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Original Research Article

Growth and Optical Analysis of Cobalt Tin Sulphide Thin Films using SILAR Technique

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ABSTRACT

In this work, cobalt tin sulphide (CoSnS) thin films were deposited on soda-lime substrates via the successive ionic layer adsorption and reaction (SILAR) method. The CoSnS films were synthesized using cobalt sulphate, tin chloride dihydrate and thioacetamide solutions as sources of cobalt (Co) tin (Sn) and sulphur (S) respectively. XRD analysis revealed that the deposited films were polycrystalline in nature with strong adherent to the substrates. The absorbance was found to be high in the ultra-violet regions of the electromagnetic spectrum and, also decreased with deposition cycles. The band gap energy was found to increase from 1.22 to 1.52 eV with deposition cycles. The refractive index (n) as well as the optical electronegativity (ϕ) were also determined and discussed. The finding indicates that the deposited material is suitable for optoelectronic devices where low optical absorbance is necessary.

1. INTRODUCTION

In recent years, tin sulphide (SnS) based semiconductors have received great attention due to their excellent optical and electrical properties (Gedi *et al.,* 2019). They are extensively used in various optoelectronic devices such as photovoltaic devices, thermoelectric, photo-detectors, gas sensors, biosensors, heat mirrors, field effect transistors, photocatalysis, water splitting, lithium-sodium ion battery and super capacitors (Sreedevi and Reddy, 2013; Mukherjee and Mitra, 2015; Trevino-Yarce *et al*., 2019; Gedi *et al.,* 2019). One of the attractions of this material is its natural availability and non-toxic nature (Nwofe *et al.,* 2012; Trevino-Yarce *et al.,* 2019).

Various physical and chemical deposition techniques have been used to prepare SnS-based thin films, such as chemical spray pyrolysis, cathodic electrodeposition, electrochemical deposition, chemical bath

deposition, hot injection, aqueous solution, colloidal route, single solid approach, precipitation electrochemical deposition and successive ionic layer adsorption and reaction (SILAR) (Jing *et al.,* 2004; Triana *et al.,* 2011; Regina *et al.,* 2011; Tariq *et al.,* 2014; Trevino-Yarce *et al.,* 2019). Among these techniques, the SILAR method enjoys advantages of low temperature, ease of controlling the deposition parameters, possibility of using any kind of substrates, large area depositions, control of deposition rate and thickness (Ghosh *et al.,* 2011; Mondal, 2013). The technique is primarily based on the solution adsorption and reaction of the ions and rinsing between each immersion with distilled water. The deposition of thin films is achieved by dipping substrates into discretely placed cationic and anionic precursors and rinsing between every immersion with ion-exchanged water (Mondal, 2013).

To enhance the efficiency of SnS for device applications, several elements have been added in various quantities. Doping tin sulphide with cobalt has been shown to enhance the electrical as well as the optical properties of SnS thin films. In the present work, the preparation of cobalt tin sulphide (CoSnS) thin films using the SILAR technique was carried out. The goal is to develop a better growth approach of new and non-toxic ternary SnS-based semiconducting material for the production of low cost solar cells. Enhancement in the properties of the material due to cobalt incorporation will play a major role in improving the device efficiency.

2. MATERIALS AND METHODS

2.1. Materials

To synthesis CoSnS thin films, chemicals of analytical grade (AR) were used without further purification and they include; thioacetamide (C_2H_5NS), ammonia solution (NH_4OH), triethanolamine ($C_6H_{15}NO_3$) tin chloride dihydrate ($SnCl_2.2H_2O$), cobalt sulphate (CoSO4), ethanol (C_2H_5OH), acetone (CH_3COCH_3), and distilled water.

2.2. CoSnS Thin Films Preparation

The successive ionic layer adsorption and reaction system used in this study consist of an adsorption solutions which are the sources of cation (i.e. $SnCl_2.2H_2O$ for Sn^{2+} and $CoSO_4$ for Co), a reaction solution which is the source of anion (i.e. C_2H_5NS for S^{2-}), and 100 ml beaker filled with distilled water. A clean glass substrate (washed in detergent solution, then in acetone, ethanol and distilled water respectively) was used for the deposition of cobalt-tin-sulphide (CoSnS) thin films. A schematic representation of the successive ionic layer adsorption and reaction technique system can be seen in Figure 1.

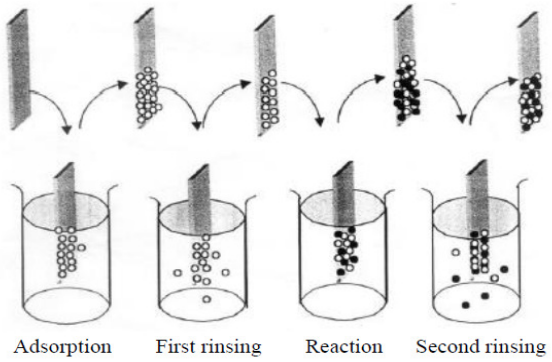

Figure 1: Schematic representation of SILAR method for the deposition of CoSnS thin films (Pathan and Lokhande, 2004)

Cobalt sulphate (2.44 g) was measured and added to a pyrex beaker containing 100 ml of distilled water and stirred till it completely dissolved as indicated in Figure 2. Tin chloride (0.22 g) was added to the cobalt

sulphate solution and stirred while heating using a magnetic stirrer hot plate till it dissolved completely. The resulting solution can be seen in Figure 3. A complexing agent (ammonia) was added to the resulting solution to increase the deposition process and stirred continuously till a uniform solution was attained. The final resulting solution formed the adsorption solution as shown in Figure 4. The reaction solution was prepared by adding 0.75 g of thioacetamide (C_2H_5NS) in a beaker containing 100 ml of distilled water without heating. Heating thioacetamide (source of sulphur) will evaporate sulphur into the atmosphere. Four beakers were used in the experimental process. The beakers containing the adsorption (cationic precursor) solution, the reaction solution and the rinsing beakers were placed alternatively, each rinsing beakers being placed between the adsorption (cationic precursor) solution and the reaction solution. A well cleaned glass substrate was first immersed in the adsorption solution for 20 seconds, and then rinsed with distilled water for 10 seconds. In the first rinsing, the glass substrate is shaken so that the loosely adsorbed ions can be rinsed away from the substrate layer. This glass substrate is then immersed in the reaction (anionic precursor) solution for 20 seconds and then rinsed again with distilled water for 10 seconds. In the second rinsing, the unreacted ions were rinsed away from the glass substrate. This process was repeated at several deposition cycles: 40, 50, 60, 70 and 80 cycles. The samples were later coded as H1 for 40 cycles, H2 for 50 cycles, H3 for 60 cycles, H4 for 70 cycles and H5 for 80 cycles.

Figure 2: Cobalt sulphate solution

Figure 3: Solution of cobalt sulphate and tin chloride

Figure 4: Adsorption solution of the mixture

2.3. Characterization of CoSnS Thin Films

The structural characterization was done using X-ray diffraction (XRD). The crystal structure of the deposited films was measured using Bruker D8 Advanced X-ray diffratometer operating with a wavelength of 1.5406Å. The diffracting angle range was between 15 to 80^o with a scanning rate of one degree per minute. Optical measurements of CoSnS thin films were done through a (UV-1800) Spectrophotometer in a wavelength range of 300 to 1000 nm at room temperature.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

The X-ray crystalline patterns of the deposited Co-Sn-S films are shown in Figure 5. The XRD spectra showed four major peaks at 15.20°, 18.95°, 24.04° and 26.68°, which correspond to the diffraction intensity of (200), (201), (211) and (221). The presence of sharp peaks in the Co-Sn-S films with narrower spectral widths indicated that the deposited materials are polycrystalline in nature (Emegha *et al.,* 2019)**.** It is also clear from the XRD analysis that the material consists of mixtures of several phases including the hexagonal structure CoS (JCPDS no 075-2023), cubic Co_9S_8 (JCPDS no 001-1279), orthorhombic Sn_2S_3 (JCPDS no 014-0619) as well as the hexagonal SnS_2 (JCPDS no 023-0677). As known, the presence of secondary phases within the Co-Sn-S system could be the direct result of the multiply phases of the binary constituents of the ternary material (Ghosh *et al.,* 2011; Abza *et al.,* 2020).

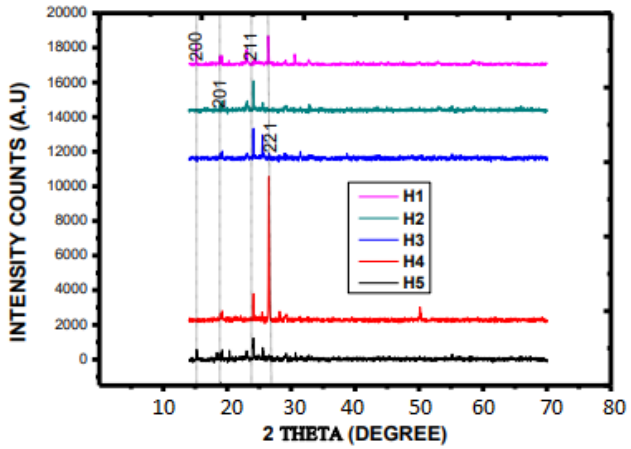

Figure 5: XRD patterns of the deposited CoSnS thin films

3.2. Optical Studies

The optical properties of the deposited thin films were assessed using ultraviolet visible spectrophotometry. The plot of absorbance against wavelength of the deposited CoSnS films is shown in Figure 6. All the absorbance spectra were in the wavelength range of 300–1000 nm. As shown in the Figure, it was observed that the absorption was high in the ultraviolet region ($\lambda < 350$ nm) of the spectrum and decreased with wavelength throughout the visible and near infrared regions. The observed high absorbance in the ultraviolet region may be attributed to electronic inter-band transitions from the filled sulphide valence band through to the empty conduction band (Olofinjana *et al.,* 2019). It may also be due to the structural defects such as surface irregularity and defect density within the CoSnS system as a result of variations in deposition cycles (Emegha *et al.,* 2021a).

Evaluation of the energy gap is based on the photon induced electronic transition between the conduction band and the valance band. Since ternary CoSnS thin film is a direct band-gap material, the absorption coefficient is related to the photon energy (hν) by the Equation 1 (Damisa et al., 2020; Emegha et al., 2021b):

$$\alpha = \left(\frac{A}{h\nu}\right)\left[h\nu - E_g\right]^n \quad (1)$$

Where, Eg is the optical energy gap, hν is the photon energy and A is a constant which depend on the transition probability.

Also, from Equation (1) the index n known as the power factor of the electronic transition mode assumed values between 1/2 and 3 depending on the nature of the electronic transition of the material. Exponent n =

1/2 for allowed direct transitions, n = 2 for allowed indirect transitions, n = 3/2 for forbidden direct transitions and n = 3 for forbidden indirect transitions (Damisa et al., 2017). Experimentally, the direct energy gap was determined by a graph of the square of absorption coefficient against photon energy, (Figure 7). Extrapolation of the linear portion of the graph to intercept photon energy axis at (αhν) = 0, gives the energy gap of the deposited CoSnS thin film (Damisa et al., 2017; Emegha et al., 2021b).

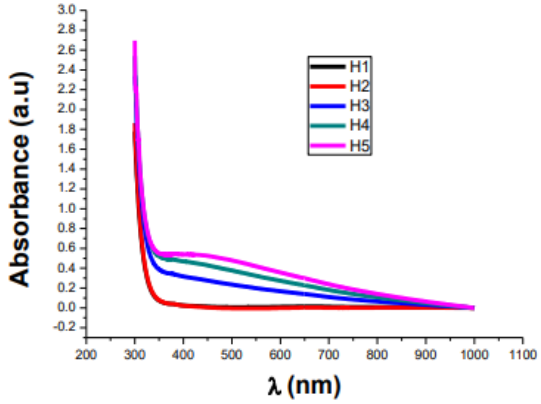

Figure 6: Absorbance against wavelength of the deposited CoSnS thin films

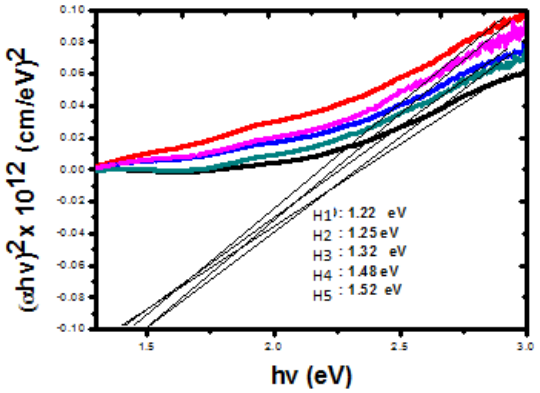

Figure 7: Square of absorption coefficient against photon energy for CoSnS thin films

The refractive index (n) is one of the fundamental properties of an optical material. The refractive index is closely related to the electronic polarization of ions as well as the local field inside the optical matrial (Hassanien and Akl, 2015). Consequently, it plays an important role in determining the material used for fabricating opto-electronic devices such as optical switches, modulation, filters as well as other electronic appliances. Based on the oscillatory theory, Harve and Vandamme proposed the following model for relating the refractive index (n) to the optical band gap (Eg) (Ahmad et al., 2013):

$$n = \left[1 + \left(\frac{A}{Eg + B}\right)^2\right]^{1/2} \quad (2)$$

The estimated value of the refractive index have been listed in Table 1 and graphically represented in Figure 8 as function of the deposition cycles of CoSnS system. It is observed that, there is a relationship between the refractive index and number of deposition cycle. The results indicate that the refractive index decreased from 3.11 to 2.94 with deposition cycles. It was observed that the refractive index of CoSnS semiconducting compounds falls between that of its binary constituents of CoS [1.4] (Govindasamy et al., 2017) and SnS [3.5 – 5.5] (Nwofe et al., 2012), and theoretically compare well with values in literature.

From the refractive index, the optical electronegativity (Φ) of the material could be determined. The optical electronegativity is an important parameter in understanding the nature of many physical properties of an optical material (Ahmad *et al.,* 2013). The optical electronegativity (Φ), which is the tendency of an atom to attract electron in ionic crystal, can be determine using a theoretical model. Duffy suggested a relation for estimating accurately the optical electro-negativity of any optical material. The model relates electronegativity (Φ) to the refractive index (n) as follows (Hassanien, 2016):

$$\Phi_{opt} = \left[\frac{A}{n}\right]^{1/4} \quad (3)$$

Where, A is a constant equivalent to 25.45 for almost all materials. The optical electronegativity values were determined and listed in Table 1, as well as graphically represented in Figure 9 against the deposition cycles of CoSnS thin films.

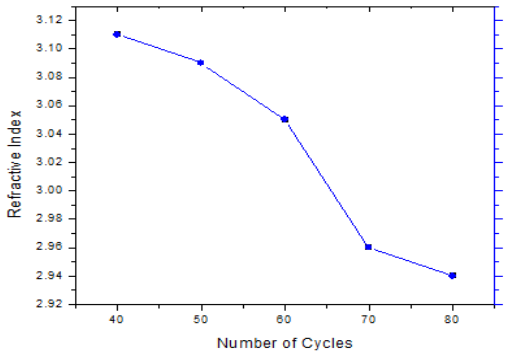

Figure 8: Refractive index against numbers of cycles of CoSnS thin films

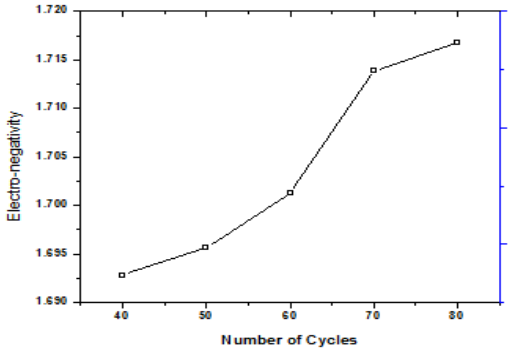

Figure 9: Electronegativity against numbers of deposition cycles of CoSnS thin films

Table 1: Some optical properties of CoSnS thin films

Samples	Band gap (eV)	Refractive index (n)	Electronegativity (□)
H1	1.22	3.11	1.6928
H2	1.25	3.09	1.6956
H3	1.32	3.05	1.7013
H4	1.48	2.96	1.7139
H5	1.52	2.94	1.7168

The Figure shows that, the Φ increased slightly from 1.6923 to 1.7168 as the deposition cycles were increased from 40 to 80. The increase in optical electronegativity of CoSnS thin films was possibly due to the dependence of the material on the refractive index, which was decreasing with deposition cycles (Hassanien, 2016). Moreover, the small magnitude of the estimated optical electronegativity as well as the relatively high refractive index values of the material could result from the nature of the bond within the CoSnS system.

4. CONCLUSION

The study showed that SILAR is an efficient method in depositing cobalt tin sulphide (CoSnS) thin films using common chemical reagents. The XRD measurements indicated a polycrystalline film with multiply phases. The band gap energy showed an allowed direct transition with values that varied between 1.22 to 1.52 eV with increasing deposition cycles. The refractive index data was found to decrease with deposition cycles and obeyed the Harve and Vandamme model. The high refractive index obtained is an indication of the bond structure within the prepared material. The determined properties confirmed that CoSnS is a potential ternary material for various optoelectronic applications.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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