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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 ($TlCl_2$) and Thiourea $(NH_2)_2CS$ which was conditioned at 80 $^{\circ}$C for about 5 hours to deposit the films. Effects of annealing on the film samples at 300 $^{\circ}$C and 350 $^{\circ}$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, Solar cells.

Introduction

The group-III elements contain thallium which forms compounds, such as TISe (tetragonal, Eg = 0.75eV), T1S (tetragonal, Eg = 1.37eV), $T1_2S$ (tetragonal, blue-black), $T1_2S_3$ (amorphous, black), $CuTlS_2$ (chalcopyrite, Eg = l.39eV, estimated), $TlBiS_2$ (rhombohedral, Eg = 0.40eV), $TlSbS_2$ (Eg = 1.42 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 the 1930s, 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, polarizers, 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 $TlSbS_2$, have reported optical band gaps (Eg) 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

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solar cells. Estrella *et al*. [4] 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 $Sb_2S_3 + Tl_2S$ and $Bi_2S_3 + Tl_2S$ 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 Bi_2S_3–CuS, Sb_2S_3–CuS and Sb_2S_3–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 lead 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 are 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 materials 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 a good-quality solar absorber that is eco-friendly. That informs the need to investigate thallium sulphide for suitability as an optoelectronic material for solar applications.

Materials and Methods

The CBD bath for Thallium Sulphide film deposition was obtained by using Trisodium citrate (TSC) ($Na_3C_6H_5O_7$) as a 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, 10 ml of 1.0 M thallium chloride ($TlCl_2$) solution and 1ml of 0.5M Trisodium citrate were added into a 100 ml beaker. Then, 40 ml 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 (NH3) 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 samples were labelled A and B for annealing 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 spectroph otometer in the range 200-1000 nm, reflectance graphs of TlS thin films are shown in Fig. 1 for the films deposited, annealed at 300 °C and at 350 °C, respectively. They were found to vary from 7 % to 15 % at initial state. Average reflect ance was found to be below 30% for all films. The film for TlS annealed at 350 °C had the lowest reflectance of about 28 % compared to the deposited film which has 30 %. The reflectan ce spectra show that the presence of heat in TlS thin films reduces reflectance of the films in the visible range, showing that annealing at higher temperature reduces the reflectance characteristi cs. This is in consonance with Wanjala *et al*. [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 λ=800 nm. This reveals that some states have been created in the Fermi-level between the conduction band and the 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.

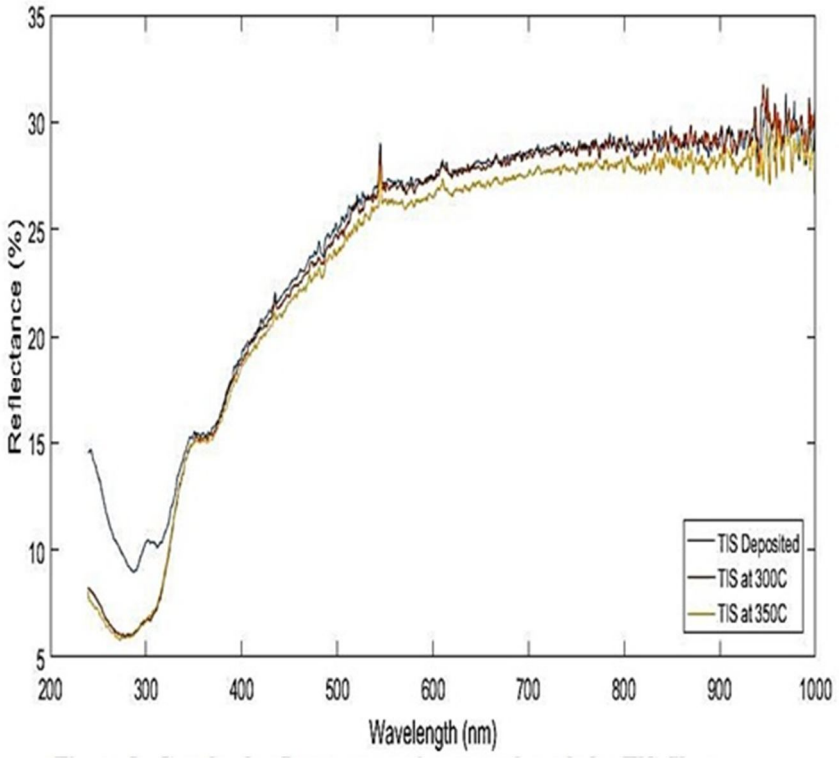

FIG. 1. Graph of reflectance against wavelength for TIS films.

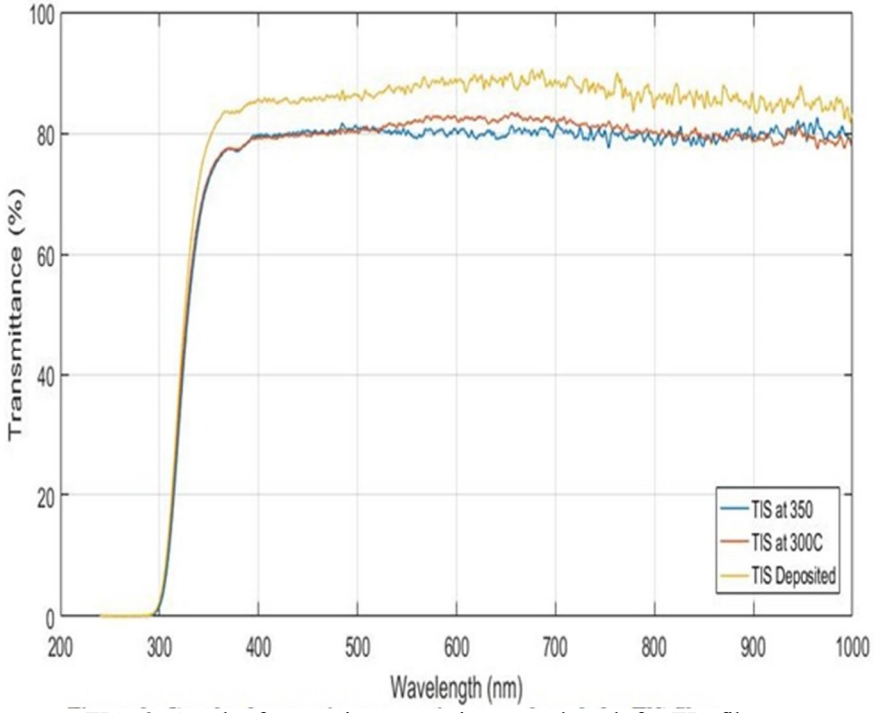

FIG. 2. Graph of transmittance against wavelength for TIS films.

In Fig. 3, it is obvious that TlS thin films have good absorbance in the short wavelength region. Records of about 3.25 %, 3.28 % and 3.3 % were obtained for films 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]:

$$T + R + A = 11$$

So that $A = 1 - [T + R]$

where;

$T = percentage\ transmittance$,

$R = percentage\ reflectance\ and$

$A = absorbance.$

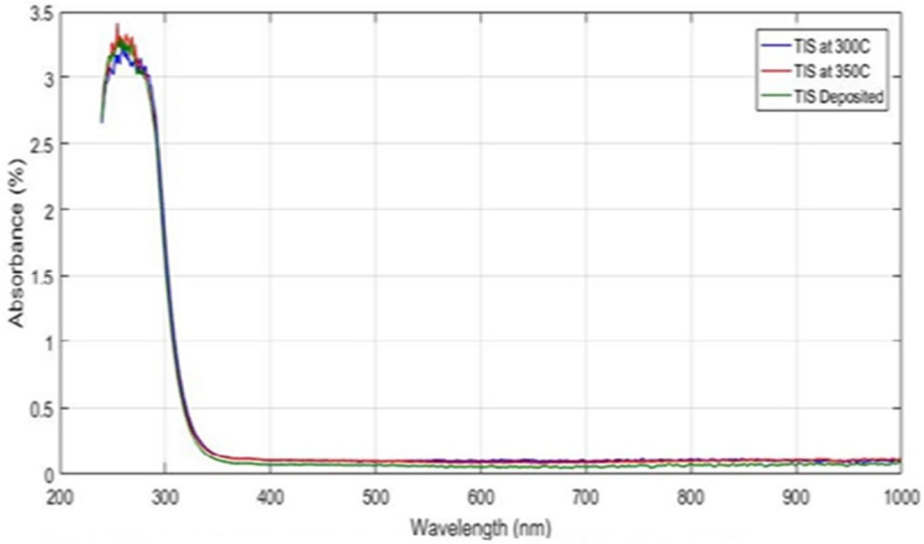

FIG. 3. Graph of absorbance against wavelength for TIS films.

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 the conduction band. The lowest absorbance of 0.2 % was recorded for TlS deposited film, while the highest of 0.25 % was recorded for TlS film annealed at 350 °C at a 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 films deposited, annealed at 300° C and annealed at 350° C. These band-gap values speak in the same direction as the results of [10] obtained in the determination of optical properties of ZnS thin films which were in the range from 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 (hv) to where $(\alpha h\nu)^2 = 0$, the value where the extrapolated line cuts energy (hv) 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 TlS films deposited and annealed samples at 300 °C and 350 °C, respectively.

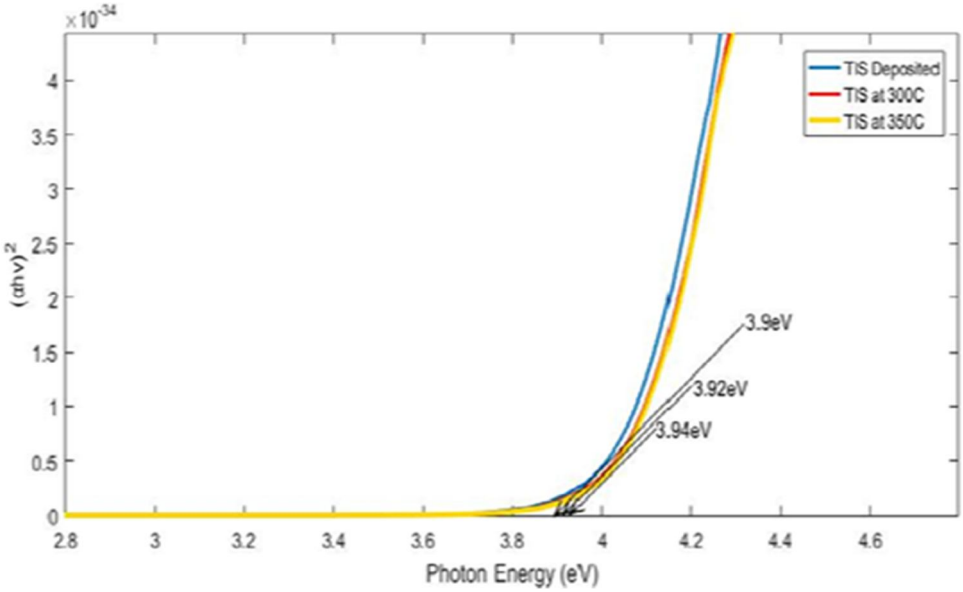

FIG. 4. Graph of $(\alpha h\nu)^2$ against wavelength for TIS films.

Electrical Properties of TlS Thin Films

The TlS 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 x 10^6 Ωm to 0.34 x 10^6 Ωm for deposited and annealed at 350 °C samples as the annealing temperature increases. The corresponding conductivity increased from 4.99 x 10^{-7} Sm^{-1} to 2.92 x 10^{-6} Sm^{-1}. This enhances the electrical property of the film and makes it useful material for solar applications [13].

TABLE 1. Electrical properties of TlS

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

Conclusion

Thallium sulphide thin films have 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 materials could be obtained at low temperatures. The film for TlS annealed at 350 ° C had the lowest reflectance of about 28 % compared to the deposited one 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 films will be good materials for window layers in solar applications. The resistivity reduces from 2.003 x 10^6 Ωm to 0.34 x 10^6 Ωm as the annealing temperature increases, while the corresponding conductivity increased from 4.99 x 10^{-7} Sm^{-1} to 2.92 x 10^{-6} Sm^{-1}. This enhances the electrical property of the film and makes it useful as a 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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