

Optical and Electrical Analyses of Thallium Sulphide Thin Films

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Abstract: In this paper, suitability of Thallium Sulphide films were investigated as an alternative to conventional silicon and germanium that were used as window layers in solar cells. Thin films were deposited on soda lime glass (SLG) substrates in a chemical bath containing Thallium Chloride (TlCl₂) and Thiourea (NH₂)₂CS which was conditioned at 80 °C for about 5 hours to deposit the films. Effects of annealing on the film samples at 300 °C and 350 °C were studied respectively by use of UV-VIS Avantes electrophotometer and Four-Point-Probe (FPP) machine in the light region with wavelength range from 200 nm to 1000 nm. The results obtained suggest that the thin films obtained are good materials for optoelectronics. The absorption spectra exhibited a relatively high energy band-gap. Materials of this nature are good for window layers which serve as passage to the absorber layer where needed charge carriers are produced.

Keywords: Thin film, Thallium Sulphide, Window layer, Optoelectronics and solar cell.

Introduction

The group-III elements contain Thallium which forms compounds such as TlSe (tetragonal, $E_g = 0.75\text{eV}$), TlS (tetragonal, $E_g = 1.37\text{eV}$), Tl₂S (tetragonal, blue-black), Tl₂S₃ (amorphous, black), CuTlS₂ (chalcopyrite, $E_g = 1.39\text{eV}$, estimated), TlBiS₂ (rhombohedral, $E_g = 0.40\text{eV}$), TlSbS₂ ($E_g = 1.42\text{ eV}$) etc. Thus, thallium could be at (+3), (+1), or mixed oxidation states, offering also the possibility of transforming oxidation states during solid state reactions. One may note that thallium sulphide as a photoconductor and photovoltaic material has been known since 1930's; but the use of thallium compounds has been almost eliminated in subsequent years [1]. However, an attraction which thallium may still offer as a Group-III heavy-element is its price. In bulk metal form of

99% purity, it costs in commercial quantities about US \$ 100 per kilogram - typically one twentieth as that of indium. The strategy to utilize thallium to replace some amount of indium and gallium in solar cell technology might relieve the pressure on the availability of these two elements indispensable in optoelectronic device technologies. Thin films have a number of applications in various fields ranging from coatings, interference filters, polarizer, narrow band filters, solar cells, photoconductors, IR detectors, waveguide coatings, magnetic and superconducting films and microelectronic devices [2; 3]. Ternary compounds of thallium, which include TlSbS₂, have a reported optical band gaps (E_g) of 1.7eV [4] and 1.85eV. Generally optical band gap in

the range between 1.00eV and 2.00eV suggests possible application as absorber materials in solar cell. [4] who deposited thallium antimony sulphide and thallium bismuth sulphide thin films produced by heating chemically deposited multi-layers. They reported the formation of these materials in thin film form by heating in nitrogen of chemically deposited $\text{Sb}_2\text{S}_3 + \text{Tl}_2\text{S}$ and $\text{Bi}_2\text{S}_3 + \text{Tl}_2\text{S}$ thin films [5]. The study was motivated by their success in producing Cu_3BiS_3 , CuSbS_2 and InSbS_3 thin films by heating chemically deposited $\text{Bi}_2\text{S}_3\text{-CuS}$, $\text{Sb}_2\text{S}_3\text{-CuS}$ and $\text{Sb}_2\text{S}_3\text{-In}$ (indium by thermal evaporation) thin film coatings at temperatures of 250 °C - 400 °C in a nitrogen atmosphere. They felt that the very fine crystalline grains (of <5nm in diameter) inherent in chemically deposited semiconductor thin films promote interfacial diffusion of the atoms and led to the formation of compounds at a temperature lower than what is required for their formation by sintering stoichiometric elemental mixtures. Given the fact that the films are of low band gaps and show poor transmission of visible light, they could find potential applications as solar cell absorbers [5]. These processes require the use of sophisticated machines and lots of time consumed. Bearing these potentials in mind, there is increasing demands for renewable energy as the alternative to present epileptic power supply for economic growth. Solar cells have been made majorly from Germanium and Indium. The idea of seeking alternative base material to give room for the vast demand for optoelectronic devices has been considered. This work is also propelled to focus on an alternative technique to produce good quality solar absorber that is eco-friendly. That informs the need to investigate Thallium sulphide for suitability as optoelectronic material for solar applications.

Materials and Methods

The CBD bath for Thallium Sulphide film deposition was obtained by using Trisodium Citrate (TSC) ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) as complexing agent for Thallium Chloride (TlCl_2) which served as precursor for Tl^{2+} and Thiourea (NH_2)₂CS which served as precursor for S^{2-} . 20 ml of 0.5M Thiourea, 10ml of 1.0 M Thallium chloride (TlCl_2) solution and 1ml of 0.5M Trisodium Citrate were added into 100 ml beaker. Then 40ml of distilled water was added to the solution and then gently stirred at room temperature to

obtain a homogenous solution. 2ml of 0.3M Ammonia (NH_3) was added in drops till an alkaline solution with pH of 8.0 was attained, as measured with Mettler Toledo AG 8603 pH meter. The mixture was immersed into a heated water bath with continuous stirring. Well prepared glass slides (3 pieces) were introduced into the mixture at 80 °C and film deposition allowed for 5 hours. After the deposition, the substrates were removed, rinsed with distilled water and allowed to dry in air. Two sample were labelled A and B for annealed at 300 °C and 350 °C respectively to study the effect of annealing on the deposited films while the third sample served as the control referred to as *deposited* subsequently.

Results and Discussion

Optical Characteristics of Thallium Sulphide Films

As obtained from Avantes UV-VIS spectrophotometer in the range 200-1000 nm, reflectance graphs of TIS thin films are shown in Fig. 1 for the deposited, annealed at 300 °C and at 350 °C respectively. They are found to vary from 7 % to 15 % at initial state. Average reflectance was found to be below 30% for all films. The film for TIS annealed at 350 °C had the lowest reflectance of about 28 % compared to the deposited which has 30 %. The reflectance spectra show that the presence of heat in TIS thin films reduces reflectance of the films in the visible range, showing that annealing at higher temperature reduces the reflectance characteristics. This is in consonance with [6] who reported ZnS:Sn thin films for use in solar cells.

The transmittances of the films vary between 80 % and 90 % with a reduction in transmittance as the annealing temperature increases. Fig. 2 shows the transmittance spectra which indicate average transmittances of 80 % at $\lambda=800$ nm. This reveals that some states have been created in the Fermi-level between the conduction and valence band. This can also be attributed to the increase in fundamental absorption as photon striking increases with increase in carrier concentration [7]. This fairly high value suggests the suitability of the films for window layers in solar cells.

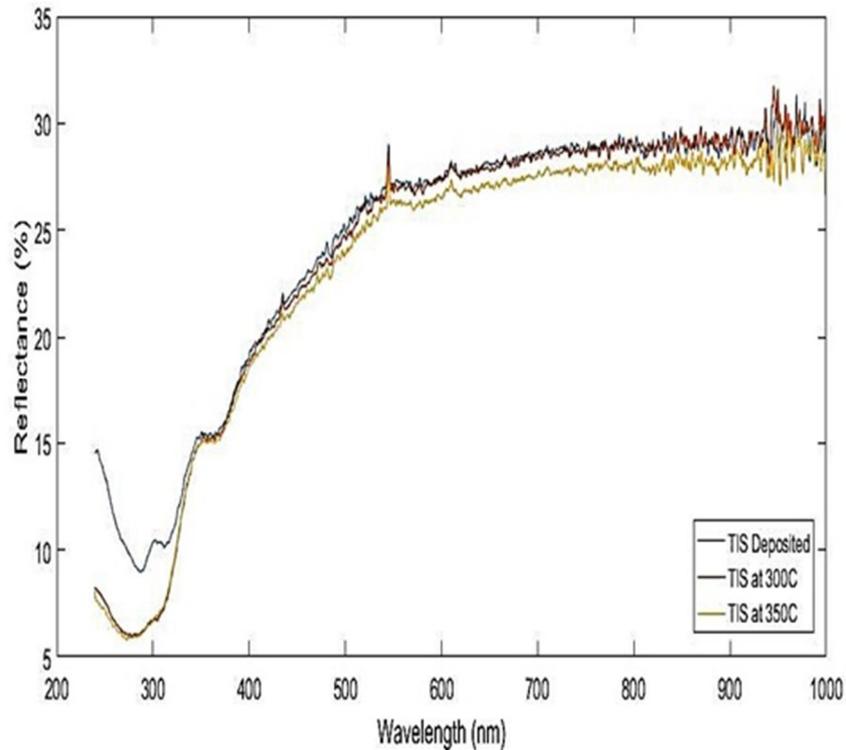


FIG. 1. Graph of reflectance against wavelength for TIS films.

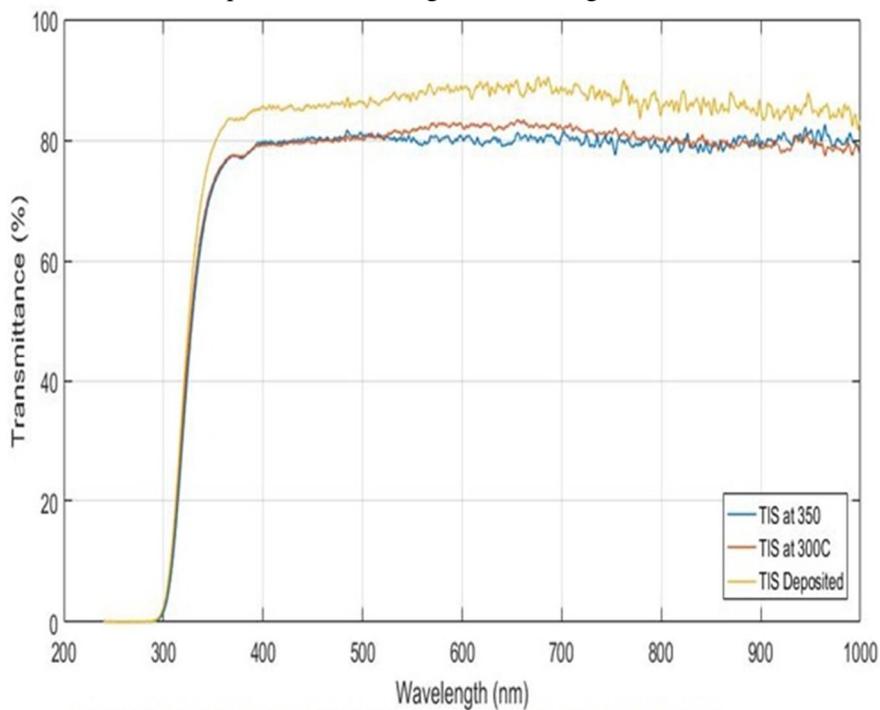


FIG. 2. Graph of transmittance against wavelength for TIS films.

In Fig. 3, it is obvious that TIS thin films have good absorbance at short wavelength region. A record of about 3.25 %, 3.28 % and 3.3 % were obtained for deposited, annealed at 300 °C and annealed at 350 °C respectively [8]. The absorbance values for all the films were calculated from transmittance and reflectance data using the expression [9]:

$$T + R + A = 11$$

$$\text{So that } A = 1 - [T + R]$$

where;

T = percentage transmittance;

R = percentage reflectance and

A = absorbance

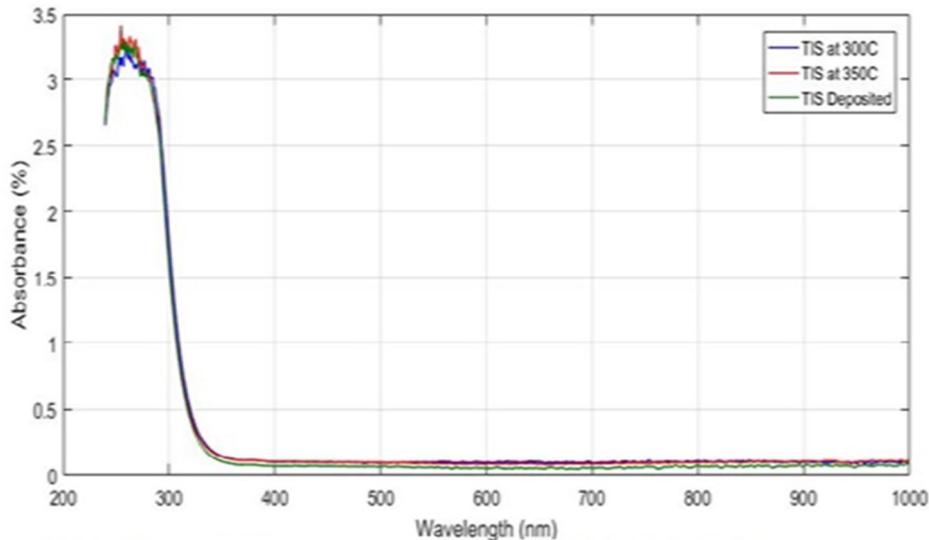


FIG. 3. Graph of absorbance against wavelength for TIS films.

The absorption decreased with increasing wavelength of solar radiation. Increase in absorption occurs when the photon energy reaches the value of the energy gap where electron transfers occur between the valence band and conduction band. The lowest absorbance of 0.2 % was recorded for TIS deposited while the highest of 0.25 % was for TIS film annealed at 350 °C at wavelength of 900 nm.

The energy band-gaps of the films were relatively high. The values obtained were 3.9 eV, 3.92 eV and 3.94 eV respectively for deposited, annealed at 300 °C and annealed at 350 °C. These band-gap values speak in the same direction with the results of [10] obtained in determination of optical properties of ZnS thin films which were

in the range 3.64 eV to 4.00 eV. Band gaps were obtained by plotting $(\alpha h\nu)^2$ against $(h\nu)$ and extrapolating the linear part. By extrapolating the linear portions of the plots of $(\alpha h\nu)^2$ against $(h\nu)$ to where $(\alpha h\nu)^2 = 0$, the value where the extrapolated line cuts energy $(h\nu)$ axis indicates the band gap [11]. The band-gap of the window layer should be as high as possible and the layer should be as thin as possible to maintain low series resistance [12]. That condition certifies the need for window layer which should not absorb any of the incident light but allows maximum photon energy to reach the absorber layer where the energy is needed for generation of electrons. Fig. 4 shows the energy band-gap graphs for TIS deposited, and annealed samples at 300 °C and 350 °C respectively.

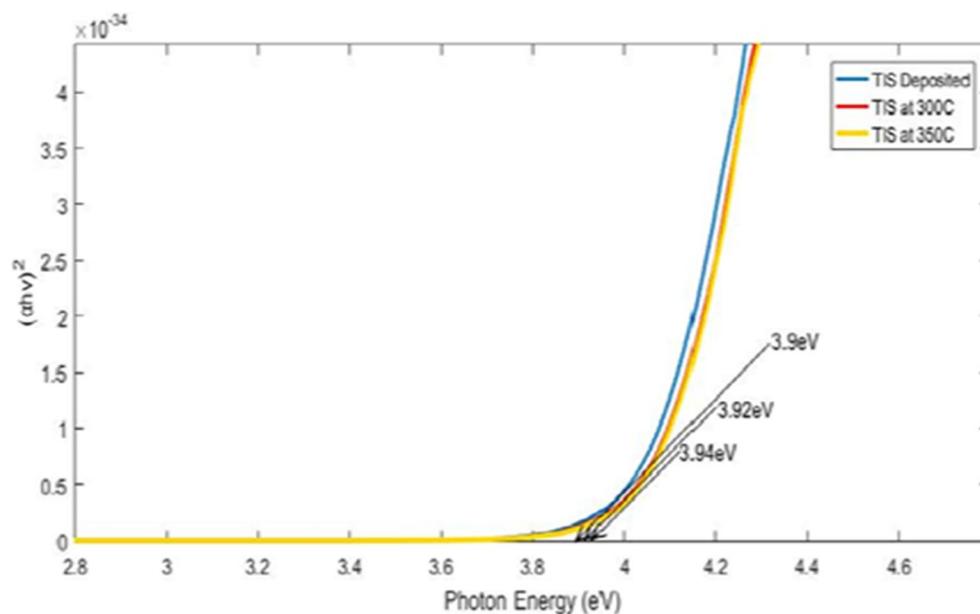


FIG. 4. Graph of $(\alpha h\nu)^2$ against wavelength for TIS films.

Electrical Properties of TIS Thin Films

The TIS samples were examined with the four point probe (FPP) machine for measurement of film current and voltage. The values for the sheet resistance (R_s), resistivity (ρ) and conductivity (σ) are presented in Table 1. The resistivity reduces from $2.003 \times 10^6 \Omega\text{m}$ to $0.34 \times 10^6 \Omega\text{m}$

for deposited and annealed at 350°C as the annealing temperature increases. The corresponding conductivity increased from $4.99 \times 10^{-7} \text{Sm}^{-1}$ to $2.92 \times 10^{-6} \text{Sm}^{-1}$. This enhances the electrical property of the film and makes it useful material for solar applications [13].

TABLE 1: Electrical Properties of TIS

Sample	Voltage (V)	Current (A)	Sheet Resistance, R_s (Ωm^{-2})	Resistivity (Ωm)	Conductivity (Sm^{-1})
Deposited	1.32×10^{-1}	5.86×10^{-8}	1.001×10^7	2.003×10^6	4.99×10^{-07}
Annealed at 300°C	3.04×10^{-1}	4.81×10^{-8}	2.87×10^7	5.74×10^6	1.74×10^{-07}
Annealed at 350°C	2.79×10^{-1}	7.41×10^{-7}	1.71×10^6	0.34×10^6	2.92×10^{-06}

Conclusion

Thallium Sulphide thin film has been successfully deposited by CBD in the laboratory. The transmittances of the films vary between 80 % and 90 % with a reduction in transmittance as the annealing temperature increases. This is an indication that good solar material could be obtained at low temperatures. The film for TIS annealed at 350°C had the lowest reflectance of about 28 % compared to the deposited which has 30 %, showing that annealing at higher temperature reduces the reflectance characteristics. The energy band-gaps of the films were relatively high. The values obtained were 3.9 eV, 3.92 eV and 3.94 eV respectively as annealing temperature increased. This implies

that the film will be good materials for window layers in solar applications. The resistivity reduces from $2.003 \times 10^6 \Omega\text{m}$ to $0.34 \times 10^6 \Omega\text{m}$ as the annealing temperature increases while the corresponding conductivity increased from $4.99 \times 10^{-7} \text{Sm}^{-1}$ to $2.92 \times 10^{-6} \text{Sm}^{-1}$. This enhances the electrical property of the film and makes it useful as material for solar applications.

It is hereby recommended that further investigations be done on the effect of concentration of the deposition bath on the quality of the films obtained for enhanced performance.

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