# Influence of selenization pressure on the growth of $Cu_2ZnSnSe_4$ films from stacked metallic layers

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$Cu_2ZnSnSe_4$ (CZTSe) is a p-type semiconductor with a high absorption coefficient, $10^4$ to $10^5$ $cm^{-1}$, and is being seen as a possible replacement for $Cu(In,Ga)Se_2$ in thin film solar cells. Yet, there are some fundamental properties of CZTSe that are not well known, one of them is its band gap. In order to resolve its correct value it is necessary to improve the growth conditions to ensure that single phase crystalline thin films are obtained. One of the problems encountered when growing CZTSe is the loss of Sn through evaporation of SnSe. Stoichiometric films are then difficult to obtain and usually there are other phases present. One possible way to overcome this problem is to increase the pressure of growth of CZTSe. This can be done by introducing an atmosphere of an inert gas like Ar or $N_2$. In this work we report the results of morphological, structural and optical studies of the properties of CZTSe thin films grown by selenization of DC magnetron sputtered metallic layers under different Ar pressures. The films are analysed by SEM/EDS, Raman scattering and XRD.

**1 Introduction** $Cu_2ZnSnSe_4$ (CZTSe) is a material that is being studied as one possible replacement for $Cu(In,Ga)Se_2$ (CIGS) in thin film solar cells. In laboratory, (CIGS) thin film solar cells have reached an efficiency of 19.9% [1]. CIGS is nowadays used by thin film PV industry but since In is a scarce element in the earth's crust, and therefore expensive, materials that could replace CIGS as absorber layer are being explored.

CZTSe thin films were first investigated by Friedlmeier et al. [2]. They reported the growth of CZTSe films with poor adhesion and with the presence of secondary phases of $Cu_{2-x}Se$ and ZnSe [2]. Several studies reported CZTSe films to have an absorber coefficient of $10^5$ $cm^{-1}$ [3, 4]. The definitive value of the band gap of CZTSe is not yet known since some groups report values between 1.44 eV [5] and 1.56 eV [6] while Grossberg et al. [7] states that it is around 1.02 eV. Theoretical calculations also point to the latter value [8]. The contradictory results are not only regarding the band gap value but the crystal structure is also in debate. While some groups report that the structure of CZTSe is stannite (space group I 2m) [5, 9], others report that the structure is kesterite (space group I) [2, 10]. One problem that occurs when analyzing XRD data is resolving CZTSe, ZnSe and $Cu2SnSe_3$ (CTSe) peaks, since these phases have almost the same lattice constant a: 5.688 Å, 5.669 Å and 5.684 Å, respectively. They have almost the same diffraction pattern and therefore identification is possible but difficult and questionable.

In a previous work [11] we have proposed Raman scattering spectroscopy to be used as complementary analysis to overcome this problem. In Raman scattering the main peaks of CZTSe, ZnSe and CTSe are found at 196 $cm^{-1}$, 251 $cm^{-1}$ and 180 $cm^{-1}$ respectively [10,11]. CZTSe has a second emission peak at 174 $cm^{-1}$ and this makes the identification of CTSe difficult since if these two peaks of CZTSe are broad they may submerge the 180 $cm^{-1}$ of CTSe.

In previous work [11] we have identified that CZTSe appears to form only at temperatures of 350ºC or higher but at those temperatures there is already loss of Sn and Zn from the precursors making the growth of stoichometric CZTSe difficult. The Sn and Zn losses were also reported by Friedlmeier et al. [2] but no suggestions were proposed to overcome this problem. Recently G. Zoppi et. al. reported [12] a CZTSe solar cell with an efficiency of 3.2 %. The CZTSe was grown at a temperature of 500 ºC by selenisation of Cu(Zn,Sn) magnetron sputtered metallic precursors. There is no mention to the selenization pressure. We believe that by increasing the selenization pressure it may be possible to reduce the evaporation losses and thereby optimize the growth conditions of CZTSe.

In this work we study the influence of the pressure from $10^{-5}$ to $10^{-2}$ mbar during the selenization of DC sputtered precursors. We then proceed to analyse a CZTSe thin film grown at $10^{-5}$ mbar with Cu poor precursors in order to overcome the problem of Sn and Zn losses.

**2.1 Sample preparation** The metallic precursors were deposited on a 3x3 $cm^2$ Mo coated soda lime glass (SLG) by DC magnetron sputtering. The precursors were deposited with the following order: SLG/Mo/Zn/Sn/Cu. The purity of the targets is 3N for Mo, 5N for Cu and 4N for Zn and Sn. All the precursors were deposited at room temperature with a power density of 0.16 $W \cdot cm^{-2}$, working pressure of $2 \times 10^{-3}$ mbar and a substrate to target distance of 10 cm. The thicknesses and deposition rates were monitored using a quartz crystal controller Intellemetrics IL 150. The selenization of the precursors was done in a separate chamber. Se was evaporated from a quartz source loaded with Se pellets of 5N purity. In this process it was ensured that the film receives an excess of Se. It is known that the required Se is absorbed while the excess is re-evaporated since the substrate temperature is higher than the Se evaporation temperature at the various working pressures. The substrate temperature could also be changed and was monitored during the process. The substrate temperature and the temperature of the Se source followed the profiles presented in Fig. 1. The maximum substrate temperature tested were 375 ºC and 500 ºC. Se was evaporated at 255 ºC. At the end of the profiles the substrate heater was turned off and allowed to cool down naturally. The Se source was turned off only when the substrate temperature reached 270 ºC. This was done to prevent Se loss by re-evaporation from the film. The pressure at which the selenization is done can be adjusted by introducing Ar into the chamber from $10^{-5}$ to $10^{-2}$ mbar.

Three sets of samples were prepared. In the first one there was a pressure variation from $10^{-5}$ to $10^{-2}$ mbar at a substrate temperature of 500 ºC. In the second set, the same pressure variation was tested but for a substrate temperature of 375 ºC. In the final test, the precursors were prepared Cu-poor and were selenized at a pressure of $10^{-5}$ mbar at 375 ºC.

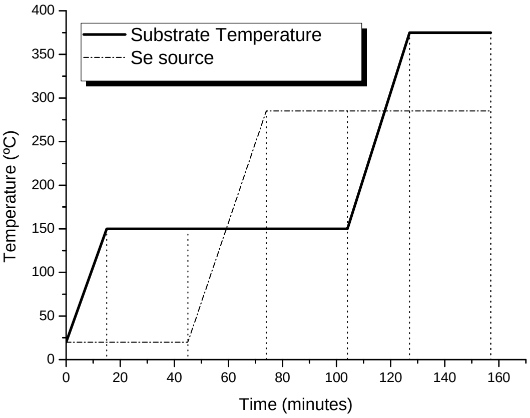

**Figure 1** Temperature profiles for the selenization process.

**2.2 Sample characterization** Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS) were used to examine film morphology and chemical composition. The system used was a S4100 Hitachi with a Rontec EDS system. The acceleration voltage used was 25 kV. Chemical composition was also analysed using a ICP-MS Thermo X Series.

X-ray diffraction (XRD) was done with a PHILIPS PW 3710 with a Cu-Kα line of 1.5406 Å. It was used to study the crystalline phases present, the crystallite size using Scherrer's equation and the lattice constants. The CZTSe films were further analyzed through Raman scattering spectroscopy using a Jobin-Yvon T64000 Raman scattering system with an Olympus microscope equipped with a 100X magnification lens and in the backscattering configuration. In the latter measurements the excitation source was an argon ion laser operating at the wavelength of 514.5 nm and at 220 mW output power. Precursor thicknesses were measured using a Dektak 150 step profiler.

**3 Results and discussion** For the pressure variation tests, the precursors were prepared stoichometric with the following order SLG/Mo/Zn/Sn/Cu. Elemental composition was measured with ICP-MS. In this step, measurements with EDS were avoided since this is a layered structure and distortion in the measurements may appear. The thicknesses of the layers were: Zn – 380 nm; Sn – 460 nm and Cu – 280 nm. The two set of precursors were selenized at 375 ºC and 500 ºC and the respective films analysed by EDS, XRD and Raman scattering. In Table 1 the values for the EDS measurements are presented. As reference we consider that there are no Cu losses for these temperature and pressure conditions and therefore study the losses of Sn and Zn by looking at the ratios of Cu by these elements.

**Table 1** Elemental composition of the films selenized at different pressures for two sets of temperatures.

| **500 ºC** | [Cu]/ ( [Zn] + [Sn]) | [Cu]/ [Zn] | [Cu]/ [Sn] | [Zn]/ [Sn] | [Others]/ [Se] |
|---|---|---|---|---|---|
| $10^{-5}$ mbar | 3.5 | 4.4 | 17.5 | 3.9 | 1.5 |
| $10^{-4}$ mbar | 2.9 | 4.7 | 7.7 | 1.6 | 1.4 |
| $10^{-3}$ mbar | 3.3 | 4.4 | 13.7 | 3.1 | 1.4 |
| $10^{-2}$ mbar | 2.7 | 3 | 21.2 | 6.9 | 1.6 |
| **375 ºC** | [Cu]/ ( [Zn] + [Sn]) | [Cu]/ [Zn] | [Cu]/ [Sn] | [Zn]/ [Sn] | [Others]/ [Se] |
| $10^{-5}$ mbar | 2.3 | 4.2 | 5.3 | 1.3 | 1.1 |
| $10^{-4}$ mbar | 2.0 | 5.0 | 3.4 | 0.7 | 1.3 |
| $10^{-3}$ mbar | 1.7 | 2.5 | 4.8 | 2.0 | 1.6 |
| $10^{-2}$ mbar | 1.6 | 2.4 | 4.6 | 1.9 | 1.7 |

For the samples grown at a temperature of 500 ºC it is possible to see that there are significantly more losses of Sn than Zn. This is probably due to the fact that Zn losses are done mainly by evaporation of elemental Zn and Sn is lost by $Sn_xSe_y$ phases. Since in the selenization profile there is a step in which the films are heated up to 250 ºC and then selenized, this encourages the formation of Se compounds and therefore promotes the evaporation of Sn over Zn. There is no pattern for the evolution of Sn with the increasing temperature. For the Zn value, the [Cu]/[Zn] seems to diminish and that also leads the value of [Cu]/( [Zn]+[Sn] ) to diminish. For these temperatures it is not evident that the increasing pressure makes more stoichiometric films because of the heavy Sn losses. These films have mostly ZnSe and $Cu_{2-x}Se$ phases which were identified by Raman scattering and XRD. Small traces of CZTSe were found in all the samples. CZTSe and ZnSe were only distinguished using Raman scattering as stated previously [11]. The presence of these phases makes the [Other]/[Se] appear to be insufficient but in fact since most of the film is $Cu_{2-x}Se$ and so those ratios cannot be close to 1.

For the samples grown at 375 ºC the ratio [Cu]/[Sn] is much lower than the one for the films grown at 500 ºC which indicates there are much less losses of Sn. For the Zn losses the variation of the [Cu]/[Zn] with increasing pressure decreases. For [Cu]/([Zn]+[Sn]) the same pattern is observed. For both temperatures at $10^{-4}$ mbar, all the ratios exhibit singular behaviour because they do not follow the trends in the other pressures and there are more Zn losses and less Sn losses. This fact is not yet fully understood due to the lack of knowledge regarding the growth thermodynamics of these systems. More data on these films and the extension of the pressure range will be published elsewhere.

Since for our actual system it is not possible to continue to increase pressure in a controlled way, we decided to prepare a set of Cu-poor precursors and selenize them with the same temperature profile described before and at 375 ºC at $10^{-5}$ mbar. Since the films grown under those conditions appear to have a [Cu]/([Zn]+[Sn]) value greater than 1 and a value of [Zn]/[Sn] close to optimum, 1.1-1.2, we decided to decrease the Cu thickness, to decrease slightly the Zn thickness and maintain Sn. The thickness of these samples were, Zn – 340 nm, Sn – 460 nm and Cu-195 nm which corresponds to the elemental composition showed in Table 2. The precursors were then selenized and the resulting films were Cu-rich and Sn-rich. In the case of $Cu_2ZnSnS_4$, it is known that the best solar cells done so far were prepared Cu-poor and Zn-rich absorbers [13], if CZTSe also follows this tendency, then the precursors need to have more Zn to achieve the desired composition.

**Table 2** Elemental composition of the Cu-poor precursors and its resulting selenized films.

| Ratios | Before Selenization | After Selenization |
|---|---|---|
| [Cu]/([Zn]+[Sn]) | 0.5 | 1.1 |
| [Cu]/[Zn] | 1.1 | 2.4 |
| [Cu]/[Sn] | 1.1 | 2.2 |
| [Zn]/[Sn] | 1.0 | 0.9 |
| [Others]/[Se] | - | 1.1 |

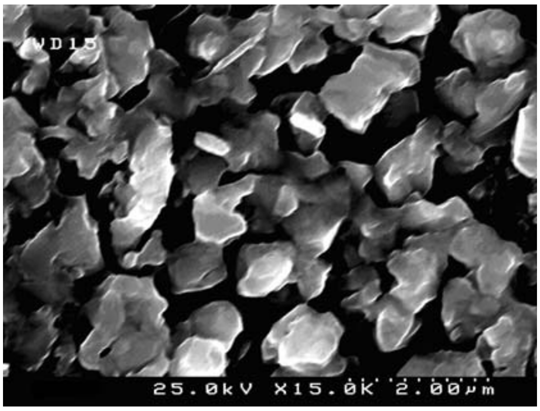

**Figure 2** SEM surface micrograph of the CZTSe film prepared with Cu-poor precursors.

The SEM surface micrograph of the CZTSe is shown in Fig. 2. It shows an open structure with relatively big voids between crystallites. This situation is due to the layer of Sn prepared by DC sputtering that is quite rough. This problem has been identified in previous work [11] and further optimization is needed. The XRD pattern of the CZTSe film is presented in Fig. 3. It is possible to see the strong peak at 27.14 º that corresponds to the direction (112). The directions (220)/(204) and (312)/(116) are not resolved. We can also see that other directions are present with minor traces: (101,) (400),(424)/(228). The lattice constants a and c of the unit cell were estimated and the values 5.683 Å and 11.342 Å were found, respectively.

These are in accordance with CZTS and for c/2a takes the value of 0.998. The crystallite sizes were estimated using Scherrer's equation and a value of 211.7 nm was obtained. Analysing the SEM surface image we see that the grains observed appear to be larger than the value obtained with Scherrer's equation. Similar differences have been found by Y.B. Kishore Kumar et al. [14]. This is probably due to the fact that the crystals seen in the SEM micrograph are agglomerates of crystallites.

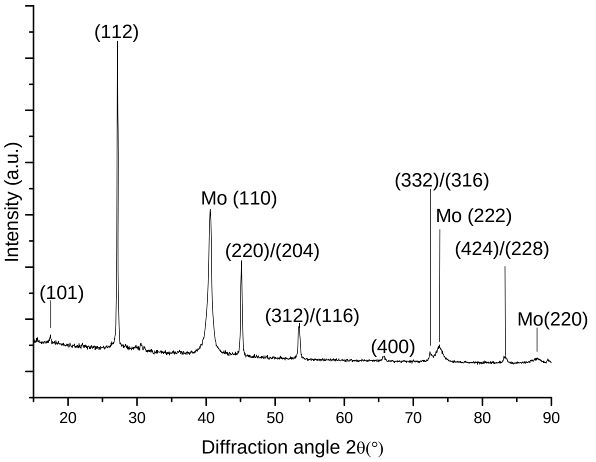

**Figure 3** X-ray diffraction patterns with the identification of CZTSe.

The Raman scattering analysis confirmed the presence of CZTSe with Raman scattering peaks at 195, 174 and 232 $cm^{-1}$ (Fig. 4). Some spots of the sample also showed small traces of $Cu_{2-x}Se$ phases. These phases were not detected in the XRD analysis. This film showed a value of [Zn]/[Sn] slightly smaller than one, which means that there is an excess of Sn, but even in those circumstances no significant traces of CTSe were found. The strongest peak of CTSe should be seen in the region of 180 $cm^{-1}$, but with the broadening of the CZTSe peaks at 195 and 174 $cm^{-1}$ it is unclear if the CTSe peak may be hidden or not be there.

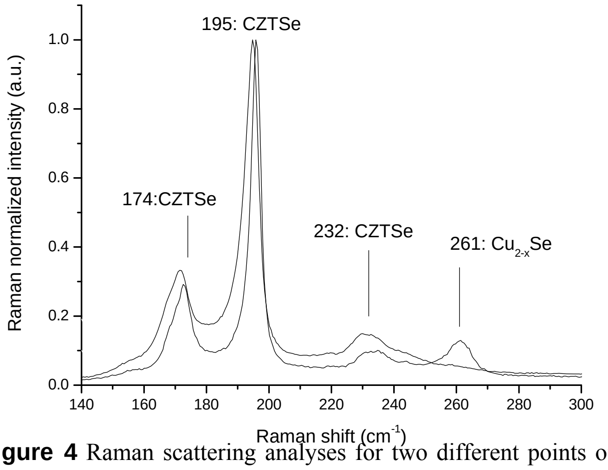

**Figure 4** Raman scattering analyses for two different points of the same sample.

## 4 Conclusions

For the set of samples prepared at 500 ºC we did not identify any pattern that suggests that increasing pressure will allow the achievement of more stoichiometric films. However for the test in which the samples were selenized at 375 ºC there are some evidences that increasing the pressure may be a solution for the evaporation losses. Further studies at higher pressures are required.

For the Cu-poor precursors, the results reported here demonstrate that it is possible to achieve CZTSe films with composition close to stoichiometry. A finer tuning of the precursors would be required to achieve the desired Cu-poor and Zn-rich final CZTSe films by increasing the initial Zn content.

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