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Annealing Effect on Optical Properties of Thalium Sulphide (Tl_2S) Thin Films

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Abstract: ***This paper investigates the effect of heat treatment on the optical properties of Thalium Sulphide (Tl_2S). Interest in the binary and ternary thin films has led to increased research in photovoltaic. Tl_2S thin films have a number of applications in various fields. The layers of thallium sulphides are commonly produced by the deposition method from chemical solutions. The chemical bath solution was obtained by preparing obtained by adding 20 ml of 0.5M Thiourea-(a precursor for Sulphur), 10ml of 1.0M Thallium chloride (TlCl) solution –(a Thalium precursor) and 1ml of 0.5M Trisodium Citrate into 100ml beaker as a complexant. 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 until a pH of 8.0 was reached. The bath pH of the solution was measured with Mettler Toledo AG 8603 pH meter. Finally, the substrates were immersed into the precursor and deposit for 6 hrs at about 70 ^oC. The substrates were removed, rinsed with distilled water and allow air-drying after the deposition. One sample was labelled as-deposited with two others annealed at temperature 300$^°$ C and 350$^°$ C respectively to study the effect of annealing on the deposited films. The results show that the presence of heat in Tl_2S thin films increases its properties such as reflectance of the films in the visible range, higher absorption and energy band-gap. Conversely, increase in heat treatment brought about decrease in transmittance properties of Tl_2S.***

Keywords: Annealing, Chemical Bath Deposition (CBD), Thalium Sulphide (Tl_2S), Thin Film, Optical properties.

1. Introduction

Thallium belongs to Group-III in the periodic table and it could form compounds like Thaliumselenide (TISe) , Thalium sulphide (T1S), Thalium II sulphide ($T1_2S$), Thalium III sulphide ($T1_2S_3$) etc. Thus, thallium could be at (+3), (+1), or mixed oxidation states, offering also the possibility of transforming oxidation states during solid state reactions. Interest in the binary thin films has led to increased research in this area. 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 (Mane *et al.*, 2000; Janickis *et al.*, 2004). Many metal sulphide compounds have excellent optical properties in the visible and IR region of solar spectrum (Gopal and Harrington, 2003). Electrical conductivity of thallium sulphide changes with exposure to infrared light, therefore making this compound useful in photocells. The layers of thallium sulphides are commonly produced by the deposition method from solutions (Estrella *et al.*, 2002). The earlier reports (Grigas *et al.*, 1976; George and Radhakrishnan, 1980; Mandaland Mondal, 1990) of antimony sulphide, is on its applications in microwave devices, switching, television cameras as target materials, and in various optoelectronic devices. Vacuum evaporation techniques (Grigas et al, 1976; George and Radhakrishnan, 1980; Mady *et al.*, 1988) and chemical bath deposition techniques (Nair *et al.*, 1998; Rodríguez-Lazcano *et al.*, 1999) have been reported for the preparation of thin films of Sb_2S_3. With an optical band gap in the range of 1.06eV to 1.88eV in crystals and in polycrystalline thin films with V_2-V_{I3} composition (Nair *et al.*, 1989), the sulphides and selenides of antimony are potential absorber materials in devices for photovoltaic conversion of solar energy.

The use of Sb_2S_3 thin films in Schottky barrier solar cells of p-Sb_2S_3 (Nair *et al.*, 1998) and n-Sb_2S_3/p-Ge (Simon, 1981) structures with conversion efficiencies of 5.5 and 7.3 %, respectively, has been reported. Tl_2S thin film was reported to have an indirect optical band gap of about 1.00eV (Madelung, 1992). Tl_2S-Sb_2S_3 films, which when annealed led to the formation of $TlSbS_2$ with direct band gap of 1.92eV has also been reported (Gasser *et al.*, 1996). Ternary compounds of thallium, which include $TlSbS_2$, have a reported optical band gaps (Eg) of 1.7eV (Estrella et al, 2002) and 1.85eV (Tauc *et al.*, 1966). Generally optical band gap in the range between 1.00eV and 2.00eV suggests possible application as absorber materials in solar cell.

2. Experimental Details

The bath for Thallium Sulphide growth was obtained by adding 20 ml of 0.5M Thiourea-(a precursor for Sulphur), 10ml of 1.0M Thallium chloride (TlCl) solution –(a Thalium precursor) and 1ml of 0.5M Trisodium Citrate into 100ml beaker as a complexant. 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 untill a pH of 8.0 was reached. The bath pH of the solution was measured with Mettler Toledo AG 8603 pH meter.Thin films were deposited on glass substrates (76.2mm x 2.5mm x 1.2mm) which were immersed vertically into the precursors contained in beakers which served as the baths for deposition. The substrates were kept vertically and at the centre of the beaker to prevent them from leaning against one another and walls of the bath. The deposition was carried out at 70 $^°$ C for 6 hours. After the deposition, the glass slides were removed, rinsed with distilled water and allowed to dry in air. It is common for the chemically-deposited samples to be contaminated with oxygen from the environment as the sample was exposed to the environment during preparation. Oxygen contamination was removed during the annealing process. One sample was labelled as-deposited which serves as control with two others annealed at temperature 300° C and 350° C respectively to study the effect of annealing on the deposited films.

3. Band Gap Estimation

The band gap of the deposited film defines how applicable the film is. The direct energy gap values were calculated by using Tauc's relation:

$$\alpha (hv) = A^* (hv - E_g^{opt})^r \quad (1)$$

where:
A = Constant,
r = ½ for direct band gap of the materials
The energy E was obtained by the relation;

$$E = \frac{hc}{\lambda} \quad (2)$$

Where;
h = planck's constant
c = velocity of light
λ = wavelength (nm) of incident beam.

The band gap energy for direct band gap materials was obtained by plotting a graph of $(\alpha hv)^2$ against photon energy, hv (eV). The value of the band gap was taken by extrapolating the linear region of the resulting curves to zero absorption coefficient (hv axis) of the graph to get the energy in eV.

4. Results

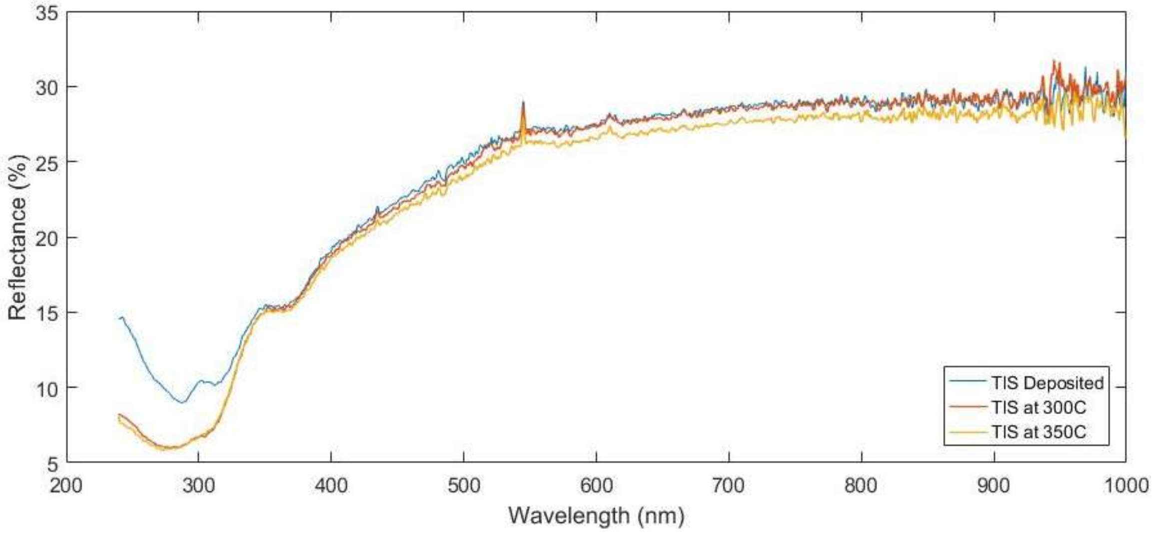

Figure 1: Graph of reflection for TlS films

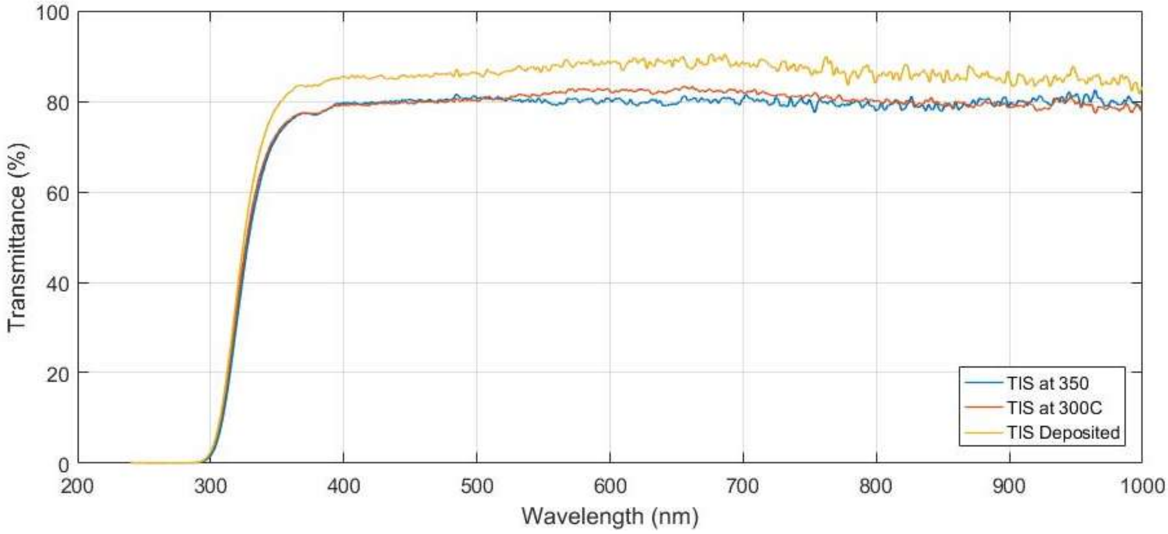

Figure 2: Graph of Transmission for TlS films

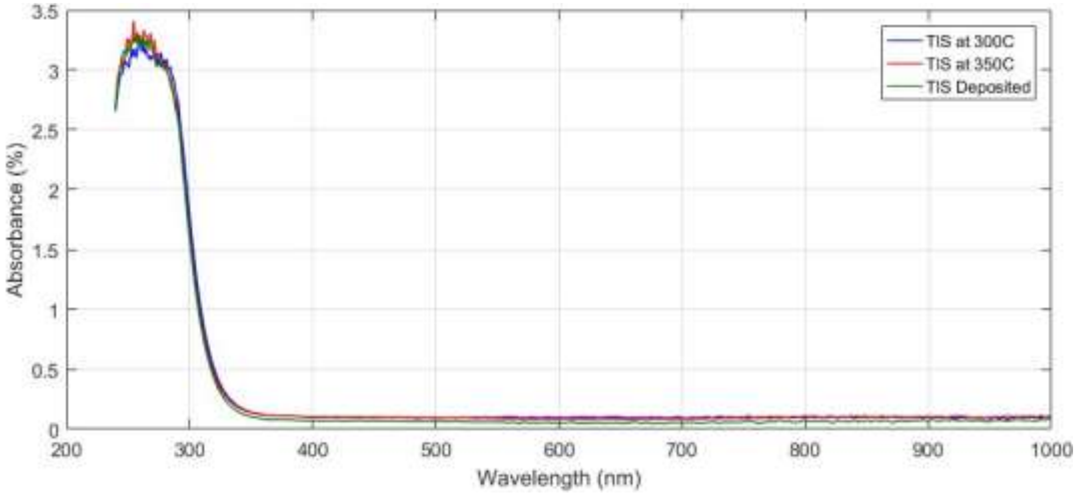

Figure 3: Graph of Absorption for TlS films

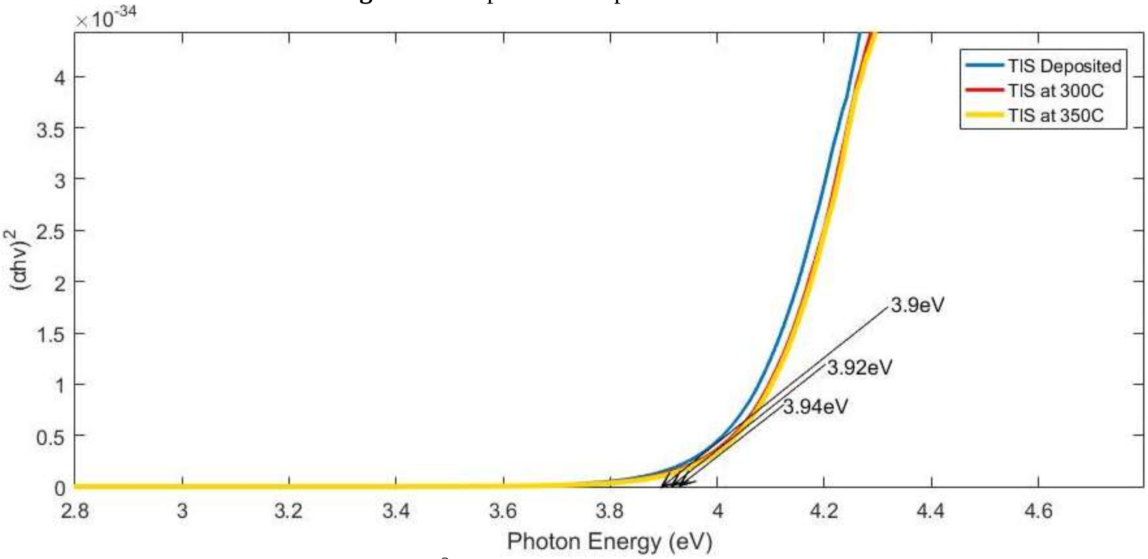

Figure 4: Graph of $(\alpha hv)^2$ against Photon Energy (Band gap) in eV for TlS

5. Discussion

The optical analyses data were obtained from Avantes UV-VIS spectrophotometer in the range 200-1000nm. Figure 1 shows the reflectance graphs of Tl_2S thin films for deposited, annealed at 300° C and annealed at 350° C. They are found to be varied from 8-15% at initial state. Average reflectance was found to be below 30% for all films. The film for Tl_2S annealed at 350 ° C had the lowest reflectance of about 28% compared to the deposited which has 30%. The results show that the presence of heat in Tl_2S thin films increases reflectance of the films in the visible range. And this proves that annealing at higher temperature reduces the reflectance properties. This agrees with the work of Wanjala *et al.* (2016), who reported that it is imperative for reflectivity to be as low as possible for solar applications. It therefore shows that the thin film is a useful material for the window layer part of the solar cell. Figure 2 reveals that all the films exhibited transmittances above 40% for wavelength above 350 nm. Below 320 nm there was a sharp fall in the percentage transmittance of the films which indicates a strong increase in photon absorption. This is in agreement with the work of Kim *et al*. (2009). It 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 (Kumar and Sankaranarayanan, 2009). Average transmittances at λ=800 nm were found to be around 80% , this high percentage of transmission suggests the suitability of the Tl_2S for window layers in solar cells. From Figure 3, Tl_2S thin films have good absorption at short wavelength region, about 3.25%, 3.28% and 3.3% for as- deposited, annealed at 300° C and annealed at 350°C respectively. The absorption decreased with increasing wavelength of solar radiation. The 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 Tl_2S deposited while the highest of 0.25% was for Tl_2S film annealed at 350° C at wavelength of 900nm. This reveals that increase in annealing temperature brought about higher absorption. From Figure 4, the band-gap graph for Tl_2S indicates relatively high energy values. The energy band gap values were 3.9eV, 3.92 and 3.94eV respectively for as-deposited, annealed at 300° C and 350° C respectively. And this shows that increase in annealing temperature, increases energy band gap of Tl_2S. These values are similar to the work Leshi, 2018 who deposited Thalium Cuprate and Thalium Sulphide thin films for renewable energy applications. Also these values are in agreement with the work of Rahdar *et al.* (2012) who obtained the range between 3.64eV and 4.00eV while determining the optical properties of ZnS. 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 (Banerjee and Chopra, 1985). This is to ensure the window layer does not absorb any of the incident light and to allow maximum photon energy to reach the absorber layer where it is needed for generation of electrons.

6. Conclusion

Thalium Sulphide (Tl_2S) thin films deposited through CBD gave high absorbance in the UV-VIS region of light where photons needed for solar application are found. Therefore they are good materials for the absorber layer of solar cells. The high band-gaps obtained from the absorption coefficients of the thin films indicate its suitability for window layers where the layer is not meant to absorb photons for generation of carriers. The results show that the presence of heat in Tl_2S thin films increases reflectance of the films in the visible range, higher absorption and energy band-gap. Conversely, increase in heat treatment brought about decrease in transmittance properties of Tl_2S which make it a good material for window layer in solar cell.

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