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Improved Optical Properties of Tin Antimony Sulphide Thin Films for Photovoltaics

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Abstract Tin antimony sulphide thin films have been synthesized as an absorber layer for solar cells. These films are deposited by vacuum thermal evaporation on glass substrate at a pressure of 10^{-5} torr. The films are then annealed at different temperatures in argon atmosphere. XRD analysis reveals that both as deposited and annealed films are found to be in polycrystalline phase. The crystallinity of the films is significantly enhanced with increasing annealing temperatures. The quantum efficiency is higher in the visible and near infrared region for the annealed films whereas the quantum efficiency of as deposited film is comparatively lower. The transmittance of the annealed films is found to be decreasing with increasing temperatures. The thickness and band gap of the films are measured by ellipsometric data. The absorption coefficient of the films is significantly higher (~10^5cm^{-1}), which is very important factor regarding solar conversion efficiency. Hot point probe measurements show that the films possess n-type electrical conductivity.

Keywords: *tin antimony sulphide, solar cell, quantum efficiency, band gap, absorption coefficient*

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1. Introduction

Photovoltaic has the potential to become a major source of energy and to have a significant and beneficial effect on the global environment. Solar energy can be converted into other forms of energy, such as heat and electricity. Photovoltaic or solar cells change sunlight directly into electricity. Sun provides 3×10^{24} joules of energy per year which is adequately (about 10^4 times) greater than human utilizations [1]. Thin films play a vital role in promoting solar cell technology due to their stability and low cost [2]. Inorganic matrix composites with special optical, electrical and photoelectrical properties have drawn attention of researchers due to their potential applications for photovoltaic and optoelectronics. Currently, thin film solar cells based on silicon, cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS) are available in market in abundance. These inorganic materials are very good absorbers materials, giving tremendous results in solar cell applications. However, there are several problems with such type of materials due to toxicity and abundance issues. In these materials, cadmium is toxic to the environment while Indium and Gallium are expensive as well as rarely available [3,4]. This problem has lead to study, identify and develop new materials, which are non-toxic and abundant in nature.

Now, the efforts have been made to develop new semiconductor materials having: (i) appropriate energy band gap (ii) good efficiency (iii) abundant in nature (iv) courteous towards environment, etc. [2]. For this purpose, metal chalcogenides are considered to be new emerging materials having wide-ranging applications in solar cell together with various other important fields. Sulfides, selenides and tellurides have also been included in this group [5]. Among them, the SnSbS (sulfosalt) appears to be the best material. SnSbS thin films have been used as an absorber material for photovoltaics due to its photo-activeness and have been the subject of considerable research due to their technological importance for thin film photovoltaic applications [6,7,8,9], phase change memory devices [10] and thermoelectric energy conversion applications [11]. Hence, sulfosalt thin films are considered to be the most suitable option for photovoltaic applications.

In this paper, tin antimony sulphide ($Sn_2Sb_2S_5$) thin films have been investigated for photovoltaic applications. It is found that all the optical parameters such as transmittance, refractive index, absorption coefficient, band gap and photoconductivity have been improved for this purpose. In addition, both as deposited and annealed films show n-type electrical conductivity.

2. Experimental

Tin antimony sulphide ($Sn_2Sb_2S_5$) thin film was deposited by common vacuum thermal evaporator by two sources technique. Initial materials prepared were tin sulphide (SnS) and antimony sulphide (Sb_2S_3). Tin sulphide was manufactured from tin and sulphur powder [12], which were grinded in pestle and mortar and annealed in quartz ampoule containing argon gas for 24 h

at 600°C. Sb_2S_3 of analytical grade was obtained from sigma Aldrich (Kurt J. Lesker) with 99.99% purity. The powdered SnS and Sb_2S_3, placed in Al_2O_3 crucibles, were evaporated simultaneously in a vacuum chamber in order to deposit thin films on glass substrates. The pressure of the chamber was sustained at approximately 10^{-5} torr. The prepared films were annealed at different temperatures such as 125°C, 175°C and 250°C.

The structural characterization of the films was performed by means of conventional JDX3532 diffractometer with Cu Kα radiation (λ=1.54Å). The optical absorption, transmission, band gap and film thickness data were obtained by the modeled ellipsometric data by using Sentech variable angle spectroscopic ellipsometer (VASE). The thickness of the film was measured as 1400 nm. The type of conductivity of the sample was examined by using hot point prob method.

3. Results and Discussions

XRD patterns of thin films of the $Sn_2Sb_2S_5$ are shown in Figure 1 before and after annealing. Surprisingly, the as-deposited $Sn_2Sb_2S_5$ film is in crystalline form which is not consistent with that of the reported ones. It has been reported [13,14] that generally a semiconducting or a dielectric material deposited by thermal evaporation method show a dominant amorphous component. Thus, we have observed an exceptional case of $Sn_2Sb_2S_5$ films. The crystallinity of $Sn_2Sb_2S_5$ films can be attributed to the low substrate temperature.

Before annealing, only the strong principal diffraction line (311) related to the $Sn_2Sb_2S_5$ phase has been appeared. After annealing, the strong principal diffraction line (311) is accompanied with a small secondary diffraction lines which are also associated to the $Sn_2Sb_2S_5$ phase [13]. It can also been seen that the intensity of the peaks is slightly increased with higher annealing temperatures. This phenomenon is attributed to the improved crystalinity of the layers with increased annealing temperatures. In order to check the effect of annealing temperature on the grain size (D) of the crystal, we used a relation between the wavelength of X-rays and grain size of crystal, which is usually given by a well known Scherrer's formula [15].

$$\mathbf{D} = \frac{0.9\lambda}{\beta Cos\theta}$$

Where D is the average grain size of crystal, λ is the wavelength of X-Rays (Cu-Kα) in angstroms λ =1.54 Å), β is the full-width at half maximum (FWHM) and θ is the diffraction angle. The average grain size of the layers was calculated using the principal diffraction line along (311) which was found to be in the range of 41.25- 43.53 nm. The grain size is slightly increased with increase in annealing temperatures.

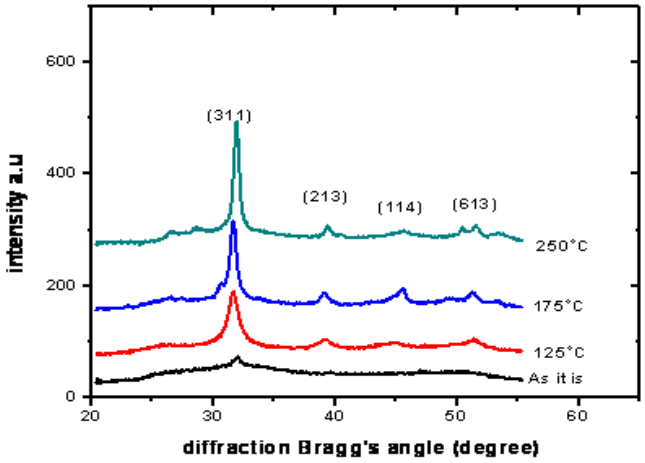

Figure 1. X-ray diffraction patterns of as-deposited and annealed $Sn_2Sb_2S_5$ thin films at various annealing temperatures

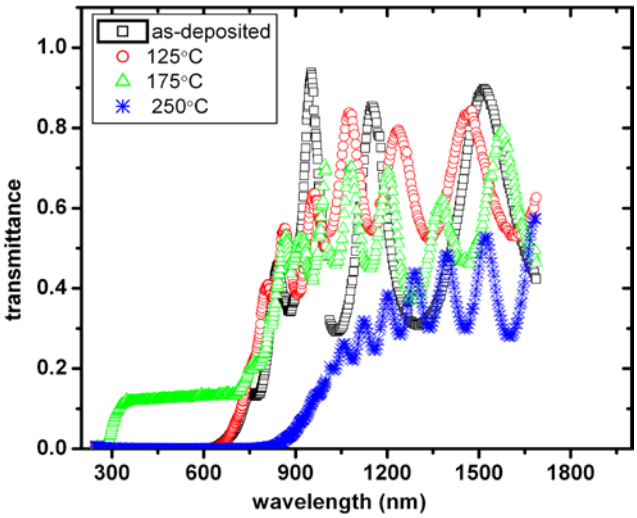

Figure 2. Transmittance spectra of $Sn_2Sb_2S_5$ thin films at various annealing temperatures

Optical properties of the $Sn_2Sb_2S_5$ thin films have been studied by Sentech spectroscopic ellipsometer in the spectral range 300-1700 nm. Transmittance spectra of $Sn_2Sb_2S_5$ thin films before and after argon heat treatment are shown in Figure 2. All the spectra do not show interference effects in the transparency region (700-1700 nm) with sharp fall of transmittance at the band edge. This plot shows that transmittance is high for as-deposited sample and low for annealed samples. It can be attributed to the fact that with increasing temperatures, crystallinity of the samples is improved by decreasing the number of defects in the films [16]. As transmittance decreases with rise in temperature, so absorbance increases.

The values of the refractive indices of the films are calculated by the following formula.

$$n = n_o + k$$

Where n_o is the refractive index indicating the phase velocity while k is called the extinction coefficient. The refractive index (n) of the $Sn_2Sb_2S_5$ films as a function of wavelength for the different annealing temperatures is shown in Figure 3. It can be seen that the refractive index increases from 3 to 3.8 by increasing annealing temperatures. This increment in the refractive index may be ascribed to the element antimony in the sample. Since it has been reported [17,18] that after annealing, materials containing antimony show an opaque aspect with high refractive indices.

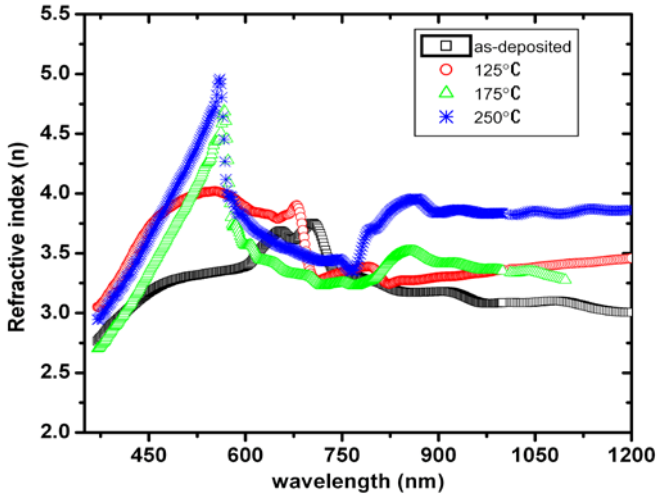

Figure 3. Refractive index (n) versus wavelength for $Sn_2Sb_2S_5$ thin films at various annealing temperatures

The absorption coefficient of the films can be investigated as follows:

$$\alpha = \frac{4\pi k}{\lambda}$$

Where α is the absorption coefficient λ is wavelength and k is the extinction coefficient of the given material found from the modeled data of ellipsometry [18]. Dependence of the absorption coefficient on photon energy is shown in Figure 4 for the $Sn_2Sb_2S_5$ thin films. It is seen that all the samples have comparatively high absorption coefficient (~ 10^5 cm^{-1}) and is found to be increasing with increasing temperatures at the same photon energy. This result is very important because the spectral dependence of the absorption coefficient is one of the important factors which influence the solar conversion efficiency.

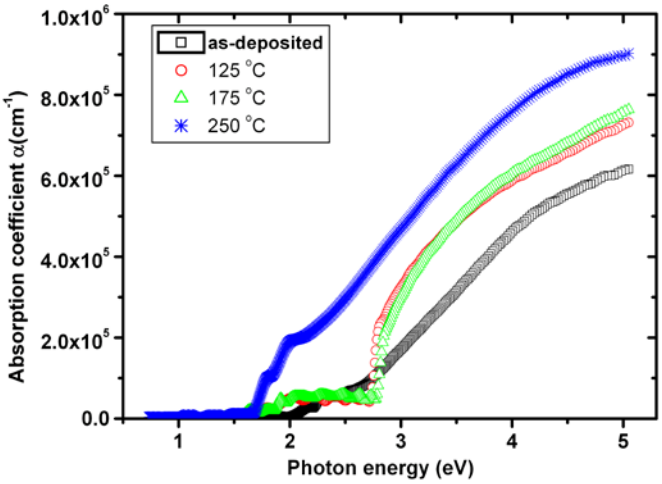

Figure 4. Absorption coefficient vs. Photon energy of the $Sn_2Sb_2S_5$ thin films at various annealing temperatures

By correlating absorption coefficient (α) and band gap energy (E_g), we can calculate the band gap of $Sn_2Sb_2S_5$ thin films through an equation [19] given by:

$$\alpha h\upsilon = A(h\nu - E_g)^n$$

Where A is a constant, h is the Planck's constant, E_g is the band gap and n is a number equal to ½ for a direct band gap and 2 for an indirect band gap semiconductor. The value of band gap (E_g) can be determined by extrapolating the straight part of $(\alpha h\upsilon)^2$ versus $h\nu$ curve to the horizontal photon energy axis [20] which is shown in Fig. 5. The estimated value of the band gap of the as deposited film is 1.80 eV, while the band gaps of the films annealed at 125°C, 175°C and 250°C are 1.72 eV, 1.69 eV and 1.60. eV, respectively (shown in Figure 5). The value of E_g for the annealed films is less than that of the as deposited film. It means that the annealing process is assumed to be helpful in enhancing the optoelectronic properties of the thin films. This is attributed to the improved crystalline quality, increase in grain size and lack of oxygen succeeding to annealing, but still the effect of these procedures is not fully identified yet [19, 20]. The crystalline size has been increased with rise in annealing temperature, due to this the radius of the particle (R) is also increased. As, there is an inverse relation between change in band gap energy (ΔE_g) of the material and radius of the particle (R), so with the increase in value of R, ΔE_g is found to be decreased [21,22].

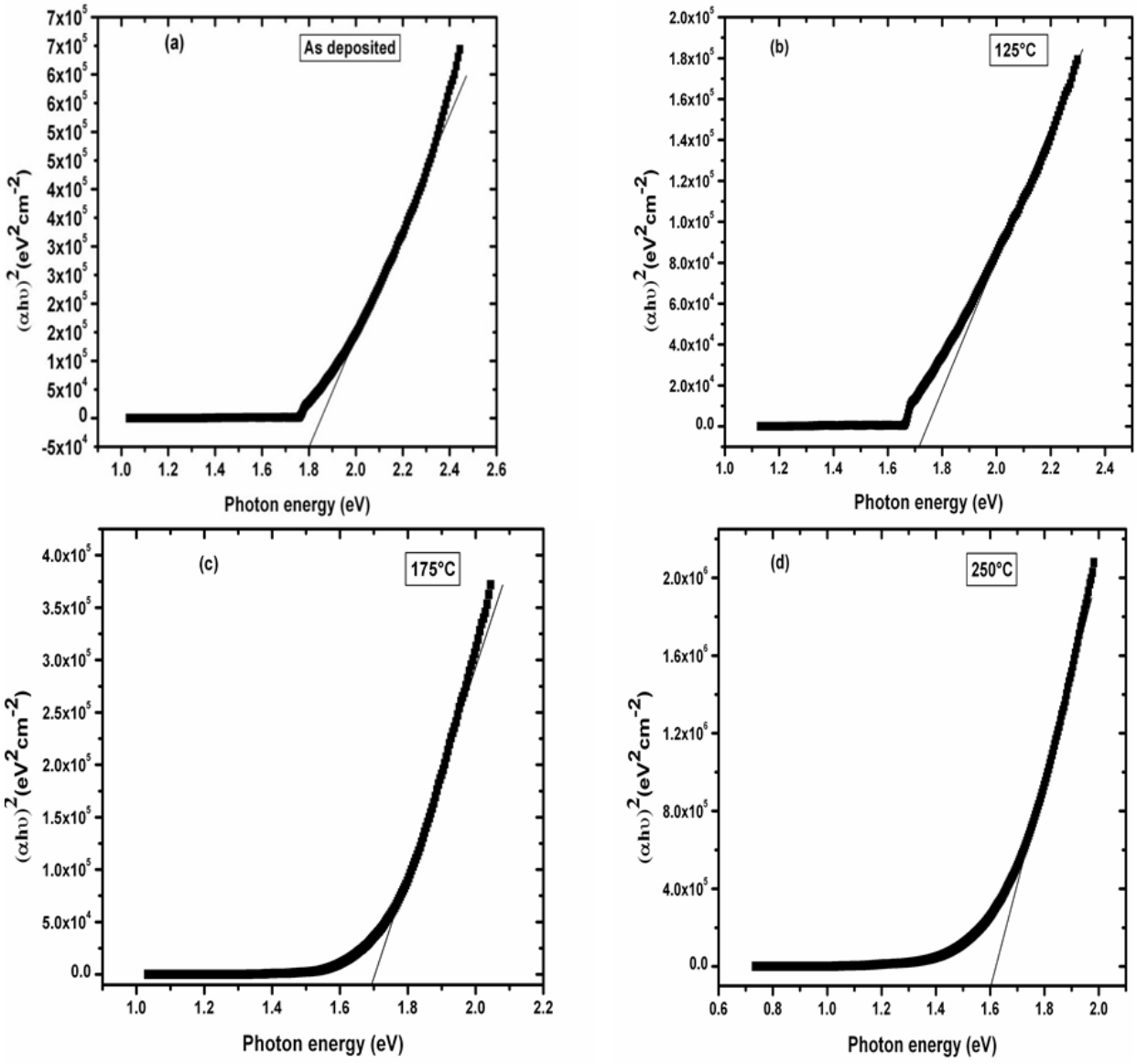

Figure 5. Plots of $(\alpha h\upsilon)^2$ versus hυ of $Sn_2Sb_2S_5$ film for band gap calculations: a) as deposited, b) annealed at 125°C, c) annealed at 175°C, d) annealed at 250°C

Figure 6 shows the variation of band gap with annealing temperatures. It can be seen that with increase in temperatures the energy gap decreases. Basic reason for this is that, when thermal energy increases, the amplitude of atomic vibrations increase which results in larger atomic spacing. An increase in interatomic spacing results in decreasing the potential seen by the electrons in the material, which in turn reduces the size of the energy band gap. The interaction between the lattice phonons and free electrons and holes also affect the band gap to some extent [23].

Quantum efficiency versus wavelength behavior of $Sn_2Sb_2S_5$ thin film is shown in Fig. 7. This behavior shows that the annealed films have good photoconductivity in the visible and near infra red (NIR) region. From this data it is also revealed that the films annealed at 175°C and 250°C have excellent photoconductivity response. That is, the photoconductivity rises with increase in annealing temperatures. Thus, we can say that the photoconductivity has been improved with the increase in grain size.

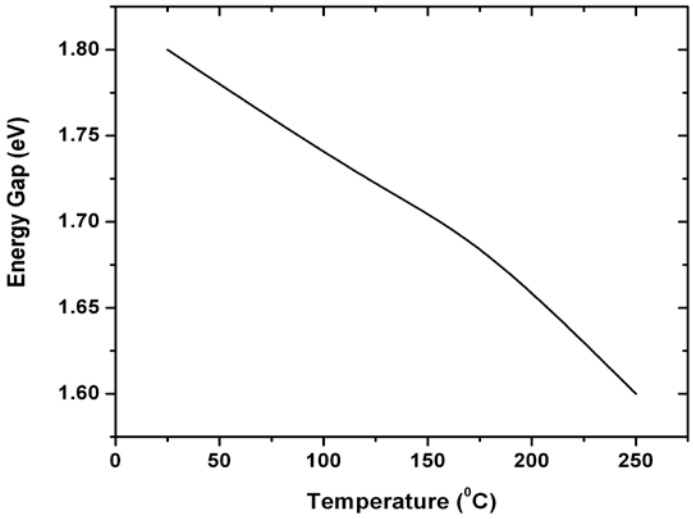

Figure 6. Band gap energy (E_g) dependence on the annealing temperature of the $Sn_2Sb_2S_5$ thin films

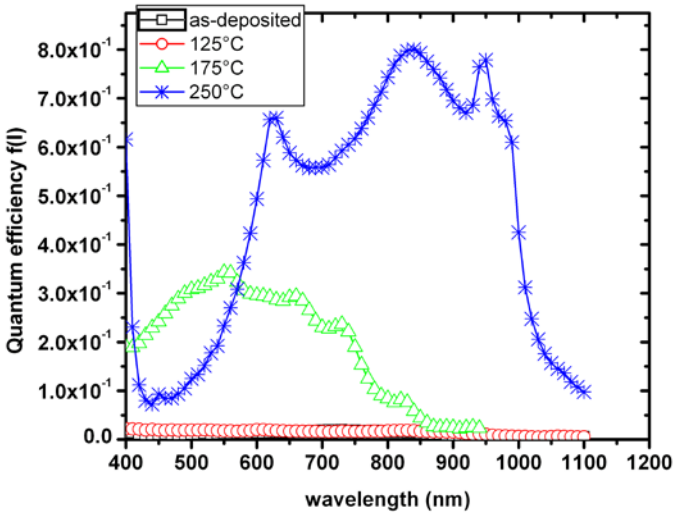

Figure 7. Plot of Quantum efficiency versus wavelength at various annealing temperatures

To find the type of conductivity of the material, hot point probe technique has been employed. First of all, the instrument was standardized for n-type Silicon and after that the type of conductivity of the $Sn_2Sb_2S_5$ film was checked [24]. It has been found that the films are having n-type conductivity before and after annealing, as shown in Figure 8.

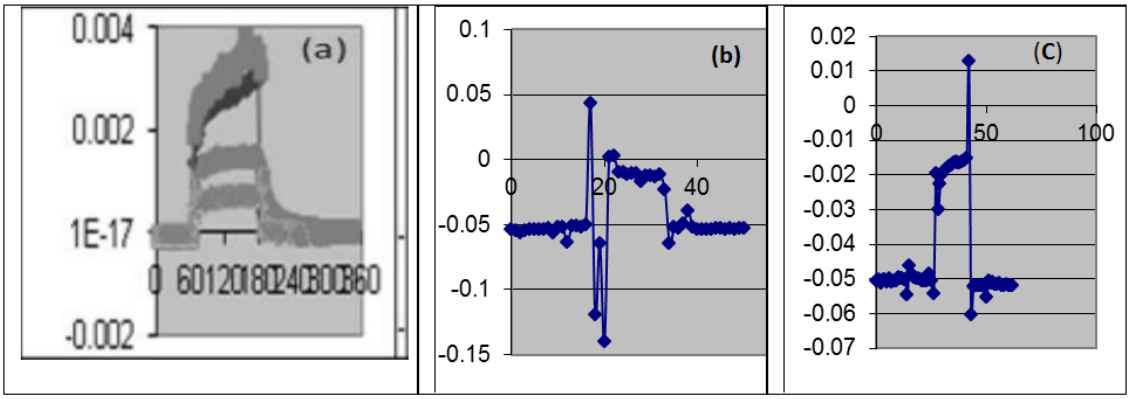

Figure 8. Hot point probe measurements (a) n-type silicon (b) as deposited $Sn_2Sb_2S_5$ film (c) annealed $Sn_2Sb_2S_5$ film

4. Conclusions

Tin antimony sulphide ($Sn_2Sb_2S_5$) thin films have been investigated as a new material for photovoltaic applications. $Sn_2Sb_2S_5$ thin film is deposited by vacuum thermal evaporator on clean glass substrate. The as deposited and annealed films both are found to be in polycrystalline ($Sn_2Sb_2S_5$) phase. The transmittance of the annealed film is found to decrease compared with as

deposited film which is a sign for changing towards the absorber layer. The photoconductivity response is found to be maximum in the visible and NIR region for the annealed films while the as deposited film is not proved to be significantly photoconductive. The thickness of the films is investigated as 1400 nm which is extracted by modeling the ellipsometry data for the films. The absorption coefficient is in the range of ~ $10^5 cm^{-1}$. The band gap of the annealed film is measured to be in the range of 1.72 eV- 1.60 eV which is an appropriate band gap for solar cell applications. It has been observed that the films have n-type electrical conductivity.

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