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Effects of sulphur and tin disulphide vapour treatments of $\text{Cu}_2\text{ZnSnS}(\text{Se})_4$ absorber materials for monograin solar cells

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Abstract

The aim of this study was to find a heat-treatment procedure for monograin powders using a controllable reactive gas phase to improve the CZTS(Se) crystal surface for effectively working *p-n* junctions. The influence of an isothermal treatment in S and SnS_2 vapour on the parameters of monograin layer solar cells is depending on the CZTS(Se) initial composition. The efficiencies of solar cells improve continuously with increasing temperatures of the absorber materials' post-annealing from 823 to 973K under constant sulphur vapour pressure of 100 Torr. The highest values of J_{sc} = 18.4 mA/cm² and V_{oc} = 720 mV were obtained for a device made from CZTS powder annealed at 1013K in SnS_2 vapour.

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1. Introduction

$\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ is theoretically derived from $\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$ by substitution of 50% of the In atoms by Zn and the other half by Sn atoms. This isoelectronic substitution produces a material with many properties being similar to the ternary compound. However, it is crucial that it no longer contains any rare or expensive elements. The desirable properties include *p*-type conductivity, a high absorption coefficient (larger than 10⁴ cm⁻¹) and a direct bandgap of about 1.04-1.5 eV (depending on the ratio of S/Se) [1]. In

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our previous reports [2, 3] we showed that monograin powders of $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSn}(\text{Se},\text{S})_4$ solid solutions can be prepared by isothermal crystallization from binary compound precursors in molten potassium iodide. A high temperature (970–1000 K) synthesis and the homogenization in the molten phase of flux material results in a uniform composition of powder crystals of these complex multicomponent compounds. Therefore, the monograin powder technology enables to grow $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ materials with homogeneous composition usable for monograin layer solar cells.

In order to achieve high-efficiency solar cells, often post-treatments of the absorber layers are required. For example, a successful method to prepare CZTS with a good solar cell efficiency is a solution-based method to deposit a precursor followed by a short annealing in sulphur at 813 K. Also evaporated thin films are often annealed in a H_2S or S atmosphere in order to improve their photovoltaic performance [4]. There are many papers [5-7] concerning the Sn loss during these annealing processes. The vapour pressure of liquid Sn is far too low to see direct evaporation of the element, but tin sulphides are volatile and decompose as following: $2\text{SnS}_2(\text{s}) \rightarrow \text{Sn}_2\text{S}_3(\text{s}) + \frac{1}{2}\text{S}_2(\text{g}) \rightarrow 2\text{SnS}(\text{g}) + \frac{1}{2}\text{S}_2(\text{g})$. Weber *et. al* [5] studied the loss of Sn from CZTS films and proposes that above 823 K CZTS decomposition occurs: $\text{Cu}_2\text{ZnSnS}_4(\text{s}) \rightarrow \text{Cu}_2\text{S}(\text{s}) + \text{ZnS}(\text{s}) + \text{SnS}(\text{g}) + \frac{1}{2}\text{S}_2(\text{g})$. So, for keeping the reactions on the left side and to avoid the decomposition of quaternary compounds it is crucial to keep the sulfur pressure high especially at the high temperatures used in annealing processes. Redinger *et. al* [6] also showed that controlling the Sn losses in the annealing environment improves the solar cell efficiency significantly and reproducibly.

In our previous studies [8], it was shown that due to the distribution of material between the liquid flux and the solid CZTS(Se) crystals during the synthesis process, some part of material is dissolved in flux material at growth temperature. In the cooling period, these dissolve species precipitate on the solid crystal surfaces. Therefore, as-grown monograins need some chemical etching and annealing before the formation of *p-n* junction. In previous studies an isothermal annealing at 1013 K was used, where the atmosphere in the ampoules was determined by the equilibrium vapour pressure formed inside closed CZTS(Se) ampoules. By varying the cooling regimes, Sn-S(Se) crystals with different compositions were deposited on the walls of the ampoules. Therefore, the isothermal arrangement was replaced by a two-temperature zone arrangement, where the atmosphere in the ampoules is controlled by the temperature of an inexhaustible S or SnS_2 source in the lower temperature zone of the post annealing system.

In this paper, the effect of annealing treatments on the structural and compositional properties and also on the parameters of the CZTS(Se) monograin layer solar cells are discussed.

2. Experimental details

$\text{Cu}_2\text{ZnSnS}(\text{Se})_4$ powder materials with different compositions were synthesized from high-purity metal sulfides (selenides) and elemental S (Se) in the liquid phase of a flux material in evacuated quartz ampoules. The details about monograin growth process can be found in [2, 3].

The post-treatments were carried out in closed ampoules additional S or SnS_2 as sulfur and/or SnS_2 sources using a two-temperature zone arrangement. The powder and the sources were in different temperature zones. For comparison, isothermal arrangement with and without additional SnS_2 were used. In a first setup, sealed ampoules were placed into a two-zone tube furnace, where the temperature of both zones were controlled and regulated precisely. In such an arrangement, the vapour pressure of the S or SnS_2 sources was determined and controlled by the lowest temperature in the system. In isothermal arrangements, CZTS powder and component (SnS_2) were in two separated chambers at the same temperature.

The bulk chemical composition of the monograin powders were analyzed by energy dispersive x-ray spectroscopy (EDS). The phase composition of the asgrown and post-treated powders was studied by room temperature (RT) Raman spectroscopy. All post-treated monograin powders were used as absorber materials in monograin layer solar cells (MGL). The MGL solar cell combines the features of a monocrystalline solar cell and a thin film solar cell. The photoactive layer is formed by the semiconductor

CZTS(Se) material with single-crystalline grains embedded into an epoxy resin called a monograin membrane. The monograin membranes are covered with CdS by chemical bath deposition followed by sputtering i-ZnO/ ZnO:Al layers. The active area of the MGL solar cells is ~ 75% of the total area. The solar cells were examined by measuring the current density versus voltage (*J-V*) characteristics and by spectral response measurements.

3. Results and discussion

In a first experiment the CZTSe monograin powders with different compositional ratios were annealed in an atmosphere of excess SnS₂ at 1013 K for 30 minutes. Figures 1a and 1b show the SEM images of a CZTSe single grain and its surface, respectively. The heat-treatment in SnS₂ atmosphere leads to a rough surface of the monograins.

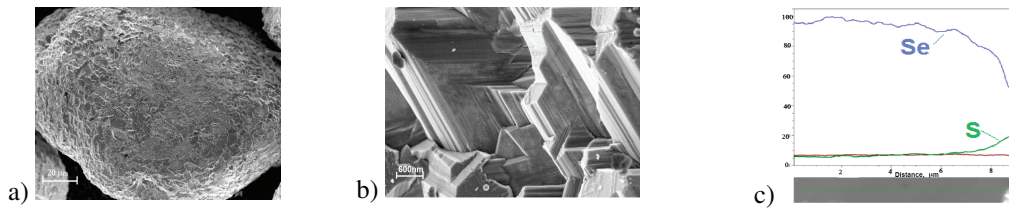


Fig. 1. SEM images of a) CZTSe monograin and b) its surface and c) EDX profile after isothermal SnS₂-treatment at 1013K

In order to clarify the depth of the sulphur diffusion at different annealing temperatures (823 - 1013K), pure CZTSe monograin powders were analyzed in cross section SEM images. Figure 1c shows the EDX compositional profile of a CZTSe monograin after annealing in SnS₂ vapour for 15 minutes at 1013K. The depth of the S diffusion increases from 0.2 to 2 μm with increasing the annealing temperature from 823 K to 1013 K. The sulphur content increases up to 10 mole % in the CZTSe powder surface according to this EDX analysis. According to EDX results, the annealing in SnS₂ vapour leads to different compositions than found for the as-grown powders. From this behaviour, we can conclude that the incorporation of Sn via SnS₂ vapour does not proceed in a random way but is determined by the phase diagram border on the SnS₂ side or by the solubility of SnS₂ in CZTS. In as-grown powders with compositional ratios of Cu/(Zn+Sn)=0.98 and Zn/Sn=1.0 secondary phases of ZnS(Se) and Cu₂S(Se) were found in Raman measurements. As long as enough Cu₂S and ZnS is present, SnS₂ from the gas phase can be incorporated into the powder to form CZTS.

Table 1. Solar cell parameters for different sulphur vapour pressures and temperatures of the CZTS zone used.

| T _{mat} [K] | p _s [Torr] | V _{oc} [mV] | J _{sc} [mA/cm ²] | FF, [%] | η _{max} [%] |
|-------------------------|--------------------------|-------------------------|--|------------|----------------------|
| untreated | | 184 | 1.8 | 27 | 0.1 |
| 823 | 100 | 645 | 15.8 | 56 | 5.6 |
| 873 | 100 | 661 | 17.4 | 61 | 6.2 |
| 923 | 100 | 627 | 13.5 | 55 | 6.1 |
| 973 | 100 | 665 | 18.0 | 62 | 6.6 |
| 973 | 30 | 542 | 10.9 | 47 | 2.6 |
| 973 | 300 | 637 | 14.6 | 56 | 4.6 |
| 973 | 1000 | 644 | 16.0 | 57 | 5.8 |

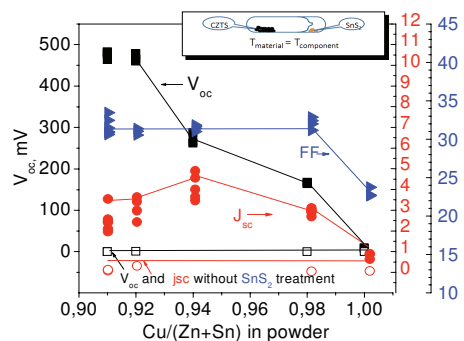


Fig. 2. Influence of an isothermal treatment in SnS₂ vapour on the parameters of MGL solar cells in dependence of the CZTS(Se) initial composition.

In order to determine the influence of the isothermal treatment in SnS₂ vapour on the solar cell parameters, several powders with different Cu/(Zn+Sn) ratios were used to prepare MGL solar cells. Figure 2 shows that the influence of the isothermal treatment in SnS₂ vapour is depending on the composition of the CZTS(Se). An improvement in solar cell parameters is remarkable if the ratio of Cu/(Zn+Sn) is in the range of 0.91-0.94 and the Zn/Sn ratio is equal or higher than one (Zn-rich samples). If the initial composition of the material is more Cu- and Sn-rich (Zn/Sn <1), the output parameters of these MGL solar cells are extremely poor. This could be due to the very low grain resistance (~100 Ω) of the Cu-rich and Sn-rich materials compared with the resistances of Cu-poor and Zn-rich materials (~1000Ω). Raman studies reveal that these low resistant materials contain CuS(Se) and SnS(Se) phases. CuS(Se) is well known as having semi-metallic nature and have a tendency to degrade the open circuit voltage [9]. Another reason for the poor performance of Zn-poor powders can be very likely be due to the presence of Cu-Sn-S phases. Cu₂SnS₃ with a band gap of about 0.95eV can result in a lowering of the open circuit voltage [10]. Therefore, these materials are not suitable for manufacturing solar cells.

With the aim to prevent the decomposition of CZTS and the Sn loss, we also investigated the influence of sulphur vapour pressure treatment of the absorber materials on their solar cell parameters. A series of powders were annealed at temperatures between 823 and 1013K. The sulphurisation time and the sulphur vapour pressures were varied from 10 to 60 minutes and from 30 to 1000 Torr, respectively. For these sulphurisation studies powders with compositional ratios of Cu/(Zn+Sn) = 0.89 and Zn/Sn=1.1 were used. Raman spectra of the sulphurised powders exhibit main peaks of CZTS at 287, 338 and 373 cm⁻¹ [11]. Also, the ZnS secondary phases were found at 353 cm⁻¹ [11]. Due to the high band gap value (3.54 eV) and the high resistivity we believe that ZnS is acting as insulator. This means that the presence of ZnS reduces the active area and the current density of MGL solar cells. Table 1 gives the maximum parameters of CZTS solar cells prepared from sulphurised materials. These MGL solar cells show V_{oc} values of up to 665 mV and FF of up to 62 %. The efficiencies of CZTS MGL solar cells improve continuously after annealing in S vapour pressures of 100 Torr at 823 to 973 K. The annealing of the absorber powders under higher S vapour pressures does not lead to a further improvements of the solar cell parameters. If the vapour pressure of S was lower than 100 Torr, the precipitation of SnS₂ on the walls of the ampoules was visible. Relatively low S vapour pressure ($P_S \leq 30$ Torr) did not prevent the tin loss from CZTS, which led to a Sn-poor surface region. The electronic structure of a Sn-depleted surface is not favourable for the formation of well working $p-n$ junction, as indicated by the poor solar cell efficiencies.

Table 2. Electrical characteristics of devices annealed at various temperatures of the SnS₂ zone ($T_{mat}=1013K$).

| T_{comp} [K] | V_{oc} [mV] | J_{sc} [mA/cm ²] | FF [%] | η_{max} [%] |
|-------------------|------------------|-----------------------------------|-------------|---------------------|
| 603 | 473 | 3.1 | 29 | 0.4 |
| 833 | 442 | 1.5 | 38 | 0.1 |
| 873 | 440 | 2.7 | 43 | 0.4 |
| 898 | 553 | 2.0 | 56 | 0.4 |
| 923 | 645 | 16. | 56 | 5.2 |
| 973 | 680 | 11.7 | 60 | 4.7 |
| 1013 | 720 | 18.4 | 60 | 7.4 |

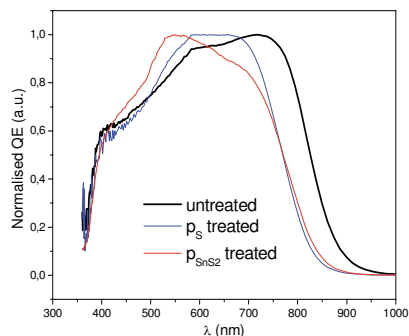


Fig. 3. QE of MGL solar cells using the a) untreated, b) sulphurised and c) annealed under SnS₂ vapor.

In order to find the optimum annealing temperature in SnS₂ atmosphere the CZTS powders were annealed at temperatures between 603 K and 1013 K for a constant time (10 min). The temperature of the CZTS zone was kept constant ($T_{mat}=1013$ K). For this study powders with an initial compositional ratios of Cu/(Zn+Sn)=0.89 and Zn/Sn=1.1 were used. EDX results revealed that the compositional ratios did not change after annealing in SnS₂ vapour. This confirms also that the annealing in SnS₂ vapour is a self

limiting process and does not have any influence on the CZTS composition if this is equal to the composition at a border in the phase diagram. We can assume that the values of the compositional ratios correlate to the border of the homogeneous phase composition. Table 2. shows the results of the best output parameters achieved from these MGL solar cells. The results show that different annealing temperatures significantly affect the photovoltaic behaviour. The highest J_{sc} =18.4 mA/cm² and V_{oc} =720 mV values were obtained from the devices with the CZTS powder being annealed at 1013 K in SnS₂ vapour. The main improvements in V_{oc} and J_{sc} values were obtained for materials annealed at temperatures higher than 923 K. The best V_{oc} is close to the highest as yet reported value for CZTS [12]. A major drawback is the low J_{sc} values obtained for the solar cell structures, which may be due to recombination losses at the active interface, i.e. between CZTS and CdS.

Fig. 3 shows the relative quantum efficiencies of the CZTS MGL devices based on untreated, S-annealed and SnS₂- annealed samples. As the result, the absorption edge of annealed CZTS shifts to shorter wavelengths. The derivatives of the QE with respect to wavelength gives rough estimation of the effective band gap of the absorber material. The estimated band gap for annealed CZTS is around 1.5 eV. and for asgrown CZTS material is around 0.1 eV lower than after annealing. Although we used Cu-poor and Zn-rich powders, it is possible that some secondary phases precipitate from the flux on the grain surface in the powder quenching processes. So, we assume that chemical pre-treatment and heat-treatment under SnS₂ vapour remove the secondary phases from the CZTS monograin surface.

4. Conclusions

It has been shown that MGL solar cell parameters improved remarkable after sulphur or SnS₂ heat-treatments of CZTSSe absorber materials. The influence of an isothermal treatment of SnS₂ vapour on the parameters of monograin layer solar cells is depending on the CZTS(Se) initial composition. Relatively low S vapour pressure ($P_S \leq 30$ Torr) and temperature of SnS₂ zone ($T_{comp} < 560^\circ\text{C}$) in two-temperature zone arrangement, did not prevent the tin loss from Cu₂ZnSnS₄, which led to a Sn-poor surface region. The electronic structure of a Sn-depleted surface is not favourable for the formation of well working *p-n* junction, as indicated by the poor solar cell efficiencies.

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