Deposition and Characterization of Antimony Tin Sulphide using Spray Pyrolysis

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Abstract

Spray pyrolysis is a method commonly used in aerosol processes for atomizing chemical precursors into aerosol droplets ready for dispersion in gas mediums to form thin films on passing through a hot reactor and getting evaporated. In this study, antimony tin sulphide was synthesized using spray pyrolysis, as it is a simpler and economical technique. Doping with antimony (Sb) showed a persistent decrease in band gap with an increase in Sb. Results showed that doping tin sulphide (SnS) with Sb enhanced the absorption spectrum of the SnS film by widening the absorption peaks of SnS (Sb) films, and consequently broadening the absorption band. The absorption spectrum of SnS film was extended from 424 nm (ultraviolet edge) to 493 nm, 517 nm, 516 nm and 512 nm (visible regions), respectively. This shows that Sb serves as an opaque material in the SnS (Sb) films, which absorb light more than transparent materials. Detailed information about the optical band gap was obtained using the dependence of the absorption coefficient on the photon energy. The bandgap was varied between 3.33 and 1.90 eV. Further results on antimony tin sulphide films at different annealing temperatures are presented. X-ray diffraction (XRD) showed a preferential peak of the plane (1 1 1) at $2\theta =$ 31.69, which was predominantly persistent in all the synthesized films. Scanning Electron Microscope (SEM), which showed the surface morphology of the synthesized SnS and SnS(Sb), indicates that the formed films were non-uniformly sparsely distributed grains, thus, depicting high-quality crystal films.

Keywords: Characterization; annealing; crystallinity; energy bandgap; spray pyrolysis.

I. INTRODUCTION

N ano particles are small-sized particles that range between 1 - 100 nm in size. They can be classified into different classes based on their properties, shape and size and have groups fullerenes, metal, ceramics, and polymeric. Their optical properties are dependent on their size as well as their reactivity, toughness, and other properties such as structural and electronic are dependent on their unique size, shape and structure [1]. Due to these properties, they are suitable for both commercial and domestic applications such as catalysis, medical applications, imaging, energy-based research and environmental applications. Nanoparticles, also known as ultrafine particles, which are found largely in nature, are usually distinguished from fine particles sized between 100 - 2500 μ m, micro particles sized (1 - 1000 μ m), and coarse particles ranging from 2500 - 10,000 μ m [2]. They drive very different physical or chemical effects, such as colloidal properties, ultrafast optical effects, etc., due to their extremely small size. Due to their small size, which is much smaller than the wavelength of visible light (380 - 700 μ m), they cannot be seen with just optical microscopes but require the use of electron microscopes or microscopes with lasers. Nanoparticles, being in transition between bulk materials and

atomic or molecular structures, often exhibit phenomena that cannot be observed at either scale, thus, the production of nanoparticles with these specific properties brings about the branch of nanotechnology [3].

Synthesis and characterization of nanoparticles is a promising area of research in nanotechnology, which aims at investigating the sizes, shapes, and compositions of nanoparticles since each of these factors plays a critical role in determining different applications. The development and fabrication of nanoparticles over a few decades have led to a wide range of advancements in the field. The utilization of nanoparticle materials to enhance physical and mechanical properties has attracted major attention and special interest in research and developing the structures of nanoparticle materials, which has also contributed to the major development of the compositions of the nanoparticle surfaces. Research on Antimony Tin Sulphide (ATS) can make significant differences in the global market in the coming years [4]. Researchers have already studied how the properties of elements vary at very small particle sizes and then used these particles to accomplish various functions. With the findings from several studies, researchers can now radically enhance everything from flexible electronics to life-saving medical processes. Antimony tin sulphide (Sn₂Sb₂S5) is a suitable combination of absorber layers playing a vital role in the fabrication of efficient functional systems [5]. Tin sulphide films are available and affordable newly discovered absorber for thin film solar cells. They were found to be semiconductor thin films and can be achieved by replacing indium and copper with copper and tin, respectively, as shown by the chemical reaction in (1).

$$2ln + 3Cu^{2+} \rightarrow 2l^{3+} + 3Cu$$
 (1)

All the constituents of Antimony tin sulphide (ATS) thin film are known to be abundant and non-toxic, which makes it safe and more comfortable for use both in the laboratory and when used for the end product for the public [6]. Chalcogenide thin films have a wide range of applications in optoelectronic devices, and as such, a lot of studies have been made in recent years for both the pure and the doped $Sn_2Sb_2S_5$ thin films, which have been used for photovoltaic devices. Their continuous improvement in photovoltaic devices has made solar energy easy and economically useful, and this is so due to their properties, such as having a direct band gap, and a high absorption coefficient, alongside their affordability and availability.

Spray pyrolysis is a thin film deposition technique where a solution containing the desired material is sprayed onto a heated substrate. Upon contact with the substrate, the solution droplets decompose, forming a thin film of the target material. This method is widely used in nanotechnology and large-scale industrial applications due to its simplicity and versatility. It allows for the easy incorporation of dopants and accommodates various elements in different proportions by adjusting the spray solution. Spray pyrolysis operates at moderate temperatures ($100 - 500 \, ^\circ$ C) and does not require

high-quality substrates, making it cost-effective and accessible. The film properties can be controlled by varying substrate type, quantity, and temperature. The process involves four stages: (i) preparing the solution, (ii) converting it into aerosol droplets via an atomizer, (iii) transporting the droplets with a carrier gas, and (iv) pyrolyzing the droplets on a heated substrate to form nanoparticles or thin films [7].

This study presents the deposition and characterization of Antimony Tin Sulphide (SbSnS) thin films synthesized via the spray pyrolysis technique. The investigation was motivated by the dual potential of these materials in both radiation shielding and photovoltaic applications. In particular, the optical and structural properties of the films were analyzed to assess their suitability as radiation-absorbing materials for occupational safety in high-exposure environments, as well as their viability as cost-effective absorber layers in thin-film solar cell technologies.

II. MATERIALS AND METHODS

A. Materials

The materials used in this study are antimony, tin, Sulphur, glass substrate, distilled water, beakers and acetone.

B. Methods

1) Preparation of the Solution

Glass slides were used as substrates to deposit the thin films. The glass slides were cleansed using acetone and ethanol. The chemicals were prepared as follows:

In beaker 1

 $SbCl_3 \rightarrow 5ml$ of acetone $\rightarrow 1.13$ g

In beaker 2

10 ml (H₂O) CH₃C₃NH₂ \rightarrow 1.50 g + 1 mg tartaric acid (complexing agent), this was stirred for 3 min. Tin and Sulphur were synthesized first as a control sample, then separated in five different beakers. Subsequently, antimony was added in the order 0.1, 0.2, 0.3, 0.4, and 0.5 wt%, respectively. The beakers were placed in an ultrasonic cleaner for a while to allow for the particles of the samples to dissociate into smaller particles. The solutions were transferred one at a time to the pipette in the locally made setup. The pipette was assembled at the pipette stand and tilted at an angle of 45 degrees. The glass substrates were placed on a palette on a controlled heater, and the solutions were sprayed at temperatures of 100 - 500 °C on the glass slide. The mass of both Sb and SnS were calculated in grams using (2), with the results depicted in Table I.

$$mass = \frac{Concentration \times Molar Weigh \times 5 ml Acetone}{Concentration \times Molar Weigh \times 5 ml Acetone}$$

| S/N | Sb | SnS | |
|-----|-----|--------|--|
| 1 | 0.1 | 0.11 g | |
| 2 | 0.2 | 0.23 g | |
| 3 | 0.3 | 0.34 g | |
| 4 | 0.4 | 0.46 g | |
| 5 | 0.5 | 0.57 g | |

(2)

III. RESULTS AND DISCUSSIONS

A. Optical Absorbance Spectrum

Ultraviolet and visible light can be responsible for an electronic transition when an energetic molecule excites an electron into an empty orbital at a higher energy level. On this note, to obtain a UV-visible spectrum, absorbance can be plotted against the wavelength. This shows the absorbance of a sample in the cuvette when scanned through various wavelengths in the UV-visible region of the electromagnetic spectrum. Both the shape of the peak(s) and the wavelength of the maximum absorbance give information about the structure of the sample. UV light has a wavelength which extends from

100 - 400 nm, and visible light has a wavelength range of 400 - 700 nm.

Fig. 1(a) - (f) shows the UV-visible absorbance spectra of the synthesized SnS and SnS(Sb) films. The SnS film showed a significant absorbance in the wavelength range of 322 nm to 419 nm. The film absorbed light from 322 nm wavelength and increased to its maximum peak at 336 nm, reaching a 15.89% absorbance height, where it immediately began falling until 363.34 nm. It again rises, forming another peak at 5.96% and an absorbance height at 374.89 nm and falls at 385.65 nm. It formed a third peak with 6.59% absorbance height at 401 nm and subsequently extended out throughout the visible region with a few small peaks, as shown in Fig. 1(a).



Fig. 1. UV-Visible absorption spectra of the synthesized (a) SnS, (b) SnS (Sb 0.1 wt.%), (c) SnS (Sb 0.2 wt.%), (d) SnS (Sb 0.3 wt.%), (e) SnS (Sb 0.4 wt.%) and (f) SnS (Sb 0.5 wt.%) films.

The synthesized SnS(Sb) films show an absorption spectrum within the range of 320 - 517 nm. The synthesized SnS (Sb 0.1 wt.%) film absorbed light from 320 nm, rose to its maximum peak at an absorbance height of 17.96% and immediately started falling. At 405 nm, the absorbance spectrum of the film widens out and extends to 492 nm, which in turn broadens the spectrum as seen in Fig. 1(b). This trend

was replicated by the other SnS(Sb) films, with varying absorbance heights for each of the films. As shown in Fig. 1(c) -(f), 19.2 % at 352 nm, 34.1 % at 375.5 nm, 47.2 % at 373.1 nm and 60.4 % at 371.5 nm are the absorbance heights with corresponding wavelengths for SnS (Sb 0.2, 0.3, 0.4 and 0.5 wt.%) films, respectively. It was found that doping of SnS with Sb enhanced the absorption spectrum of the SnS film by

(3)

widening the absorption peaks of SnS(Sb) films and consequently broadening the absorption band. It is observed that doping Sb with SnS extends the absorption spectrum of SnS film from 424 nm (ultraviolet edge) to 493 nm, 517 nm, 516 nm and 512 nm (visible region) for SnS (Sb 0.1 wt.%), SnS (Sb 0.3 wt.%), SnS (Sb 0.4 wt5) and SnS (Sb 0.2 and 0.5 wt.%) films, respectively. This interprets that Sb serves as an opaque material in the SnS(Sb) films and opaque materials absorb light more. Similar results have been reported in [8] and [9].

B. Transmittance Spectra

The transmittance of the synthesized SnS and SnS(Sb) films was calculated from the absorbance data using (3) [10], which

$$T = 10^{-A}$$

Where A is the absorbance and T is the transmittance.

Fig. 2(a) – (f) shows the transmittance spectra of the synthesized SnS and SnS(Sb) films. From Fig. 2(a), the SnS film is seen to transmit light from 319.74 nm and continues to increase in wavelength, where it attains 74.14% and begins dropping till 70.61 nm, just before it rises again to 79.2% and begins to increase again. This wavy pattern of transmittance was maintained until it attained a maximum transmittance of 82.98% through the region. The SnS(Sb) films transmitted light at close to 600 nm and increased to 800 nm where it spread out uniformly throughout the region. This trend is identical to the SnS (Sb 0.2, 0.3, 0.4 and 0.5 wt.%) films.



Fig. 2. Transmittance spectrum of the synthesized (a) SnS, (b) SnS (Sb 0.1 wt .%), (c) SnS (Sb 0.2 wt %), (d) SnS (Sb 0.3 wt %), (e) SnS (Sb 0.4 wt %) and (f) SnS (Sb 0.5 wt %) films.

It was observed that the introduction of Sb resulted in a variation in the transmittance value of the SnS film. The transmittance value decreased with increasing content of Sb. When 0.1 wt.% content of Sb was doped with SnS film, the transmittance value was reduced to 80.9%, as shown in Fig.

2(b). Similarly, as shown in Fig. 2(b) - (f), the transmittance value was reduced to 79.9%, 66.1%, 52.1% and 39.4% when 0.2 wt.%, 0.3 wt.%, 0.4 wt.% and 0.5 wt.% content of Sb was added, respectively. Consequently, it unambiguously affirms just as earlier stated in the absorbance spectra, that Sb material

in SnS(Sb) film behaved as an opaque body, as an increase in the Sb content decreases the transmittance value of the SnS(Sb) films. This conforms with reports in [6] and [11].

C. Reflectance Spectra

The reflectance spectrum of each film was calculated using (4) [12]. Equation (4) is a result of the law of conservation of energy, which establishes the relationship between absorbance, transmittance and reflectance given as:

$$A + T + R = 1 \tag{4}$$

Where A is the Absorbance, T is the transmittance, and R is the reflectance.

Fig. 3(a) - (f) below shows the reflectance spectra of the synthesized SnS and SnS (Sb 0.1, 0.2, 0.3, 0.4 and 0.5 wt %)

films. The SnS film started reflecting light at a wavelength of 320 nm at a maximum reflectance value of 1.15%. The reflectance decreased with increasing wavelength, exhibiting a wavy form as shown in Fig. 3(a). This trend was repeated by the SnS(Sb) films. The reflectance values, as shown in Fig. 3(b) – (f), 1.09%, 0.98%, 0.84%, 0.71% and 0.15% are the maximum values for SnS(Sb 0.1, 0.2, 0.3, 0.4 and 0.5 wt%) films respectively. The values of reflectance are very low due to the high absorption rate. However, the decrease in the reflection coefficient with increasing wavelength may be attributed to the dispersion in the semiconductor materials. This agrees with a study by [13].



Fig. 3. Reflectance spectrum of the synthesised (a) SnS, (b) SnS (Sb 0.1 wt %), (c) SnS (Sb 0.2 wt %), (d) SnS (Sb 0.3 wt %), (e) SnS (Sb 0.4 wt %) and (f) SnS (Sb 0.5 wt %) films.

D. Optical Absorption Coefficient

The optical absorption spectrum data were used to evaluate the absorption coefficient, optical band gap energy and nature of transition in the films. The absorption coefficient entails how easily a material (film) can be penetrated by a beam of light and can strongly affect the solar conversion efficiency [5]. The transmittance, reflectance and film thickness are related to the absorption coefficient by the relation given in (5) [14].

$$\alpha = \frac{1}{d} \ln \left(\frac{(1-R)^2}{T} \right) \tag{5}$$

Where, α = the absorption coefficient, d = the film thickness, T = the transmittance and R = the reflectance.

Fig. 4(a) – (f) shows the optical absorption coefficient (α) of the synthesized SnS and SnS (Sb) thin films. Fig. 4(a) shows the synthesized SnS has an absorption coefficient value of 3.94×10^4 cm⁻¹ and gradually decreases with increasing wavelength in a wavy manner. The SnS (Sb) films replicated a similar trend. SnS (Sb 0.1 wt %) film has an absorption coefficient value of 4.85×10^4 cm⁻¹ as shown in Fig. 4(b). Similarly, SnS (Sb 0.2 wt %) film has 4.99×10^4 cm⁻¹ as seen in Fig. 4(c). It is also seen in Fig. 4(d), where the SnS (Sb 0.3 wt %) film had an absorption coefficient value of 2.34×10^5 cm⁻¹. Absorption coefficient values 2.68×10^5 cm⁻¹ and 2.78×10^5 cm⁻¹ were observed for SnS (Sb 0.4 and 0.5 wt%)

films, respectively, as shown in Fig. 4(e) and (f). The thicknesses (in nm) with a step of 0.5 nm measured, 115.21, 115.27, 115.32, and 115.28 nm, respectively. However, the absorption coefficient value was seen to drastically increase when Sb contents (0.3, 0.4 and 0.5 wt %) were added to the SnS film. Thus, introducing Sb into the SnS film improved the absorption edge of the synthesized SnS (Sb) films from 3.94×10^4 cm⁻¹ to 2.78×10^5 cm⁻¹. This is evident in the absorption spectrum of the films. The higher value of absorption coefficient in the range of $10^4 - 10^5$ cm⁻¹ is in line with the high absorbance and low transmittance values, thus, depicting that the films can be used as a good absorber material for solar cell applications.



Fig. 4. Absorption coefficient of the synthesized (a) SnS, (b) SnS (Sb 0.1 wt%), (c) SnS (Sb 0.2 wt%), (d) SnS (Sb 0.3 wt%), (e) SnS (Sb 0.4 wt%) and (f) SnS (Sb 0.5 wt%) films.

E. Refractive Index (η)

The refractive index (n) was calculated from the transmittance and reflectance spectra using (6) [5-6], [12], [15-26]

$$\eta = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{6}$$

Where η is the refractive index, R is the reflectance, and k is the extinction coefficient.

Fig. 5(a) - (f) shows the plot of the refractive index versus the wavelength for the synthesized SnS and SnS(Sb) films. The SnS film has a maximum refractive index of 4.5 and gradually varies to 0.5 as seen in Fig. 5(a). This pattern is

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identical in the SnS(Sb) films except for SnS(Sb 0.1 wt%) film where at 900 nm it becomes uniform and remains uniform throughout the region. The values of refractive indices 4.0, 3.8, 3.65, 3.48 and 1.99 are recorded for the SnS(Sb 0.1, 0.2, 0.3, 0.4 and 0.5 wt%) films respectively as shown in Fig. 5(b) - (f). It is observed that the refractive index of the prepared films decreased with increasing wavelength and a wavy pattern along the trend. This may be attributed to the increase of absorption coefficient indicating the normal dispersion behaviour of the studied films. This strongly agrees with [16].



Fig. 5. Refractive index of the synthesized (a) SnS, (b) SnS (Sb 0.1 wt%), (c) SnS (Sb 0.2 wt %), (d) SnS (Sb 0.3 wt %), (e) SnS (Sb 0.4 wt %) and (f) SnS (Sb 0.5 wt %) films.

F. Optical Bandgap Energy (E_g)

The Tauc and Davis-Mott relation shows the optical band gap dependence on the absorption coefficient (α) as given by (7). This relation is used to study the optical band gap of thin film samples from UV-visible absorption spectroscopy. To obtain detailed information about the optical band gap of the samples, the dependence of the absorption coefficient on the photon energy is analyzed in the high absorption region ($\alpha > 109 \text{ cm}^{-1}$).

$$(\alpha h v)^2 = A \left(h v - E_g \right) \tag{7}$$

Where α is the absorption coefficient, hv is the incident photon energy, n is the nature of transition, E_g is the optical band gap energy of thin film material and A is an energy-independent constant (a parameter that depends on the transition probability also called Tauc parameter). The extrapolations of the linear part of the curve to the "hv" axis determine the E_g . The optical energy gap (E_g) and nature of band transition were obtained in the high absorption region by the Tauc relation [11], [16], [9]. The value of 'n' determines the mechanism of optical absorption whose value is 1/2 for direct allowed transition and 2 for indirect allowed transition [16], [9]. The linear fitting of the data points of the linear portion by taking n = 2 indicates the direct allowed transition between valence and conduction bands in the film. The plot of $(\alpha hv)^2$ versus (hv) gives a straight line and the intercept gives the optical band gap.

Fig. 6(a) - (f) shows the plot of $(\alpha hv)^2$ versus (hv) revealing how the values of E_g for the prepared SnS and SnS (Sb) films were estimated. The E_g in this case was direct (n = 2) and varied between 3.33 and 1.90 eV as presented in Table II. The E_g value of the synthesized SnS was estimated to be 3.33 eV. Consequently, the introduction of Sb into the SnS film varied the Eg values. It is observed that the decrease in the band gap of the SnS (Sb) films was persistent with increasing Sb content. This may be interpreted as due to the phase changes with higher concentrations and incomplete healing during the annealing process is another possibility for

the variation in the E_g . This is very close to the experimental values of E_g 3.31 eV, 2.3 - 2.85 eV and 2.04 - 1.89 eV reported in [6], [15-16], and [26].

| Table II. Estimated values for bandgap (Eg) and Urbach | ι |
|--|---|
| energies (Eu) for the prepared SnS and SnS (Sb) film. | |

| chergies (Eu) for the prepared Sh5 and Sh5 (S0) fifth. | | | | |
|--|---------|-----------|-----------|--|
| Sample | SnS(Sb) | Sb (wt %) | $E_g(eV)$ | |
| 1 | SnS | 0 | 3.33 | |
| 2 | SnS(Sb) | 0.1 | 3.01 | |
| 3 | SnS(Sb) | 0.2 | 2.84 | |
| 4 | SnS(Sb) | 0.3 | 2.71 | |
| 5 | SnS(Sb) | 0.4 | 2.69 | |
| 6 | SnS(Sb) | 0.5 | 1.90 | |



Fig. 6. Optical band gap energy of the synthesized (a) SnS, (b) SnS (Sb 0.1 wt %), (c) SnS (Sb 0.2 wt %), (d) SnS (Sb 0.3 wt %), (e) SnS (Sb 0.4 wt %) and (f) SnS (Sb 0.5 wt %) films.

G. Structural Investigation using X-Ray Diffraction (XRD) Analysis

Fig. 7(a) – (f) shows the XRD patterns of the synthesized SnS and SnS(Sb) films deposited on a glass substrate. The SnS film has peaks at $2\theta = 26.70^{\circ}$, 30.10° , 31.61° , 33.55° , 39.68° ,

42.25°, 47.92°, and 51.86° corresponding to (2 0 1), (0 1 1), (1 1 1), (6 3 1), (3 1 1), (1 0 2), (0 2 0) and (2 0 2) lattice planes respectively, as seen in Fig. 7 (a). These peaks perfectly match the Joint Committee on Powder Diffraction Standards, JCPDS card No: 00-001-0538. Revealing that the sample is

Herzenbergite-SnS with the crystal structure of orthorhombic and falls under the Pbnm space group. Similarly, the synthesized SnS(Sb) films' XRD pattern also matched with the JCPDS card No: 00-005-0562. The matching of the XRD patterns with JCPDS standards endorses and demonstrates the polycrystalline nature of the films.

The 2 θ values of the major peaks for each sample are presented in Table III. When 0.1 wt% of Sb was added to the SnS film, it was observed that new peaks emerged at $2\theta = 29.33^{\circ}$ and 45.41° corresponding to (4 1 6) and (0 2 0) lattice plane respectively, as shown in Fig. 7(b). Also, in addition to

the existing peaks of the SnS (Sb 0.1 wt %) sample, a new peak at $2\theta = 40.79^{\circ}$ appeared when 0.2 wt% of Sb was added to the SnS film as shown in Fig. 7(c). A peak at $2\theta = 49.36^{\circ}$ with a plane (3 0 2) was seen when 0.3 wt% of Sb was added to the SnS film as shown in Fig. 7(d). The emergence of new peaks is identical as Sb content was increased to 0.4 and 0.5 wt% respectively, as shown in Fig. 7(e) and (f). This is due to lattice distortions caused by doping with sb, thereby promoting the ordering and nucleation of crystalline domains, and stabilizing the crystallographic phases.



Fig. 7. Typical XRD patterns of the prepared samples of SnS and SnS(Sb 0.1, 0.2, 0.3, 0.4 and 0.5 wt %) films.

A preferential peak with the plane $(1\ 1\ 1)$ at $2\theta = 31.69^{\circ}$ was predominantly persistent in all the synthesized films (see Table III). The summary of the major peaks with their peak positions (2 θ) and intensities is presented in Table III. It was observed that the peak position of the peaks slightly increased as the intensity of the synthesized films increased with increasing Sb content. Consequently, the increase in the 2 θ of

the peaks indicates broadening of the peaks and translates into enhancement of the crystallinity of the samples [1-4], [6-12], [14-15], [27-41]. Sb has a remarkable effect on the synthesized SnS(Sb) films, such that, the crystallinity of the films increases with increasing Sb content. These results agree with the results reported in [1-4], [6-12], [14-15], and [27-41].

| Sample SnS | 2θ (°) | Intensity (a.u) | Sample SnS | 2θ (°) | Intensity (a.u.) |
|---------------|--------|-----------------|---------------|--------|------------------|
| (Sb 0.0 wt %) | 26.70 | 27.851 | (Sb 0.3 wt %) | 21.96 | 18.074 |
| | | | | 26.70 | 28.879 |
| | 30.10 | 23.307 | | 30.26 | 20.610 |
| | 31.61 | 24.570 | | 31.97 | 25.116 |
| | 33.55 | 22.543 | | 33.55 | 21.105 |
| (Sb0.1 wt %) | 26.83 | 27.810 | (Sb 0.4 wt %) | 21.96 | 22.292 |
| | 29.33 | 23.314 | | 25.65 | 24.109 |
| | 30.79 | 21.838 | | 26.57 | 20.475 |
| | 31.97 | 24.373 | | 31.19 | 26.774 |
| | 33.55 | 22.660 | | 33.42 | 15.840 |
| (Sb 0.2 wt %) | 21.82 | 19.223 | (Sb 0.5 wt %) | 22.04 | 15.840 |
| | 26.55 | 26.909 | | 25.88 | 17.097 |
| | 30.96 | 20.204 | | 26.10 | 14.584 |
| | 31.75 | 24.307 | | 31.30 | 26.774 |
| | 33.79 | 19.877 | | 33.79 | 13.039 |

Table III. Summary of the major peaks with their Peak Positions and Intensities.

H. Scanning Electron Microscopy (SEM)

Fig. 8(a) - (f) shows the surface morphology of the synthesized SnS and SnS(Sb) films as revealed by SEM. It was observed that the surface morphology of SnS and the SnS(Sb) samples were different, due to Sb doping.



The doped films had higher thickness than undoped films as determined using cross-sectional SEM. The films formed were of non-uniformly and sparsely distributed grains, indicating incomplete coalescence during film growth. The morphology exhibited relatively increased densification with the increase in the Sb content and consequently, showed that the addition of Sb content has significant effects on the Sb₂S₃ films. It can be interpreted by the fact that increasing the dopant content increases the kinetic energy and the mobility of the adsorbed atoms on the surface of the films. Hence, adsorbed atoms consequently gain sufficient energy to start a

crystallization process and eventually bring about the growth of grains on the surface of the sample. These results prove that SnS(Sb) films are suitably employable materials for optoelectronics and solar cell applications. This agrees with [32].

I. Energy Dispersion X-ray Spectroscopy (EDXS)

Fig. 9 shows the obtained experimental measurements of the elemental composition of the synthesized SnS and SnS(Sb) films resulting from EDX spectroscopic obtained through EDX analysis. The varying elemental composition of different elements (Sn, Sb, and S) in the SnS(Sb) composite is presented in Table IV. It is observed that the percentage of sulphur varied as seen in the synthesized films. There is no indication of the formation of oxides, so the phase of the deposited material is strictly sulphide.



Fig. 9. EDXS of the Synthesized SnS and SnS(Sb) films. However, with Sn decreasing in atomic percentage, Sb performed contrarily and was seen to increase along the

atomic percentage axis, compared to Sn. This can be attributed to the antimony doping effect, in SnS(Sb), where the Sb atoms could preferentially replace Sn sites or create secondary phases. This substitution can appear as a reduction in Sn content in the primary phase, or it could also be due to the segregation of elements, whereby Sb may form clusters or segregate at grain boundaries, altering the EDX measurements and showing an apparent decrease in Sn concentration. This proves that the addition of Sb content, in an increasing manner to SnS film, had effectively reduced Sn in the film by replacing the Sn atoms Therefore, EDXS analysis validates the increase of Sb content in the compositional ratio of the synthesized SnS(Sb) thin films. This conforms with [9-10], [27-28].

Table IV. The elemental composition of different elements (in atomic percentage (%)) present in the SnS(Sh) composite

| Silb(Sb) composite | | | |
|--------------------|---|--|--|
| S % | Sn % | Sb% | |
| 61.01 | 38.99 | 0 | |
| 54.81 | 34.38 | 10.81 | |
| 54.23 | 31.94 | 13.83 | |
| 54.36 | 28.62 | 17.02 | |
| 56.68 | 21.56 | 21.76 | |
| 57.09 | 18.44 | 24.47 | |
| | S % 61.01 54.81 54.23 54.36 56.68 57.09 | S % Sn % 61.01 38.99 54.81 34.38 54.23 31.94 54.36 28.62 56.68 21.56 57.09 18.44 | |

IV. CONCLUSION

Antimony tin sulphide thin film has been successfully deposited on a glass substrate using spray pyrolysis as the deposition technique. This investigation was conducted to determine how the resulting material finds application in photovoltaics as absorbing materials and to be useful as radiation protection materials for workers in high-radiation environments. The films were annealed at 100 - 400 °C. The optical absorption spectrum shows that the doping of SnS with Sb enhanced the absorption spectrum of the SnS film by widening the absorption peaks of SnS(Sb) films and consequently broadening the absorption band. From the transmittance spectra it was observed that the introduction of Sb varied the transmittance value of SnS film, the value decreased with increasing content of Sb. It can be seen from the XRD that the position of the peaks slightly increased as the intensity of the synthesized films increased with increasing Sb content. The surface morphology of the synthesized SnS and SnS(Sb) films shows that the surface morphology of SnS and the SnS(Sb) samples were different due to Sb doping. The results obtained indicate that the as-prepared films can be applied for radiation protection.

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