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Opto-Electrical Characterization of Chemically Deposited Tin Bismuth Sulphide (TBS) Thin Film for Solar Energy Application

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Abstract*— Research on Tin Bismuth Sulphide (SnBiS2)(TBS) attracts a lot of interest due to its many applications. Chemical bath deposition (CBD) is a relatively inexpensive, simple and convenient technique for large area deposition of thin films at low temperatures. CBD emerges as an excellent technique for elaboration of several semiconductor thin films. The chemical bath solution was obtained by preparing 20ml of 0.5M stannum chloride (SnCl2), 20 ml of 0.5M of Zinc chloride solution with 5ml of Triethanolamine (TEA) (N(CH2CH2OH)3) and 20ml of 0.5M of Thiourea was added into 100ml beaker, NaOH(aq) which was added until a pH of 10 and temperature of the mixture was monitored with the aid of Mettler Toledo AG 8603 pH meter. And, 30ml of distilled water was added into the solution to make final volume of 100ml in the beaker. The mixture was gently stirred at the temperature to obtain a homogenous solution. Finally, the substrates were immersed into the precursor and deposit for 4hrs at about 70oC. The substrates were removed, rinsed with distilled water and allow to dry in air after the deposition. Three of the samples were annealed at 250 oC, 300 oC and 350 oC in an electric furnace. The reflectance graphs of TBS thin films revealed that average reflectance was below 28% for all films. TBS annealed at 350 0C thin films had the greatest reflectance of about 27% than all other films. This made the thin film to be a good material in being the window layer part of the solar cell. From the reflectance spectra, discontinuities were observed at wavelength above 900 nm. All TBS films demonstrated transmittance above 50% for wavelength above 800 nm. Below 800 nm there was a fall in the percentage transmittance of the films, an indication of a strong increase in absorption. The optimized transmittance at λ=900 nm was found to be 60%. TBS films have good absorption at short wavelength region, the absorption decreased with increasing wavelength of solar radiation. The extrapolated band gaps energy values for TBS thin films varies from the range of 3.82 to 3.91 eV. The resistivity increased with increase in heat treatment and it ranged between 5.48 × 106 Ωm and 3.05 × 106 Ωm. The thin films deposited through chemical bath deposition technique (CBD) were found to have high absorbance in UV-VIS regions while the films absorbance increases as the thickness increased, thus they could be find applications in solar radiation absorbers for solar cell applications. The high band gap properties indicate that the films can be used as a window layer in the fabrication of thin film hetero-junction solar cell and other optoelectronic devices. The low reflectance properties make them good materials for antireflection coatings, solar cell absorbers, thermal control and photosynthetic coatings.

***Index Terms*— Characterization, Chemical Bath Deposition (CBD), Tin Bismuth Sulphide (TBS), Thin Film, Solar Energy.**

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I. INTRODUCTION

Nanocrystalline SnO_2 thin films have garnered attention since higher quality synthesis of SnO_2 thin films was achieved (Saeideh *et al.*, 2011). The photoconductivity in bismuth sulphide (BiS_3) was reported by Case in 1917 based on studies on mineral samples-bismuthinite or bismuth glance. This ascribes to bismuth sulphide the status of one of the earliest photoconducting materials known until the early 1920s as reported by **(**Begum *et al*., 2011). One notes that the anodic formation of bismuth sulphide films was reported by Miller *et al*. 1978 and the chemical bath deposition technique for these films was reported in Pramanik and Bhattacharya, 1980. The application of such films in photoelectrochemical solar cells has been descried in **(**Bhattacharya and Pramanik, 1982) and surveyed in (Kalyanasundaram, 1985). Nanocrystalline semiconductors are of great interest for scientific research due to their important applications in advanced electronic and optoelectronic devices. Bismuth sulfide (Bi_2S_3) is one of the most attractive semiconducting materials for a wide variety of applications in photovoltaic converters, photodiode arrays, thermoelectric cooling technologies based on the peltier effect (Miller *et al* ., 1978; Robin *et al* ., 2006). The direct band gap value (Eg=1.7 eV) (Mane *et al* ., 2000) of Bi_2S_3 falls in the region of the visible region of energy spectrum and makes it an ideal candidate for solar energy conversion devices. Bi_2S_3 is one of the earliest materials known to exhibit photoconducting properties. As compared to methods such as thermal evaporation (Rincon *et al*., 1998), the hot wall method, hydrothermal synthesis (Shao *et al* ., 2001), ultrasonic method (Wang and Du, 2002), solvothermal decomposition (Deshpande *et al*., 2008), reactive evaporation (Nuli *et al*., 2003), spray pyrolysis (Hori *et al*.,1994), cathodic and anodic electrodeposition microwave irradiation (Lee *et al*., 2001) etc, for the preparation of Bi_2S_3 thin films, chemical bath deposition (CBD) method offers the advantages of economy, convenience, large area deposition of thin films at relatively low temperature and pressures (Mane *et al*., 2000).

II. EXPERIMENTAL DETAILS

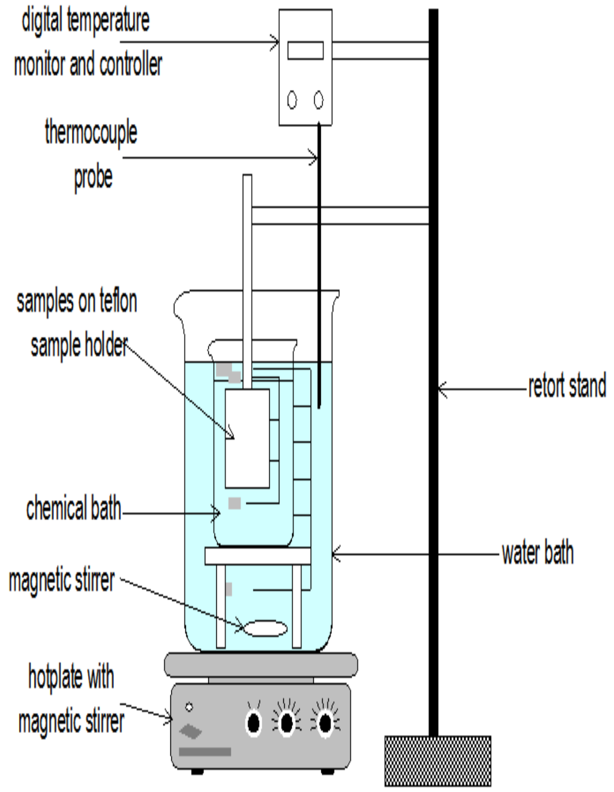

Figure 1: Schematic experimental set-up for Chemical Bath Deposition of Tin Bismuth Sulphide (TBS).

The chemical bath solution were obtained by preparing 20ml of 0.5M stannum chloride ($SnCl_2$), 20 ml of 0.5M of Bismuth Nitrate ($BiNO_3$) with 5ml of Triethanolamine (TEA) ($N(CH_2CH_2OH)_3$) and 20ml of 0.5M of Thiourea were placed into 100ml beaker, NaOH(aq) which was added until a pH of 10 and temperature of the mixture was monitored with the aid of Mettler Toledo AG 8603 pH meter. Then, 30ml of distilled water was added into the solution to make final volume of 100ml in the beaker. The mixture was gently stirred at the temperature to obtain a homogenous solution. The substrates were kept vertically and at the centre of the water bath to prevent them (substrates) from leaning against one another and walls of the bath. The deposition were carried out for 4 hours at about 70 ^{o}C. After the deposition, the substrates were removed, rinsed with distilled water and allow to air-dry. It is common for chemically deposited samples to be contaminated with oxygen from the environment as the sample usually exposed to the environment during preparation. Oxygen contamination was removed during the annealing process. One of the samples, labeled A was as-deposited and others labeled B, C and D were annealed at 250^{o}C, 300^{o}C and 350^{o}C respectively to study the effect of annealing on the deposited films.

III. RESULTS AND DISCUSSION

A. Optical Characterization

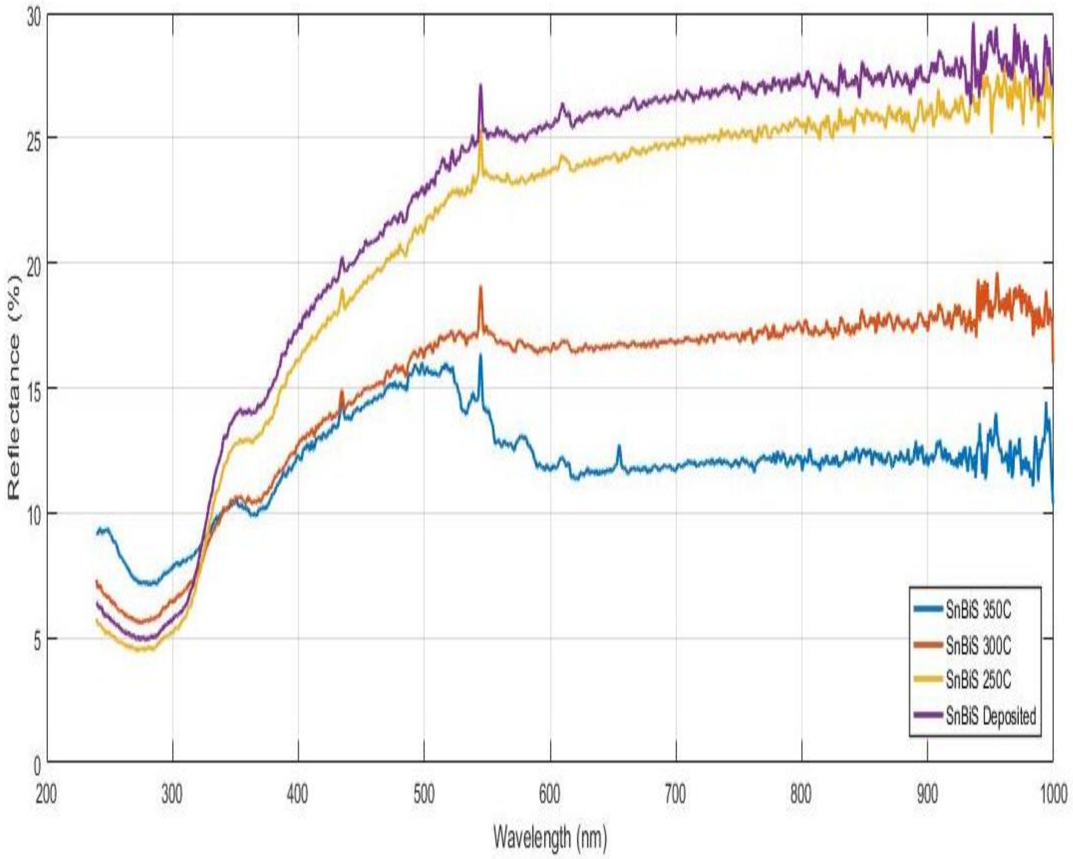

Figure 2: Graph of reflectance against wavelength for TBS

Figure 2 shows the reflectance graphs of SnBiS (TBS) thin films. The reflectance were found to vary from 10-27%, 10-25%, 10-17% and 10-16% for as deposited, annealed at 250^{0} C, 300^{0} C and 350^{0} C respectively. It was observed that average reflectance was below 28% for all films. The as-deposited TBS thin film had the greatest reflectance of about 27% compared to all other films. This is in agreement with Wanjala *et al* (2016) who reported ZnS:Sn thin Films for

Solar Cell Application. Results from reflectance graph show that the presence of heat in TBS thin films decreases reflectance of TBS thin films in the visible and infrared range except in some cases. To reduce the reflectance characteristics, it is imperative that reflectivity is supposed to be as low as possible (Wanjala *et al*., 2016), this made the thin film to be a good material in being the window layer part of the solar cell. From the reflectance graph, discontinuities were observed at wavelength above 800 nm.

B. Transmittance Results

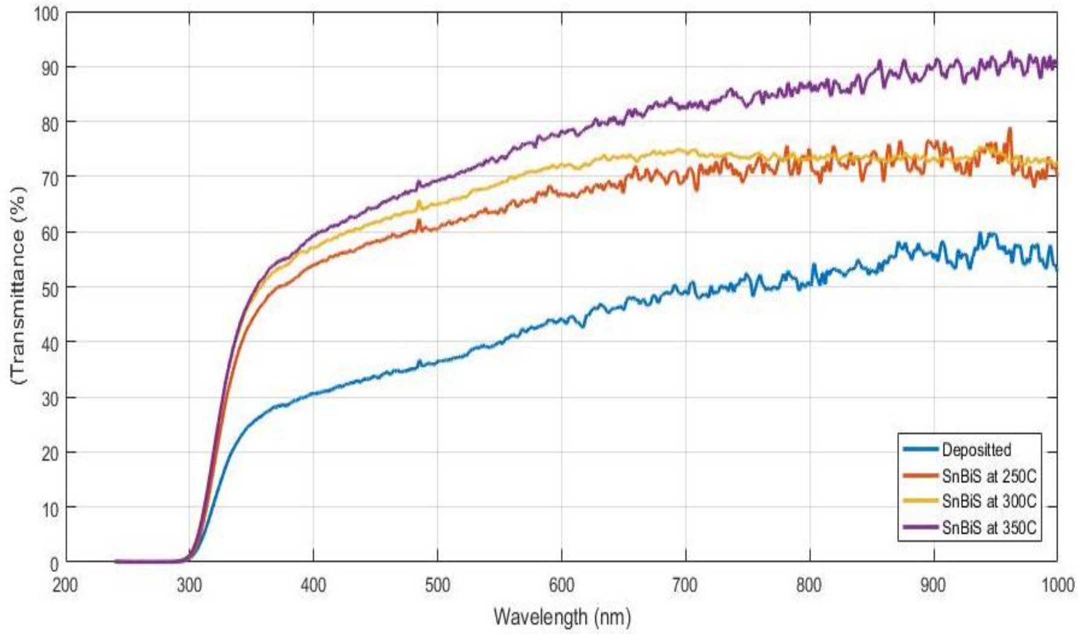

Figure 3: Graph of transmittance against wavelength for TBS

Figure 3 shows the transmittance for SnBiS (TBS) thin films. Transmittance values of 60%, 70%, 75% and 90% were observed for as deposited, annealed at 250^0 C , 300^0 C and 350^0 C respectively. All films exhibited transmittance above 50% for wavelength above 800 nm. Below 780 nm there was a fall in the percentage transmittance of the films around 950 nm, an indication of a strong increase in absorption (Kim *et al.*, 2009). This is attributed to rapid change in the optical absorption coefficient, and is an indication that some states have been created in the region 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). The optimized transmittance at λ=900 nm was found to be 90%. This transmittance value of the thin film is good for the window material to be used in solar cells. This value of high transmittance is in agreement with the values for doped ZnS thin films deposited by Wanjala *et al*., 2016.

C. Absorbance Results

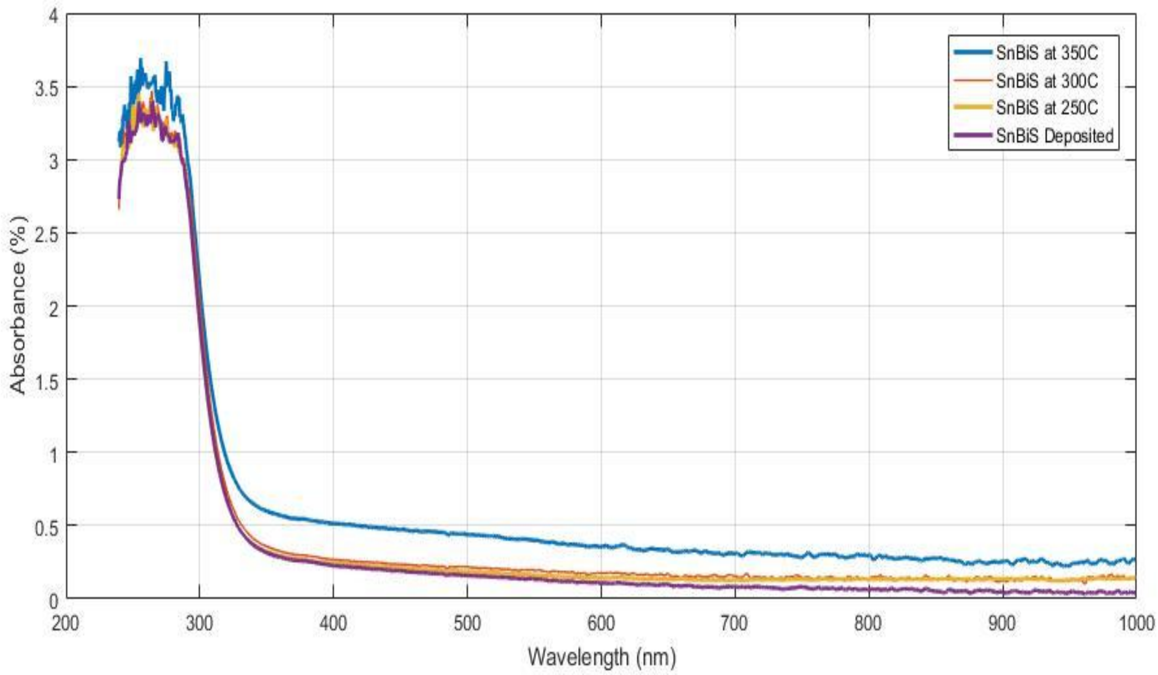

Figure 4: Graph of absorbance against wavelength for TBS

Figure 4 shows that SnBiS (TBS) films have good absorption at short wavelength region between 250 nm and

450 nm. The absorption decreased with increasing wavelength of solar radiation. From the figure there was a decrease in absorbance up to a wavelength, λ=990nm, then a slight increase in absorption. And this result is in agreement with the work of Wanjala *et al*. (2016) who reported that the increase in absorption occurs when the photon energy is equal to the value of the energy gap when electronic transfers between the valence band and conduction band begin. As deposited TBS Thin film has the lowest of absorbance of 3.4% at wavelength 270 nm whereas TBS thin film annealed at 350 ^{0}C has the highest absorbance of 3.6% at wavelength 250 nm. And this implies that increase in annealing brings about increase in absorption.

D.Bandgap Estimation

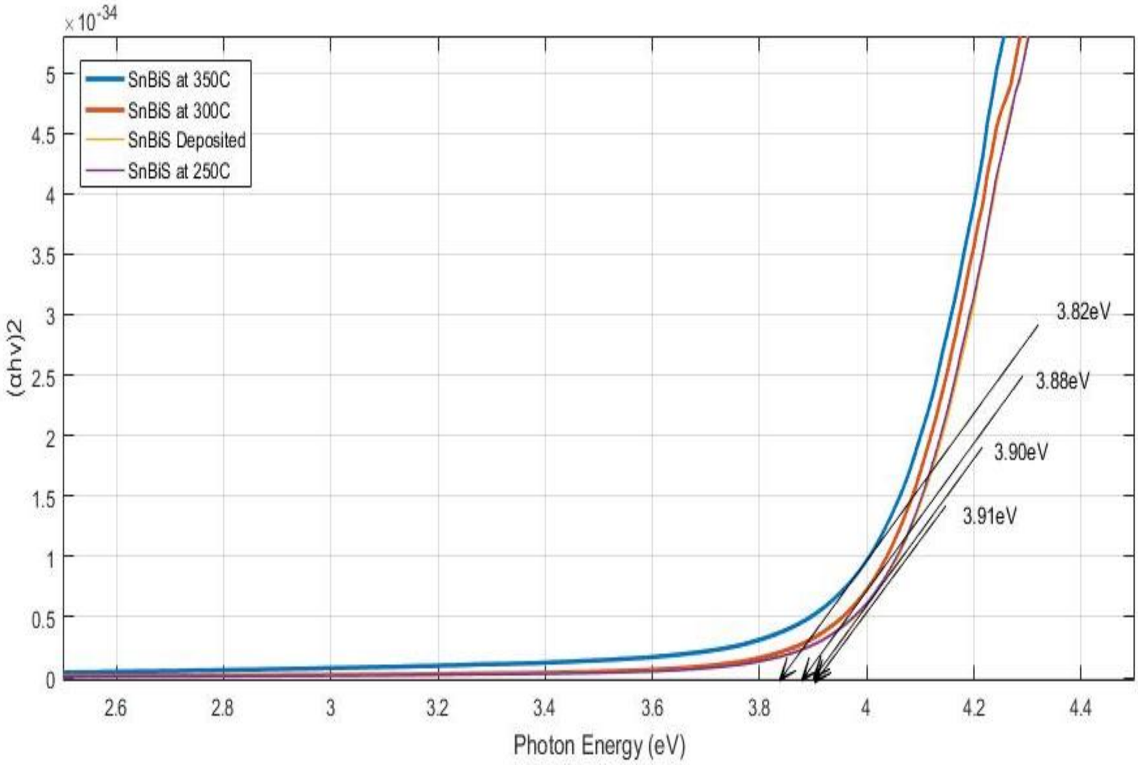

Figure 5: Graph of $(\alpha h v)^2$ against wavelength for TBS

Figure 5 shows the estimated energy band gap values 3.91 eV, 3.90 eV, 3.88 eV and 3.82 eV for as deposited, annealed at 250^0 C , 300^0 C and 350^0 C thin films respectively. The extrapolated band gaps energy values for SnBiS (TBS) thin films varies from the range of 3.82 eV to 3.91 eV. These Band gap values are in agreement with Rahdar *et al* (2012) obtained in determination of optical properties of ZnS thin films which were in the range of 3.64 eV to 4.00 eV. 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 (Chopra *et al.*, 2004).

Electrical Characterization

Table 1: Electrical results of TBS

Samples	Voltage (v)	Current (A)	Sheet resistance, R_s (Ω/m^2)	Resistivity (Ωm)	Conductivity (Sm^{-1})
TBS as deposited	0.35	5.8 x 10^{-8}	2.74 x 10^7	5.47 x 10^6	1.83 x 10^{-7}
TBS annealed at 250 ^{0}C	0.26	1.8 x 10^{-7}	6.55 x 10^6	1.31 x 10^6	7.64 x 10^{-7}
TBS annealed at 300 ^{0}C	0.18	9.1 x 10^{-8}	8.97 x 10^5	1.79 x 10^6	5.58 x 10^{-7}
TBS annealed at 350 ^{0}C	0.42	1.25 x 10^{-8}	1.52 x 10^{-8}	3.05 x 10^6	3.28 x 10^{-7}

Table 1 shows the sheet resistance calculated from the I-V characteristics for the TBS as deposited, annealed at 250 ^{0}C , 300 ^{0}C and 350 ^{0}C with values of 2.74 × 10^7 Ωm to 1.52 × 10^8 Ωm respectively. From the table, it was observed that resistivity increased with increase in heat treatment and it was between 5.48 × 10^6 Ωm and 3.05 × 10^6 Ωm. Though the film resistivity increases it can be used for photovoltaic applications with adjustments on resistivity either by further doping with dopants that reduce resistivity or introducing low resistivity grids. Similar sheet resistivity measurements for

ZnS were obtained using Van der Pauw technique in the order of 10^1 Ω-cm to 10^2 Ω-cm and electrical conductivity of 10^{-2} to 10^{-3} $(\Omega\text{-cm})^{-1}$ by Shinde *et al* . (2011). The resistivity should not be too high or low due to the inevitable defects in solar cells fabricated during the actual production process (Ikihioya, 2015). The respective conductivities are 1.83 x 10^{-7} Sm^{-1}, 7.64 x 10^{-7} $Sm^{-1}$and 3.28 x 10^{-7} Sm^{-1}. This shows that conductivity increases as the heat treatment increased which enhances the electrical properties of TBS thin films. This surely made the TBS a good material for solar cell fabrication.

IV. Discussion

The reflectance graphs of TBS thin films revealed that average reflectance was below 28 % for all films. TBS annealed at 350 ^{0}C thin films has the greatest reflectance of about 27 % than all other films. This made the thin film to be a good material in being the window layer part of the solar cell. From the reflectance spectra, discontinuities were observed at wavelength above 900 nm. All TBS films demonstrated transmittance above 50 % for wavelength above 800 nm. At below 800 nm there was a fall in the percentage transmittance of the films, an indication of a strong increase in absorption. The optimized transmittance at λ=900 nm was found to be 60 %. This transmittance value of the thin film is good for the window material to be used in solar cells. TBS films have good absorption at short wavelength region, the absorption decreased with increasing wavelength of solar radiation. The extrapolated band gaps energy values for TBS for as deposited and annealed thin films varies from the range of 3.82 to 3.91 eV. The resistivity increased with increase in heat treatment and it ranged between, 5.48 × 10^6 Ωm and 3.05 × 10^6 Ωm. Though the film resistivity increases it can be used for photovoltaic applications with adjustments on resistivity either by further doping with dopants that reduce resistivity or introducing low resistivity grids.

V. Conclusion

The thin films (TBS) deposited through chemical bath deposition technique (CBD) were found to have high absorbance in UV-VIS regions while the films absorbance increases as the thickness increased, thus they could be found to have numerous applications in solar radiation absorbers.

The high band gap properties indicate that the films can be used as a window layer in the fabrication of thin film hetero-junction solar cell and other optoelectronic devices. Conversely, their low reflectance properties make them good materials for antireflection coatings, solar cell absorbers, thermal control and photosynthetic coatings.

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