

Optical and Electrical Characterization of Tin Sulfide

Okinyi, D.O¹, Gwaro, J.O², Munji M³, Njoroge, W⁴.

^{1,3,4} Kenyatta University, ²Maasai Mara University

Correspondence: dokinyi@gmail.com

Abstract

Alternative sources of clean and more efficient energy are desirable to replace fossil fuels for sustainable

development. Photovoltaic technologies have become major players in the development of renewable sources of

energy using thin film solar cells. In this study, tin sulfide (SnS) films were prepared and deposited using

chemical bath. The preparation of tin chloride was done by weighing different masses to obtain various

concentrations in the range (0.05 - 0.25) M. Tin chloride was then dissolved by adding HCL (5mL). Addition of

HCL made the solution to be transparent. 20mL of 0.1M NA2EDTA acting as a complexing agent was added

into the transparent solution in the beaker and the solution stirred using a glass rod for 4 minutes. Next 20mL

of 0.6M of sodium thiosulfate (source of sulphide) was added and the solution stirred for 4 minutes. Ammonium

was added to the solution to make it alkaline and clean glass slides were vertically placed in the solution without

disturbing it. Optical properties of thin film samples prepared such as transmittance, absorbance and reflectance

in the range of 200nm to 1200nm were measured using UV-VIS NIR Solid Spec 3700 DUV Spectrophotometer

in the range 200nm to 1200nm. The optical measurements were calculated using SCOUT software to determine

absorption coefficient and band gap for all the thin films that were prepared. The sheet resistivity of all the thin

films prepared were measured by using 4-point probe. The tin sulfide films were prepared at a concentration of

0.1M of tin chloride with a thickness of 62 nm used to fabricate the photovoltaic solar cells. The optical and

electrical properties measurements showed that the fabricated solar cell has low transmittance, high absorbance

and suitable narrow band gap for an absorber layer. Based on the optical and electrical values obtained, a p-n

junction was fabricated suitable for solar cell applications.

Keywords: Band Gap, Photovoltaic, P-N Junction, Solar Cell.

Received: 14 July,2022 Accepted: 24 Aug 2022

Published: 9th

Nov 2022



Introduction

The photovoltaic industry is experiencing a lot of research activities that are directed towards the development of new alternative ways of meeting energy demands, since more energy is expected to be consumed by industries and domestic use (Kui-Jui, 2010). Solar energy is available in plenty naturally from the sun hence it has high potential of meeting a large fraction of renewable energy demands. Conversion of solar energy into electricity will be crucial to ever increasing energy demands (Mohd *et al.*, 2011).

Solar energy is an environmental friendly and economically viable clean source of renewable energy. Its tapping is crucial in obtaining an environment free from carbon emissions (Makori, 2013).

Ongoing research on thin film solar cells is mainly on CdTe-CdS and CIGS-CdS due to its high achieved efficiencies of 22.1 % (De Elisa, 2016) and 23.4% (Gedi et al., 2021) respectively. The research has a major setback due to presence of harmful elements (cadmium and selenium) and Tellurium, Indium and Gallium being scarce and expensive (Gedi et al., 2021). In view of the above factors, efforts have been made in developing an environmental friendly absorbers and buffers that are not harmful and abundant in nature. Tin sulfide has drawn much interest in research due to its abundance being non-poisonous and cost effective. It is viewed as a favorable absorbing layer for thin film solar cells because of its magnificent optical and electrical properties. It is a double compound semiconductor comprising of non-poisonous and earth bountiful materials. The band gap energy is 1.35 eV which is near to the optimum value 1.5 eV for maximum absorption of solar energy. The absorption coefficient in the visible region is high (greater than 104 cm-1) (Jacob et al., 2015). The theoretical efficiency is about 32% which is almost equal with silicon based sunlight cells (Araujo et al., 1994). The efficiency recorded so far for SnS based solar cells is merely 4.6% (Sinsermsuksakul et al., 2014). Subsequently, a superior comprehension of the underlying structural, chemical and actual qualities of SnS is expected to accomplish higher efficiencies.

Tin sulfide films have been prepared and deposited using a number of techniques such as thermal evaporation (El-Nahass *et al.*,2002), successive ionic layer deposition (Ghosh *et al.*, 2011) Chemical bath deposition (Sinsermsuksakul *et al.*,2013), spray pyrolysis (Ninan *et al.*, 2016) and atomic layer deposition (Sinsermsuksakul *et al.*, 2014). Films deposited by atomic layer deposition have recorded the best efficiency so far, though the method is slow and expensive. The chemical bath technique has been reported to be a favorable substitute method of deposition (Chao *et al.*, 2011) because it is simple in depositing the low cost of constituent materials of SnS and the fact that the films obtained can occupy large areas.



Optimizing growth conditions (time for deposition and concentration of the solution) is important in order to avoid unnecessary precipitation and any loss of materials during deposition (Higareda-Sanchez *et al.*, 2021).

This research focused on investigating the effect of concentration of tin chloride on the thin films deposited. Effects of varying the concentration on the precursor on optical and structural aspects were studied. Concentration was varied from 0.05~M-0.20~M and deposition time maintained at 50~minutes. SnS thin films of better crystallinity were obtained at 0.1M~SnCl2.

The tin sulfide thin films were prepared by chemical bath technique.

Methodology

Chemical bath technique was used in depositing the tin sulfide thin films. The films prepared by this method were of high quality. This technique of preparing thin films can be deposited on a broader area. The set up below of chemical bath technique was used in the deposition of SnS.

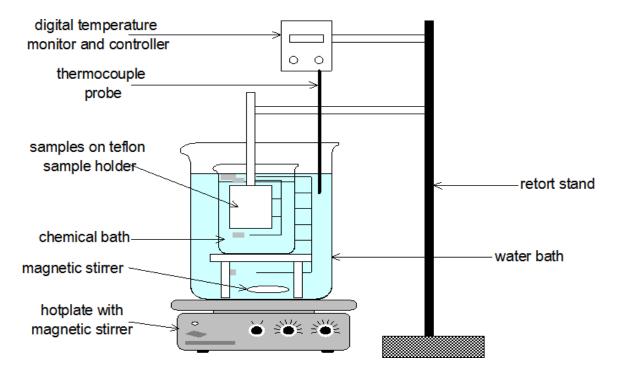


Fig. 1: Set up of Chemical Bath Technique

The following chemicals were used for preparation of SnS thin films; sodium thiosulfate, tin chloride and di-sodium ethylene diaminetetraacetic (Na2EDTA), ammonia and HCl. Tin was obtained from tin chloride. Tin chloride was dissolved by adding hydrochloric acid. Sulfide ions were obtained from sodium thiosulfate. Di-sodium



ethylenediaminetetraacetic (Na2EDTA) was used as a complexing agent. Ammonium was used to change pH of the precursor solution. The complexing agent was to chelate with tin ions. The microscopic substrates were cleaned before deposition by immersing them in ethanol for 10 minutes and later cleaned using distilled water for another 5 minutes.

In order to prepare SnS, specified amount of tin chloride was weighed in a beaker to obtain different concentrations (0.05 M to 0.20 M). The tin chloride was dissolved by adding 5 ml of HCL making the solution transparent. 20 ml of complexing agent (0.1M Na2EDTA) was then added and the mixture stirred well for 2 minutes, 20 ml of sodium thiosulfate of 0.1M concentration added and the solution stirred by using a magnetic stirrer. To change the pH of the solution 1 ml of ammonium was added and obtained solution kept at a constant temperature of 80oC. The substrates were kept vertically for a duration of 50 minutes for deposition to take place. After 50 minutes of deposition, the substrates were removed and cleaned by immersing in distilled water and cleaned deposited films dried for analysis.

Table 1 below shows summary of deposition parameters

Table 1: Deposition parameters of SnS

Parameters/Chemicals	Quantities/Conditions
SnCl2.H2O	25 ml
Na2S2O3	25ml
Na2EDTA	25ml
HCL	5ml
NH3	1ml
Deposition temperature	80oC
Deposition time	50 min
рН	12



Results and Discussions

Optical characterization

The solid spec DUV spectrophotometer was used to obtain reflectance and transmittance data in the wavelength range of 200 nm to 1200 nm. The transmittance data was used in the Scouts software to obtain band gap energy, absorption coefficient and refractive index. Results recorded from Scouts Software were used to determine absorption. The absorption results were also used to determine band gap using equation

(1) below,

$$a hv = (hv - Eg)1/2 (1)$$

where α is absorption coefficient, h is planck's constant (h = 6.63 x 10-34 Js) and v is frequency of incoming photon.

From the graph of (αhv) 2 against hv, band gap was obtained by extrapolating the region that is linear in the graph.

Electrical Characterization

Resistivity of films were measured using 4-point probe method connected to Keithley 2400 source meter. Sheet resistivity was calculated from sheet resistance.

a. Transmittance



The graphs of transmittance against wavelength are as shown in the figure 2 below;

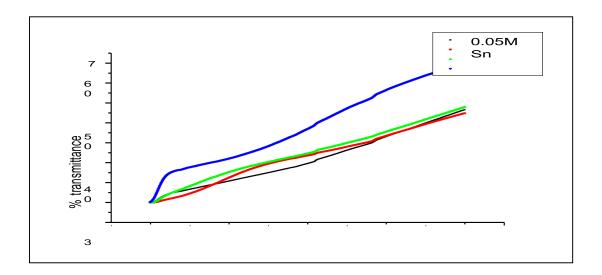


Figure 2: Graphs of transmittance against wavelength at different molarity

From the data obtained, transmittance was changing as the molarity of the tin chloride was changing. Generally, transmittance was between 0.2 – 44% for photons of wavelength between 200 – 1200 nm. The lowest transmittance was obtained for the films deposited with 0.1M SnCl2 and highest was achieved with 0.2M SnCl2. The results can be explained in terms of surface 'roughness'. When the concentration increases, surface 'roughness' increases which reduces transmittance but increases for higher concentrations. The increase in surface roughness is caused by increase of optical scattering that is caused by rough surface morphology.



b. Reflectance

The graphs of reflectance against wavelength at different concentrations is as shown in figure 3

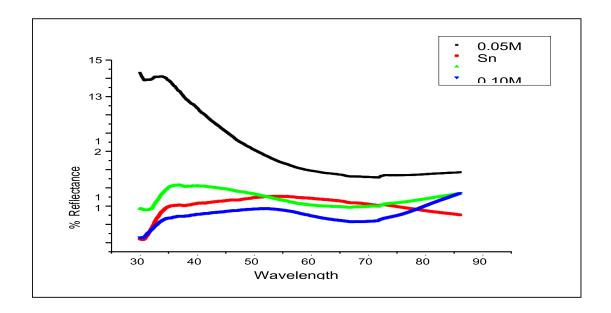


Figure 3: Reflectance versus wavelength at different concentrations

The films obtained showed reflectance ranging between 3-12%. There was a slight increase within the visible region and decreased beyond this region. The lowest

c. Absorption

Absorption of the films samples decreased as the wavelength increased. Absorption of the films was high when the photon energy was greater than the band gap energy. Graphs of absorption against wavelength are as shown in figure 4



The values of absorbance were tabulated within the visible region and recorded as presented on the table 2.

Table 2: Average absorbance and molarity values

Molarity of SnCl2	Average absorption within VIS	Film thickness
0.05	62.45	45.5
0.10	65.98	62.3
0.15	63.68	73.2
0.20	54.31	86.70

The graph of average absorption within the visible region versus concentrations was plotted as shown in figure 5:

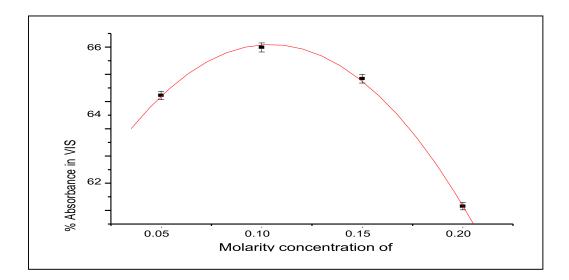


Figure 5: Average absorption versus concentration.

Average absorption is highest at 0.1M SnCl2 which is suitable for an absorber layer.

d. Band gap energy

The band gap energy was obtained by use of equation (1) at various concentration as shown on table 3 below,

Table 3: Band gap energy values at different molarity

Concentration of SnCl2	Band gap, eV
0.05M	1.68



0.10 M	1.61
0.15 M	1.33
0.20 M	1.27

The band gap energy was decreasing as the concentration was increasing. This was due to increase in density of localized states which increases due to increase in film thickness. Band gap against concentration graphs was as shown in figure 6.

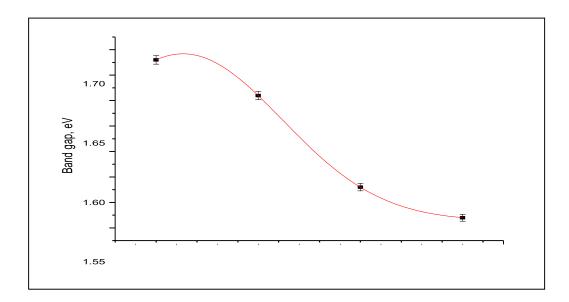


Fig. 6. Band gap energy against molarity for SnCl2.



Table 4: Optimum parameters used in fabrication

Parameter	Unit
Temperature of deposition	80oC
Concentration of SnCl2	0.1 M
Time of deposition	50 minutes
pН	12

e. Resistivity

The 4-point probe method connected to Keithley 2400 source meter was used to obtain resistivity values and recorded on table 5. Conductivity was obtained from resistivity values.

Table 5: Values of resistivity and conductivity

Concentration of SnC12	Resistivity x 10 3 (Ω cm)	Conductivity x 10-3 (Ω cm)-1
0.05	4.078	0.245
0.10	2.081	0.481
0.15	0.337	2.967
0.20	0.335	2.982

From the values of resistivity and conductivity values obtained, the graphs were obtained as in figure 7

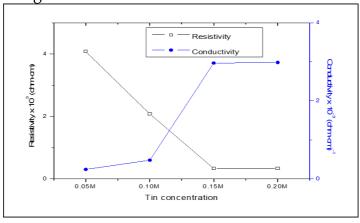


Fig.7: Resistivity and conductivity versus concentration of SnCl2 graphs

As the concentration of SnCl2 increased, resistivity of films decreased. The decrease in resistivity is explained by use of petritz barrier model. Petritz barrier that talks about crystallites not being able to grow large enough at low temperature and that the inter



crystalline regions offer high resistance to movement of charge carriers. The decrease in resistivity is also due improvement of crystallinity of films at higher concentrations (Kumar *et al.*, 2012).

Conclusions

SnS films were successfully deposited on the glass substrate using chemical bath technique. Deposition was done under different conditions (varying concentrations of SnCl2). The electrical and optical properties were studied when molarity of tin chloride was varied. Transmittance of the films within the visible was between 2 – 44%. The films showed a decrease in band gap energy (1.68- 1.37eV) as molarity of tin chloride was increasing (0.05M – 0.20M). Resistivity of deposited films was decreasing (4078 Ω cm - 335 Ω cm).

Recommendation

0.1 M tin chloride was chosen for fabrication of the solar cell due to high absorption and low band gap which is suitable for an absorber layer.



References

- Araujo, G.L., Marti, A. (1994) Absolute limiting efficiencies for photovoltaic energy conversion. *Solar Energy Mater. Sol. Cells* 33, 213-240.
- Chao, G., Honglie, S., Lei, S. (2011) Preparation and properties of zinc blende and orthorhombic SnS films by Chemical bath deposition. *Appl. Surf. Sci*, 257: 6750-6755.
- De Elisa, R. (2016) Cadmium telluride solar cells: Sellenium diffusion unveiled. *Nat. Energy* 1:16143-16146
- El-Nahass, M.M., Zeyada, H.M., Aziz, M.S., El-Ghamaz, N.A. (2002) Optical properties of thermally evaporated SnS thin films. *Opt. Mater* 20: 159-170.
- Gedi, S.; Minnam Reddy, V.R; Kotte, T.R.R; Park, C.; Kim, W.K. (2021) Fundamentals Aspects and Comprehensive Review on Physical properties of chemically grown tin-based binary sulfides 11:1955.
- Ghosh, B., Chowdhury, S., Banerjee, P., Das, S. (2011) Fabrication of CdS/SnS heterostructured device using successive ionic layer adsorption and reaction deposited SnS. *Thin solid Film*. 519: 3368-3372.
- Higadera-Sanchez, A., Mis-Fernandez, R., Rimmaudo, I., Camacho-Epinosa, E., Pena, J.L. (2021) Evaluation of pH and deposition mechanisms effect on tin sulfide thin films deposited by chemical bath deposition. *Superlattices Microstruc*. 151: 106831.
- Jacob, A., Maykel, C., Osvaldo, V. (2015) SnS-based thin film solar cells: Perspectives over the last 25 years. *J. Mater, sci. Electron.* 26: 4541-4556.
- Kuo-Jui H, (2010). *Electron Reflector strategy for CdTe thin-film solar cells*. PhD Thesis. Colorado State University, Department of Physics, USA.
- Makori N.E. (2013). Characterization of SnSe-CdO:Sn p-n Junction for solar cell applications. Msc Thesis. Kenyatta university, Department of Physics, Kenya.
- Mohd A., Syafiq Y., Zainal T. and Wan Y. (2011). Annealing and light effect on structural and electrical properties of thermally evaporated Cu2SnSe3 thin films. *Chemical Engineering and Materials Science*, 2: 103-109.
- Ninan, G.G., Kartha, C.S., Vijayakumar, K.P. (2016) Spray pyrolysed SnS thin films in n and p type: Optimization of deposition process and characterization of samples. *J. Anal. Appl. Pyrolysis* 120: 121-125.
- Sinsermsuksakul, P., Hartman, K., Kim, S.B., Heo, J. (2013) Enhancing the efficiency of SnS Solar cells via band-offset engineering with zinc oxysulfide buffer layer. *Appli. Phys. Letter.* 102: 053901.



Sinsermsuksakul, P., Sun, L., Lee, S.W., Park, H.H., Kim, S.B., Yang, C., Gordon, R.G. (2014) Overcoming Efficiency Limitations of SnS-based solar cells. *Adv. Energy Mater.* 4: 1400496.