Formation of a phase pure kesterite CZTSe thin films using multisource hybrid physical vapour deposition

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Abstract
Copper Zinc Tin Selenide (CZTSe) absorber films were obtained by growing CZT films with simultaneous RF and DC magnetron sputtering followed by thermal evaporation of Selenium. The deposition of CZTSe films was performed with different sputter powers with in-situ and post annealing of the deposited films at 400 °C in order to get uniformity and phase purity. Detailed GIXRD analysis concluded that a phase pure CZTSe film was obtained for in-situ annealed sample with Cu-Sn deposited through RF sputter power of 250W and Zn deposited through pulsed DC power of 200W. In conclusion from Raman scattering measurements, phase pure Raman active A mode of Kesterite CZTSe was observed for the same sample. Compositional analysis by EDS and XPS clearly showed that the CZTSe films are having Cu poor and Zn rich composition, favoring shallow Cu-vacancy which is highly desirable as p-type absorber layers for solar cells. The optical bandgaps ($E_g$) of the films calculated using Tauc plots were within the reported bandgap value of 1.0–1.35eV. The present deposition approach using hybrid PVD tool helps to control individual fluxes (Cu-Sn, Zn, Se), more precisely without the need of extra selenization step, leading to one step reduction in production process.

1. Introduction

Fabrication of a phase pure thin film of a quaternary compound is a very challenging task. Among quaternary compounds, Kesterite and Chalcopyrite type materials have been proven to be the main functional materials in thin film solar cells. Chalcopyrites have accomplished the highest efficiencies of 22.6% (Copper Indium Gallium Diselenide - CIGS) and 22.1% (Cadmium Telluride-CdTe) and have already acceded to their production stage. However, extensive use of this class of materials is still trailing because of high material cost, availability and toxicity which in-turn limits their mass production [1–4]. Therefore researchers are focusing on replacing the rare earth Indium and Gallium in CIGS with Zn and Sn with suitable stoichiometry and improved crystallization such as, Copper Zinc Tin Sulphide (CZTS) and selenide (CZTSe). Because of their crystal structure, these class of materials are known as Kesterite based materials and are inherently good alternative for polycrystalline CIGS and CdTe [4–10]. CZTSe materials have an adjustable bandgap of 0.85–1.5eV and high absorption coefficient in the range $10^5$ cm $^{-1}$ which makes it a dependable semiconductor absorber layer in thin film solar cells [11, 12]. The fluctuations in the bandgap of the material is responsible for the origin of the band-tailing in kesterite which reduces the open circuit voltage and in-turn limits the efficiency of the solar device [1]. The variation in the bandgap of the material mainly depends upon the selenide alloying and chemical composition variations at nanoscale. Recently, quaternary Chalcogenides have been showing promising thermoelectric properties owing to their intrinsically low thermal conductivities and good electrical conductivity suitable for waste heat recovery applications [13].

In general, CZTSe films are fabricated using conventional non-vacuum based methods such as ball milling, sol-gel, electro deposition, spray-pyrolysis and vacuum based techniques such as co-evaporation, sputtering, e-beam evaporation methods etc [14–19]. For solar cell applications the films fabricated by hydrazine-based
solution process have achieved a maximum power conversion efficiency of 12.6% [20, 21]. This method is still not in extensive use due to the toxic processing nature of hydrazine route which hinders its mass production [19]. For mass manufacturing, vacuum based physical vapour deposition techniques such as thermal evaporation and sputtering methods are highly desirable. Initially Katagiri et al [7] reported the power conversion efficiency of 0.66% for a thin film solar cell with CZTSe absorption layer deposited by using vacuum based technique. Subsequently, the composition Cu$_2$ZnSnSe$_4$ was deposited using vacuum based co-evaporation technique with a reported solar cell power efficiency of 11.6% [19, 20, 22]. During the fabrication of the solar cell, the most crucial process is the deposition of high quality absorber layer. By using conventional methods such as spin coating and spray pyrolysis needs high temperature annealing and the formation of a phase pure kesterite CZTSe is very challenging. So in this aspect our main focus is to achieve an optimized synthesis to form a phase pure CZTSe thin film in a single step process without any ex-situ high temperature selenization process. Considering the industrial fabrication of Kesterite thin film solar cells, the processes developed must assure inherent purity and industrial scalability [23].

There are reported literature about the low solar cell efficiencies obtained from this class of materials fabricated completely using sputtering process [24]. These are mainly attributed to high concentration of lattice defects formed due to complete sputtering of selenide materials. In order to avoid defect formation due to sputtering we intend to utilize hybrid approach involving simultaneous use of co-sputtering and evaporation. Co-sputtering is an effective approach by which one can easily control the desired thin film composition by varying the source power without affecting the thin film properties and it has been found successful even in composition sensitive systems such Ni-Ti thin films [13, 25]. By using hybrid physical vapour deposition (PVD), CZT (Cu Zn Sn) is deposited through co-sputtering of Cu-Sn alloy and Zn targets and later selenium is deposited through evaporation. Afterwards the film is annealed to obtain single phase CZTSe. It is also possible to obtain high quality dense thin film of CZTSe absorber layers by performing these deposition with in-situ substrate heating. The main advantage of the in-situ formulation of CZTSe film is that it is more suitable for large area production and thus for industrial manufacturing. This work involves fabrication of high quality crystalline CZTSe films using multiple deposition approach. This approach has better flexibility in terms of controlling the individual composition than single-target sputtering method. Basically the interest in this synthesis method using hybrid PVD is to avoid the ex-situ selenization process. However it is also expected to have advantages for large area deposition, less plasma damage due to bombardment of anion, and precise control of film composition by manipulating each flux independently. This approach is expected to favor the fabrication of kesterite semiconductors and its related alloy thin films suitable for high efficiency solar cells and other applications.

One of the major challenges in this particular work is to obtain a high quality, impurity free and phase controlled CZTSe thin films. The improved efficiencies of polycrystalline solar cells is mainly due to the increased grain size and the deep defect for absorber material [26]. Cu-poor and Zn-rich CZTSe absorbers showed good optical and electronic properties and were successfully fabricated into solar cells with high efficiency of 6.7% by Nagaoka team [27]. However, the single phase composition range is much narrower for CZTSe than for CIGS. The formation of undesirable ternary and binary phases and unfavorable defects in their crystal structure are some of the factors affecting the phase stability of the CZTSe quaternary compound [28]. In this particular work the CZTSe films deposited under various conditions and deposition rates are correlated to their basic structural, optical and electrical properties. The process-property correlation of CZTSe quaternary compound deposited using a multi-source hybrid PVD tool is studied in detail. The structural, optical and electrical properties of this film obtained with in-situ annealing are compared with the film annealed after the deposition (post annealed).

2. Materials and methods

The custom built PVD instrument used in this study is mainly commissioned with its 6 sources integrated in DANVEC glove box. By using this cluster tool, it is possible to control individual fluxes from different targets (Cu, Zn, Sn, Se) more precisely in one chamber without the need of extra selenization step, leading to one step reduction in production process. Another advantage of using this tool is that it is possible to develop high purity and multilayer films with sputtering and co-evaporation of metals and oxides with in-situ heating using its in-built substrate heater. The precursor metal targets and selenium shots with 99.9% purity were supplied by SRC metals, china. Cu-Sn alloy (Cu (60%)-Sn (40%)) and Zn (100%) targets with 3inch diameter and 4mm thickness were employed as precursor sources for co-sputtering to form CZT films. Selenium shots weighing 0.6g were placed inside a tungsten boat as the source for thermal evaporation. RCA (Radio Corporation of America) cleaned soda lime glass (SLG) substrates were loaded inside the chamber. In the present study, co-sputtering was used with Cu-Sn alloy deposited through RF sputtering, Zn through DC sputtering and selenium through...
thermal evaporation as shown in the graphical representation in figure 1. The detailed procedure for deposition of films through co-sputtering is as follows.

The deposition chamber was evacuated to a base pressure of \(4.3 \times 10^{-6}\) mbar. Argon gas was fed inside the chamber with a flow rate of 10sccm. The working pressure inside the chamber was maintained at \(5.0 \times 10^{-3}\) mbar. To obtain better surface homogeneity of films, the substrates were rotated at 20 rpm during the entire deposition. The deposition of Cu-Sn was carried out with a varying RF sputter power of 150W, 200W and 250W to optimize the film thickness and stoichiometry. The deposition of Zn was carried out in pulsed DC mode with a constant sputter power of 200W. Pulsed DC mode induces a periodic target voltage reversal that suppresses the arc formation at the target. Before the actual deposition, the targets were pre-sputtered in Argon atmosphere for 15 min in order to remove any oxide layer that could be present on their surface and the shutter was opened for 30 min for CZT (Cu-Zn-Sn) deposition. Subsequently, thermal evaporation of selenium was performed at a deposition rate of 27–28 W power. The deposition rate was monitored using a quartz crystal monitor inside the chamber. The prepared samples were later annealed at 400° C in same atmosphere for 1 h for the diffusion of selenium into the CZT layer and forming CZTSe compound. These samples will be addressed as post annealed samples in the forthcoming part of the article. For comparison, thermal evaporation of Se on CZT precursor films were carried out with in-situ (simultaneous) substrate heating condition at 400° C. These samples will be called as in-situ annealed samples.

The deposition parameters and the corresponding ranges for the deposition of CZTSe films are given in table 1

3. Characterization studies

The crystallographic studies of CZTSe thin films were characterized by x-ray diffraction (XRD, DMAX 2500 V) with Cu Kα radiation (\(\lambda = 0.15418\) nm). The data was collected with a step scanning mode of \(2\theta\) (diffraction angle) ranging from 20° to 90° with a step size of 0.05° at room temperature. Raman scattering spectroscopy (Raman, LabRAMHREvolution) with laser wavelength of 532 nm was employed to reassert the phase purity of the deposited films. The chemical analysis of the films was carried out by an Energy Dispersive x-ray Spectroscopy/EDS (EMAX-Horiba, Japan) attached to a Scanning Electron Microscope/SEM (Zeiss Ultra). The optical transmission spectra of CZTSe thin films were investigated by using a UV/Visible spectrophotometer (Shimadzu) with a spectral range of 300–1200 nm at room temperature. The average surface roughness of the samples were characterized using Atomic force microscopy (Agilent Technologies, Singapore, 5500 series). X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II, ULVAC-PHI Inc., USA) equipped with micro focused (200 μm, 15 KV) monochromatic Al-Kα x-ray source (\(hν = 1486.6\) eV) were used for investigation. Both survey spectra and narrow scan (high-resolution spectra) were recorded. Survey scans were recorded with
an x-ray source power of 50W and pass energy of 187.85 eV. High-resolution spectra of the major elements were recorded at 46.95 eV pass energy.

4. Results and discussion

4.1. Morphological and Compositional studies of co-sputtered CZT precursor films

4.1.1. RF sputtered Cu-Sn alloy film: Compositional studies using EDS

Cu-Sn thin films were separately deposited for different RF power (100 to 200 W) and substrate temperature (300 to 450 °C) to understand the influence of the process parameters on stoichiometry of Cu-Sn. Energy Dispersive x-ray spectroscopy (EDS) analysis was performed to estimate the presence of Cu and Sn in the thin films deposited with and without substrate heating. Figure 2 indicates that there is no significant variation in the compositions of Cu and Sn in both films. The average composition in the films deposited without substrate heating is 62% Cu and 38% Sn and those with substrate heating is 70% Cu and 30% Sn. Though the composition of the target is 60% Cu and 40% Sn, the films deposited without substrate heating using this target appears to

| Sample name | Sputter power | Thermal evaporation | Time (mins) | Working pressure (mbar) | Heat treatment          |
|-------------|---------------|---------------------|-------------|-------------------------|-------------------------|
|             | Cu-Sn RF (W)  | Zn DC (W)           | Selenium shots |                          |                         |
| C1          | 150           | 200                 | 28          | 30                      | 5*10⁻³                  |
| C2          | 200           | 200                 | 28          | 30                      | 5*10⁻³                  |
| C3          | 250           | 200                 | 28          | 30                      | 5*10⁻³                  |
| C4          | 150           | 200                 | 28          | 30                      | 5*10⁻³                  |
| C5          | 200           | 200                 | 27          | 30                      | 5*10⁻³                  |
| C6          | 250           | 200                 | 27          | 30                      | 5*10⁻³                  |

Post annealed at 400 °C

In-situ annealed at 400 °C

Table 1. Parameters for the deposition of Cu-Sn, Zn and Se.

Figure 2. Consolidated EDS data of Cu-Sn alloy deposited with different (a) sputter power and (b) substrate heating temperatures (right).
have lower percentage of Sn than expected. This could be due to the re-evaporation of the Sn because of its lower vapour pressure. Moreover, the Sn loss in the films with substrate heating is higher when compared to those without substrate heating as illustrated in figures 2(a), (b). However, this percentage ratio is under the tolerance limit for their applications in kesterite based compositions [29].

4.1.2. Pulsed DC sputtered Zn thin film
Figures 3(a), (b) show the AFM, SEM and EDS results of Zn films deposited with continuous DC power of 100 W and pulsed DC power of 200 W. The data clearly shows that the deposition of Zn is poorer in continuous DC mode. This is mainly because in continuous DC mode there are possibilities of charging of the target. This in-turn discharges in high voltage arcs into plasma forming droplets causing defects in the thin film quality. Whereas the Zn film deposited in pulsed DC mode shown in figure 3(b) comprises of uniform sized well dispersed particles forming a continuous non-porous layer. In pulsed DC mode the arc formation at the target was suppressed. This happens mainly because the pulsed DC mode operates in a periodic target voltage with negative and positive pulse. During the initial part of the pulse trigger a strong negative pulse is employed sputtering off target atoms and igniting plasma glow. Later in positive pulse, the voltage is turned off or kept at low value. During this time it cleanses the target from a charge build-up [30]. EDS results of Zn thin films deposited in pulsed DC mode in figure 3(b) reveal 100 atomic weight percentage of Zn, whereas in the film deposited in continuous DC mode (figure 3(a)) only small atomic weight percentage of Zn was observed. Presence of elements from the glass substrate in the EDS data of the film deposited in continuous DC mode also indicates that the film is not sufficiently thick and continuous. SEM and AFM images in figures 3(a) and (b) also

Figure 3. (a) SEM AFM and EDS results for Zn deposited on SLG using (i) continuous DC mode, (ii) pulsed DC mode.
show that the films deposited in pulsed DC mode have a denser microstructure with well dispersed particles without any pores due to the higher deposition rate so that the larger number of species arriving at the substrate.

4.2. Structural analysis using XRD

Under thermodynamic growth conditions the stability range of CZTSe is very narrow, forming a phase pure material of the required composition is challenging. Beyond the narrow phase stability range, defects and secondary phases are easily formed during the growth of in-situ annealed films. The most common crystallographic phases observed in such cases are stannite and kesterite phases. Apparently, since the formation energies of both stannite and kesterite phases are similar, their formation happens simultaneously.

Figure 4 shows the XRD patterns of CZTSe films with varying sputter power (refer table 1).

However diffractograms obtained from one of the in-situ annealed (C4) and all post annealed (C1, C2, C3) samples (figure 4(a)) exhibited secondary phases along with CZTSe phase. All the possible secondary phases such as CuSn, ZnSe, Cu2Se and SnSe (marked with red color) at 2θ values of 13.02°, 37.5°, 51.96° and 68.18° can be seen in all the post-annealed samples. From x-ray diffractograms of post annealed samples, it can be observed that the crystallization behavior of these compounds mainly depend upon the growth process. In figure 4(b), the films deposited with in-situ substrate heating (C5 & C6) exhibited three major crystallographic peaks at 27.14°, 45.08° and 53.34° which corresponds to (1 1 2), (2 0 4) and (3 1 2) planes of Kesterite CZTSe phase [30]. This is mainly because at high annealing temperature of about 400°C, the eutectic liquid mixture of Cu2Se and SnSe will react with solid ZnSe and gaseous Se2 to form CZTSe [31, 32]. It can also be noticed that as the sputter power is increased, the diffraction peak intensities of films developed with in-situ substrate heating are improved, possibly due to the improvement in grain size and film thickness of the deposited samples. However the potential secondary phases such as ZnSe and the ternary phase Cu2SnSe3 overlap with the Braggs peak of CZTSe in XRD patterns [33]. Therefore more advanced characterization methods have to be performed in-order to rule out their presence.

4.3. Raman spectroscopy

The indistinguishable phase identification for a Cu-Zn-Sn-S-Se system can be easily performed using Raman spectroscopy as the Raman spectra of the secondary phases are rather distinct due to the editions of vibrational displacements in their lattice symmetry [34]. To confirm the presence of CZTSe, the in-situ and post annealed samples were further analyzed using Raman spectroscopy. For CZTSe, the main Raman vibrational peak is designated at 174 cm⁻¹, 193 cm⁻¹ and 232 cm⁻¹ which indicates the formation of polycrystalline Kesterite (KS) structure [34–36]. Figure 5(a) clearly shows that in post annealed samples C1 & C2 there is no indication of the formation of CZTSe phase. While the Raman shift at 151 cm⁻¹ and 219 cm⁻¹ observed in these samples indicate the presence of ZnSe and SnSe secondary phases. The broadening of the peak in Raman spectra might be due to the increased quantity of crystallographic defects. However, as shown in figure 5(b), all the samples developed in-situ annealing clearly indicate the presence of dominant vibrational peak at 174 cm⁻¹ with weaker modes at 231 cm⁻¹ which accounts to the phonon mode of the spectra of KS Cu2ZnSnSe4 phase. The Raman shift at 151 cm⁻¹ observed in all the samples is basically due to the presence of ZnSe secondary phase. Whereas the
Figure 5. Raman spectra of (a) post-annealed and (b) in-situ annealed CZTSe films with varying sputter powers.

Figure 6. Morphology of post annealed and in-situ deposited CZTSe samples.

Table 2. Elemental composition CZTSe samples obtained from EDS analysis.

| Samples | Cu   | Zn   | Sn   | Se    | Cu/(Zn+Sn) | Zn/Sn |
|---------|------|------|------|-------|------------|-------|
| C1      | 23.15| 12.87| 14.62| 49.36 | 0.84       | 0.88  |
| C2      | 23.82| 13.06| 13.84| 49.28 | 0.89       | 0.94  |
| C3      | 25.32| 12.74| 13.28| 48.66 | 0.97       | 0.96  |
| C4      | 25.70| 13.38| 11.34| 49.58 | 1.04       | 1.18  |
| C5      | 19.86| 16.63| 12.01| 51.5  | 0.69       | 1.38  |
| C6      | 20.32| 17.18| 12.5 | 50    | 0.68       | 1.37  |
in-situ annealed C6 sample developed with 250W power showed the presence of pure CZTSe phase at 174 cm$^{-1}$ which support the Raman active Asymmetry mode of KS CZTSe [35].

4.4. Scanning electron microscope and EDS analysis of CZTSe films
Morphologies of post annealed and in-situ annealed films through SEM analysis are depicted in figure 6. The image in figure 6(a) shows agglomerated small grains on the surface of the post annealed samples. The post
annealed sample with higher sputter power: C3 exhibits these agglomerated grains in the form of platelets similar to that of the morphology reported by Kevin et al. [32]. This might be imputed due to the formation of secondary and ternary phase, whereas the samples deposited with in-situ annealing as depicted in figure 6(b) showed well dispersed uniform morphology without any pores.

The Cu Zn/Sn ratio in high efficiency solar cells reported till now are in the range Cu/(Zn+Sn) = 0.70–0.85 and Zn/Sn =1.1–1.30. Table 2 shows the results obtained from EDS analysis of the CZTSe thin films. One of the major challenges in this work is to obtain the desired stoichiometry. The post annealed CZTSe sample C3 showed a Cu rich and Zn poor condition. Since the desirable Cu/Zn ratio is less than 1, it is not suitable for high efficiency solar cell applications [29, 37]. If Cu and Zn are not in the desired stoichiometry there is a possibility of formation of vacancies and other defects in their crystal structure which affect their characteristic features. Due to the similar ionic radii of Cu (0.73 Å) and Zn (0.74Å) cations, Cu with +1 or +2 oxidation states can occupy divalent Zn sites resulting in the formation of defects. The CuZn antisite defects in CZTSe lead to Cu poor and Zn rich conditions which are highly desirable for solar cell applications. This defect gives rise to band tail states that forms a deep acceptor level which makes it a p-type semiconducting material.

4.5. XPS analysis of in-situ annealed C6 sample
X-ray photoelectron spectroscopy (XPS) were carried out to study the exact composition and the valence states of in-situ developed phase pure C6 sample. Figure 7(a) shows the full survey spectrum analysis for the identification of four constituent elements present in the film. The atomic weight percentage of the deposited samples are shown in the inset of figure 7(a). The obtained results showed a Cu poor and Zn rich condition which cordially support with the required stoichiometry to behave as a good active layer for kesterite thin film solar cells. The high resolution spectrum in figure 7(b) indicates the presence of two peaks at 931.8eV and 951.7eV which accords to Cu 2p has split into two peaks with 2p3/2 and 2p1/2 with an observed valence state of +1 ion. Whereas two strong peaks at 1019.9eV and 1042eV in figure 7(c) corresponds to the Zn 2p3/2 and Zn 2p1/2 peaks. The observed binding energy values Zn 2p supports the characteristic of Zn2+ ions. Figure 7(d) shows that the Sn 3d peak split into peaks located at 486eV and 494 eV respectively having a valence state of +4 ion. Finally the peak located at 54.1eV in figure 7(e) is due to Se 3d with a valence of 2. The observed results cordially supports to the values reported in literature [38].

4.6. Optical characterization
UV-Vis-NIR absorption spectroscopy was used to evaluate the optical properties of the deposited thin film samples and the data is depicted in figure 8. The observed absorbance ranges of the CZTSe samples are from 300nm to 1000nm which covers a wide band absorbance in mid UV and visible region. As illustrated in figure 8(b) the C6 sample deposited with in-situ annealing showed similar absorbance spectrum as reported for CZTSe materials (inset of figure 8(b)) [39]. There is a significant decrease in the absorbance value for the samples deposited with in-situ annealing. This can be attributed mainly to the presence of multiple phases and morphology of the deposited films. The optical band gap energy was determined in figure 9 by extrapolating the linear region of the plot of (αhν)2—the square of the absorption coefficient (α) multiplied by the photon energy (hν) versus hν and taking the intercept, evaluated using the equation (1). Where Eg is the band-gap of the material, A is the absorbance and n is the power factor which takes the value of 0.5 for direct transitions [39].

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

(1)
UV absorbance studies (figures 8(a), (b)) clearly indicate that annealing plays a major role in the desirable phase formation and thus the optical characteristics. It can be concluded that in-situ annealing can give better quality thin films with more suitable energy band characteristics than films obtained through post annealing. The optical band gap values of the all samples are shown in figure 9. A wide range of band gap values from 0.85 to 1.5 eV have been reported for CZTSe films deposited by different methods [39]. The band gap energy values obtained from CZTSe films in this work are within this range. The phase pure thin film with required stoichiometry C6 exhibits a bandgap value of 1 eV. The CZTSe thin film with optimized process parameters synthesized in this work has the required characteristics to be used as an absorber layer for solar cells which can absorb majority of the photons using visible to infrared radiation with high conversion efficiency. The intrinsic defects present in the films generate absorption centres for photons having energy within the energy gap which contribute to the generation of electron-hole pairs.

5. Conclusion

This work has introduced a new path for the formation of CZTSe absorber layer without extra selenization step. The multi-source hybrid PVD tool used in this study is capable of producing high quality CZTSe absorber layers leading to one step reduction in the production process. XRD, Raman spectroscopy and optical characterization confirms that the stacking method (post annealing after depositing individual layers) with these power conditions cannot produce phase pure and uniform thin films for the quaternary alloys like CZTSe. Single phase CZTSe quaternary compound can be effectively made into good quality thin film if deposited with single vacuum chamber with all the constituent elements deposited simultaneously from different sources along with in-situ substrate heating.

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