

**OPTICAL PROPERTIES DEPENDENT SILAR DEPOSITED CuSFe, PbSFe, AND ZnSFe THIN FILMS FOR LABORATORY STERILISATION**

**BY**

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**ABSTRACT**

The doping influence of iron on optical properties of lead sulphide(PbS), Zinc Sulphide(ZnS) and Copper Sulphide (CuS) thin films deposited on glass substrates via successive ionic layer adsorption (SILAR) Technique using lead acetate,  $Pb(CH_3COO)_2$ , Zinc acetate,  $Zn(CH_3COO)_2$  and Cupric Acetate  $Cu(CH_3COO)_2$ , thioacetamide ( $S_2H_5NS$ ), Iron (II) Chloride dehydrate( $FeCl_2 \cdot 2H_2O$ ), ethanol and ammonia by in alkaline medium annealed between 283K and 500K were investigated. Our interest in this study in the fire alarm sensing and brooding optical properties of the deposited thin films. 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  $Cu_2S$  thin films and cubic and hexagonal crystalline natured CuSFe thin films with the preferential (111),(002)(004) (311) orientations while the Zn.SFe thin films were nanocrystalline and tetragonal as confirmed by XRD Analysis.

Keywords : PbSFe;ZnSFe; CuSFe; fire-alarm sensing optical properties;;structural and morphological properties, SILAR Technique

**INTRODUCTION**

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. 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. 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 ( $Cu_2S$ ) 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 ZnS,  $(ZnS)_x(Fe)_{1-x}$  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. 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)

## 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 ZnS, PbS and CuS involved four steps while that of ZnSFe, 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.

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  $CuK\alpha$  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.

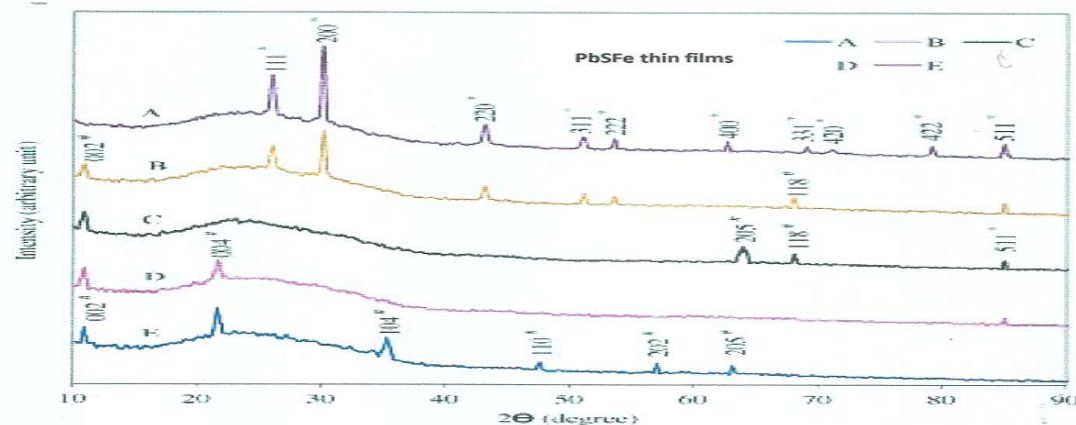
### 3.0 Results, discussion and Conclusions

A simple, cheap and convenient SILAR method was employed to deposit good quality CuSFe, ZnSFe and (PbS)<sub>x</sub>(Fe)<sub>1-x</sub> 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 structural characterizations of (PbS)<sub>x</sub>(Fe)<sub>(1-x)</sub> and (CuS)<sub>x</sub>(Fe)<sub>(1-x)</sub> 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. The crystallite size of the deposited material was calculated by using Debye- Scherer's formula (equation 1)

$$D = K\lambda / \beta \cos \theta, \quad (1)$$

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.



The compositional analysis was done using energy dispersive spectroscopy(EDS). EDS Studies showed that in (PbS)<sub>x</sub>(Fe)<sub>1-x</sub> composite thin films, the composition of iron was 21.8wt%, that in while in (CuS)<sub>x</sub>(Fe)<sub>1-x</sub> composite thin films, iron composition was 20.8wt% and in (ZnS)<sub>x</sub>(Fe)<sub>1-x</sub> thin film, the iron content was 20.5wt%. The XRD and morphological studies revealed

that ZnSFe, 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, for ZnSFe thin films between 14 and 22 and for PbSFe thin films 34 and 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(11), Udejah and Onah(2018)(12), Udejah and Onah (2020)(13). The samples annealed at different temperatures (383K-500K) never showed any prominent peaks structurally and morphologically as confirmed by studies done by udejah(14), Udejah and onah(15), udejah and onah(16), udejah and onah(17), Onah et al.(18), and He et al.(19-28) From literature, considerable changes can be seen for temperatures up to 700 <sup>0</sup>K by Mote (29-31). The high absorbance displayed by PbSFe films may be used as spectrally selective coating for solar thermal application for sterilisation in hospitals and warming poultry farms. 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(32-37). 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 sterilisation in hospitals and for warming young chicken in poultry farms(38-44). These properties can be well used in solar energy conversion devices and optoelectronics.

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#### REFERENCES

1. Bala, E.J., Ojosu, J.O., and Umar, I.H., Government Policies and Programmes on the Development of Solar PV Sub-sector in Nigeria.(2008) *Nigeria Journal of Renewable Energy*, 8(1 and 2): 1-6

2. Whitefield, D. (2000). Solar Dryer System and the Internet Important Resources to Improve food preparation. A Paper presented at *International Conference on Solar Cooking, Kimberly, South Africa*, and 24th June, 2000.
3. Nwoke, O. O., Okonkwo, W. I. and Oparaku, O. U. (2008). Solar Energy Use in Nigeria: constraints and Possible Solutions. *Nigeria Journal of Solar Energy*, 19(1), 90-93.
4. Jesuleye, A.O. and Siyanbola, W.O. (2008). Solar Electricity Demand Analysis for Improved Access to Electricity in Nigeria.. *Nigeria Journal of Solar Energy*. (1): 136-141.
5. Liang,W and Whangbo, M.H(1993): Solid State Communications. 85 (1993) 405
- 6.Chattarki AN, Kamble SS, Deshmukh LP (2012). Role of pH in aqueous alkaline chemical bath deposition of lead sulfide thin films. *Mater. Lett.* 67:39-41.  
<http://dx.doi.org/10.1016/j.matlet.2011.08.105>.
7. Koao LF, Dejene FB, Swart HC (2014). Synthesis of PbS nanostructures by chemical bath deposition method. *Int. J. Electrochem. Sci.* 9:1747-1757
8. Preetha KC, Deepa K, Dhanya AC, Remadevi TL (2015). Role of complexing agents on chemical bath deposited PbS thin film characterization. *Mater. Sci. Eng.* 73.  
<http://dx.doi.org/10.1088/1757-899X/73/1/012086>
9. Valenzuela, J., J'auregui, R., Ram'irez-Bon, A., Mendoza-Galva'n, M. and Sotelo-Lerma, A. (2003). Optical properties of PbS thin films chemically deposited at different temperatures. *Thin Solid Films*, 1441: 104-110.
- 10.Lambert-Beer's law Source (online: <http://www.wikilectures.eu/index.php?oldid-24362>
- 11.Igweoke, A.E., Augustine, C. Idenyi, N.E., Okorie, B.A. and Anyaegbunam, F.L.C. (2018). Influence of processing conditions on the optical properties of chemically deposited zinc sulphide (ZnS) thin film, *Materials Research Express*, 5, 1-12.
- 10.Kumar, V., Sharma, M.K., Gaur, J. and Sharma, T.P. (2008). Polycrystalline ZnS thin films by screen-printing method and its characterization, *Chalcogenide Letters*, 5(11), 287-295.
- 11.Agbo, P. E. and Nnabuchi, M. N. (2011). Core-Shell TiO<sub>2</sub>/ZnO Thin Film: Preparation, Characterization and effect of temperature on some selected properties, *Chalcogenide Letters*, 8(4), 273-278
- 12.Augustine, C., Nnabuchi, M.N., Anyaegbunam, F.N.C and Nwachukwu, A.N. (2017). Study of the effects of thermal annealing on some selected properties of HeterojunctionPbS-NiO core-shell thin film, *Digest Journal of Nanomaterials and Biostructures*, 12(2), 523-531.
- 13.Augustine, C. and Nnabuchi, M.N. (2018). Optical and solid state characterization of chemically deposited CuO/PbS double layer thin film, *Materials Research Express*, 5(2), 1-11
- 14.Udejah (2020). Morphological and structural of PbSFe thin films deposited by SILAR Method, published in nigerian association of mathematical physics, vol 55,2,18-32
- 15 Udejah, V. N and Onah, D.U. (2020), "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, published in the International Institute for Science, Technology and Education (IISTE)- Journal of Advances in Physics theories and Applications in January 2020,82,21-28.
- 16.Udejah, V. N and Onah, D.U. (2019), "Comparative studies on transmittance, absorbance a structural properties of iron copper sulphide(CuS-Fe) and iron lead sulphide(PbS-Fe) thin Films by chemical method (SILAR), published in International Journal of Physical

Sciences Research, 3,2, 19-33.Published by ECRTD UK

- 17.Udejah, V.N and Onah, D.U.(2019) Influence of iron on structural and optical properties of lead sulphide(PbS) thin films synthesized by Successive ionic layer adsorption and reaction (SILAR) method published in GIRD International Journal of Sciences and Technology, 4, 1, 2019. ISSN: 2384-5600
- 18.Onah, D. U., Ugwu, E.I. and Ekpe, J. E. (2015). Optical Properties of Nanocrystalline TiO<sub>2</sub>/CuO Core-Shell Thin Films by Thermal Annealing, *American Journal of Nano Research and Applications*, 3(3), 62-65.
- 19.Petkov, K., Todorov, R., Kozuharova, D., Tcky, I., Cernoskova, E. and Ewen, P.J.S. (2006). Changes in the physiochemical and optical properties of chalcogenides thin films from the system of As-S to As-S-Ti, *Journal of Material Sciences*, 39:961
- 20.Shinde, M.S., Ahirrao, P.B., Patil, I.J. and Patil, R.S. (2011). Studies on nanocrystalline ZnS thin films prepared by modified chemical bath deposition method, *Indian Journal of Pure and Applied Physics*, 49, 765-768.
- 21.Sunil, H.C., Deshpande, M.P. and Jiten, P.T. (2014). Characterization of CuS nanocrystalline thin films synthesized by chemical bath deposition and dip coating techniques, *Thin Solid Films*, 550(1), 291-297.
- 22.Uhuegbu, C.C. (2010). Solution growth technique for iron copper sulphate ternary thin film and its optical characteristics, *American Journal of Scientific and Industrial Research*, 1(3), 392-396.
- 25.Boer, K.W.,(1977), *Physica Status Solidi*. A40, 435.
- 26.Chaudhuri, T. K. and Chatterjes, S. (1992). Ternary Thin Films, *Proceedings of the International Conference on Thermoelectronics*. New Jersey, N.Y, 11: 40.
- 27.Fernandes, P.A., Salome, P.M. and Cunha, A.F. (2010). A study of ternary Cu<sub>2</sub>SnS<sub>3</sub> and Cu<sub>2</sub>SnS<sub>4</sub> thin Films prepared by sulphurizing stacked metal precursors, *Journal of Physics D: Applied Physics*, 43, 1-11.
- 28.He, Y, Yu, X and Zhao, X. (2007), *Materials latter*, 61, 3014
- 29.Ibrahim, S. G. and Salame, P. H. (2016). Thickness Dependent Physical Properties of lead Sulphide thin Films, *Int. J. Chemistry*, 6:5-11
- 31.Mote, V., Y. Purushotham, Y., and Dole, B.(2012), The morphological, optical and electrical Properties of nanocrystalline PbS thin films., *J. Theor. Appl. Phys.* 6, 1 7.
- 32.Nicolau, Y. F, Dupuy M, Brunnel, M (1990): *Journal of Electrochemical society*, 137, 2915.
- 34.Nair, M T.S, Alvarez-Garcia,G., Estrada-Gasva C.A. and Nair, P.K(1993); *Journal of Electrochemical Society*. 140, 212.
35. Nair, P.K., Garcia, V.M., Fernandez, A. M. Ruiz H.S and Nair, M.T.S (1991), *Journal Of Physics D*. 24, 441.
- 36.Han, Z.H. Li, Y.P., Zhao, H.Q., Yu, S.H., Yin, Y.L., and Qian, Y.T(2000), *Materials Letters*. 44, 366.
- 38.Qadri, S. B. , Singh, A. and Yousuf, M.(2003): Structural stability of PbS Films as a function of temperature, *Thin Solid films*, 431(432),506-510
- 39.Wang, S.Y, Wang, W,Lu,Z.H(2003):*Material Science and Engineering*, B10,3184

42. Smith, G. B., Ignatiev, A. and Zajac, G.(1980).Copper sulphide nanocrystalline thin films at room temperature, *Thin Solid films*, 514, 132-137.
43. Ubale, A.U., Bhute, M.V., Malpe, G.P., Raut, . P.P., Chipade, K.S. and. Ibrahim, S.G (2014)“Physical properties of nanostructured (PbS)<sub>x</sub>(CuS)<sub>1-x</sub>composite thin films grown by successive ionic layer adsorption and reaction method”, *Journal of Saudi Chemical Society*, 1-14
44. Yucel, E., Yucel, Y., Beleli, B.(2015). Process optimization of deposition conditions of PbS *Appl. Phys. Lett.*, 56, 51-53.S

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