Near-optimal composition of CZTS thin film via exploration of copper and thiourea molar concentration in spray pyrolysis technique

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Abstract

Attaining the optimal composition of Cu$_2$ZnSnS$_4$ (CZTS) thin film is a pre-requisite for photovoltaic application. Herein, the near-optimal composition of spray pyrolyzed CZTS thin film has been obtained by varying copper and thiourea molar concentrations in the precursor solution. Different characterization techniques such as x-ray diffraction (XRD), UV–vis spectroscopy, Scanning electron microscopy (SEM) and Energy-dispersive x-ray spectroscopy (EDS) have been employed to determine the changes in absorber layer properties. The CZTS thin films synthesized using Cu-0.016 M exhibits higher crystallinity with the direct band gap of 1.52 eV. Apart from that, the reduction of copper molar concentration in precursor solution minimizes the segregation of surface secondary phase. The variation of thiourea molar concentration facilities the growth of CZTS and reduces the formation of secondary phases. Besides that, the optical studies revealed that the increment in thiourea molar concentration leads to a broadening of band gap from 1.52 eV to 1.61 eV. The CZTS thin films synthesized using copper and thiourea molar concentrations of 0.016 M and 0.12 M showed appropriate absorber layer properties with near-optimal Cu-poor and Zn-rich ratio i.e., Cu/(Zn +Sn) = 0.81 and Zn/Sn = 1.26.

1. Introduction

Thin-film solar cells have been acquired considerable attention from researchers due to its optimal properties, such as direct band gap and high absorption coefficient compared to silicon-based solar cells [1–3]. Thin-film based solar cells technologies such as Copper Indium Gallium Sulfide (CIGS), Gallium Arsenide (GaAs), Cadmium Telluride (CdTe) reached the competitive power conversion efficiency to Si, Though the presence of rare (i.e., Ga, In, Te) and toxic elements (i.e., Cd) limits the large scale commercial production of photovoltaic (PV) [3–7]. Therefore, In and Ga elements in CIGS are replaced using zinc and tin elements, respectively, to form Cu$_2$ZnSnS$_4$ (CZTS) material [8, 9]. The abundance and non-toxic elements present in the CZTS made this material a perfect competitor for other PV materials [10–12]. Moreover, CZTS exhibits a suitable band gap of ~1.5 eV and a higher absorption coefficient of ~10$^4$ cm$^{-1}$ to act as an efficient absorber layer [13–15].

Even though CZTS based solar cell demonstrates optimal properties, the highest achieved power conversion efficiency was limited to 12.6% with partial substitution of sulfur with selenium [16]. Moreover, the Shockley–Queisser limit predicts that CZTS solar cells can reach a power conversion efficiency of ≈32% [17]. The difference between the experimental and theoretical power conversion efficiency is high. Besides, CZTS solar cell performance mainly suffers due to its higher open-circuit voltage deficit [18, 19]. The synthesis of single-phase CZTS is complicated due to its narrow chemical potential region. Therefore, binary and ternary phases such as Cu$_2$S, ZnS, SnS, SnS$_2$ and Cu$_2$SnS$_3$ can occur in CZTS thin film [20, 21]. Apart from that, deep defects present in the band gap facilitates the non-radiative recombination, and it is deleterious to device performance. Furthermore, Elemental composition present in CZTS film took a decisive role in the formation of secondary phase and defect complexes [22, 23].
In general, CZTS films synthesized at copper-poor and zinc-rich composition exhibited higher power conversion efficiency as compared to the film synthesized at stoichiometric composition. The reduction in secondary phases and defect complexes in Cu-poor and Zn-rich CZTS films improves device performance [24, 25]. Therefore, optimization of element composition of Cu/(Zn+Sn) ≈0.8 and Zn/Sn ≈1.2 present in CZTS is the key to control the formation of secondary phases and defect complexes. CZTS thin films were synthesized using various techniques such as Thermal Evaporation [26], Sputtering [27], Pulsed Laser Deposition [28] and Spin Coating [29]. Amid these techniques, spray pyrolysis is a relatively simple, low-cost technique and have the ability to deposit the film in a large area that is suitable for industrial-scale production [30].

Researchers have devoted their enormous effort towards the achievement of the optimal composition ratio of CZTS thin film by spray pyrolysis technique. Patel M et al synthesized CZTS thin films using the spray pyrolysis technique and studied the effect of the various molar concentration of precursor solution. Their results concluded that the thin films synthesized using Zn-rich and S-rich precursor solution exhibits optimal optoelectronic properties as compared to the films synthesized with other precursor concentration [31]. Vigil-Galán et al investigated the role of precursor composition on electrical properties and secondary phase formation in CZTS thin film synthesized using the spray pyrolysis technique. The film synthesized using the non-stoichiometric composition of Cu-poor and Zn-rich precursor exhibits enhanced physical properties with less secondary phase. Thus, it exhibits enhancement in device performance [32]. The physical properties were studied for the stoichiometric and optimal composition of CZTS thin films by Courel et al. The films synthesized at stoichiometric composition resulted in the formation of more secondary phases, and the films synthesized at optimal Cu-poor and Zn-rich composition showed minor secondary phases with enhanced physical properties [25].

The surface of the absorber layer has a substantial role in decisive performance of solar cells which is mainly due to its interface with the buffer layer. The presence of secondary phase segregation on the surface of CZTS thin films leads to adverse band alignment in the absorber-buffer interface. This causes the large interface recombination, as a result, the photovoltaic device exhibits less open circuit voltage and short circuit current.

The occurrence of Cu,S secondary phase on the surface of CZTS thin film corresponds to the different Zn/Sn ratio has been examined by Kaur et al. Their results concluded that CuS secondary phase was significantly reduced for the films synthesized at less Zn/Sn ratio of 1.10 [35].

The above reports have elucidated the importance of the optimal composition ratio of CZTS thin films and the presence of surface phase segregation. Thus, so far, the achievement of the optimal composition ratio of CZTS thin film by spray pyrolysis technique is not completely explored using molar concentrations of the precursor solutions. To harness the CZTS thin film in the photovoltaic application, the optimal composition ratio of Cu/(Zn+Sn) ≈0.8 and Zn/Sn ≈1.2 has to be achieved. Moreover, the study of surface secondary phases present in the CZTS thin film deposited using spray pyrolysis is not conclusive. The present study explores the role of the distinguished molar concentration of copper and thiourea on spray pyrolyzed CZTS thin film and are presented with a comparison to the existing reports. The phase segregation present in CZTS thin film surface with respect to the different copper and thiourea molar concentration was also examined and discussed.

The secondary phases are found to be diminished in CZTS thin film under the optimized molar concentration of copper and thiourea. The correlation is scrutinized for surface segregation with respect to the copper and thiourea molar concentration. Our results pave the way to the optimal Cu/(Zn+Sn) ≈0.8 and Zn/Sn ≈1.2 of CZTS thin film along with the assist of different molar concentrations of the precursor solution. The acquired results in this study will give insight into the surface phase segregation present in the CZTS absorber layer deposited using the spray pyrolysis technique.

2. Experimental details

The automatic chemical spray pyrolysis deposition technique was used to synthesis CZTS thin film, and the instrument details are given in our previous work [37]. Two series of experiments were performed in order to optimize copper and thiourea molar concentration. The aqueous precursor solution is prepared using CuCl2.2H2O as a copper source, ZnCl2 as a zinc source, SnCl4.5H2O as a tin source, and SC(NH2)2 as a sulfur source. Since deposition is performed in an ambient atmosphere, we have used 1.6 bar compressed air through the tube as a carrier gas to create droplets from the precursor solution. The soda-lime glass was used as a substrate and the optimized substrate temperature of 325 °C was maintained. Nozzle to substrate distance was
maintained at 15 cm and the solution flow rate was kept as 1.75 ml min$^{-1}$. Spray deposition is carried out as a cyclic process. A gap is given in between each cycle to maintain the substrate temperature. The spray process was done for the duration of 20 min. The copper molar concentration is varied as 0.02 M, 0.018 M, 0.016 M and 0.014 M, and corresponding samples were named Cu-0.020, Cu-0.018, Cu-0.016 and Cu-0.014. ZnCl$_2$, SnCl$_4$.5H$_2$O, SC(NH$_2$)$_2$ molar concentrations in precursor solution are maintained at 0.01 M, 0.01 M and 0.08 M, respectively. To compensate for the sulfur loss in the as-deposited films, twice the amount of thiourea molar concentration was used in 0.08 M, as compared to its stoichiometric molar concentration i.e., 0.04 M.

In the second series of the experiment, the optimized molar concentration of copper 0.016 M was used, and the thiourea molar concentration is varied from 0.08 M – 0.14 M in order to study the molar concentration effect in a wide range of magnitude for as-deposited CZTS thin films. The rest all the spray parameters are kept the same as used in the previous experiment. The thiourea molar concentration is varied as 0.08 M, 0.10 M, 0.12 M and 0.14 M, and the samples named as for S-0.08, S-0.10, S-0.12 and S-0.14, respectively. CuCl$_2$.2H$_2$O, ZnCl$_2$ and SnCl$_4$.5H$_2$O molar concentration in chemical solution is 0.016 M, 0.01 M and 0.01 M, respectively.

X-ray diffraction (XRD) data were collected using an x-ray diffractometer (Rigaku mini flex 600) which uses Cu k$\alpha$ (\(\lambda = 1.5406 \text{ Å}\)) radiation. The optical absorption, as well as transmittance spectra, were obtained using a UV–vis spectrometer (Shimadzu UV-1800) in the wavelength range of 190–1100 nm. Surface morphology was analyzed using a scanning electron microscope (SEM) (EVO MA18). The atomic percentage of elements were calculated using energy dispersive x-ray spectroscopy (Oxford EDS) attached to the SEM with an accelerating voltage up to 15 kV. Bruker dektak xt stylus profilometer is employed to evaluate the thickness of the deposited films.

![Figure 1. XRD pattern of Cu-0.02, Cu-0.018, Cu-0.016 and Cu-0.014.](image-url)
3. Results and discussion

3.1. Optimization of copper molar concentration

3.1.1. X-ray diffraction (XRD) studies

Figure 1 depicts the XRD pattern for samples of Cu-0.02, Cu-0.018, Cu-0.016 and Cu-0.014. * and # symbols are used to allude to the secondary phases of CuxS and ZnS, respectively. The acquired XRD pattern is compared with the standard JCPDS of CZTS (26–0575). The existence of hkl planes (112), (200), (220) and (312) matches with standard JCPDS of CZTS and corroborates the formation of the polycrystalline kesterite phase. Furthermore, the films exhibit preferential orientation along the (112) plane. Besides that, the formation of pure CZTS is complicated due to its narrow chemical potential region, and it is more prone to the occurrence of binary and ternary secondary phases such as CuS, ZnS, SnS2 and Cu2SnS3 [38]. The existence of the minor CuxS phase is observed in the XRD pattern. The existence of the CuxS phase must be ascribed to the formation of a copper-rich film and evident compositional results were given in the EDS analysis. The intensity of the CuxS secondary peaks is diminished with respect to the reduction in copper concentration. The film deposited with Cu-0.016 M exhibits the less intense secondary phases, whereas the films deposited with Cu-0.014 M showed the existence of the ZnS along with Cu0S secondary phases. The occurrence of ZnS might correspond to the higher amount of zinc present in the Cu-0.014 M sample. The presence of the Cu0S secondary phase might short the solar cell, and the existence of the ZnS secondary phase reduces the active area of the solar cell [20]. So, evading the existence of unwanted phases is more pivotal to facilitate the performance of the solar cell.

The Scherer formula is employed to evaluate the crystallite size of the synthesized CZTS film. 

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]

\[ \lambda = \text{Incident wavelength of the CuK}\alpha (1.5406 \text{ Å}) \]

\[ \beta \] is the FWHM, \( \theta \) is the Bragg angle. The microstrain (\( \varepsilon \)) is calculated using the following relation 

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]

The dislocation density (\( \delta \)) is evaluated using Williamson and Smallman’s formula \( \delta = 1/D^2 \) [15].

### Table 1. Crystallite size, microstrain, dislocation density and lattice parameters of Cu-0.02, Cu-0.018, Cu-0.016 and Cu-0.014.

| Sample name | \( \theta (°) \) | FWHM (°) | The crystallite size (nm) | Microstrain \( \times 10^{-3} \) | Dislocation Density \( \times 10^{14} \) lines \( \text{m}^{-2} \) | Lattice parameters |
|-------------|-----------------|----------|--------------------------|-------------------------|-----------------------------------|-------------------|
| Cu-0.020    | 28.07           | 0.27     | 29.5                     | 1.17                    | 11.47                             | a(Å) 10.82        |
| Cu-0.018    | 28.14           | 0.26     | 30.7                     | 1.12                    | 10.55                             | 5.45  10.85       |
| Cu-0.016    | 28.22           | 0.25     | 32.1                     | 1.07                    | 9.67                              | 5.44  10.88       |
| Cu-0.014    | 28.25           | 0.29     | 27.3                     | 1.26                    | 13.36                             | 5.44  10.90       |

![Figure 2. \( (\alpha h\nu)^2 \) versus \( h\nu \) plot of Cu-0.02, Cu-0.018, Cu-0.016 and Cu-0.014](image-url)
The lattice parameter of the tetragonal crystal structure is calculated using the following relation

\[
\frac{1}{d^2} = \left( \frac{h^2 + k^2}{a^2} \right) + \frac{l^2}{c^2}
\]

Where \(h, k\) and \(l\) are miller indices and \(d\) is an inter-planar spacing \[26\].

The crystallite size, microstrain and dislocation density values of the CZTS thin films deposited at various copper concentrations are depicted in table 1. The films synthesized at a stoichiometric copper molar solution of 0.02 M showed a crystallite size of 29.5 nm. The crystallite size was increased to 30.7 nm for films synthesized using 0.018 M of copper solution. The observed improvement in the crystallinity might correspond to the reduction of the Cu$_x$S secondary phase compared to films synthesized using stoichiometric composition. Further, an increment in crystallite size of 32.1 nm was obtained for films synthesized using a copper molar solution of 0.016 M. Consequent reduction in the Cu$_x$S secondary phase might be the cause for an enhancement in crystallinity. The CZTS thin films deposited using Cu-0.014 M precursor solution exhibits less copper element ratio of Cu/(Zn+Sn) = 0.70. The observed copper reduction facilitates the formation of additional secondary phases i.e., ZnS. The occurrence of this secondary phase might promote the strain in lattice and reduce the crystallinity of CZTS \[25, 39\]. The film deposited at Cu-0.016 M exhibits a higher crystallite size of 32.1 nm with less microstrain and dislocation density compared to the films deposited with other copper concentrations. The calculated lattice parameters of \(a = 5.44\) Å and \(c = 10.88\) Å was obtained for CZTS thin film deposited using Cu-0.016 molar concentration.

### 3.1.2. UV–vis spectroscopy

The optical properties were determined using UV–vis spectroscopy. Figure 2 depicts \((\alpha h\nu)^2\) versus \(h\nu\) for Cu-0.02, Cu-0.018, Cu-0.016 and Cu-0.014. Tauc’s relation is employed to evaluate the band gap for a synthesized film. \(\alpha h\nu = A(h\nu - E_g)^n\). \(\alpha\) is the absorption coefficient. \(A\) is a constant. \(h\) is Planck’s constant. \(\nu\) is the photon energy. \(n = 1/2\) for a direct allowed transition \[26\].

The thin film deposited at 0.02 M of copper concentration has a wider band gap of 1.62 eV compared to the standard CZTS band gap of \(\sim 1.50\) eV. The occurrence of the Cu$_x$S phase is the chief cause for existed wide band gap of the material. The Cu$_x$S has a band gap in the range 1.7 eV–2.16 eV \[40\]. Moreover, the band gap is found to be getting narrow for films deposited with less copper molar concentration compared to the stoichiometric concentration. The thin films synthesized at a copper molar concentration of Cu-0.018 showed the narrow band gap of 1.56 eV as compared to band gap of 1.62 eV, for the films synthesized at Cu-0.020 M. Further the band gap getting narrow as 1.52 eV and 1.49 eV for films synthesized using Cu-0.016 and Cu-0.014 M respectively. The obtained narrowness in the band gap might correspond to the reduction in Cu$_x$S secondary phase for the films synthesized with less copper molar concentration. Those obtained results insisted that the composition of copper present in the film have a pivotal role in defining its optical properties. The thin film deposited at a copper concentration of 0.016 M has a direct band gap of 1.52 eV is near to the reported CZTS direct band gap of \(\sim 1.50\) eV.

Figure 3. Transmittance spectra of Cu-0.02, 0.018, 0.016 and 0.014.
Figure 3 depicts the transmittance spectra of Cu-0.02, Cu-0.018, Cu-0.016 and Cu-0.014 Samples. The films have a very less transmittance percentage, i.e., 3% on the wavelength region of 400–700 nm regardless of the copper concentration. The obtained less transmittance attributes to the higher absorption in this region. This higher absorption is an important fundamental property for the absorber layer. All the CZTS thin films have a thickness of around $\sim 1.3 \mu m$.

The absorption coefficient of CZTS thin film for various copper concentrations is given in figure 4. The absorption coefficient was calculated using the basis of lambert’s law $\alpha = 2.303 A/t$. where $A$ is the absorbance; $t$ is the film thickness [41]. The absorption coefficient is found to be around $10^4 \text{cm}^{-1}$ for all the deposited films. It has been observed that films with less copper elements exhibit a higher absorption coefficient compared to films that have a higher amount of copper elements.

3.1.3. Scanning electron microscopy (SEM)
As seen in figure 5, distinct spherical grains were obtained in the SEM micrographs for CZTS thin films. Besides that, the pinholes and voids are found to be reduced with a decrease in copper molar concentration. The
observed spherical grains belong to copper-rich secondary phases and the evident elemental results were discussed in the EDS analysis. The CZTS thin film deposited using Cu-0.020 M and Cu-0.018 M showed a higher number of spherical grains on the film surface. When the copper molar concentration decreased to 0.016 M, a significant reduction in the number of spherical grains has been observed. The films deposited using Cu-0.014 M showed a minor presence of spherical grains as compared to the films synthesized using 0.020 M copper concentration. A notable reduction in the number of spherical grains was observed for the films synthesized with less copper molar concentration. The reduced number of spherical grains attributes to the minimization of secondary phases [42]. The calculated average spherical grain size for CZTS thin films synthesized using various copper concentrations was ~0.79–1.3 μm.

3.1.4. Energy dispersive x-ray spectroscopy (EDS)

Figure 6 depicts the EDS spectra of CZTS thin film and its quantitative weight percentage. The observed results show that copper weight percentage in the film is decreased, corresponds to the reduction of copper concentration in the precursor solution.

Figure 7. Atomic Percentage of elements present in Cu-0.02, Cu-0.018, Cu-0.016 and Cu-0.014.
The atomic percentage and composition ratio of Cu-0.02, Cu-0.018, Cu-0.016 and Cu-0.014 are shown in figures 7 and 8, respectively. Copper atomic percentage in CZTS thin film was found to be reduced as expected due to a reduction of copper molar concentration in the precursor solution.

Table 2 shows the atomic percentage of elements and its ratio of CZTS thin film. The copper element atomic percentage of 33.12 was obtained for the films synthesized using 0.020 M copper precursor solution. The copper element percentage for Cu-0.018, Cu-0.016 and Cu-0.014 M reduced to 30.93, 28.95 and 26.94 respectively. Moreover, zinc atomic percentage is found to increase with the reduction in copper molar concentration.

Besides that, Cu/(Zn + Sn) molar ratio is reduced from 1.09–0.70 with respect to the reduced amount of copper molar concentration in the precursor solution. The reduction of the tin element in the as-deposited film might correspond to its evaporation during the spray pyrolysis process. The variations in the tin composition might be attributed to the formation of SnS which is ascribed to its higher vapour pressure [43, 44]. The various reports showed that Cu/(Zn + Sn) ≈ 0.8 and Zn/Sn ≈ 1.20 is optimal for CZTS solar cells to achieve higher power.
conversion efficiency [45]. The reduction of secondary phase formation in the film synthesized at optimal composition ratio is the main cause for the enhancement in device performance. The profuse copper present in the film is the cause for the obtained copper-related secondary phase of Cu_xS in the XRD pattern. Besides that, all the films exhibited sulfur deficiency regardless of all the experimented copper concentrations. The sulfur evaporation process during spray pyrolysis is the cause of sulfur deficiency [36]. CZTS thin film synthesized using Cu-0.016 M was found to have a copper-poor and the zinc-rich composition ratio of Cu/(Zn + Sn) = 0.83 & Zn/Sn = 1.32.

Figure 9(a) Shown EDS point scan area of spherical grains presented in the CZTS thin film. The respective qualitative spectra and quantitative weight percentage were shown in figure 9(b). The qualitative EDS spectra display the profuse enrichment in the copper element. The spherical grains comprise the element percentage of Cu:Zn:Sn and S are 45.7:13.2:5.43 and 35.6 respectively. The abundant copper element present in the spherical grains indicates the possible presence of Cu_xS secondary phases. The possible Cu_xS phase is consistent with the acquired XRD pattern as well. Therefore, the combined XRD and EDS results elucidated that the spherical grains belong to Cu_xS phases.

The origin of the surface segregation of secondary phases during the spray pyrolysis technique was ambiguous. The possible causes for the observed surface segregation of CZTS thin films synthesized using spray pyrolysis techniques were discussed based on the existing reports. Jung et al revealed SnS evaporation during sulfurization lead to the decomposition of the CZTS phase, which is the primary cause for the surface segregation of the CuS phase [46]. Based on their study, we speculate that in our case, the decomposition of CZTS might arise due to the evaporation of Sn during spray pyrolysis. Consequently, the CuS phase might segregate to the surface of the thin film.

Kaur et al investigated the role of the Zn/Sn ratio on the surface segregation of the Cu_{2-x}S phase. According to their proposed mechanism, SnS_x evaporation promotes the uncompensated Cu_xS phase which segregates to the surface of CZTS thin film. The respective chemical equation is mentioned below.
In our study, the surface phase segregation might also arise due to the uncompensated Cu$_x$S present in the CZTS thin film. The reduction of the copper element in as-deposited films suppress the formation of Cu$_x$S secondary phase and, thus it might consequently, minimize phase segregation.

3.2. Optimization of Thiourea molar concentration

3.2.1. X-ray diffraction (XRD) Studies

Figure 10 depicts the XRD pattern for films synthesized with various thiourea concentrations of S-0.08, S-0.10, S-0.12, and S-0.14. All the films showed the formation of the CZTS compound with the existence of minor secondary phases. Moreover, The Cu$_x$S secondary phase peak intensity is found to be reduced with an increase in thiourea concentration from 0.08 M to 0.12 M. The increase of thiourea molar concentration in precursor solution facilitates the growth of CZTS. Furthermore, the presence of a minor ZnS Secondary phase is observed for the films synthesized using 0.14 M thiourea concentration. The reaction between zinc and surplus sulfur present on higher thiourea concentration solution might be the cause for ZnS secondary phase formation.

Table 3 shows the crystallite size, microstrain, dislocation density and lattice parameters of S-0.08, S-0.10, S-0.12, and S-0.14. The crystallite size of 32.1 nm has been observed for the films synthesized using S-0.08 M. The further increment in the sulfur precursor solution to S-0.12 M, S-0.14 M leads to decrease in the crystallite size of 23.1 nm and 19.1 nm respectively. The increase of thiourea molar concentration in precursor solution might induce the strain in the lattice which causes the reduction in crystallite size. The microstrain was increased as $1.07 \times 10^{-3}$ to $1.81 \times 10^{-3}$ with the increase in thiourea molar concentration. Even though the crystallite size was reduced with respect to the increase in thiourea molar concentration whilst, the film deposited using S-0.012 M shows a negligible amount of secondary phase. The lattice parameter of tetragonal crystal structure i.e., $a = 5.43$ Å and $c = 10.94$ Å was calculated for CZTS thin films deposited using S-0.12 M.

![Figure 11. $(\alpha h \nu)^2$ versus $(h \nu)$ plot of S-0.08, S-0.10, S-0.12 and S-0.14.](image)

\[
\text{Cu}_2\text{S} + \text{SnS}_2 \rightarrow \text{Cu}_3\text{SnS}_4[35]
\]
3.2.2. UV–vis spectroscopy

Figure 11 shows the calculated band gap for films synthesized at various thiourea concentrations. The band gap was calculated using the aforementioned Tauc’s relation. The CZTS thin film deposited using a sulfur molar concentration of 0.08 M exhibits a band gap of 1.52 eV. The band gap was found to be broadened to 1.54 eV for the films deposited using S-0.10 M. The continuous broadening in the band gap was obtained as 1.58 eV and 1.61 eV, corresponding to the increase in thiourea molar concentration of S-0.12 M and 0.14 M respectively. Besides that, the presence of a secondary phase might be responsible for the observed wide band gap of 1.61 eV for the films deposited at 0.14 M thiourea concentration [36].

Figure 12 depicts the transmittance spectra for the films synthesized using various thiourea concentrations of S-0.08, S-0.10, S-0.12 and S-0.14. The transmittance percentage of the as-deposited films is less than 3% in the wavelength range between 400–700 nm. The increase in the transmittance percentage was observed corresponds to the increase in thiourea molar concentration.

Figure 13 represents the absorption coefficient of CZTS thin-film S-0.08, S-0.10, S-0.12 and S-0.14. Based on lambert’s law absorption coefficient was calculated. The absorption coefficient is around $10^4$ cm$^{-1}$ for all the deposited films, and it is found to decrease with an increase in thiourea concentration.
3.2.3. Scanning electron microscopy (SEM)

Figure 14 depicts SEM micrographs for the CZTS thin film deposited with various thiourea concentrations. Spherical grains were observed on the surface of the samples. The increase in the thiourea concentration shows a reduction in voids and pinholes on the thin film. Moreover, the thin film deposited using S-0.10 M and 0.12 M

Figure 14. SEM micrographs of S-0.08, S-0.10, S-0.12, and S-0.14.

Figure 15. EDS spectra of (a) S-0.08, (b) S-0.10, (c) S-0.12 & (d) S-0.14 with inset images of the quantitative weight percentage.

Table 4. Compositional atomic percentages and ratio of S-0.08, S-0.10, S-0.12, and S-0.14.

| Sample name | Cu (25%) | Zn (12.5%) | Sn (12.5%) | S (50%) | Cu/(Zn+Sn) | Zn/Sn | S/(Cu+Zn+Sn) |
|-------------|----------|------------|------------|---------|------------|-------|--------------|
| S-0.08      | 28.95    | 19.72      | 14.91      | 36.41   | 0.83       | 1.32  | 0.57         |
| S-0.10      | 27.92    | 20.72      | 14.95      | 36.27   | 0.78       | 1.38  | 0.57         |
| S-0.12      | 27.60    | 18.96      | 14.95      | 38.49   | 0.81       | 1.26  | 0.62         |
| S-0.14      | 28.65    | 19.77      | 14.13      | 37.44   | 0.84       | 1.39  | 0.59         |

3.2.3. Scanning electron microscopy (SEM)

Figure 14 depicts SEM micrographs for the CZTS thin film deposited with various thiourea concentrations. Spherical grains were observed on the surface of the samples. The increase in the thiourea concentration shows a reduction in voids and pinholes on the thin film. Moreover, the thin film deposited using S-0.10 M and 0.12 M
Table 5. Summary of the composition variation works in CZTS thin films synthesized using spray pyrolysis technique.

| Metal salts | Precursor solution variation | Conclusion |
|-------------|-----------------------------|------------|
| Cupric chloride Zinc acetate Stannic chloride Thiourea [48] | Cu\(^{0.007-0.01} M\) Zn\(^{0.005} M\) Sn\(^{0.005} M\) Thiourea | Near-Stoichiometric composition is obtained at Cu\(^{0.009} M\), Zn\(^{0.0045} M\), S\(^{0.05} M\) |
| CuCl\(_2\)·2H\(_2\)O ZnCl\(_2\)·SnCl\(_4\) Thiourea [31] | Cu\(^{0.007-0.01} M\) Zn\(^{0.005} M\) Sn\(^{0.005} M\) Thiourea | Zn rich and sulphur-rich precursors exhibit enhanced optical and electrical properties |
| CuCl\(_2\)·2H\(_2\)O ZnCl\(_2\)·SnCl\(_4\)·5H\(_2\)O [49] | Cu\(^{0.007-0.01} M\) Zn\(^{0.005} M\) Sn\(^{0.005} M\) Thiourea | Cu-17 mmol dm\(^{-3}\) Exhibits higher solar power conversion efficiency |
| CuCl\(_2\)·2H\(_2\)O ZnCl\(_2\)·SnCl\(_4\)·5H\(_2\)O (CS(NH\(_2\))\(_2\)) [50] | Cu\(^{0.007-0.01} M\) Zn\(^{0.005} M\) Sn\(^{0.005} M\) Thiourea | Cu-0.0122 M exhibits enhanced properties over other films with different copper concentration |
| CuCl\(_2\)·2H\(_2\)O (ZnCl\(_2\)·2H\(_2\)O)·2H\(_2\)O [51] | Cu\(^{0.003-0.02} M\) Zn\(^{0.005} M\) Sn\(^{0.005} M\) Thiourea | Cu-0.015 M is suitable for CZTS thin film solar cell |
| CuCl\(_2\)·2H\(_2\)O ZnCl\(_2\)·SnCl\(_4\)·5H\(_2\)O (CS(NH\(_2\))\(_2\)) [This work] | Cu\(^{0.007-0.01} M\) Zn\(^{0.005} M\) Sn\(^{0.005} M\) Thiourea | Cu-0.016 M S\(^{0.012} M\) exhibits optimal properties |
has demonstrated a minimal number of spherical grains, which might be ascribed to the less segregation of secondary phases on the surface compared to the thin films deposited with other thiourea molar concentrations. Incorporation of the sulfur element in CZTS film ameliorates the surface with fewer spherical grains. Further, an increase in the thiourea molar concentration to 0.14 M leads to an increment in spherical grains, which indicates the occurrence of a higher amount of secondary phase. The calculated spherical grains size vary from ~0.8–1.6 μm for films deposited using various thiourea molar concentration.

3.2.4. Energy dispersive x-ray spectroscopy (EDS)

Figure 15 shows the EDS spectra of CZTS thin film and quantitative weight percentage of elements. A higher amount of sulfur weight percentage was observed for CZTS thin film synthesized using 0.012 M.

Table 4 shows the atomic percentage of elements present in the CZTS thin films. The S/(Cu+Zn+Sn) molar ratio is varied from 0.57–0.62 with respect to thiourea concentration on the precursor solution. The formation of SO₂ volatile species during the spray pyrolysis technique reduces the incorporation of sulfur in CZTS thin film [47]. Consequently, slight changes in sulfur element percentage were obtained. The CZTS thin film with higher sulfur atomic percentage, i.e., 38.49 obtained for the S-0.12 sample. Even though an excess amount of thiourea is used on the precursor solution, still the films are sulfur deficient. This is consistent with earlier reports [48, 49]. The sulfur deficiency on the film leads to the formation of vacancy of sulfur (V₅) defect. The presence of V₅ defect formed mid-gap defects state, which acts as an effective recombination center and is deleterious for solar cell performance [20]. The stoichiometric composition of sulfur is required to reduce the V₅ defect on the CZTS thin film. Sulfurization is an alternative process to enhance sulfur content in the film and to obtain the stoichiometric composition of sulfur. The precursor solution deposited with S-0.12 M exhibits a near-optimal composition ratio of Cu/(Zn+Sn) = 0.81 and Zn/Sn = 1.26.

Table 5 Shows the composition optimization works done in CZTS thin films synthesized using the spray pyrolysis technique. The various types of metal salt precursors such as chloride, nitrate, and acetate were used to synthesis CZTS thin film. The films synthesized using copper-poor and zinc-rich composition exhibits the optimal properties to synthesis CZTS thin-film solar cell. In this work, we have obtained CZTS thin films with the near-optimal composition of (Cu/Zn+Sn) = 0.81 and Zn/Sn = 1.26.

4. Conclusion

In summary, the CZTS thin films synthesized using Cu-0.016 M and S-0.12 M show a near-optimal compositional ratio of Cu/(Zn+Sn) = 0.81 and (Zn/Sn) = 1.26. The thin films deposited using Cu-0.016 M exhibits a higher crystallinity compared to the films deposited at other precursor concentration. Subsequently, the band gap is varied in the range between 1.62 eV–1.49 eV with respect to copper concentrations. The phase segregation of the secondary phases was reduced regarding appropriate copper and thiourea molar concentration. Moreover, the relative reduction in secondary phases and higher composition of sulfur were observed for the CZTS thin films synthesized using S-0.12 M. This result triggers the importance of understanding the various molar concentrations of precursor solutions on pyrolyzed CZTS thin films. On the basis of the obtained results, a further critical investigation is needed in the synthesis of CZTS thin film using the spray pyrolysis technique to attain negligible amount phase segregation on the surface.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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