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Optimization of Zinc to Tin Ratio in a Sol Gel Precursor Solution on the Growth and Properties of Annealed CZTS Thin Films

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Abstract

CZTS thin films were deposited by sol–gel spin coating method using precursor solutions prepared by dissolving copper acetate dihydrate, zinc acetate dihydrate, tin chloride and thiourea in methanol and monoethylamine then annealed in RTP furnace at 500 °C. Sol–gel precursor solutions were prepared with different Zn/Sn in a precursor solution and were annealed at different time intervals; and their effects on the optical and electrical properties of CZTS (Cu_2ZnSnS_4) films were investigated. The optical band-gap values were estimated to be between 1.30 and 1.88 eV while the absorption coefficients were in the range of 10^4 cm^{-1} in the visible region. The resistivity and carrier concentrations ranged from 13.12 to 2634 kΩ/□ and 10^{17} to 10^{20} cm^{-3}, respectively. The influence of Zn/Sn ratio and annealing time on structural properties of CZTS thin films are also discussed.

Keywords: CZTS, Cu_2ZnSnS_4, Kesterite, Zn/Sn ratio

Introduction

Cu_2ZnSnS_4 (CZTS) thin films have been drawing much attention over $CuInGaS_2$ (CIGS) and CdTe as solar absorber materials for the production of cheap thin-film solar cells. The interest in CZTS is due to large optical absorption coefficients in the order of 10^4 cm^{-1}, a tunable direct band gap energy 1.4 – 1.5 eV coupled with the uses of natural abundance and non-toxicity constituents (Michael 2012, Mkawi et al. 2013).

CZTS is a p-type semiconductor material and is obtained by replacing half of the indium atoms in chalcopyrite $CulnS_2$ with zinc, and the other half with tin. The constituents of CZTS (copper, zinc, tin, and sulfur) are all abundant in the earth's crust, indicating that CZTS will not be limited by material constraints for large-scale power generation. The abundance of Zn and Sn in the earth's crust is 1500-times and 45-times greater than that of In, respectively, and the price of In is almost two orders of magnitude higher than that of Zn and Sn (Wang 2011).

Several techniques that have been reported for growing CZTS thin films for solar cell applications including evaporation, sputtering, electrodeposition, nano crystal ink deposition, Sol gel method and spray pyrolysis (Isah et al. 2013, Majula 2014). Up to now 12.6% conversion efficiency has been reported for non-vacuum techniques, and 9.2% for vacuum based techniques (Chiril et al. 2013, Wang et al. 2014**)**. However until now, it is still difficult to control the formation of secondary phases. Thus, further investigation on the optimum composition of various precursor materials used in the CZTS solar cells, particularly Zn/Sn ratio, needs to be done for better deposition of CZTS for thin film solar cells. Furthermore, although few attempts for optimization of annealing time for CZTS have been done before (Singh et al. 2014,Vidyaet al. 2014, Longa et al. 2015, Aldalbahi et al. 2016), still more studies on the influence of annealing time are needed for further improvement of both structure and stoichiometry of the CZTS thin films.

In this work, CZTS thin films were prepared using the sol gel method in a spin coating method. The influence of Zn/Sn in a precursor solution and annealing time on the structural, optical and electrical properties of the CZTS thin films are discussed.

Materials and Methods

CZTS thin films were deposited by sol–gel spin coating method using precursor solutions prepared by dissolving copper acetate dihydrate, zinc acetate dihydrate, tin chloride and thiourea in methanol and monoethylamine solvent and stabilizer, respectively. To optimize the Zn/Sn ratio in a precursor solution, sol–gel precursor solutions with different Zn/Sn molar ratios were deposited on SLG glass substrates using a spin coater rotated at 2100 rpm for 30 sec on SLG substrate. The resulting films were dried in air on a hot plate at 150 °C for 5 minutes to remove the residual organic materials. The deposition process to drying was repeated 8 times to attain film thickness of ~0.8 µm. The molar ratios of Zn/Sn in a mixture solution were 0.8, 0.9, 1.0, 1.1, 1.2 and 1.3. The as-deposited films were inserted in RTP furnace and then annealed at 500 °C in nitrogen atmosphere for 30 minutes. Before annealing the as deposited films were sealed in a graphite boat together with sulfur powder (Figure 1) for reducing sulfur loss. For further study of influence of annealing time on CZTS films, the films with optimal Zn/Sn molar ratios were then annealed at different time intervals in the range of 30, 60, 90 minutes following the annealing profile shown in Figure 2.

The structural, surface topology and morphology of the films were examined using X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). The optical and electrical measurements were determined using UV/Vis/NIR spectrophotometer Perkin Elma Lambda 9/19 and Ecopia HMS 3000 Hall Measurement System, respectively.

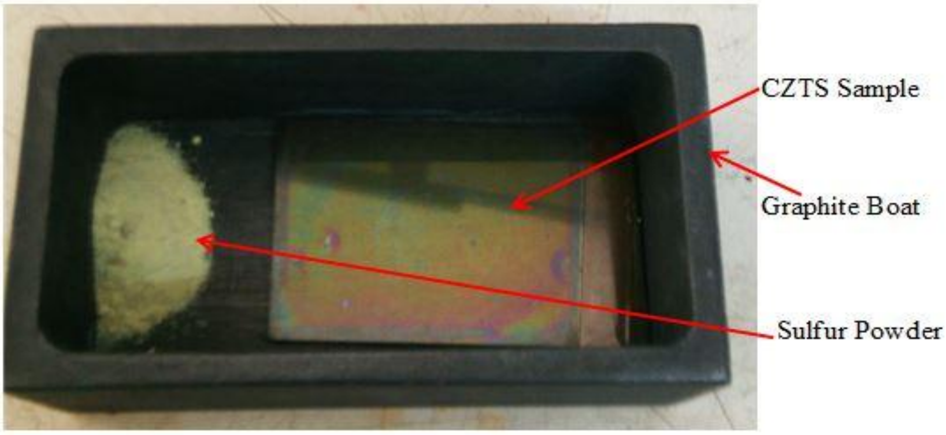

Figure 1: The CZTS sample and sulfur powder in unsealed graphite boat.

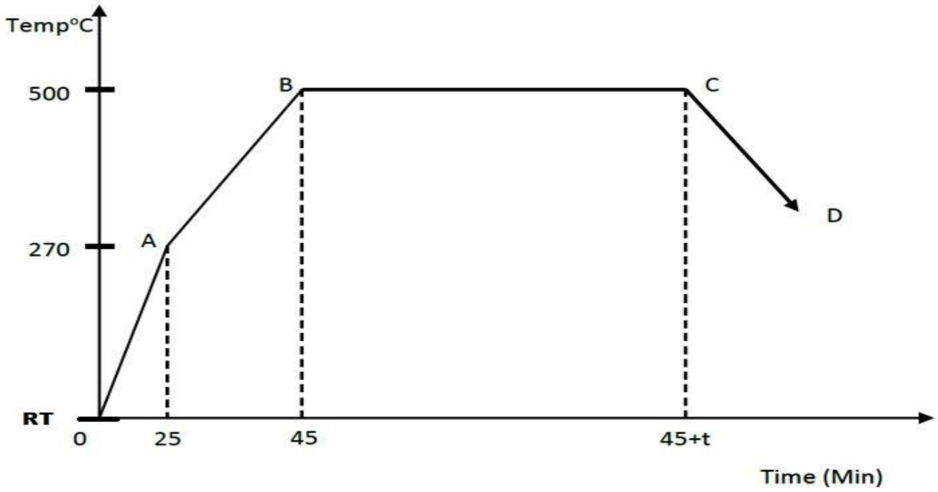

Figure 2: The temperature elevation profile for annealing process of CZTS samples (t = annealing time).

Results and Discussion

The deposited CZTS thin films appeared yellow-brown in color (Figure 3). These were associated with different amounts of Zn/Sn ratios in the precursor solutions, pre-annealing and annealing conditions as suggested in other studies (Majula et al. 2015).

Figure 4 (a) shows the X-ray pattern of the CZTS thin films prepared with different Zn/Sn ratios in the precursor solution.

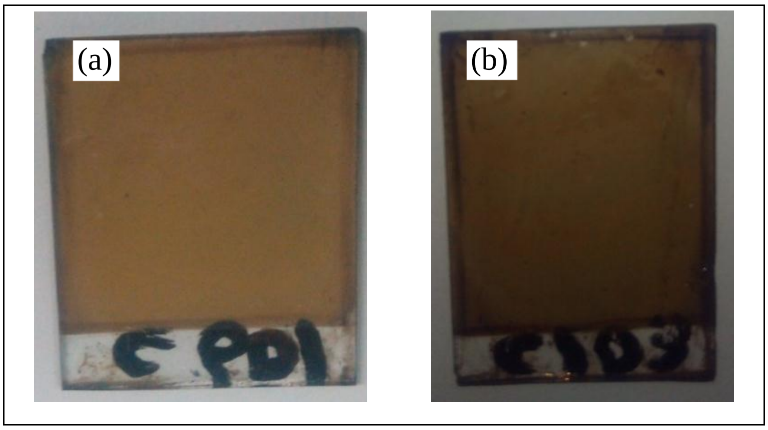

Figure 3: Appearance of annealed CZTS thin films with (a) smooth and uniform color (b) unsmooth and non-uniform color.

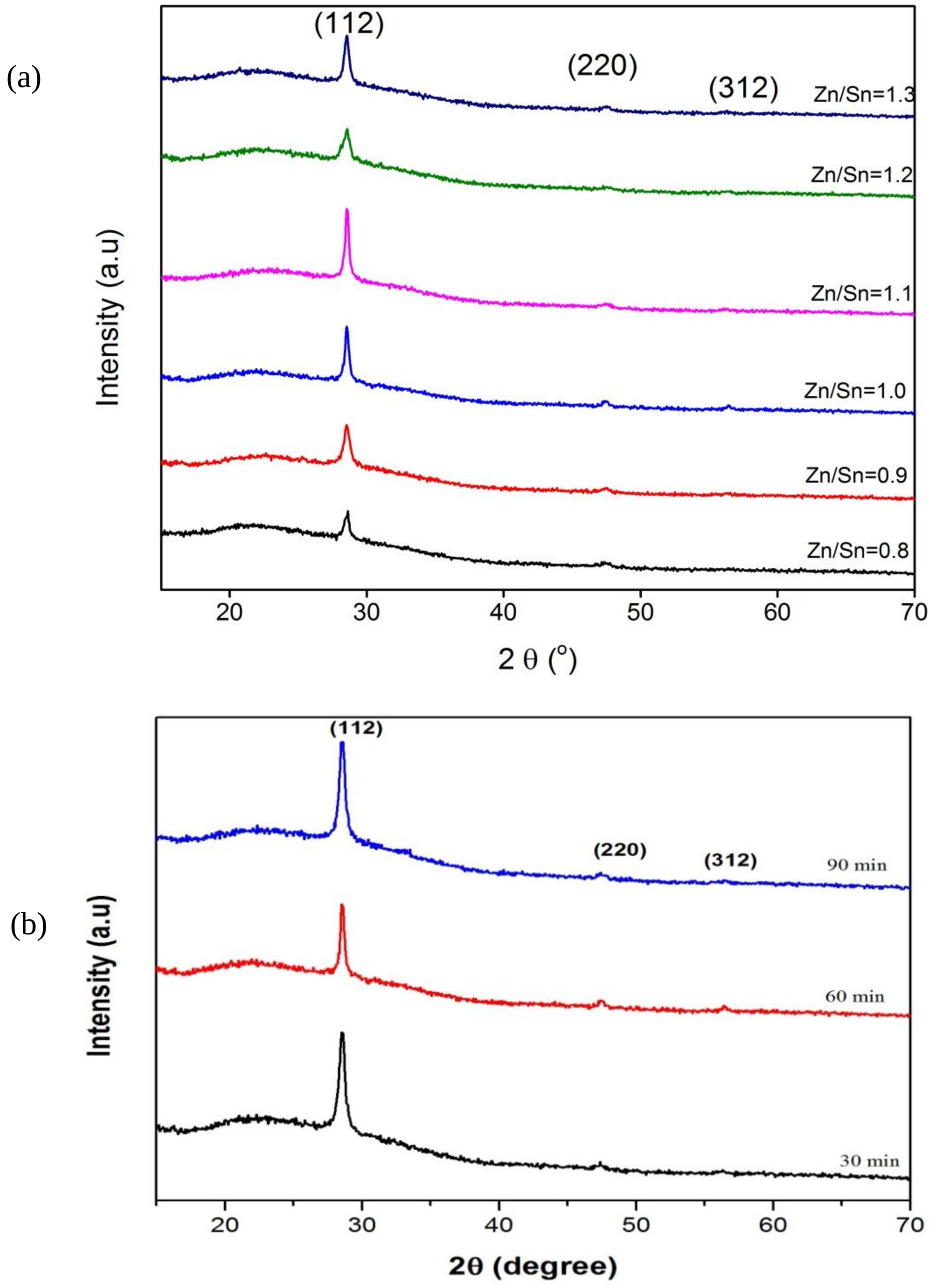

Figure 4: XRD patterns of CZTS thin films (a) prepared with different Zn/Sn ratios (b) annealed at different time intervals.

The major XRD diffraction peaks appeared at 2θ ≈ 28.6°, 47.6°, and 56.7°, associated with (112), (220), (312) planes of the CZTS phases, respectively (JCPDS data base card no. 26-0575) with preferred orientation on (112) plane which are in good agreement with features of characteristic kesterite CZTS films reported by other studies (Hemalatha et al. 2014, Majula et al. 2015). The calculated lattice constants reveal a tetragonal unit cell with a = 5.451 Å and c = 10.721 Å as c/2a = 1 (Deokate et al. 2013). No characteristic peaks were detected for other phases/impurities such as ZnS, CuS or Cu_2S, even though it is difficult to detect the presence of other secondary phases with XRD only due to overlap with major CZTS diffraction peaks. The intensities of major XRD diffraction peaks seem to be increasing with Zn/Sn ratios from 0.8 to 1.1 and then decreased as Zn/Sn ratios increased from 1.1 to 1.3. The CZTS thin films annealed at different time intervals (Figure 4b) show the increases of broadness and intensity of the peaks with annealing time, which was associated with increase in grain size and overall improvement in crystallinity with annealing time (Singh et al. 2014, Tchognia et al. 2016).

Most of the deposited films consisted of uniform and substantial densely packed grains. Moreover, SEM images (Figure 5), show the variation in sizes of the grains, which may be associated with the variation of zinc and tin concentrations in a precursor solution (Guan et al. 2013, Malerba et al. 2013). The film with Zn/Sn = 0.8 (Figure 6 (a)) was rough and had large grains compared to others; this can be associated by the presence of rich tin content in the films.

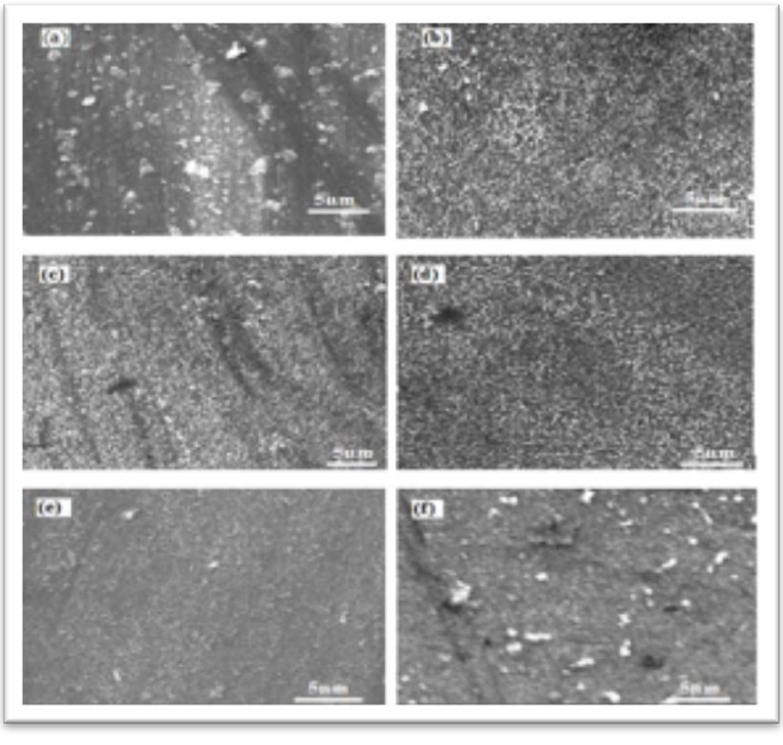

Figure 5: SEM images for samples with different Zn/Sn ratio.

According to Hreid et al. (2015) tin has larger nucleation size when compared to zinc and copper. Normally increase in tin content makes the films rougher and more porous. Moreover, the SEM micrographs (Figure 6) show that the grain sizes increase with increase in the annealing time as was also observed in other studies (Guan et al. 2013, Rajeshmon et al. 2013, Singh et al. 2014). AFM images (Figure 7) show that the grain sizes increased from 1561.8 nm^2 to 11691 nm^2 with annealing time. The surface roughness increased from 5.6 nm to 28.1 nm with the increase in annealing time which may be attributed to the increase in grain size (He et al. 2013).

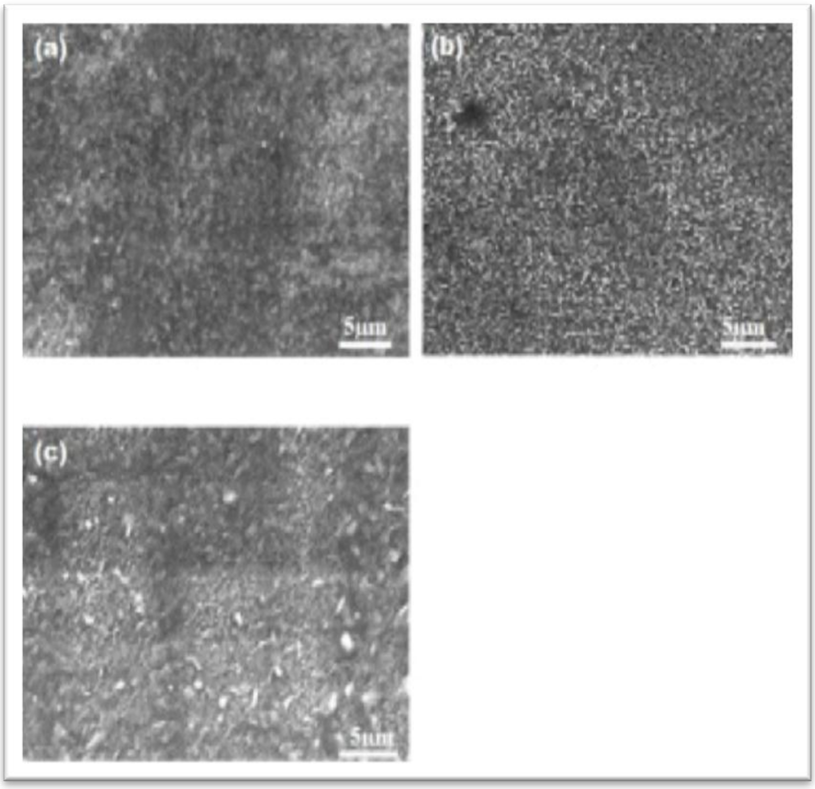

Figure 6: SEM images for samples annealed at different time intervals.

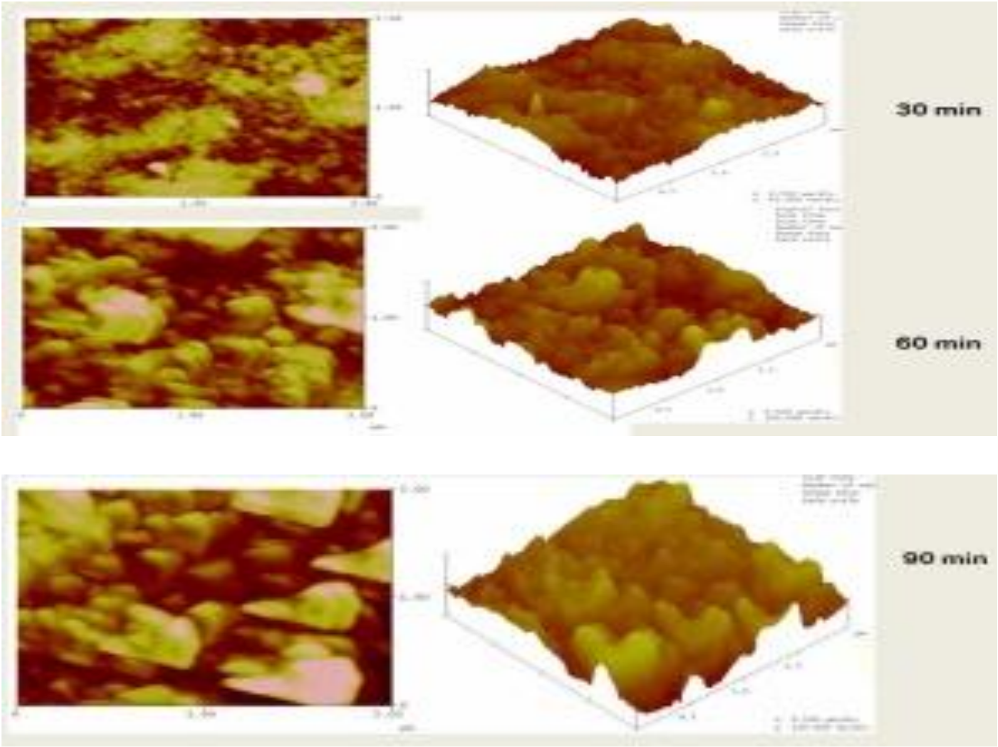

Figure 7: AFM images for samples annealed at different time intervals.

The fabricated CZTS films exhibit an average transmittance less than 51% (Figure 8) over the range of 300 – 1800 nm, which is in good agreement with prior reported studies (Michael 2012, Marleba et al. 2013). The low transmittances behaviour is associated with crystal defects that include vacancies, antisite and interstitials. Secondary phases that might develop could also contribute to lowered transmittance. These normally introduce absorption sites within the band gap as was observed by earlier studies (Marleba et al. 2013).

The films with Zn/Sn ratios of 1.0 and 1.1 had relatively lower transmittances than all other samples with Zn/Sn ratios below and above of 1.0 and 1.1, and this shows that the films with Zn/Sn = 1.0 – 1.1 absorbed most photons falling on them compared to others. The average transmittance registered for the films with Zn/Sn ratios of 1.0 and 1.1 were 40.3% and 39.1%, respectively.

The band gap values were found to be ranging between 1.30 and 1.88 eV. These differences may be caused by the deviation from stoichiometric composition (Tanaka et al. 2007 Rajeshmon 2013). The sample with Zn/Sn = 1.0 and Zn/Sn = 1.1 showed energy band gaps that are quite close to the recommended energy gap value of CZTS thin films (~1.5 eV) as suggested by most literatures on CZTS thin film solar cells (Tanaka et al. 2007, Oyola et al. 2013, Jiang et al. 2012, Majula et al. 2015). This indicates that the fabricated films are suitable for photovoltaic applications.

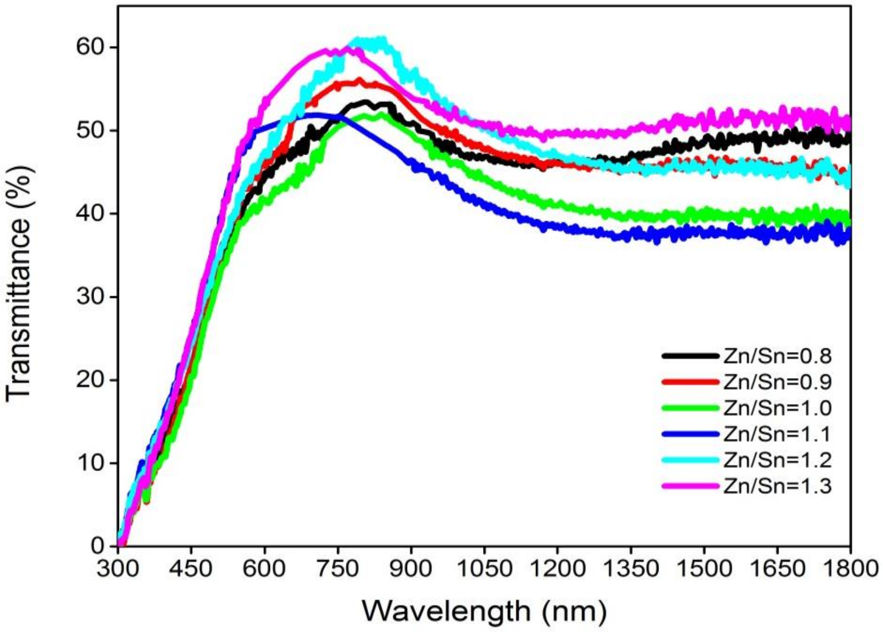

Figure 8: Optical transmittances for samples with different Zn/Sn ratios in a precursor solution annealed at 500 °C for 30 minutes.

The absorption coefficient α values of the CZTS thin films were computed using Equation (1) from measurements of spectral transmittance measured by UV/Vis/NIR lambda 9/19 spectrophotometer and the thickness measured by the Alpha Step stylus IQ surface profiler.

$$\alpha = \frac{1}{t} In\left(\frac{1-R}{T}\right) \ldots \ldots (1)$$

Figure 9 reveals that the absorption coefficients in a visible and near infrared region were above 10^4 cm^{-1} whereby the samples with Zn/Sn = 1.1 had the highest absorption coefficients. These values are in good agreement with the previous published studies (Katagiri et al. 1997, Tanaka et al. 2005, Rajeshmon 2013, Malerba 2014), indicating that they are suitable for use as the absorber layers for the thin film CZTS solar cells (Jiang et al. 2012, Seo and Lim 2013, Oyola et al. 2013, Majula 2014).

Figure 10 shows the Tauc plots for the CZTS thin films prepared.

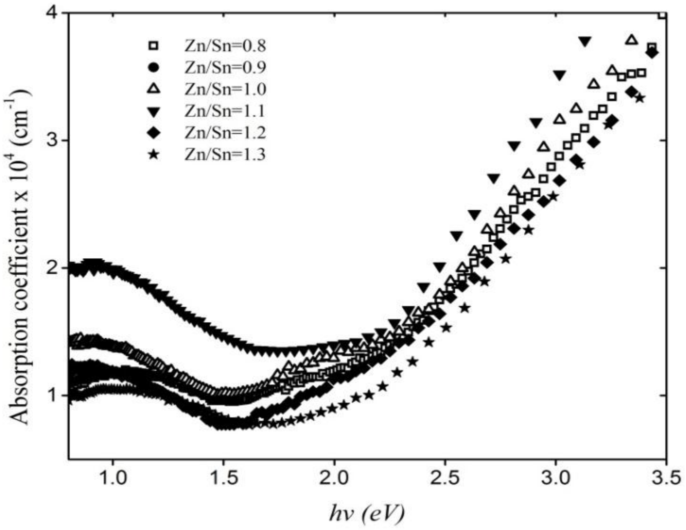

Figure 9: Absorption coefficients for samples with different Zn/Sn ratios in a precursor solution. All samples were annealed at 500 °C for 30 minutes.

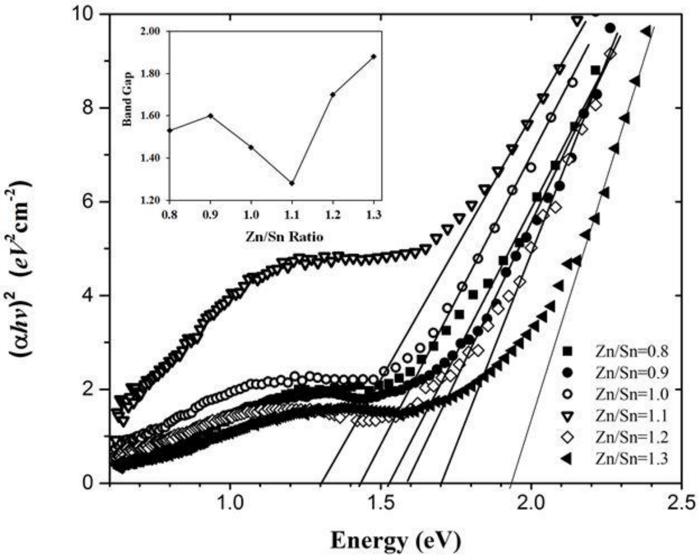

Figure 10: Tauc plots for CZTS thin films prepared using different Zn/Sn ratios in a precursor solution and annealed at 500 °C for 30 minutes.

Figure 11 depicts the absorptance of the CZTS thin films in the wavelength range of $300\ \text{nm} \leq \lambda \leq 1800\ \text{nm}$. The plots reveal that there is a slight change in the absorptance of the films with variation of Zn/Sn ratios in the starting precursor solution. This might be associated with different composition of metals in the starting precursors. The sample with Zn/Sn ~1.0 shows high absorption coefficient in the visible region and Zn/Sn ~1.1 had a highest absorptance in the near infrared region when compared to the other samples, suggesting that the optimal Zn/Sn ratio lies between these values.

The results show that there is a decrease in transmittance with the increase in annealing time (Figure 12); however, there is an increase of absorptance and absorption coefficients with the increase of annealing time (Figure 13 and Figure 14). Again a significant evolution of the band gap towards the recommended optimal band gap for the CZTS thin films with an increase of annealing time was observed (Figure 15). These effects may be associated with improvement in crystallinity of the CZTS thin films and the reduction of the secondary phases in samples that may be evolved during the formation of CZTS. By increasing the annealing time, the secondary phases get converted to CZTS quaternary phase (Linnala 2008, Singh et al. 2014, Longa et al. 2015, Singh et al. 2016).

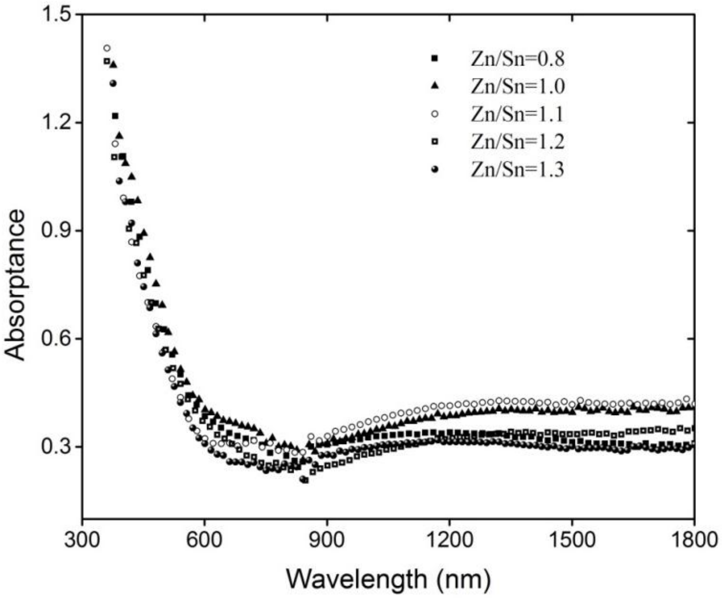

Figure 11: Absorptance of CZTS thin films with different Zn/Sn ratios in a precursor solution. All samples were annealed at 500 °C for 30 minutes.

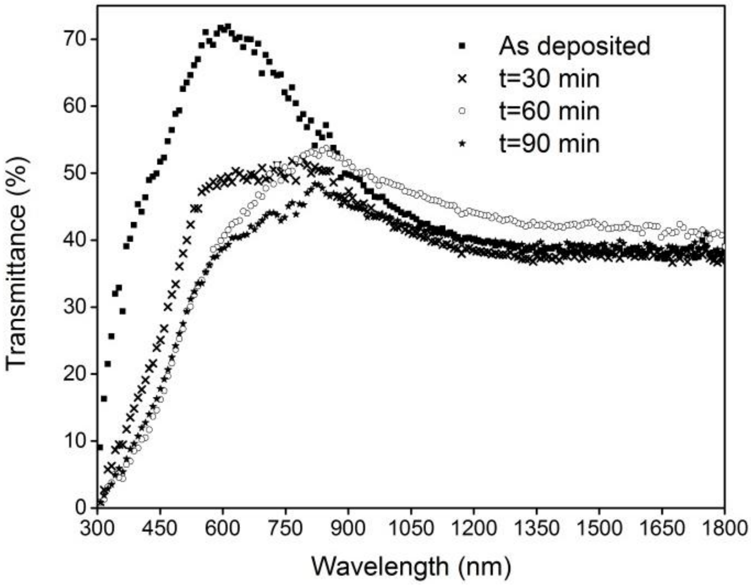

Figure 12: Transmittance of CZTS samples with Zn/Sn = 1.1 ratios in a precursor solution annealed at 500 °C for different time intervals.

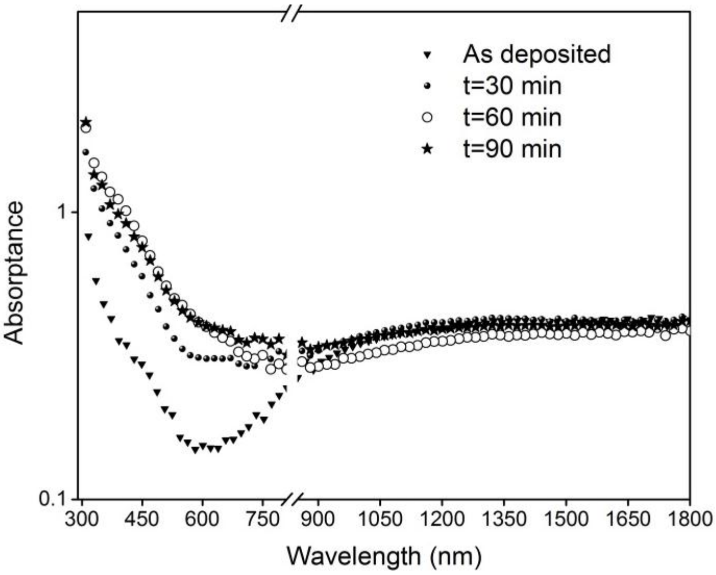

Figure 13: Absorptance of CZTS samples with Zn/Sn = 1.1 ratios in a precursor solution annealed at 500 °C for different time intervals.

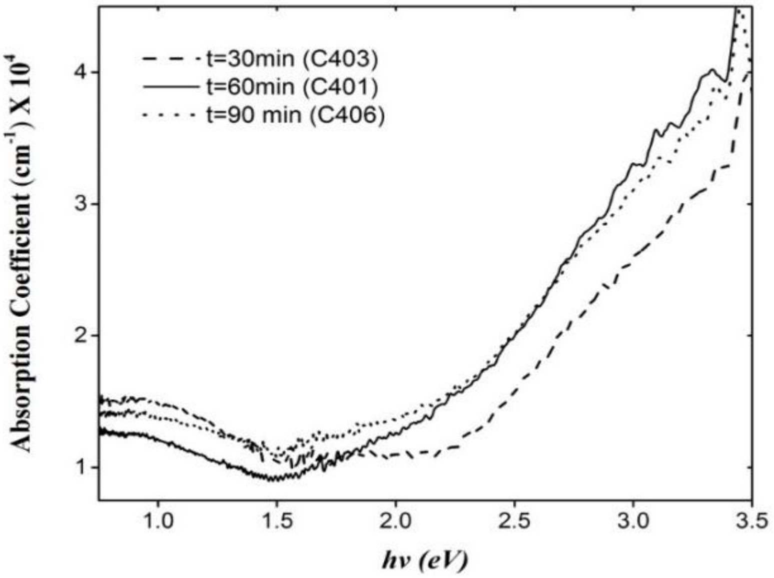

Figure 14: Absorption coefficients, for CZTS thin films with Zn/Sn = 1.1 ratios in a precursor solution for different annealing time intervals.

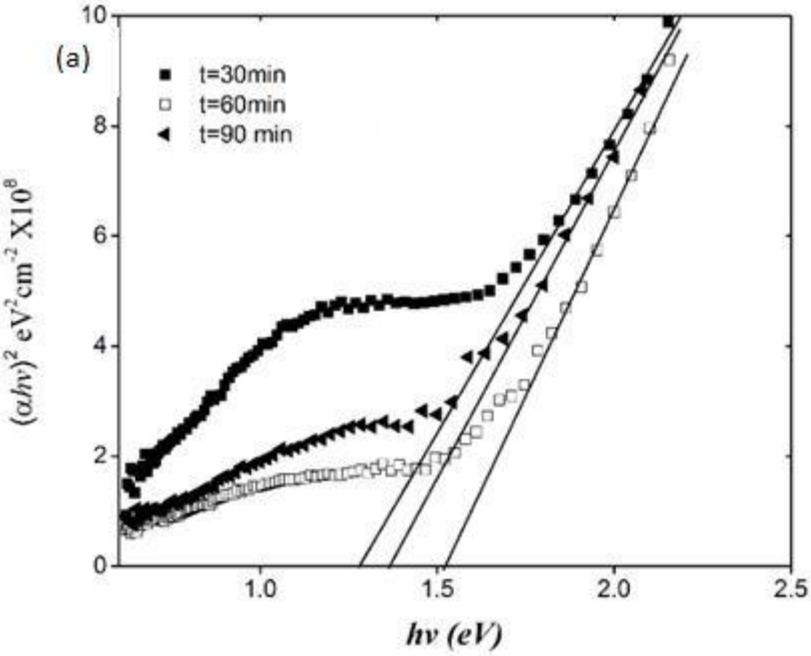

Figure 15: Tauc' plots for CZTS thin films with Zn/Sn = 1.1 ratio in a precursor solution for different annealing time intervals.

All the CZTS films showed positive values of the Hall coefficient, indicating *p*-type conductivity. The resistivity ranged between 0.341 and 9.643 Ωcm and sheet resistance ranged between 13.12 and 2634 k□/sq. A general trend showed a significant increase in resistivity and sheet resistance with increase in Zn/Sn ratio in the precursor solution. The charge mobility values ranged from 0.1334 to 11.88 cm^2/Vs, which are in good agreement with the results reported in previous studies (Fella 2014). The general trend of conductivity was found to decrease with increase in the Zn/Sn ratios and ranged between 0.126 and 2.932 Ω cm^{-1}.

The carrier concentrations for the prepared CZTS films ranged between 10^{16} and 10^{20} cm^{-3}. These results are in good agreement with that of kesterite CZTS thin films reported by other studies (Majula 2014, Singh et al. 2014). Moreover, the general trend showed the decrease in carrier concentrations with the increase in Zn/Sn ratios.

Conclusions

The fabrication of CZTS thin films by sol gel method was succeeded. In this study the Zn/Sn molar ratio in a precursor solution was optimized. The XRD results showed that all the films had a kesterite CZTS structure and a preferred orientation on (112) plane. All the films exhibited transmittances below 65% and had band gap values in the range of 1.30 to 1.88 eV and coefficient of absorptance in the order of 10^4 cm^{-1}. Moreover, the films with Zn/Sn ratios of 1.0 and 1.1 showed the optimal transmittances, absorptance and optical band gap values. The CZTS thin films exhibited *p*-type conductivity, resistivity ranged between 13.12 and 2634 kΩ/sq and carrier concentrations ranged from 10^{16} to 10^{20} cm^{-3}. The improvements in structural, optical and electrical properties of optimal CZTS films with the increase of annealing time were observed.

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