Comparative Studies of the Optical Absorbance and Structural Properties of Iron-copper Sulphide (CuS-Fe) and Iron Lead Sulphide (PbS-Fe) Thin Films Deposited 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 acetate, Pb(CH$_3$COO)$_2$, Cupric Acetate Cu(CH$_3$COO)$_2$, thioacetamide (S$_2$H$_3$NS), Iron (II) Chloride dehydrate(FeCl$_2$, 2H$_2$O), ethanol and ammonia by 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 UV-visible studies were done using spectrometer in the Technical University, Ibadan. 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: Copper Sulphide thin Films: Lead Sulphide thin Films: Absorbance: structural properties
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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 (Bala et al. 2008). 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 (Whitefield, 2000). Solar energy, an energy obtained from the sun, is the world’s most abundant and cheapest source of energy available from Nature (Nwoke et al, 2008). 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 (Jesuleye and Siyanbola, 2008). 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 (Liang and Whangbo, 1993) 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 (Chatterki et al. (2012), koao et al. (2014), Preetha et al.(2015)).

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.(Valenzuela, 2003)

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 0.05M 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 acetate solution for 35 minutes, 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 35 seconds, 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 and Fe 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 35 seconds, 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 35 seconds.

After repeating for sufficient number of cycles (90 cycles), PbS and Fe composite thin films were deposited. The number of deposition cycles for PbS and Fe were adjusted to obtain various compositions of PbS and Fe thin films (see table 1 below).

Table 1: Deposition scheme for the growth of PbS and Fe thin films

| Preparative Parameter | Cationic precursors | Anionic precursor |
|-----------------------|--------------------|------------------|
| Concentration(M)      | Pb(CH₃COO)₂         | S₂H₃NS           |
| pH                    | 11.5               | 11.5             |
| Immersion time (seconds) | 35                | 35               |
| Rinsing time (seconds) | 35                | 35               |

Table 2: PbS and Fe thin films composition

| Films      | Composition parameter(x) | Number of SILAR cycles Fe | Thickness (nm) |
|------------|--------------------------|---------------------------|----------------|
| PbS        | 1.00                     | 90                        | 00             | 397            |
| PbS₀.₈₀Fe₀.₂₀  | 0.80                     | 80                        | 10             | 393            |
| PbS₀.₅₀Fe₀.₅₀  | 0.50                     | 70                        | 20             | 283            |
| PbS₀.₂Fe₀.₈₀  | 0.20                     | 60                        | 30             | 299            |
| PbS₀.₁₀Fe₀.₉₀  | 0.10                     | 45                        | 45             | 230            |

The thickness of the composite PbSₙFeₙ thin film was measured by weight difference method. The density of PbS was taken as 4.9g/cm³ and iron as 5.2g/cm³.

The densities of the composite PbSₙFeₙ 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 PbSₙFeₙ films measured using sensitive microbalance is listed in table 2 above. 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 PbSₙFeₙ 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 thin films, 0.05 M cupric acetate solutions were taken as cationic precursor and 0.05 M thioacetamide 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 react 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 acetate solutions taken as cationic precursor, then rinsed in deionised water for 35 seconds before immersing into 0.05 M thioacetamide, 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) Chloride 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 35 seconds. It is worthy to note that the substrate was again immersed in thioacetamide 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 |
|-----------------------|---------------------|-------------------|
|                       | Cu(CH\(_3\)COO)\(_2\) | FeCl\(_2\).2H\(_2\)O | S\(_2\)H\(_5\)NS |
| 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 Tables 1 and 2 below. The crystallite size of the deposited material was calculated by using Debye- Scherer’s formula (equation 2)

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]

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, \(\lambda\) is the X-ray wavelength used (0.1542 nm), \(\beta\) is the angular line width of half-maximum intensity (FWHM) of the diffraction peak, and \(\theta\) is the Bragg’s angle in degrees. See tables 1 and 2 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)\(_{0.10}\)(Fe)\(_{0.90}\), (D) CuS

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

| Film composition | Thickness (nm) | Grain Size (nm) | Dislocation density \((\delta \times 10^{19})\) 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)\(_{0.50}\)(Fe)\(_{0.50}\) | 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           |

Table 2. Thickness, grain size, strain and dislocation density of (CuS)\(_{x}\)(Fe)\(_{1-x}\) thin films.

| Film composition | Thickness (nm) | Grain Size (nm) | Dislocation density \((\delta \times 10^{19})\) lines/cm\(^2\) | Strain \((\varepsilon \times 10^{-4})\) |
|------------------|----------------|-----------------|-------------------------------------------------|-----------------|
| A CuS            | 386            | 35              | 10.47                                           | 10.17           |
| B (CuS)\(_{0.80}\)(Fe)\(_{0.20}\) | 300            | 33              | 14.66                                           | 11.30           |
| C (CuS)\(_{0.50}\)(Fe)\(_{0.50}\) | 298            | 30              | 15.92                                           | 13.77           |
| D (CuS)\(_{0.20}\)(Fe)\(_{0.80}\) | 287            | 19              | 17.57                                           | 14.99           |
| E (CuS)\(_{0.10}\)(Fe)\(_{0.90}\) | 273            | 17              | 32.47                                           | 21.34           |

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:
Figure 3. 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) \((\text{PbS})_{0.80}(\text{Fe})_{0.20}\) at 10 µm (HFW=124 µm)

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

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

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

Figure 5. EDS of \((\text{PbS})_x(\text{Fe})_{1-x}\) composite thin films:
Figure 6. EDS of (CuS)$_x$(Fe)$_{1-x}$ composite thin films:

3.3 Optical characteristics

Fig 7: Plots of absorbance against wavelength for PbSFe thin film

Fig 8: Plots of absorbance against wavelength for CuSFe thin film

Fig.7 shows the plots of absorbance against wavelength of PbSFe thin films while Figure 9 depicts the plots of transmittance against wavelength. Figure 8 shows the plot of absorbance against wavelength of CuSFe thin films. The absorbance spectra of PbSFe thin films (Fig.7) vary in a manner, decreasing continuously from 1.40 (a.u) at 400nm to about 0.50 at 900nm. This range of absorbance is in agreement with the reports of Uhuegbu (2007) for FePbS thin films, Agbo and Nnabuchi (2011) for TiO$_2$/PbO thin films, and Onah, Ugwu and Ekpe (2015) for TiO$_2$/CuO thin films. The absorbance spectra of CuSFe thin films (Fig.8) shows that the thin films decreased within 400-500nm and then remained fairly constant within the wavelength range 550-700nm. Thereafter, it increased within the wavelength range 750-900nm. The maximum absorbance is about 0.5 (a.u.) at 400nm. This value of absorbance is below the maximum of 1.50 (a.u) by Uhuegbu (2007) for FeCuS$_2$ thin films. The high absorbance displayed by PbSFe films may be used as spectrally selective coating for solar thermal applications. Solar collectors for heating fluids require increasing the reception area of the solar radiation, and/or to increase the absorbance of the surface coating in order to improve thermal efficiency (Oliva, Maldonado, Diaz and Montolvo, 2013). These findings are in agreement with the report of Augustine and Nnabuchi (2018) for CuO/PbS thin films. SUMMARY: X-ray diffraction patterns of CuS-Fe 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 20 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 20 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. 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.

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. Their dislocation density(δ) 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, 27,19,17. The variation in the strain and dislocation density may influence the properties on the nanostructures. The compositional analysis showed that the iron content of the SILAR synthesized PbSFe thin films was 21wt % and CuSFe thin films was 20.8wt%.

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 (Qadri et al. 2003).

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(Qadri et al. 2003). 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 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 pure PbS 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 Wang et al. 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., From literature, considerable changes can be seen for temperatures up to 700 0K (Mote, 2012). The high absorbance displayed by PbSFe films may be used as spectrally selective coating for solar thermal applications. Solar collectors for heating fluids require increasing the reception area of the solar radiation and/or to increase the absorbance of the surface coating in order to improve thermal efficiency. The relatively high transmittance of PbSFe and CuSFe thin films in the infrared region suggest that they may be used for coating the walls and roofs of poultry houses to facilitate the transmission of infrared radiation in order to generate the heat required for warming young chicken. These properties can be well used in solar energy conversion devices and optoelectronics.

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