Study of kesterite Cu₂ZnSnS₄ (CZTS) thin films deposited by spray technique for photovoltaic applications

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ABSTRACT

For the synthesis of an absorber crystalline layer of the solar cell device, the Cu₂ZnSnS₄ (CZTS) absorber is fabricated by using the sol–gel method and the spray deposition technique. The proposed method in this study aims to synthesize stoichiometric CZTS thin films without the sulfurization process and use of a toxic atmosphere. Thin films CZTS were sprayed on the substrates annealed at different temperatures, that are 250, 300 and 350 °C, for solar cell applications. This study highlights the effect of the substrate temperature on the structural, morphological and optical properties of the CZTS deposited films. Therefore, in this study, at the higher substrate temperature, which is 350°C, a semi-optimal band-gap value of $E_g = 1.3$ eV was obtained. For all prepared CZTS thin films, the structural and optical properties were discussed in the light of the variations in the observed microstructure at different substrate temperatures.

1. Introduction

It is a crucial point for the success of the commercialization of solar cells to achieve a high efficiency, and the used materials should be inexpensive and environment friendly. These criteria can be fulfilled by performing a rapid research in the field of thin film solar cells based on the quaternary compound Cu₂ZnSnS₄ (CZTS). In fact, CZTS has drawn attention because of its promising properties and thus becomes a promising candidate for solar cell applications. The abundant presence of this compound, its low cost and the presence of non-toxic elements in its structure makes it an optimal choice as an absorber layer in solar cells [1]. Moreover, it has attractive characteristic optical properties with a direct band-gap energy of $E_g = 1.5$ eV and a large absorption coefficient on the order of $10^4$ cm⁻¹ [2,3].

CZTS films have been prepared by several deposition methods such as sputtering [4,5], electrodeposition [6,7], sol–gel method [8–11], pulse laser deposition [12] and spray pyrolysis [13, 14]. One of the attractive non-vacuum techniques is the spray pyrolysis method. This method has different characteristics such as its versatility and easiness to deposit films over a large area [15]. Different studies revealed that the usage of the spray pyrolysis technique shows the success of fabrication of CZT (S, Se)-based thin-film solar cells [16]. However, most of the CZTSSe-based solar cells were reported in the literature employed CZTSSe films with selenium-rich compositions. In view of the toxicity issue, the use of pure sulphide compound (i.e. CZTS) would be preferable [17]. In other words, to avoid the toxicity issue due to the presence of the selenium element, it would be preferable to use a pure sulphide compound, that is, CZTS [17]. Elaborating CZTS thin films with free annealing sulfurization onto indium-doped tin oxide-coated glass substrates for solar cell applications has been performed in the studies done by Azmi et al. [18,19]. But, on the other hand, using a spray technique to fabricate...
CZTS thin films with free annealing sulphurization is also of great interest. That’s mainly because, in this method, the deposition process starts with the deposition of a thin film by spraying a solution onto a preheated substrate in which the constituents will react to form the required chemical compound. Moreover, the spray pyrolysis process is simple and it has a number of advantages which can be concluded as the following: (i) the first advantage of using the non-vacuum technique as a deposition method. (ii) Secondly, the spray pyrolysis process does not require any high-quality targets and/or substrates. (iii) The most important and useful advantage is the controlling of the stoichiometry of prepared films. This can be achieved easily by changing the concentrations of the precursors in the starting solution. (iv) Additionally, an easy doping can be done by adding the soluble salt of a dopant to the precursor solution. (v) Moreover, the absence of the restrictions related to the dimensions of the film’s substrate or on its surface profile. (vi) Large area deposition is possible. (vi) Finally, with this technique, a vacuum isn’t required at any stage during the deposition and is able to deposit thin films on a large scale; resulting in great advantages for industrial applications [20]. The required chemical compound in the deposited thin films by spraying a precursor solution on preheated substrates in a range between 250 and 650°C will be formed upon the reaction of the constituent elements. For example, recently, in 2016, the highest efficiency of 8.1% was recorded for an optimal Cu-poor and Zn-rich composition of a pure sulphide CZTS thin film. In this case, the film was fabricated on an Mo-coated glass substrate; and the fabrication process was done by utilization of the spray pyrolysis to spray an aqueous precursor solution containing Cu(NO$_3$)$_2$, Zn(NO$_3$)$_2$, Sn(CH$_3$SO$_3$)$_2$ and thiourea followed by sulphurization at 600°C for 30 min [21]. In general, a sol–gel solution has usually been prepared by using 2-methoxyethanol (C$_3$H$_8$O$_2$) as a solvent, which is expensive, toxic and needs low-temperature processing [22]. To overcome these difficulties, an alternative solvent in the preparation of a gel solution was suggested. This solvent is dimethyl sulfoxide (DMSO), which is known to have good characteristics such as being a low cost and non-toxic solvent [23–25]. It has been shown that this alternative solvent will truly assist to achieve the fabrication of low cost and safe solar cells. DMSO has been reported as a promising solvent that can dissolve many metal salts and thiourea. Good controlling of the metal composition as well as the precursor solution can be obtained by using DMSO solvent, and thus, desired metal composition of the absorber could be obtained [26].

The main challenge to produce CZTS solar cells is the production of a single-phase CZTS film. That’s simply because the phase diagram of CZTS indicates that stoichiometric single-phase CZTS has a very small region so that the synthesis of an impurity-free, stoichiometric, single-phase CZTS film is a main challenge for the production of CZTS solar cells [27]. Thus, many parameters have to be adjusted during the spray deposition procedure. The atomic ratio of the constituent elements in the prepared solution, the carrier gas pressure, the spray rate and the speed of movement of the spray head are the important parameters which have to be optimized in order to improve the quality of the prepared films. However, the most significant parameter in the spray deposition procedure is the substrate temperature. The optimization of the substrate temperature is truly needed during the spray deposition procedure and usually results in the reduction of the formation of secondary phases as well as bulk and grain boundary states. In this context, one should note that the improvements in the physical properties of CZTS films as well as the solar cell efficiency usually associated with compositional ratio values of Cu/(Zn + Sn) and Zn/Sn are between 0.8 and 0.9 and 1.2 and 1.3, respectively [28].

In the view of the cost-effectiveness, a complete avoidance of vacuum technology is required; and non-vacuum techniques are more preferable because they are generally cheaper. Generally, in these techniques, deposition of CZTS thin films have been achieved by using the lower cost machines which are suitable for the deposition of thin films. For example, the spray pyrolysis technique has been proved to be an extraordinarily flexible and practical materials synthesis method. However, the resulting material usually includes more impurities. Moreover, in such a deposition method, a multiple coating and cracks are expected [29].

In order to synthesize a stoichiometric CZTS thin films without sulphurization process and/or use of toxic atmosphere such as H$_2$S or "S" vapour, the aim of this study is to synthesize a stoichiometric CZTS thin film prepared by a non-toxic DMSO-based sol–gel solution and deposited by using the spray technique at three different substrate temperatures, that are, 250, 300 and 350°C. The CZTS thin films were investigated in terms of their structural, compositional, morphological and optical properties. The proposed approach in this study showed that there is a possibility of the result in the development for the synthesis process of CZTS films to be easy, toxicless and low cost. Additionally, the proposed method will ensure the resulting material will be free from impurities, and the presence of a multiple coating and cracks will be eliminated.

2. Materials and methods

The preparation of the CZTS precursor solution involves dissolving 0.88 M CuCl$_2$·2H$_2$O (Sigma Aldrich, 99%), 0.52 M ZnCl$_2$ (Sigma Aldrich 98%), 0.25 M SnCl$_2$·2H$_2$O (Sigma Aldrich 99%) and 2.36 M CH$_3$N$_2$S (Sigma Aldrich,
99.0%) in 5 mL DMSO (Sigma Aldrich, 99.8%). The preparation steps of the CZTS precursor solution are shown in Figure 1. Adding different metal salts into the solvent sequentially to prepare the precursor solution was illustrated in Figure 1(a). A deep-green suspension was observed to be transformed into a clear solution with a very light-yellow colour after adding thiourea. This observation might denote the reduction of Cu$^{2+}$ to Cu$^+$ which is usually associated with the stabilization of metal ions due to the presence of the DMSO and/or chloride anions. Little Cu$^{2+}$ might remain in the solution after adding thiourea. This expectation is due to the observation of the final light-yellow solution, and this can be clarified by the formation of CuCl$_4^{-}$ as a species which has a yellow colour from the unreacted Cu$^{2+}$ in a solution with a high Cl$^-$ concentration [30]. The preparation of the solution was done at a slightly elevated temperature between 50 and 60 °C while applying stirring to ensure the good mixing of the constituent elements. After obtaining a homogeneous and clear solution, it was sprayed at a flow rate of 2.5 mL/min with a 1.5 bar air blast atomizer pressure and 17 cm for the nozzle-to-substrate distance. Once again, the spray pyrolysis technique is an atmospheric pressure chemical synthesis of the materials, in which a precursor solution of chemical compounds was prepared in the proper solvent and then sprayed onto the heated substrate in order to eliminate impurities in the resulted films. The used substrates in which the films were sprayed were made from soda-lime glass. These substrates were cleaned with methanol and then dried with a clean soft fabric. During the spraying procedure, the annealing of the substrates occurred at 250, 300 and 350 °C for 3 min in air (Figure 1(b)). The prepared films are named: CZTS-250, CZTS-300 and CZTS-350. Furthermore, the final solution was transferred to the glass substrate, dried and then powder from this solution was separated. This powder was washed with ethanol and analysed by transmission electron microscope (TEM- JEOL 1400). The TEM micrographs of the separated powder are shown in Figure 2. Figure 2(a) reveals the presence of the nanoparticles with dispersion in their sizes. Gradually increasing the TEM image magnification in Figure 2(b,c) better illustrates the presence of nanoparticles with different sizes, ranging between 2 and 4 nm. This observation confirms the synthesis of the crystalline CZTS nanoparticles, which has been composed entirely of non-toxic, inexpensive and abundant elements using sol–gel solution.

The obtained CZTS films were investigated by means of an X-ray diffraction (XRD) by using Shimadzu Lab X XRD-6000 diffractometer with a Cu–K$\alpha$ ($\lambda = 1.5406$ Å) radiation source in the 2$\theta$ range between 20° and 80° in order to investigate their structural properties. By using the International Centre for Diffraction Data (ICDD) database, the phase determination was done by a comparison of the experimentally measured inter-plane distances with those in the database. Raman scattering was performed at room temperature using a Bruker Optics SENTERRA dispersive Raman spectrometer equipped with 532 nm (5 mW) excitation laser. Using field-emission scanning electron microscopy (FESEM, Model: Quanta 250) with an energy dispersive X-ray (EDX) analyzer, an insight was given into the morphology and elemental analysis of the CZTS films. Moreover, the morphology of the film surface was analysed with a Vecco (Digital Instrument CP-II) atomic force microscope (AFM). The thickness of films was measured by the

![Figure 1](image-url)

**Figure 1.** Preparation steps of the CZTS precursor solution: (a) photographs of the precursor solution for the CZTS preparation by adding different precursors into the solvent sequentially, (b) schematic of the formation of the CZTS thin films via thermal decomposition and reaction by using the spray technique.
Figure 2. TEM micrograph of the separated powder from the final solution shown in Figure 1(a). (a) TEM image at low magnification. (b,c) TEM image by gradually increasing magnification.

Figure 3. XRD patterns of sprayed CZTS thin films deposited at different substrate temperatures.

3. Results and discussion

3.1. Structural properties

Patterns of the XRD measurements for the CZTS thin films prepared at the three selected substrate temperatures, that are 250, 300 and 350 °C, are shown in Figure 3. The presence of polycrystalline CZTS diffraction peaks assigned to the (112), (200), (220) and (312) according to (PDF) #00-026-0575 of CZTS kesterite. The observed diffraction angles (2θ) for the recorded peaks are: 28.2° for the (112) atomic plane, 32.7° for the (200) atomic plane, 47.1° for the (220) atomic plane and 55.9° for the (312) atomic plane. The resulting patterns indicate that the Cu2ZnSnS4 thin films present the typical tetragonal structure of kesterite. Once again, the locations of the observed angle of each peak well match the powder diffraction file (PDF) #00-026-0575. The relatively intense and sharp peaks are observed to become more pronounced as the annealing substrate temperature increases. As the peaks in the XRD pattern intensified, the FWHM has been observed to be reduced. This observation confirms the improvement of the crystallinity of the films which has been induced by the increment in the substrate temperature. Based on the calculations, the films possess the lattice constants of $a = 5.4127$ Å and $c = 10.8465$ Å, which shows the value of $a = 2c$ and indicates the association of the kesterite structure with a tetragonal unit cell.

Calculating the size of the crystallites is done by using the Scherrer formula according to the location and the FWHM of the main diffraction peak (112) by using this equation [31]:

$$L = \frac{k\lambda}{\beta \cos \theta}$$

By considering the Scherrer’s constant $k = 0.94$ for the FWHM of spherical crystals with cubic symmetry; $\lambda$ is the wavelength of the X-ray; $\beta$ is the width of the diffraction peak at its half maximum and $\theta$ is the Bragg diffraction angle, the size of the crystallites can be obtained [32]. The variation in the crystal size upon increasing the heating substrate temperature can induce variations in different related properties, including the dislocation...
density ($\delta$), microstrain ($\epsilon$) and texture coefficient (TC). The calculation of the dislocation density ($\delta$), which is known as the number of dislocation lines per unit volume of the crystal, can be obtained by the inversion of the square of the crystallite size according to this equation [32]

$$\delta = \frac{1}{L^2}$$

While the origin of microstrain ($\epsilon$) is associated with the deposition conditions and can be calculated from [33]

$$\epsilon = \frac{\beta \cos \theta}{4}$$

The value of the microstrain is an indicator of the compressive stress as well as the local distortion in the lattice planes due to the presence of the plastic deformation. Finally, the texture coefficient (TC) is a parameter that is often used to determine the degree of texture or preferred orientation in the sample. Calculation of the texture coefficient can be done by using the formula [34]:

$$TC_{hkl} = \frac{l(hjKj)}{l_0(hjKj)} \frac{1}{n} \sum_{j=1}^{n} \frac{l(hjKj)}{l_0(hjKj)}$$

The count of intensity for the observed peak is $l(hjKj)$, while the count of the standard relative intensity obtained from the crystallography open database is $l_0(hjKj)$. Finally, $n$ is the number of the plane’s peaks observed in the acquired XRD pattern.

The results of the calculations, in which the crystallite size ($L$) is obtained by using Equation (1); the dislocation density ($\delta$) is acquired by using equation (2); the microstrain ($\epsilon$) is achieved by using equation (3) with the main diffraction peak, the (112) and the texture coefficient (TC) for three crystallographic planes, the (112), (220) and (312), are determined by using equation (4), are shown in Table 1. Interestingly, the reduction of the values of $\delta$ and $\epsilon$ are found with increasing substrate temperature. Thus, the lower values of $\delta$ and $\epsilon$ are recorded for the CZTS-350 film. This result confirms that a higher substrate temperature allows CZTS to develop more perfect microstructures. This development of the microstructure is due to the releasing of the stresses that have built-up in the layers, as the substrate temperature increases. Finally, the TC values for all sprayed films indicate that the (112) plane is preferentially aligned parallel to the substrate, with the recorded value higher than one. In this context, one should note, also, that a higher TC value in the (112) plane is also found for the CZTS-350 film. This fact confirms the well-developed characteristic microstructure of this film, with a relatively high crystal size in (112) direction according to Table 1.

The confirmation of the kesterite CZTS phase has been done by using the Raman scattering measurement. Figure 4 shows the major Raman peak at 331 cm$^{-1}$ that corresponds to the CZTS compound and is in good agreement with the reported observations by Ziti et al. [35] and by Chen et al. [36]. Thus, at various annealing temperatures for substrates, the formation of CZTS films was confirmed by the XRD and Raman scattering measurements. The FWHM ($\beta$) of the Raman mode might provide information about the crystal quality. The tendency of increasing crystalline quality with the substrate temperature from 250 to 350°C is clear. This is because the FWHM ($\beta$) of CZTS-350 is found to be decreased from 45 to 38 cm$^{-1}$ at a higher substrate temperature, indicating an improvement in the crystallinity [37]. The consistency of these results with the XRD analysis is clearly observed. However, the “CZTS-300” sample shows a non-uniformity in the peak shape. This might be explained by the presence of several less-crystalline sulphide compounds [17].

The determined sizes of the crystallites ($L$) in Table 1 were directly obtained from the measured XRD patterns and well match the morphological studies by using SEM micrographs which give insight on the film’s microstructure, and by using the AFM technique for the topographical features. Figure 5 displays the SEM

![Figure 4. Raman spectra of sprayed CZTS thin films deposited at different substrate temperatures.](image)

| Sample | Crystallite size/L (nm) (112) | Dislocation density/\delta (lines/m²) (112) | Microstrain/\epsilon (112) | Texture coefficient/TC$_{112}$ | Texture coefficient/TC$_{220}$ | Texture coefficient/TC$_{312}$ |
|-------|-----------------------------|-----------------------------------------|----------------------|-----------------------------|-----------------------------|-----------------------------|
| CZTS-250 | 6.2 ± 0.1                   | 0.0254                                   | 0.0057               | 1.5                         | 0.8                         | 0.6                         |
| CZTS-300 | 7.7 ± 0.1                   | 0.0022                                   | 0.0016               | 1.5                         | 1.0                         | 0.4                         |
| CZTS-350 | 18.2 ± 0.1                  | 0.00099                                  | 0.00096              | 2.9                         | 0.08                        | 0.01                        |
micrograph and AFM images for the CZTS-250 film. The SEM micrograph in Figure 5(a) reveals that the surface morphology of this film exhibits agglomerations of small grains with some voids in between. The presence of the grain agglomerations in this film might be due to the presence of nanocrystals of the CZTS compound. As the annealing temperature and the time are relatively small, an observation of separate grains has not been recorded. The presence of different voids in this film might degrade its performance as an absorber layer. This observation has been confirmed by having a clear view of the topographical features in 2D and 3D AFM micrographs in Figure 5(b,c), respectively. Figure 5(b) illustrates the topographical 2D AFM image of the CZTS-250 film, in which the presence of spherical grains homogeneously through the films was observed as well as the presence of some voids in the film’s surface. The 3D AFM image of this film is shown in Figure 5(c). According to this image, the wide column structures were observed, which are in good agreement with the observed agglomerations of grains in the SEM micrograph (Figure 5(a)).

Moving to CZTS-300 film, SEM images of its morphology as well as the AFM images of its topographical features are shown in Figure 6. The microstructure of the prepared CZTS-300 film is shown in Figure 6(a) which reveals the presence of a dense surface associated with the presence of the porous structure as well as significant clear grains. Furthermore, the clearer view of the observed grains in Figure 6(a) compared to those exist in the CZTS-250 film’s morphology in Figure 5(a) was observed. Such observation confirms the development of the crystallinity nature of the film’s morphology. This development was achieved upon increasing the substrate temperature. The observed topographical features of the CZTS-300 film are shown in the 2D AFM image (Figure 6(b)) and in the 3D AFM image (Figure 6(c)). According to these figures, the presence of spherical grains homogeneously through the films accompanied by some voids in the film’s surface was observed. Additionally, observation of the wide column structures was also recorded.

SEM micrograph, 2D and 3D AFM images for the CZTS-350 film are shown in Figure 7. According to the SEM micrograph in Figure 7(a), the morphology of this film exhibits the presence of separate grains that tend to grow by coalescing together. This observation is in good agreement with the XRD structural calculation results, which reveal a larger crystal size for this film, are in Table 1. The good crystallinity of this film is attributed to the relatively high substrate temperature that induces the growth of CZTS compound. The 2D AFM image (Figure 7(b)) and the 3D AFM image (Figure 7(c)) illustrate the topographical data for the CZTS-350 film clearly showing that the column structure becomes sharper and denser. This is due to the initial growth stage which has been induced by increasing substrate temperature. In this case, the grains become sharper.
and tend to coalesce together as it has been shown in the SEM micrograph in Figure 7(a).

The composition of the three prepared films was obtained by using EDX at different zones on the surface of each sample, and the corresponding average values of the atomic percentages of Cu, Sn, S and Zn elements are shown in Table 2. Knowing that the composition ratios of the optimized CZTS solar cell efficiency are Cu/(Zn + Sn) = 0.8–0.9, Zn/Sn = 1.1–1.3 and S/metal = 0.9–1 [38], the atomic ratios of Cu/(Zn + Sn), Zn/Sn and S/metal for the three prepared films are found to be close to these composition ratios, with slightly Cu-poor and Zn-rich compositions. In this context, one should note that a poor Cu and rich Zn compositions for a CZTS absorber layer was found to minimize the presence of the secondary phases while keeping optimal electrical properties of the films [39].

Average roughness values of the prepared CZTS films were observed in the 3D AFM and were estimated to be 32.9 nm for CZTS-250, 0.08 for CZTS-300 and 25.4 nm for CZTS-350. These values show a large variation and do not depend on the substrate temperature. The relatively high values for the CZTS-250 and CZTS-350 thin films might be indicative of vertical growth, while the low value for CZTS-300 might be due to the lateral growth of the film.

3.2. Optical properties

Investigation of the CZTS films revealed the presence of different values of transmittance (T) and diffuse reflectance (R), and these values for the prepared films are shown in Figure 8. According to Figure 8(a), the maximum transmittances at wavelengths λ > 1.8 µm are 5, 15 and 30% corresponding to the samples with substrates annealed at 300, 250 and 350°C, respectively. Knowing that the thicknesses of the prepared films are: 16 µm for the CZTS-250 film, 19 µm for the CZTS-300 film and 14 µm for the CZTS-350 film, the low transmittances for the sprayed films might be explained in terms of their high thicknesses. Moreover, the observed microstructure of the prepared films reveals the presence of small grains, which are agglomerated together, as shown in the SEM micrographs in Figures 5(a), 6(a) and 7(a). Thus, the light cannot be transmitted easily. However, the increased transmittance of the CZTS-350 film might be explained in terms of the presence of separate grains with certain voids in its microstructure (Figure 7(a)). Additionally, the diffuse reflectance (R) values of the sprayed films for the wavelength range from 200 to 2700 nm are shown in Figure 8(b). According to this figure, all three sprayed films have similar diffuse reflectance values, which are lower than 5%. However, in the region above the material band gap, that is, above a wavelength of 800 nm, the reflectance slightly increases for all sprayed films. In this context, one should note that reduction in the diffuse reflectance of the sprayed films is due to the increase in the thickness of the films; this property leads to the scattering of the incident light, resulting in a decrease of their reflectance.

Other important optical parameters for the determination of the optical behaviours of the respective sprayed films are the absorbance (A) (which is calculated from \( A = 1 - (T + R) \)) and the absorption coefficient (\( \alpha \)), which is calculated from

\[
\alpha = \frac{1}{d} \left[ \ln \left( \frac{1 - R}{T} \right) \right] \quad (5)
\]

**Table 2. Metallic compositions of CZTS films fabricated from precursor solutions at different substrate temperatures.**

| Sample   | Atomic composition (%) | Atomic ratios | Composition  |
|----------|------------------------|---------------|--------------|
|          | Cu     | Zn     | Sn     | S       | Cu/(Zn + Sn) | Zn/Sn | S/metal |               |
| CZTS-250 | 22.64  | 12.56  | 13.03  | 51.77   | 0.88        | 0.96  | 1.07    | \( Cu_{1.8}Zn_{1.1}Sn_{1.3}S_{4.1} \) |
| CZTS-300 | 23.13  | 14.99  | 11.84  | 50.04   | 0.86        | 1.26  | 1.00    | \( Cu_{1.8}Zn_{1.1}Sn_{0.9}S_{4} \) |
| CZTS-350 | 22.27  | 12.86  | 13.98  | 50.89   | 0.82        | 0.91  | 1.03    | \( Cu_{1.7}Zn_{1.1}Sn_{1.5}S_{4} \) |
where $d$ is the thickness of the prepared films [40]. The recorded curves of absorbance ($A$) and the calculated absorption coefficients ($\alpha$) are shown in Figure 9. According to the absorbance data curves in Figure 9(a), all sprayed films showed a good absorbance of the visible wavelengths. However, above the material band gap, that is, above a wavelength of 800 nm, the absorbances are observed to decrease for all films, which indicate that the most absorbent wavelengths are the ones matching CZTS’s band gap. More insight into the absorption behaviour of our respective sprayed films can be obtained by calculating their absorption coefficients ($\alpha$), which are shown in Figure 9(b). This figure reveals that all sprayed films show a maximum value of $\alpha$ between $1 \times 10^3$ cm$^{-1}$ and $2 \times 10^3$ cm$^{-1}$ at photon energy values between 1.5 and 4 eV, as obtained by plotting the absorption coefficient as a function of photon energy. Compared with the maximum values of the absorption coefficient recorded in the previous and similar study [35], which is $10^4$ cm$^{-1}$, the obtained values of $\alpha$ for the sprayed films are relatively low.

The direct optical band-gap energy $E_g$ can be obtained from the Tauc formula relation [41]:

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

Figure 8. Transmittance and reflectance of sprayed CZTS thin films deposited at different substrate temperatures: (a) optical transmittance spectra and (b) optical reflectance spectra.

Figure 9. Absorption behaviour of sprayed CZTS thin films deposited at different substrate temperatures: (a) optical absorption spectra and (b) absorption coefficient spectra.

Figure 10. Determination of optical band gap by extrapolation method from the variation of $(\alpha h\nu)^2$ as a function $(h\nu)$ of the sprayed CZTS thin films deposited at different substrate temperatures.
where $hv$ is the photon energy, $A$ is a constant and $m$ takes the value of 2, for allowed direct transitions [42]. To obtain the direct band gap of the films, $(\alpha hv)^2$ was plotted against the photon energy $hv$, and the linear part of this plot is extrapolated to the photon energy axis at $(\alpha v)^2 = 0$. Graphs of the band gaps are shown in Figure 10. As shown in this figure, the direct optical band gaps of the CZTS thin films, which were deposited at 250, 300 and 350°C, are deduced to be 1.80, 1.60 and 1.36 eV, respectively. Obviously, the band-gap values decreased gradually with the increase in the substrate temperature. The obtained band gaps for the three sprayed films and their reduction with the increase in substrate temperature are drastically different from the observed behaviour for the band gaps obtained by other studies [42,43]. According to these studies, the band-gap values were observed to increase with the substrate temperature, which was explained in terms of losing sulphur during the annealing procedure. However, the observation of the decreasing of the band gaps upon increasing the annealing temperature has been recorded for the CZTS thin films elaborated by a single-step electrodeposition method without the sulfurization process [18,19]. It was demonstrated that the increase in annealing temperature leads to a decrease in the phase impurity presence; and the morphology of the CZTS thin-film surface was improved. In a similar way, our observed band gaps show an optimal behaviour in which increasing the substrate temperatures causes a reduction in the band-gap value, and the tendency to be closer to the optimum value for photovoltaic applications occurs at the higher substrate temperature in this study, that is, 350°C. This observation confirms the improvement in the crystallinity and microstructure of the prepared films upon increasing substrate temperature. Moreover, the presence of a stoichiometric composition without any secondary phases in film’s microstructure plays an important role in achieving a band-gap value close to the optimal one. Similar results were, also, obtained by Bhosale et al. in which the band-gap values shift to lower energies with the increase in the substrate temperature [44]. In terms of these motivating results, it is shown that this preparation strategy for CZTS this film might be more efficient for the photovoltaic solar cells.

4. Conclusions

Spray technique was used with reproducible parameters to deposit CZTS thin films on substrates annealed with different temperatures of 250, 300, and 350 °C by using a DMSO-based sol–gel in the ambient. High-quality CZTS films were prepared by optimizing the substrate temperature conditions. A single phase of (Cu2ZnSnS4) was observed in the prepared films with the characteristic diffractions of the (112), (220), and (312) planes as it has been revealed by the XRD analysis. Thus, the existence of the kesterite CZTS structure as well as polycrystalline nature with an average crystallite size of 6–18 nm were confirmed. The Raman spectra of the films show a single primary Raman peak at 331 cm$^{-1}$ that corresponds to the CZTS compound. For the sake of investigation of the optical properties, transmittance, reflectance and absorbance spectra were measured for all the prepared films. The obtained results confirm that the film formed with a low substrate temperature exhibits a high band-gap value (~ 1.8 eV) with a porous microstructure, a relatively high dislocation density, and microstrain. Increasing the substrate temperature to 300°C reduces the band-gap value to 1.6 eV and improves the film’s microstructure with the presence of significant clear grains of CZTS and relatively lower values for the dislocation density and microstrain. However, in this study, the best properties are obtained at a higher substrate temperature, that is, 350°C. For this film, the calculated band-gap value is observed to be close to the optimum value for photovoltaic applications, with $E_g = 1.3$ eV. Moreover, the film’s structure shows a perfect microstructure with very small values of dislocation density and microstrain and the presence of nanocrystalline CZTS that tend to coalesce and grow. In general, the motivating results obtained in this study confirm the ability of the preparation of a low cost and environmentally friendly Cu2ZnSnS4 absorber layer, and hence, an optimization of the engineering processes of CZTS solar cell devices can be achieved.

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