Post-growth annealing effect on the performance of Cu$_2$ZnSnSe$_4$ monograin layer solar cells


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A B S T R A C T

In this work, we investigated the effect of annealing of absorber powder on the conversion efficiency of Cu$_2$ZnSnSe$_4$ (CZTSe) monograin layer solar cells. CZTSe powders were synthesized from binary compounds and elemental Se in the liquid phase of KI in evacuated quartz ampoules at 740 °C. In order to study the effect of post-treatments of the absorber material different annealing parameters such as Se and/or SnSe$_2$ vapor pressure, annealing time and temperature were varied with the aim to gain uniform, good quality absorber materials for monograin layer solar cells. The annealing temperature was found to be crucial for the performance of CZTSe monograin layer solar cells. The conversion efficiency of solar cells improved significantly after the heat treatment. The effect can be attributed to the change of the absorber material composition and the crystals surface properties suitable for the effective $p$–$n$ junction formation. The best CZTSe monograin layer solar cell showed conversation efficiency of 4.4%.

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1. Introduction

The Cu$_2$ZnSnSe$_4$ (CZTSe) compound has attracted a considerable attention as an alternative absorber in thin film solar cells because CZTSe is a $p$-type semiconductor with a band gap of 1.0 eV and has an absorption coefficient that is larger than $10^4$ cm$^{-1}$, which matches the prerequisites for a solar absorber material [1].

Recently, the record efficiency of liquid-processed CZTSe solar cell yielded 10.1% [2]. However, although device performance was greatly improved, basic researches on CZTSe material itself are insufficient. For example, fabrication of compositionally uniform CZTSe film is still a hard task due to Sn-loss during annealing process. Usually, a high temperature annealing in chalcogen atmosphere is essential to form a well-crystallized and single phase CZTSe. It is well known that CZTSe quickly decomposes at temperatures higher than 400 °C [3–5]. The decomposition rate, however, depends drastically on the experimental conditions such as temperature, total pressure inside the annealing container and partial pressures of all involved volatile species. As monograin powder synthesis is an isothermal process, the Sn loss in the synthesis process is not a problem. The problem rises in the post-treatment step. In our previous studies [6], it was shown that due to the distribution of material between the liquid flux and the solid CZTSe crystals during the synthesis process, some part of material is dissolved in molten flux at growth temperature. In the cooling period, the dissolved part precipitates on the solid crystal surfaces. Therefore, as-grown monograins need some chemical etching and annealing before the formation of $p$–$n$ junction. It has been found that Br$_2$–methanol treatment followed by immersion in an aqueous solution of KCN [7] and annealing in SnSe$_2$ or Se vapors heals crystals' surfaces to the device quality.

Considering that high efficiency CZTSe solar cell can be realized just with Cu-poor and Zn-rich CZTSe [8], the proper adjustment of chemical composition of CZTSe is a prerequisite for well working solar cells. Hence, systematic annealing experiments under controlled temperature and atmosphere come to be significant.

Here, we report the effect of post-growth annealing and sequential etching of CZTSe monograin absorbers with different compositions on the performance of CZTSe monograin layer (MGL) solar cells.

2. Experimental details

The CZTSe absorber materials, used for MGL solar cells in this study were synthesized by isothermal recrystallization method in molten flux. The details about monograin growth process could be found in [9].

After the removal of flux, the post-treatments were carried out in closed quartz ampoules using two-temperature zone arrangement. Elemental Se or SnSe$_2$ pellets were placed into the lower temperature zone of the ampoules. CZTSe powder was heated in the higher temperature zone. The temperatures of both zones were regulated and controlled independently. The lowest temperature in the ampoule determined the vapor pressure of Se or SnSe$_2$. After annealing, the ampoules were taken out of the furnace and cooled down on a ceramic plate at room temperature.
Prior to CdS deposition, the post-treated monograin powders were sequentially etched with fresh-made 1% bromine in methanol and in the 10% aqueous solution of KCN at room temperature in order to remove secondary phases. Bromine etching is an oxidative and leaves elemental Se on the crystals’ surface [7] that was removed by following cyanide etching. After etching, the crystals were washed in deionized water.

The bulk chemical compositions of the monograin powders were analyzed by energy dispersive X-ray spectroscopy (EDX) on ZEISS HR SEM ULTRA 55 with accelerating voltage 7 kV and a beam current 3 nA. The phase composition of the asgrown and post-treated powders was studied by room-temperature (RT) micro-Raman spectroscopy using Horiba’s LabRam HR spectrometer with incident laser light with wavelength 532 nm. The narrow granulometric fraction of the post-treated monograin powders was used as absorber materials in MGL solar cells. The MGL solar cell combines the features of a single crystalline solar cell and a thin film solar cell. Embedding the CZTSe grains into a layer of epoxy resin formed the photoactive layer called a monograin membrane. The monograin membranes were covered with CdS by chemical bath deposition followed by sputtering of i-ZnO/ZnO:Al layers. Solar cell structures were completed by vacuum evaporation of 1–2 mm thick indium grid contacts onto the ZnO window layer. The active area of the MGL solar cells was ~75% of the total area. The solar cells were characterized by measuring the current density versus voltage (I–V) characteristics by Keithley 2400 electrometer under standard test conditions (AM 1.5, 100 mW/cm²).

3. Results and discussion

As reported earlier by different authors [3–5], CZTSe decomposes at temperatures higher than 400 °C. According to Redinger et al. [4] the loss of Sn cannot be compensated by any significant SnSe partial pressure. Scragg et al. [3] showed by two different kinetic models that ambient vapor phase with both components – chalcogen and Sn-compound – is a prerequisite for stability of Cu2ZnSnSe4 (CZTS) surface. Both proposed models predicted that if the product of the sulfur and Sn vapor pressures exceeds a certain value, the CZTS surface would be completely stabilized. It is therefore important to determine this critical value, in order to produce CZTSe with good surface quality that is vital for solar cell performance. In the present study, SnSe2 or Se sources to produce and regulate the gas phase composition were used.

Following reactions describe the decomposition of CZTSe (1) and formation of gas phase above CZTSe by heating. SnSe2 as a separate source decomposes at high temperatures according to the reactions (2) and (3) providing SnSe and Se into gas phase. It is known that Se in saturated gas phase consists of oligomers Seₙ(g), where n = 2, 3, 5, 6, 7, 8, and the proportions of them are depending on temperature [10].

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\begin{align*}
\text{Cu}_2\text{ZnSnSe}_4(s) & \rightarrow \text{Cu}_2\text{Se}(s) + \text{ZnSe}(s) + \text{SnSe}_2(s) \quad (1) \\
\text{SnSe}_2(s) & \rightarrow \text{SnSe}(s) + \frac{1}{n}\text{Se}(g) \quad (2) \\
\text{SnSe}(s) & \rightarrow \text{SnSe}(g) \quad (3) \\
\text{Cu}_2\text{ZnSnSe}_4(s) & \rightarrow \text{Cu}_2\text{Se}(s) + \text{ZnSe}(s) + \text{SnSe}(g) + \frac{1}{n}\text{Se}(g) \quad (4)
\end{align*}
\]

Where Kp = equilibrium constant and P = partial pressure of components.

As analyzed by mass-spectrometry [11] vapor phase above solid SnSe(s) (melting point 861 °C) consists mainly from SnSe atoms described by the equilibrium (3). The equilibrium vapor pressure of pure SnSe is more than 4 orders of magnitude lower than the vapor pressure on pure SnSe2 or pure Se as can be seen in Fig. 1 (constructed on the base of data published in [10]). From the equation of equilibrium (4) it can be derived that the reaction (4) is shifted to the left side if \(\lg P_{\text{SnSe}} > \frac{1}{n} (\lg K_{\text{CZTSe}} - \lg P_{\text{SnSe}})\) and the incorporation of Sn from the gas phase of SnSe2 into the crystal of CZTSe could occur. If applied vapor pressure of Se is lower than determined by the equilibrium of reaction (4) in a closed ampoule with CZTSe, the composition of CZTSe changes due to the decomposition process by an extent determined by the applied Se pressure.

Fig. 2 displays typical Raman spectra of asgrown and annealed CZTSe monograin powder with compositional ratios of \([\text{Cu}] / ([\text{Zn}] + [\text{Sn}]) = 0.81\) and \([\text{Zn}] / [\text{Sn}] = 1.13\). Annealing was done in SnSe2 vapor at 740 °C. RT Raman spectra of both CZTSe powder crystals revealed four main peaks at 196, 173, 223 and 234 cm⁻¹ which are characteristic for CZTSe [12]. Raman analysis showed that a secondary phase with the Raman peak at 186 cm⁻¹ [13] was formed on the surface of CZTSe monograin after annealing. It can be attributed to SnSe2 or to some Cu–Sn–Se ternary compound. EDX analysis from mechanically polished
crystals showed that Cu-content decreased 0.5 at.% from 23.2 to 22.7 at.%, Zn content decreased from 15.3 at.% to 14.9 at.% and Sn content increased from 13.5 at.% to 13.8 at.% after annealing in SnSe2 vapor. In order to remove the formed secondary phase, the sequential etching with bromine in methanol and with cyanide solution on the annealed CZTSe monograins was performed.

Fig. 3 illustrates a typical etch pattern observed on the monograin surface after the sequential etching. The bromine etchant produced well-defined triangular pits on some faces of crystals and crystal columns on the other type of faces. After bromine etching, the dark red liquid is usually visible on the surface of monograins. This liquid could be either Br2Se3 or Br4Se2 [14]. After the second etching, the powder was washed in water. Se excess from the surface was etched off in a cyanide solution. The Raman scattering peak at 186 cm\(^{-1}\) (Fig. 2) completely disappeared after the sequential chemical etching while no change was observed in the main peaks of CZTSe at 173, 196, 222 and 234 cm\(^{-1}\). Also ZnSe peak at 252 cm\(^{-1}\) remained [12].

Fig. 4 shows the I–V characteristics of a) asgrown, b) SnSe2-annealed c) SnSe2-annealed and etched with bromine in methanol and d) annealed and etched with two etchants CZTSe-based MGL solar cells. After the SnSe2-annealing and sequential etching before CdS deposition, the open circuit voltage (\(V_{oc}\)), current density (\(j_{sc}\)) and fill factor (FF) improved remarkably. Therefore, sequential etching was used in all following annealing experiments before CdS deposition.

In order to elucidate the optimal conditions of post-annealing of absorber powders for CZTSe MGL solar cells, different Se or SnSe2 vapor pressures were applied for several periods starting from 10 min up to 16 h. The optimal annealing time was found to be 30 min. The temperature of material zone was varied from 550 °C to 740 °C. The ratios of metal concentration in the used un-treated CZTSe powder were [Cu]/([Zn] + [Sn]) = 0.81 and [Zn]/[Sn] = 1.13. After annealing in SnSe2 vapor, both compositional ratios decreased to 0.80 and 1.10, respectively. Se-vapor treatment of CZTSe absorber in the temperature range 550–650 °C was beneficial for \(V_{oc}\) and FF values as shown in Fig. 5. The values of \(V_{oc}\) and FF of solar cells based on Se-treated CZTSe absorbers were lower than those of MGL solar cells based on SnSe2-annealed absorbers. CZTSe annealing in both atmospheres over 650 °C, decreased the solar cell parameters continuously with increasing the temperature of the material zone.

The composition of CZTSe absorber has strong influence on the performance of solar cells. Therefore, to confirm clearly the effect of absorber composition to CZTSe MGL device performance, we annealed powders of a large deviation of compositional ratios: 0.79 < [Cu]/([Zn] + [Sn]) < 0.95 and 0.93 < [Zn]/[Sn] < 1.2. The annealing temperature in the material zone was 650 °C and in component zone was 600 °C.

Fig. 6 shows the dependence of powder composition on the device performance after annealing in Se or SnSe2 atmospheres. The values of \(V_{oc}\) were depending on the [Cu]/([Zn] + [Sn]) and [Zn]/[Sn] ratios in powder. The highest \(V_{oc} = 350\) mV was gained with Cu-poor ([Cu]/([Zn] + [Sn]) = 0.81–0.83) and Zn-rich ([Zn]/[Sn] = 1.1) powders. The values of \(j_{sc} = 23.8\) mA/cm\(^2\) were also the highest in these regions. The performance of solar cells is very poor if the powder’s compositional ratio [Cu]/([Zn] + [Sn]) > 0.85. In our previous study [9], it was found that by increasing the Cu content in powders, the [Zn]/[Sn] ratio decreased and the CZTSe materials were Sn-rich ([Zn]/[Sn] < 1). There is a high probability that Cu- and Sn-rich materials contain secondary phases and due to this the solar cells showed very low performance.

By using the optimized SnSe2-annealing conditions, such as temperature in the material zone of 650 °C and temperature of SnSe2 zone of 600 °C, powder compositional ratios of [Cu]/([Zn] + [Sn]) = 0.81 and [Zn]/[Sn] = 1.12, and the CZTSe MGL solar cell with 4.4% efficiency were obtained.
4. Conclusion

The results of this study suggest that the composition of the absorber material can be tuned and the quality of MGL solar cells can be improved by post-treatment of CZTSe powders in Se and/or SnSe₂ vapors. The annealing temperature was found to be crucial for the final performance of CZTSe MGL solar cells. The conversion efficiency of solar cells improved significantly due to heat treatment procedure in SnSe₂ atmosphere and the sequential chemical etching before CdS deposition. The highest efficiencies of MGL solar cells were gained with Cu-poor ([Cu]/([Zn]+[Sn]) = 0.81–0.83) and Zn-rich ([Zn]/[Sn] = 1.1) powders.

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