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ANALYSIS OF SILAR- DEPOSITED CuSFe THIN FILMS FOR OPTOELECTRONICS APPLICATION

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ABSTRACT

*The iron doping influence on Copper Sulphide (CuS) thin films deposited on glass substrates via successive ionic layer adsorption and reaction (SILAR) Technique using copper acetate,$Cu(CH_3COO)_2$, thiourea***,** *Iron (II) Chloride dehydrate($Fe\ Cl_2 . 2H_2O$) and Iron nitrate respectively, ethanol and ammonia in alkaline medium annealed between 283K and 500K were 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 CuS thin film,polycrystalline Cu_2S thin films and cubic and nanocrystalline natured CuSFe thin films with the preferential (111),(002)(004) (311) orientations . The relatively high transmittance of CuSFe thin films in the infrared region suggest that they may be used in physiotherapy for strained gyratrics patients bodies and joints. They are generally used in medical rehabilitation.*

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

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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. Copper Sulphide (Cu_2S) are groups 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 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)

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 CuS involved four steps while that of CuSFe thin films involved six steps. After pre-treatment of the substrates, the synthesis were done using .05M lead acetate and thiourea solution. Ammonia was used to control the pH. It was done between pH between 8.5 and 11.5. The copper ions were got from cupric acetate. It was equally deposited in alkaline environment too.

Copper Sulphide and Copper Sulphide Iron thin films.

For the SILAR deposition of $(CuS)_{(1-x)}$ thin films, 0.05 M copper chloride 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 thiourea 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 copper 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 nonahydrate 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 $(Fe)_{1-x}(CuS)_x$.

3.0 Results and discussion

The results are reported below: The crystallite size of the deposited material(CuS and CuSFe thin films) was calculated using Debye- Scherer's formula (equation 1)

$$D = K\lambda / B\cos\theta, \qquad (1)$$

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 , 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.

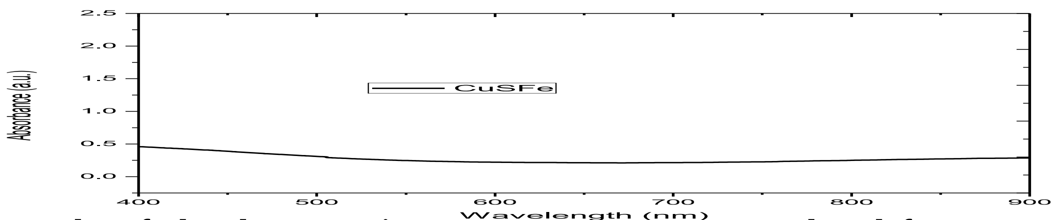

Figure 1 : Plot of absorbance against wavelength for CuSFe thin films

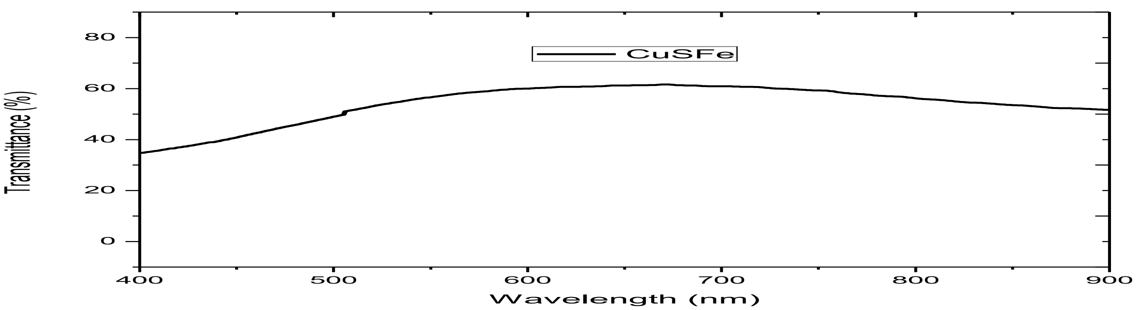

Figure 2 : Plot of Transmittance against wavelength for CuSFe thin films

3.1 Optical Properties of CuSFe Thin Films

The absorption spectra, is direct and the simplest method for probing the band structure of semiconductors. The UV–visible optical absorption measurements for composite $(CuS)_x(Fe)_{1-x}$ films were carried out using spectrophotometer. The wavelength range was between 400 and 900 nm. Figure 1 showed the variation of absorbance (αt) with wavelength for $(CuS)_x(Fe)_{1-x}$ films whiile Figure 2 showed transmittance plot.

4..1. Absorbance

The graph of absorbance against wavelength for CuSFe thin films are shown in Figure 1. The absorbance of CuSFe thin films is maximum with a value of about 2.40 (a.u.) in the visible region in the wavelength range 475-575nm and minimum value of about 1.15 (a.u) in the infrared red region corresponding to 900nm. The maximum absorbance is above the value of 2.0 (a.u) stipulated by Lambert-Beer's law (http://www.wikilectures.eu/index-php).This may be attributed to the concentration of reagents used in the deposition of CuSFe thin films. At high concentration, the assumptions of Lambert-Beer law no longer hold (http://www.wikilectures.eu/index-php). Particle attractive forces come into play at high concentration, the particles may not act independently of one another so far as absorbing light. Thus, most of the light is absorbed by the particles thereby reducing the transmission of light as it passes through the sample(http://www.wikilectures.eu/index-php). The range of absorbance of CuSFe thin films is in agreement with that of Udeajah and Onah(2019) and Udeajah(2020). This result is in agreement with the reports of Onah,Ugwu and Ekpe (2015) for TiO_2/CuO thin films. The absorbance spectra of CuSFe thin films (Fig.1) shows that the decreased with wavelength 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 CuSFe 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, Udeajah,2020).

5.1.2 Transmittance

The graph of transmittance against wavelengthis the inverse of the absorbance. The transmittance spectra for CuSFe thin films (Fig. 2) vary in different manner, increasing from about 35% at 400 nm to about 58% in the wavelength range 550nm and then remained fairly constant in the wavelength range 575-750nm. Thereafter, it decreases to about 52% at 900nm. Generally, CuSFe thin films transmit higher compared to ZnSFe thin films. The relatively high transmittance of 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 and as physiotherapy for strained gyratrics patients bodies and joints. These thin films may generally be used in medical rehabilitation. This has the potential to reduce the cost of energy consumption associated with the use of electric bulbs, stoves and infra red lamps. These findings are in agreement with the report of Udeajah (2021) and Augustine and Nnabuchi (2018) for CuO/PbS thin films.

4.0 Conclusions

A simple, cheap and convenient SILAR method was employed to deposit good quality CuSFe composite thin films. The deposited thin films were uniform and adherent to the substrate. Their structural and morphological properties of those composite thin films were studied. The compositional analysis was done using energy dispersive spectroscopy(EDS). EDS Studies showed that in $(CuS)_x\,(Fe)_{1-x}$ composite thin films, iron composition was 20.8wt%. The XRD and morphological studies revealed that CuSFe 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 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.(2003). 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.*,2011. From literature, considerable changes can be seen for temperatures up to 700 ^{0}K (Mote, 2012). The relatively high transmittance of 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 and in the treatment of stressed and strained bodies during physiotherapy as it take the place of infra-red lamps. These properties can be well used in solar energy conversion devices and optoelectronics.

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