Cu₂ZnSn(S,Se)₄ absorber layer formation and characterization using solution dip coating and selenization method

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Abstract
In the present study, Cu₂ZnSn(S,Se)₄, popularly known as CZTSSe (Copper Zinc Tin Sulfo-Selenide) film is prepared from the low cost, nontoxic solution by mixing of CuCl₂ (Copper Chloride), ZnS (Zinc Sulfide), SnCl₂ (Tin Chloride), thioacetamide in ethylene glycol to form a precursor solution. Here, we have used for the first time the ZnS compound as a zinc source in place of conventional ZnCl₂ as its binding energy with other constituents is more. The results imply that high quality of CZTSSe film could be feasible by infusing selenium during annealing of the film in selenium atmosphere in the temperature range of 500 °C—520 °C. The formed films shows perfect kesterite structure with a balanced interplanar spacing at the above-mentioned environment. The one-step annealing with selenisation of the as-deposited film shows improved crystallite size, microstrain, and lattice parameters. From the compositional analysis results, the infusion of selenium on annealing at high temperature shows the decrease in Cu/(Zn + Sn) ratio and an increase in Zn/Sn ratio as compared to as-deposited films confirming the required stoichiometric ratio for photovoltaic applications. The SEM image confirms the formation of a compact regular surface when the film is subjected to the annealing process. The bandgap of the film was calculated from UV-vis spectrophotometer and there is an increase in conductivity and mobility of the annealed absorber layer is found from the Hall measurement system.

1. Introduction
In the last 10 years, the thin film based solar cells have attained a substantial momentum due to zero emissions and zero use of fossil fuels. CIGS (Copper Indium Gallium Sulfur) and CIS (Copper Indium Selenide) have record conversion efficiencies of 22.6% [1] and 14.28% [2] respectively. However the constituents In (Indium), Ga (Gallium) are scarce in the Earth’s crust. The paucity of elements drives the researchers to strive for alternative sources such as CZTS which have been explored and are valued as reliable candidates because of the suitable band gap (1.0–1.5 eV), the large absorption coefficient of 10⁴ cm⁻¹, low toxicity and earth abundant material [3–5]. It has been demonstrated that wet chemical route at low temperature is useful for the fabrication of CZTS/Se with considerable efficiency. CZTSSe solar cells can be formed with the hydrazine-based spin coating route with the highest efficiency, but still, it cannot be used for practical applications as hydrazine is highly hazardous. Generally, vacuum-based high-temperature methods suffer from the high volatility of constituents as well as narrow compositional stability window of CZTS [6]. In the present work, CZTSSe compound with good compositional stability i.e. Cu/(Zn+Sn) ≤ 1 and Zn/Sn ≥ 1, Band gap ranging from 1.0 eV to 1.5 eV, and the large optical absorption coefficient of 10⁴ cm⁻¹ is formed using the Ethylene glycol-based precursor solution route which is non-toxic in nature. The precursor solution used to form the CZTSSe films has constituents such as CuCl₂, ZnS, SnCl₂, and thioacetamide (TAA). We have proposed a unique constituent ZnS in place of ZnCl₂ to exploit the binding energy feature. We report the formation of CZTSSe compound by dip coating method and further formation of CZTSSe using selenization procedure in the present manuscript using ZnS as a source of zinc and sulfur. The films were characterized by XRD and Raman (Phase Analysis), SEM
2. Experimental process

All chemicals were of analytical grade and are used as received without further purification. Copper chloride (CuCl₂·2H₂O 99.0%), Zinc Sulphide (ZnS 99.99%), Tin(II) Chloride (SnCl₂·2H₂O 97.02%), Thioacetamide (CH₃CSNH₂ 99.0%) & Ethylene Glycol was from Alfa Aesar. Here in this synthesis, we used ZnS as a Zinc source in place of ZnCl₂ which is conventionally used. As we know, ZnS can be used as a source of zinc as well as for sulfur. So we tried to substitute ZnCl₂ with ZnS to see whether we are having any difference in the properties of absorber layer shown by ZnCl₂. Also, Chlorine is the impurity in the material. Our focus was to reduce the content of Chlorine in the film so that it should not hamper the film properties. Copper(II)chloride (0.007 moles), Zinc Sulphide (0.003 moles), tin(II) chloride (0.004 moles) and thioacetamide (0.026) were dissolved in ethylene glycol (20 ml) to form the precursor solution at room temperature. After that, the precursor solution was covered with aluminium foil and was kept for two to three days in dark to increase its viscosity. Further, the glass substrate was dipped in the above precursor solution to attain the required thickness. The dip coated film was subsequently dried at 100 °C for 30 min and finally, the obtained CZTS films were Selenized in one-step annealing process at 520 °C for 2 min in vacuum (4 × 10⁻² mbar) using selenium shots. The excess Se is mostly got deposited at both the ends of the furnace (which is at lower temperature < 100 °C). After annealing, the sample was slowly cooled to room temperature using the slow cooling mechanism. The details of the experimental process adopted is shown in figure 1. The CZTS film obtained from dip coating deposition method is subjected to annealing in selenium atmosphere at 520 °C to obtain CZTSe film. To analyze the film preparation, both CZTS and CZTSe films were subjected to different characterization methods. The Structural characterization and phase determination of the films was performed by x-ray diffraction (XRD, Shimadzu-6100) with CuKα radiation having λ = 1.54 Å. The compositional analysis of the deposited and the annealed films were done by ED-XRF (Shimadzu EDX-7000). The Raman Analysis of both the films was done using Nd: YAG 532 nm laser to confirm the XRD data. The optical properties were studied by UV–vis Spectrophotometer and the electrical properties were measured by the Hall Effect Measurement system (HMS-3000).
3. Results and discussion

3.1. Structural analysis

To ascertain the phase of the grown samples, XRD analysis was carried out. The XRD patterns of the obtained CZTS precursor film before and after selenization is shown in figure 2. For the as-deposited sample, the major peak is observed at 28.48° indexed to (112) along with few other minor peaks of CZTS were observed at 2θ = 32.6°, 47.3° and 56.1° [JCPDS card no. 52-0868] indexed to (200), (220), (224) respectively. Confirming the formation of CZTS. XRD data with 2θ = 28° to 29° was convoluted and ascertained the presence of CZTS peak with a binary peak of ZnS. The film after selenization shows escalated peak at (112) which conforms to the formation of CZTSSe compound. The minor peaks found in the as-deposited sample vanished when the film is annealed which is again validated from the deconvoluted plot shown in figure 3. The narrow, sharp peak formed at 28.48° confirms the increase in crystallinity of the film. The main peak at (112) is narrow and the increased intensity indicates that CZTSSe thin film has kesterite structure with a crystallite size of 10.57 nm which is calculated from the XRD data (table 1). [7]

Figure 2. XRD patterns of thin film (a) as deposited and (b) after annealing under Se atmosphere at 5200 for 2 min.

Figure 3. XRD patterns of thin film with deconvolution (a) as deposited and (b) after annealing under Se atmosphere.
cannot distinguish the binary phases perfectly but it is not sufficient to identify most of the minor or overlapping phases present. Also, from the XRD graph, we cannot distinguish the binary phases perfectly. So, Raman analysis (Nd:YAG 532 nm laser) is done for the confirmation of the presence if there is any binary phases present in the films. The Raman spectra for the as-deposited and annealed films are shown in figure 4. The spectra indicate a strong peak at 335 cm$^{-1}$ and a weak peak at 229 cm$^{-1}$ which stands for the CZTS compound for the as-deposited sample [11]. As the sample is annealed in the selenium environment as discussed in the experimental process the film shows bimodal spectra [12]. The annealed films show two major peaks at 326 cm$^{-1}$ and 208 cm$^{-1}$ which clearly reveal that the shifted Raman spectra 326 cm$^{-1}$ and 208 cm$^{-1}$ attributed to the CZTS and CZTSSe compounds [13]. The shift in the spectrum can be due to the infusion selenium [14].

3.2. Raman analysis

XRD is generally used as the basic tool to analyze the structure of different compounds formed by phase analysis, but it is not sufficient to identify most of the minor or overlapping phases present. Also, from the XRD graph, we cannot distinguish the binary phases perfectly. So, Raman analysis (Nd:YAG 532 nm laser) is done for the confirmation of the presence if there is any binary phases present in the films. The Raman spectra for the as-deposited and annealed samples are shown in figure 4. The spectra indicate a strong peak at 335 cm$^{-1}$ and a weak peak at 229 cm$^{-1}$ which stands for the CZTS compound for the as-deposited sample [11]. As the sample is annealed in the selenium environment as discussed in the experimental process the film shows bimodal spectra [12]. The annealed films show two major peaks at 326 cm$^{-1}$ and 208 cm$^{-1}$ which clearly reveal that the shifted Raman spectra 326 cm$^{-1}$ and 208 cm$^{-1}$ attributed to the CZTS and CZTSSe compounds [13]. The shift in the spectrum can be due to the infusion selenium [14].

3.3. Compositional analysis

The elemental analysis and thickness of films were studied by ED-XRF (SHIMADZU-7000) as shown in figures 5(a)–(b) indicate the elemental peaks of both the as-deposited and for the annealed at different energy levels. The table 2 shows each constituent’s atomic percentage and it is clearly evident that after annealing the appropriate stoichiometric ratio is obtained which is suitable for photovoltaic applications [15] i.e. Copper poor and zinc rich, satisfying the ratio of Cu/(Zn+Sn) ≤ 1 and Zn/Sn ≥ 1. The measured thickness of the as-deposited and annealed sample is 1.53 ± 0.05 um and 2.33 ± 0.6 um respectively.

3.4. Morphological analysis

The morphological characteristics were studied through SEM analysis where we can see a noticeable change in the grain size increment from as-deposited (a) to the annealed sample (b) figures 6(a)–(b) [16]. The presence of irregularity (unevenness) pattern, cracks and voids in the as-deposited sample may be due the air space present.

Table 1. Structural Properties of the film.

| Sample/Parameters | As deposited film | Annealed film |
|-------------------|-------------------|---------------|
| Miller Indices (hkl) | (112) | (112) |
| 2 theta | 28.27 | 28.38 |
| FWHM(2θ) | 0.96 | 0.81 |
| Interplanar Spacing (d)(Å$^2$) | 3.15 | 3.14 |
| Lattice constant (Å$^2$) | 2.18 | 2.58 |
| Dislocation density (nm$^{-2}$) | 12.57 | 8.95 |
| Micro Strain | 0.23 | 0.19 |
| Average crystallite size (nm) | 8.92 | 10.57 |

The micro strain(s) of the films were estimated by using the relation,

$$d_{hlkl} = \frac{k \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

$$S = \frac{\beta \cos \theta}{4}$$ \hspace{1cm} (2)

Where $\lambda$ is the wavelength of the x-ray radiation (1.5405 Å), $\theta$ is the Bragg’s angle of the related peak, $\beta$ is the FWHM (Full Width Half Maxima) in radian, $k = 0.9$ which is a constant. The average crystallite size was estimated from XRD pattern using Debye-e Scherer’s formula and is found to be 8.92 nm and 10.57 nm for as-deposited and annealed samples respectively. From table 1, we observe that crystallite size is increased upon selenization. The micro-strain of the selenized sample was found to be comparatively lower than that of the as-deposited sample. The stress generated, affects the structural properties which can lead to the geometric abnormality between the films and the substrate [8], this stress can lead to micro strain ($\delta$) in the films. Now, the lattice imperfection in a crystal associated with the improper alignment of the lattice of the crystals [9] is termed as the Dislocation density ($\delta$) which is quite less for the annealed film than the as-deposited one conforming a more compact structure. It can be calculated by using the following formula,

$$\delta = \frac{1}{d^2}$$ \hspace{1cm} (3)

Where, $\delta$ is dislocation density and d is the interplanar spacing. The unit cell of the as-deposited and annealed samples shows the basic tetragonal structure with the miller indices (112).
during deposition but is gradually decreasing after annealing is carried out. It is notable to see that the
irregularity of the deposited film reduces and the annealed film becomes more compact with less number of
grain boundaries and voids which is highly necessary for photovoltaic applications \[17\]. The compact grain

**Figure 4.** Raman spectra of the films.

**Figure 5.** (a) Compositional analysis of as-deposited film. (b) Compositional analysis of annealed film.
growth is basically due to the annealing environment with selenium which is crucial for the formation of CZTSSe absorber layer.

3.5. Optical properties

The optical properties of the annealed sample were studied by UV–vis Spectrophotometer (Shimadzu UV-2450). The band gap is calculated from UV-Spectrum using Tauc formula.

\[
(\alpha h\nu)^n = C (h\nu - E_g)
\]

where \(\alpha\) is the absorption coefficient, \(A\) is absorbance, \(t\) is the thickness of the film, \(C\) is a constant and \(n\) is class the transition process. Here \(n = 2\) and \(1/2\) represent the direct band gap and indirect band gap, respectively. The optical band gap of CZTSSe (direct band gap material) approximately calculated by the slope of \((\alpha h\nu)^2\) versus \((h\nu)\) plots to \((h\nu)\) axis at \((\alpha h\nu)^2 = 0\) is shown in figure 7. The band gap of CZTSSe film selenized at 520 °C is found to be 1.38 eV.

3.6. Electrical properties analysis

The hall effect of the as-deposited and selenized annealed samples was characterized by using the hall measurement system (Ecopia HMS-3000). The hall effect measurement is basically used to confirm the polarity of the samples through the positive hall coefficients\((R_{HI})\) for both as-deposited and annealed absorber layers.
which is of P-type. The procedure involves placing the sample in the magnetic field of 0.55 Tesla oriented perpendicular to the direction of the current which results in a voltage developed across the sample in a direction perpendicular to both the magnetic field depicted. The direction of the current which is in accordance to the given below governing equations

\[ F_B = q\nu \times b \]  

(6)

Where \( F_B \) is the exerted force, \( q \) is the electronic charge \( b \) is the magnitude of the magnetic field and \( \nu \) is the drift velocity. The Hall coefficient

\[ R_H = \frac{1}{ne} \]  

(7)

Where \( R_H \) is the Hall coefficient is the carrier concentration is the electronic charge[18]. The carrier concentration measured from the hall measurement setup for as-deposited sample was found to be \( 2.38 \times 10^{19} \) cm\(^{-3} \) which was further increased to \( 3.2 \times 10^{19} \) cm\(^{-3} \) may be due to compact nature of annealed sample as discussed in the surface morphology section. The mobility of the selenized sample varied from 2.17 cm\(^2\)V\(^{-1}\)s\(^{-1} \) for as-deposited to 2.59 cm\(^2\)V\(^{-1}\)s\(^{-1} \) for annealed sample ascertaining the perfect mobility parameter condition of photovoltaic application. The conductivity and hall coefficient from the as-deposited to the annealed sample as shown in table 3, these changes are attributed due to the formation of the crystalline structure of the CZTSSe as confirmed from earlier measurements.

4. Conclusion

We have shown a novel route for homogeneous CZTSSe absorber layer formation through ethylene glycol based solution dip coating method by replacing the source for Zn from ZnCl\(_2\) to ZnS with an aim to reduce chlorine content from the solution. The film after annealing at 520 °C, we have achieved the CZTSSe structure which is corroborated by Raman Spectra. The compositional analysis data shows the ratio of Cu/(Zn+Sn) \( \leq 1 \) and Zn/Sn > 1 which is suitable for the devices. The surface morphology indicates the disappearance of voids from as-deposited to annealed sample and the compactness of the film is increased. The band gap of the film is found to be \( \sim 1.38 \) eV. The electrical properties show an increase in the mobility & conductivity of the film after annealing. From all the above observations we can state that the film annealed at 520 °C for 2 min can also be further processed for photovoltaic applications.
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