

$\text{Cu}_2(\text{Zn}_x\text{Sn}_{2-x})(\text{S}_y\text{Se}_{1-y})_4$ MONOGRAIN MATERIALS FOR PHOTOVOLTAICS

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ABSTRACT

In monograin solar cells powders replace wafers or thin films. This allows for cheaper and much more efficient materials production and minimize materials loss. The separation of materials formation from the module fabrication - allowing for all temperatures and purity precautions- is the very important advantage of the monograin layer based technology. Large area module fabrication proceeds without any high temperature steps in a continuous roll-to-roll process. No up-scaling problems arise as is typical of thin-film technologies since a homogenous powder leads to homogenous modules. The influence of different technological parameters to the materials properties was studied and from CZTS= $\text{Cu}_2(\text{Zn}_x\text{Sn}_{2-x})(\text{S}_y\text{Se}_{1-y})_4$ monograin powders solar cells have produced with parameters V_{oc} up to 690 mV, fill factors up to 65 % and I_{sc} more than 20 mA/cm². It was founded that changing of the sulfur/selenium ratio allows a change of 1.04 and 1.72 eV the band gap of $\text{Cu}_2(\text{Zn}_x\text{Sn}_{2-x})(\text{S}_y\text{Se}_{1-y})_4$.

INTRODUCTION

Climate change and insecurity of power supplies are among the greatest problems for humankind at the moment and solutions are to be found within only a few decades. Large-scale introduction of renewable power systems in combination with a strong increase of power efficiency and saving will be the only way out. For example, in order to stabilize the world's climate a continuous growth of PV by at least about 20 % per year will be needed during the coming decades that will lead to PV installation of at least ten TW_p before 2050. To realize these plans new abundant materials and cheap technologies are needed [1].

The technologies used today for manufacturing solar cells are the wafer and the thin film technologies [2]. The wafer technology is based on the growth and use of very large monocrystals or the casting of ultrapure silicon or A3B5 materials. This is a very expensive process not only in terms of money but also in terms of energy input. Later these large single or polycrystals with a high degree of chemical purity and physical perfection have to be sawn into wafers which are subjected to sophisticated methods of oxidation, diffusion and chemical treatment in order to form localized regions of different types of conductivity needed for highly efficient solar cell structures. The idea of making crystalline solar cells by growing very large crystals and then cutting them into thin wafers is in fact not the most intelligent way to obtain perfect materials and structures. Thin film technologies of solar cells production can be applied, but the technical parameters of thin film solar cells are as a rule much worse than those of crystalline solar cells. On the other hand, thin film technologies are, in general, much cheaper than monocrystalline materials based technologies, both with respect to financial expenses and energy costs.

Although silicon as semiconductor material is still dominating even in the thin film solar cell production, photovoltaic cells based on more complex compound semiconductor materials are becoming increasingly important. Unconventional solar cell materials that are abundant but much cheaper to produce than silicon could substantially reduce the overall cost of solar photovoltaics. Currently the most widely used compound solar cell materials, cadmium telluride (CdTe) and copper indium diselenide, copper indium gallium diselenide or the respective sulfides (CIGS), contain resource-limited elements (Te and In) that are already today about ten times more expensive than other metals and do not allow for the provision photovoltaic energy in amounts needed for the very large scale applications in future [3]. One of the currently available most promising new unconventional materials is CZTS, here meaning all copper zinc tin sulfo-selenides including e.g.

$\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ with their abundant and nontoxic constituents. With a direct band gap that depends on the ratio of sulphur to selenium it can be tuned to the optimum for solar energy conversion even for tandem structures. These materials have also a high optical absorption coefficient ($> 10^4 \text{ cm}^{-1}$) [4]. This makes these materials ideal as adsorber layers for low cost high efficiency terrestrial photovoltaic devices [5].

A number of reports have been published on the properties of CZTS materials prepared as thin films by various vacuum as well as low-cost chemical preparation techniques. The most important are sputtering and vacuum evaporation of metals or constituent metal binaries followed by chalcogenization [6, 7, 8], electrodeposition [9, 10], chemical spray pyrolysis [11], and soft chemical technologies [12, 13]. The efficiency of developed polycrystalline films solar cells is lower than theoretically possible. However, in a recent paper Todorov, Reuter and Mitzi achieved a 9.6 % solar efficiency confirmed by NREL [13]. As a result the optimization of growth conditions are regularly discussed by different authors [14, 15]. In addition to the above, the manufacturing of thin films with a large surface area, suitable stoichiometric composition and good reproducibility is a technically complicated task and is not up to end solved even on the laboratory level.

In addition to the monocrystalline and the thin film approach, the third alternative to prepare solar cell structures is the use of powder materials [16]. Powder technologies are the cheapest technologies for materials production. At the same time, although several companies and research institutions have made considerable efforts, powder methods for solar cell applications have not found widespread use yet. It has been shown that isothermal recrystallization of initial powders in different molten fluxes appears to be a relatively simple, inexpensive and a convenient method to produce CIS and CZTS powders with an improved crystal structure, that are prerequisite for solar cell use [16-19]. Powders consist of small single crystalline grains. In monograin solar cells powders replace monocrystalline wafers or thin films. This allows for cheaper and much more efficient materials production that minimizes materials loss. The separation of materials formation from the module fabrication - allowing for all temperatures and purity precautions- is an additional very important advantage. Large area module fabrication could be done without any high temperature steps in a continuous roll-to-roll process. Homogenous powders lead to homogenous modules and do not result in up-scaling problems.

EXPERIMENTAL

Monograin powder materials were synthesized from metal binaries ($\text{CuSe}(\text{S})$, $\text{ZnSe}(\text{S})$, $\text{SnSe}(\text{S})$ and elemental selenium or sulphur, respectively) in a molten flux using an isothermal recrystallization process. The precursors were thermally annealed in evacuated quartz ampoules. The evolution of crystal shape and morphology of the monograin powders was analyzed by electron imaging using a high-resolution scanning electron microscope (SEM) Zeiss ULTRA55 with the compositional contrast detector EbS. The chemical composition and the distribution of components in powder crystals were determined using an energy dispersive X-ray analysis (EDX) system). XRD patterns were recorded by using a Bruker AXS D5005 diffractometer using monochromatic Cu K α radiation.

Monograin layer (MGL) solar cells (graphite/CZTSSe/CdS/ZnO) were made from grains with diameters of 56–63 μm [19-21]. Powder crystals were covered with chemically deposited CdS buffer layers. For the MGL formation a monolayer of CZTS powder crystals was glued together by a thin layer of epoxy. After polymerization of this epoxy, i-ZnO and ZnO:Al were deposited by RF-sputtering onto the open surface of the layer. Solar cell structures were completed by vacuum evaporation of 1–2 μm thick In grid-contacts onto the ZnO window layer. Subsequently, the layer was glued onto glass substrates. The opening of the back contact areas of the crystals that were originally inside the epoxy was done by etching the epoxy in H_2SO_4 and by abrasive treatment. Graphite paste was used for the back contacts. The solar cell efficiency was measured in an Oriel class A solar simulator. I–V curves were measured using a Keithley 2400 source meter.

RESULTS AND DISCUSSION

The structural, morphological, electrical and optical properties of Cu₂ZnSn(S,Se)₄ materials depend strongly on the composition and on the additional thermal and chemical treatments. Fig. 1 shows the morphologies of CZTS powder crystals grown in the KI flux. The crystals have tetragonal shape with rounded grain edges. A change in the chemical nature of the flux leads to variations in crystals shape.

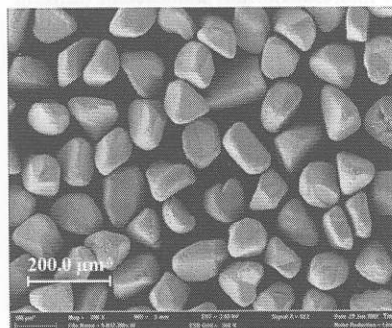


Fig. 1. SEM micrographs of Cu₂ZnSn(S,Se)₄ monograin powder crystals grown in KI flux.

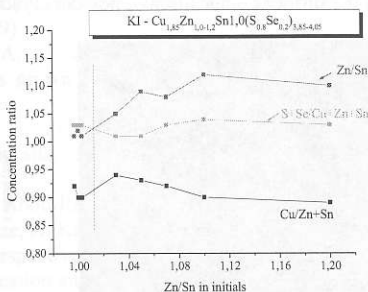


Fig. 2. Dependence of Cu₂ZnSn(S,Se)₄ monograin powder composition on precursor composition.

Fig. 2 shows the results of the compositional analyses of as-grown Cu₂ZnSn(S,Se)₄ materials as a function of the initial precursor composition. With the Zn/Sn compositions ratio increasing in the precursors the obtained powders contain an increased ratio of Zn to Sn but a decreased amount of Cu. At the same time the content of chalcogens (S+Se) in the materials does not depend on the Zn/Sn ratio. At stoichiometric ratios of 25%, 12.5%, 12.5% and 50% for Cu, Zn, Sn, and S+Se, in Cu₂ZnSn(S,Se)₄ respectively, all studied materials were Zn-rich and Cu-poor and have an stoichiometric content of (S+Se). An overstoichiometric chalcogen amount in the starting materials leads to an increase of the relative contents of Zn and Se in the as-grown powders (Fig. 3).

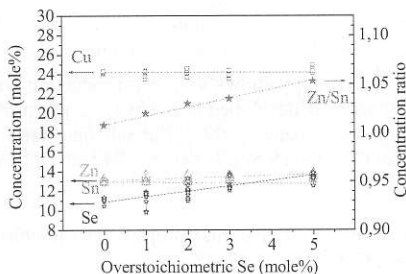


Fig. 3. The influence of the chalcogen (Se) content on the composition of Cu₂ZnSn(S,Se)₄ powders

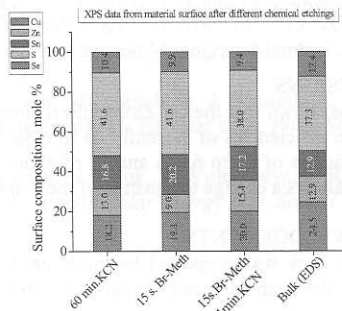


Fig. 4. Surface composition of etched in different etchants Cu₂ZnSn(S,Se)₄ powders

By comparing as-grown powders crystal surface compositions with the bulk compositions it was found that the surface of as-grown Cu₂ZnSn(S,Se)₄ crystals was Sn-rich while the bulk of crystals was Zn-rich. This was the result of the contamination of the powder crystals by

components of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ dissolved in the flux. In order to remove these contaminations (other phases) from the surfaces and to improve the developed $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ solar cells performance, the chemical treatments in different etchants (HCl, KCN, Br-MeOH and NH_4OH) were performed. It was found that etching with KCN or HCl increases the ratio of Zn to Sn on the surface. At the same time HCl etching leads to a slightly chalcogen-poor surface. Treatment with KCN dissolves mainly Cu, Sn and chalcogen, and ammonia solution remove selectively Cu and chalcogen in an approximate ratio of 1:2. Fig. 4 shows the results of this influence of different etchants on the surface composition of powder crystals.

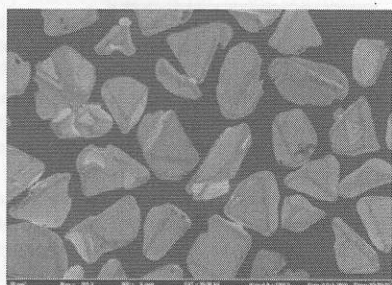


Fig.5. EBIC picture of MGL solar cell from material composed of $\text{Cu}_{1.85}\text{Zn}_{1.0}\text{Sn}_{0.95}(\text{S}_{0.8}\text{Se}_{0.2})_{3.95}$

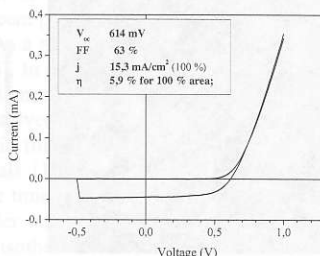


Fig.6. I-V dependence of the $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ monograin layer cell (certified in the Calibration Lab of Fraunhofer ISE, Freiburg, 2009)

Electron beam induced current (EBIC) investigations of MGL solar cells indicate that all crystals in MGL operate with nearly the same efficiency. Fig. 5 represents EBIC picture for the MGL solar cell from the material composed of $\text{Cu}_{1.85}\text{Zn}_{1.0}\text{Sn}_{0.95}(\text{S}_{0.8}\text{Se}_{0.2})_{3.95}$. Current-voltage dependences of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ MGL solar cells show V_{oc} values of over 690 mV, fill factors of up to 65 %, and short circuit currents of up to 20 mA/cm^2 . Efficiencies of the active area of these solar cells of up to 6.4 % were determined, total area efficiencies of 5.9 % were certified by calibration lab measurements (fig. 6). Varying the S/Se ratio in the material allows one to control the band gap of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ materials and with this the quantum efficiency of the solar cell made on their base.

CONCLUSIONS

It is shown that the $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ monograin technology allows solar cell production with conversion efficiencies of currently up to 6 %. The solar cells developed here have V_{oc} up to 690 mV, fill factors of up to 65 % and I_{sc} of about 20 mA/cm^2 . Changing the sulfur/selenium ratio in materials allows a change the change of the band gap of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ between 1.04 and 1.72 eV.

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