Luminous Transmittance Of Silar Deposited Iron Lead Sulphide(PBS) Thin Films For Photovoltaic Applications In Ebonyi State, Nigeria

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ABSTRACT

The lead sulphide (PbS) thin films were successfully deposited on glass substrates via successive ionic layer adsorption and reaction (SILAR) Technique using lead Nitrate, $Pb(NO_3)_2$ and thiourea which provided the PbS ions; Iron (II) Chloride dehydrate($FeCl_2 . 2H_2O$) was used to provide the iron ions while sodium hydroxide(NaOH) was the pH adjuster . There was post-deposition annealing between 283K and 500K. The X-ray diffraction (XRD) Analysis, scanning electron microscopy(SEM) and Uv-vis spectroscopy were studied to determine the structure, morphology and optical properties respectively for use in photovoltaic applications in Ndiebor Agbaja Unuhu and Ishiagu- Ebonyi State. The XRD showed PbS thin films being cubic and crystalline nanoparticles. The transmittance was high and the absorbance low.

Keywords: Doping: lead sulphide structure; XRD studies; SEM Analysis and optical properties

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I. 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 thin films 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)

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 synthesis 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 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 thioure 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), $PbS_x Fe_{(1-x)}$ 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 equations of reaction)

$$Pb(NO_3)^2 + 4NaOH \rightarrow$$
$$[Pb(OH)_4]^{2-}+Na++2NO^{3-} \quad (1)$$

$$[Pb(OH)_4] \quad MnO_2$$
$$2OH- +CN_2H_2 + 2H_2O \quad (2)$$
$$PbS+2OH-+CN_2H_2+2H_2O+ 2FeCl_2.2H_2O \rightarrow \quad 2PbSFe(s)\downarrow+4HCL+6H_2O \quad (3)$$
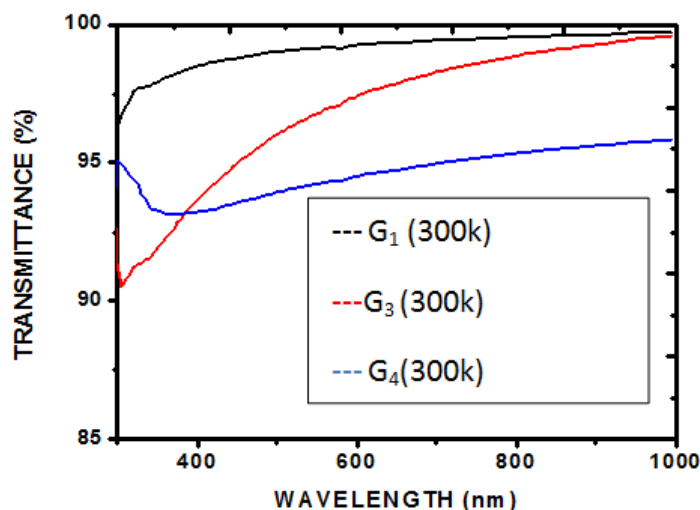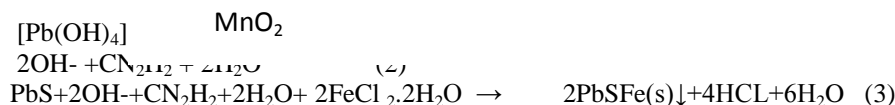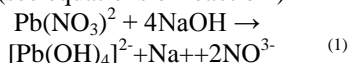

Figure 1: Plot of Transmittance against Wavelength for PbS-Fe thin Films
(43rd NIP conference 2021)

Characterisation:

The structural characterizations of $(PbS)_x(Fe)_{(1-x)}$ 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 . Using the PbSFe as case study, detailed analyses are given in Tables1 and 2. The crystallite size of the deposited material was calculated by using Debye- Scherer's formula (3)

$$D = K\lambda / B\cos\theta, \hspace{4cm} (3)$$

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.

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 excluded. . The cubic lattice are distinct in pure PbS 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 $(PbS)_{0.5}(Fe)_{0.5,}$ 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 using transmittance values (Allah *et al.* 2007) 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 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(26). The optical studies carried out showed that it had high absorbance and low transmittance in the ulra-violet and near infra red regions. These properties were advantageous in lighting of poultry farms at Asa Road Ishiagu, Ebonyi state, Nigeria to warm chicken as the walls and roof of the place were glazed with the material.

II. 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 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 were also composition dependent. Similar observation has been reported by Wang et al (2009), Udeajah (2020) and Udeajah(2021) (21-30) 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 700 ^{0}K (31). These properties can be well used in solar energy conversion devices and poultry farm lighting and warming as the case in Ishiagu and Ndiebor Agbaja-Unuhu, located in Ebonyi State and Obudu in Cross River State, Nigeria.

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