Formation of Properties of CuInSe₂ and Cu₂ZnSn(S,Se)₄ Monograin Powders Synthesized in Molten KI

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Declaration: Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any academic degree.

Kristi Timmo

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Kaaliumjodiidsulandaja keskkonnas kasvatatud monoterapulbrite $\text{CuInSe}_2$ ja $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ omaduste kujundamine

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LIST OF PUBLICATIONS

The present doctoral thesis is based on the following papers, which are referred to in the text by their Roman numerals I-VI.


In Appendix A, copies of the following papers are included.
Author’s own contribution

I Part of the experimental work (CuInSe2 monograin powder preparation, determination of CuInSe2 solubility in KI, granulometric analysis), analysis of the results and major part of writing

II Part of the experimental work (CuInSe2 monograin powder preparation)

III Part of the experimental work (CuInSe2 monograin powder preparation, doping with sodium) and characterization (I-V curve measurements), analysis of the results and major part of writing

IV Part of the experimental work (Cu2ZnSn(S,Se)4 monograin powder preparation, chemical etching, CBD-CdS deposition) and characterization (Raman spectroscopy, I-V curve measurements), analysis of the results and major part of writing

V Part of the experimental work (Cu2Zn1-xCdxSn(Se1-ySy)4 monograin powder preparation, CBD-CdS deposition) and characterization (I-V curve measurements)

VI Part of the experimental work (Cu2ZnSn(S,Se)4 monograin powder preparation, chemical etching, CBD-CdS deposition) and characterization (I-V curve measurements), analysis of the results and major part of writing

List of abbreviations and symbols

MGL Monograin layer
CISe CuInSe2
CZTS Cu2ZnSnS4
CZTSe Cu2ZnSnSe4
CZTSSe Cu2ZnSn(S,Se)4
RF Radio frequency
RT Room temperature
EDXRD Energy dispersive X-ray diffraction
PL Photoluminescence
$E_g$ Bandgap energy
MGP Monograin powder
I-V Current-voltage
$\eta$ Solar cell efficiency
$j_{sc}$ Short circuit current density
$V_{oc}$ Open circuit voltage
$FF$ Fill factor
$\Phi_b$ Barrier height of p-n junction
$V_L$ Volume of liquid phase
$V_S$ Volume of solid phase
XRD X-ray diffraction
ICP-MS Inductively coupled plasma mass spectrometry
<table>
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<th>Abbreviation</th>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SE SEM</td>
<td>Secondary electron mode of SEM</td>
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<tr>
<td>EsB SEM</td>
<td>Energy selective backscattering mode of SEM</td>
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<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
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<td>QE</td>
<td>Quantum efficiency</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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INTRODUCTION

The increasing demand for energy, the limited supply of fossil fuels and their unfavourable effect on the environment are the main reasons why the search for alternative sources of power is imperative. Given that there is a vast amount of energy available from the sun, devices that convert light energy into electrical energy are becoming increasingly important. Since the 1970s, solar electricity, also known as photovoltaics (PV), has shown that human race can get a substantial portion of its electrical power without burning fossil fuels (coal, oil or natural gas) or creating nuclear fission reactions. Photovoltaics has shown that it can generate electricity for a wide range of applications, scales, climates, and geographic locations [1].

For large–scale terrestrial photovoltaic applications, cost-effective processes and materials are needed. One approach to bring down the costs of solar cell production is to develop cheap non-vacuum technologies: one of them is the monograin layer (MGL) solar cell technology.

The research in this thesis is mainly directed to the regularities of the synthesize-growth of CuInSe2 and Cu2ZnSn(S,Se)4 monograin powders in liquid potassium iodide as absorber materials for monograin layer solar cells. The aim of the study was to modify absorber material properties for improvement of monograin layer solar cell parameters.

This thesis is divided into four Chapters. After introduction, literature is briefly reviewed in Chapter 1. Chapter 2 describes the preparation of the CuInSe2 and Cu2ZnSn(S,Se)4 monograin powders and the design of monograin layer solar cells on their bases. Additionally, the used experimental technological approaches and characterization methods are given. Chapter 3, divided into four different parts, presents experimental results and their discussion. In the first part the growth parameters of CuInSe2 powder particles in potassium iodide are described. The second part deals with the effect of sodium doping to the properties of CuInSe2 monograin powder as absorber material in monograin layer solar cells. The third part of this chapter presents the results of chemical treatment of Cu2ZnSn(Se1–xSx)4 monograin powder surface. The morphological and compositional properties of CZTSSe crystals surfaces depending on the chemical nature of the etchant are given in this part of the work. The fourth part describes the formation of Cu2ZnSn(Se1–xSx)4 solid solutions and how the concentration ratio of Se/S in the absorber material influences the solar cell parameters.

Finally, Chapter 4, summarizes the main results.

The work is financially supported by Estonian Science Foundation grants 6160, 6179, 7678 and SF0140099s08. Financial support was also received from Enterprise Estonia, World Federation of Scientists National Scholarship Programme and Estonian Doctoral School of Materials Science and Materials Technology (MMTDK). This doctoral thesis is based on 6 published papers.
1. LITERATURE REVIEW AND AIM OF THE STUDY

1.1 CuInSe₂ based solar cells

The chalcopyrite CuInSe₂ is a I-III-V₂-semiconductor. It can be deposited as a polycrystalline thin film or grown as a single crystal. As a semiconductor, CuInSe₂ inhibits a high absorption coefficient $10^9 - 10^5$ cm⁻¹. Conversion efficiencies between 12 and 15% have already been achieved for devices based on pure CuInSe₂/CdS/ZnO heterojunction [2,3]. The bandgap of the absorber material can be changed by using solid solutions of CuInSe₂ with CuInS₂ and CuGaSe₂. The bandgap of the resulting Cu(In,Ga)(S,Se)₂ compound semiconductor can be adjusted over a wide range: from 1.04 eV for pure CuInSe₂ over 1.5 eV and 1.68 eV for CuInS₂ and CuGaSe₂ [4].

The highest efficiency to date for Cu(In,Ga)Se₂ solar cells is 20.3%, reported by Centre for Solar Energy and Hydrogen Research (ZSW) in Stuttgart [5].

1.1.1 Cu₂ZnSnSe₄ and Cu₂ZnSnS₄ based solar cells

Since the availability of indium is an object of discussion regarding the large-scale production of CuInSe₂ solar cells, its replacement with other elements, for instance with Zn and Sn, is reconceived. Cu₂ZnSn(S,Se)₄ (CZTSSe) is a new type of an absorber material for thin film solar cells. CZTSSe consists of elements that are abundant in the crust of the earth and most of them are nontoxic. This semiconductor compound can be obtained by replacing half of the indium atoms in chalcopyrite CuInSe(S)₂ with zinc and the other half with tin. The abundance of zinc, tin, and indium in the crust of the earth is 75, 2.2, and 0.049 ppm, respectively [6]. In 1988, Ito and Nakazawa for the first time recorded the photovoltaic effect in the heterodiode that consisted of a cadmium-tin-oxide transparent conductive film and a CZTS thin film on a stainless steel substrate. They reported the value of open-circuit voltage as high as 165 mV [7]. In 1989, by annealing the same device in air, they achieved the open-circuit voltage of 250 mV and the short-circuit current of 0.1 mA/cm² [8]. In 1997, Friedlmeier et al. fabricated CZTS thin films by thermal evaporation of the elements and binary chalcogenides in high vacuum. To form the heterojunction on this film they deposited $n$-CdS and ZnO window layers and reported the highest conversion efficiency of 2.3% and the highest open-circuit voltage of 570 mV [9]. In 2003, Seol et al. prepared CZTS thin films by RF magnetron sputtering. They reported that the refractive index of CZTS was 2.07, the absorption coefficient was about $10^4$ cm⁻¹, and that the band gap energy was about 1.51 eV [10]. Katagiri et al. attained the conversion efficiency of 5.45% in 2003 [11]. In 2007, they reached up to the conversion efficiency of 5.74% [12] and in 2009 up to 6.77% using a three-sources RF co-sputtering for metal film deposition followed by annealing in sulfur...
containing atmosphere [13]. At present, the best conversion efficiency of the Cu$_2$ZnSn(S,Se)$_4$ thin film solar cells achieved by Mitchi et al. is 9.66% [14].

1.2 Crystal structures of CuIn(S,Se)$_2$ and Cu$_2$ZnSn(S,Se)$_4$

The compounds A$^I$B$^{III}$X$_2$V$^I$ (A = Cu,Ag; B = Al,Ga,In; X = S,Se,Te) crystallize in the tetragonal chalcopyrite-type structure (space group $I\bar{4}2d$) [15]. The unit cell of CuInSe$_2$ is shown in Figure 1. The values measured for lattice parameters of ClSe at room temperature are $a = 5.784$ Å and $c = 11.618$ Å [16].

![CuInSe$_2$](image)

Figure 1. Chalcopyrite type unit cell of CuInSe$_2$ [15].

Lowering the symmetry one step further leads to the stannite-type structure (space group $I\bar{4}2m$) named after the mineral stannite Cu$_2$FeSnS$_4$ [17,18]. A symmetry decrease is not only achieved by an ordered substitution of the metals, but also by changing the metal ordering, i.e. the arrangement of the cations on the structural sites of the unit cell. By doing so the kesterite type structure (space group $I\bar{4}$) can be deduced from the stannite-type structure, which is named after the mineral kesterite Cu$_2$ZnSnS$_4$ [18,19]. These two structures, the stannite and kesterite type structures (see Figure 2), differ only in the distribution of Cu$^+$ and Zn$^{2+}$ [19,20].
Figure 2. Crystal structures of Cu$_2$ZnSnSe$_4$ in kesterite and stannite phases [20].

The discussion in literature centres on photovoltaics based on In-free absorber materials, as for instance compounds belonging to the stannite-type or also kesterite-type structure family [21,22]. Chen et al. found that kesterite structure is the ground state structure for both CZTS and CZTSe, whereas stannite structure has higher total energies [23]. Although the kesterite structure possesses lower energy, the energy difference between the kesterite and stannite structure is small, about 3 meV/atom [23,24]. This indicates that kesterite and stannite ordering may coexist in the synthesized samples.

The calculated bandgap of CZTSe is about 0.4 eV smaller than CZTS in the same crystal structure, which is consistent with our common expectation that the selenides have smaller bandgaps than the corresponding sulfides but disagrees with the interpretation of experimental absorption data showing that the bandgaps of CZTSe are nearly the same as CZTS at about 1.5 eV [25,26,27]. The estimated energy gaps are $E_g = 1.56$ eV for kesterite CZTS, 1.42 eV for stannite CZTS, 1.05 eV for kesterite CZTSe, and 0.89 eV stannite CZTSe [24].

Another problem reported concerns the bandgap energy of CZTSe, where there are large discrepancies between the reported values. Several research groups have found that Cu$_2$ZnSnSe$_4$ has bandgap energies from 1.44 to 1.56 eV [7,25,27,28]. On the other hand, Raulot et al.[29] have performed ab initio calculation of the electronic structure of CZTSe and found a bandgap around 0.8 eV and Zoppi et al.[30] stated that this value ranges from 0.88 to 0.94 eV.
1.2.1 Phase diagrams

The isoelectronic, pseudobinary Cu$_2$Se-In$_2$Se$_3$ tie line provides a good overview of the phases involved in CuInSe$_2$ growth. The most contemporary and the most relevant for thin-film CuInSe$_2$ growth, Cu$_2$Se-In$_2$Se$_3$ phase diagram, is the one from Haalboom in 1998 [31] shown in Figure 3. This investigation had special focus on temperatures and compositions relevant for the preparation of thin-films. The phase diagram in Figure 3 represents the four different phases which have been found to be relevant in this range: the $\alpha$-phase CuInSe$_2$, the In-rich $\beta$-phase CuIn$_3$Se$_5$, the $\delta$-phase (the high-temperature sphalerite phase) and Cu$_2$Se. For the $\alpha$-phase the existence range extends from 24-24.5 at.% Cu at room temperature [32]. At higher temperatures, the existence range of single-phase CuInSe$_2$ is broadening to the In side and does not involve the stochiometric composition with 25% Cu, as reported in [33,34]. The $\alpha$-phase and Cu$_2$Se already coexist at a Cu content below 25 at.%. Cu$_2$Se is the only secondary phase present in Cu-rich compositions. For more extreme In-rich compositions, in addition to the $\beta$-phase, other ternary In-rich Cu-In-Se phases can also form (e.g. Cu$_2$In$_4$Se$_7$, CuIn$_3$Se$_5$ and Cu$_3$InSe$_4$) [35].

![Figure 3. Quasi-binary phase diagram Cu$_2$Se-In$_2$Se$_3$ in the range of 15-30 at.% Cu and 20-900°C [31].](image)

There is no simple way to draw a quaternary phase diagram, and only few papers have been published in this regard for Cu-Zn-Sn-S/Se. Phase equilibria in the Cu$_2$Se-Cu$_2$SnSe$_3$-ZnSe system were investigated by L.V.Piskach et al. [36]. The quaternary
compound Cu$_2$ZnSnSe$_4$ has a homogeneity range and undergoes a polymorphous transformation (δ↔δ') in the temperature interval 856–892 K (see Figure 4). In contrast to CuInSe$_2$, where it is clear that only Cu$_2$Se is present for compositions with [Cu]/[In] ≥ 1, the formation of secondary phases in Cu$_2$ZnSnSe$_4$ for [Cu] 25 at.% depends also on the Sn content (on the [Sn]/[Zn] ratio). The polythermal SnSe$_2$–Cu$_2$ZnSnSe$_4$ section is quasi-binary in the subsolidus part. Its liquidus consists of two fields of primary crystallization of the β-solid solution (ZnSe) and the γ-solid solution (SnSe$_2$). The secondary crystallization L↔γ+β and L+β↔δ is completed on the horizontal plane at a temperature of 892 K corresponding to a ternary peritectic processes. The SnSe$_2$–Cu$_2$ZnSnSe$_4$ section is a tie line in the quasiternary system and, hence, the three-phase fields 4 and 5 can be contiguous with the single-phase fields 10 and 7, respectively. The polymorphous transformation of Cu$_2$ZnSnSe$_4$ occurs at 856 K and its homogeneity range is smaller than 3 mol.% SnSe$_2$.

Figure 4. SnSe$_2$–Cu$_2$ZnSnSe$_4$ section (B, 50 mol.% Cu$_2$Se, 50 mol.% ZnSe): (1) L, (2) L+β, (3) L+γ, (4) L+β+γ, (5) L+β+δ, (6) γ+δ, (7) δ, (8) δ+δ', (9) δ', (10) γ, (11) γ+δ' [36].
Figure 5. Isothermal section of the Cu$_2$Se–ZnSe–SnSe$_2$ system at 670 K [36].

The isothermal section of the quasi-ternary Cu$_2$Se–ZnSe–SnSe$_2$ system at 670 K (Figure 5) consists of the homogeneity ranges of the $\alpha$-, $\beta$-, $\gamma$- and $\delta'$-solid solutions of Cu$_2$Se, ZnSe, SnSe$_2$ and of the low-temperature modification of the quaternary compound Cu$_2$ZnSnSe$_4$. The solubility of Cu$_2$ZnSnSe$_4$ in Cu$_2$Se is lower than 2 mol.% and is elongated along the Cu$_2$Se–SnSe$_2$ boundary side, in ZnSe and SnSe$_2$ it is lower than 1 mol.%, in Cu$_2$SnSe$_3$ lower than 0.5 mol.%. The miscibility gap of Cu$_2$ZnSnSe$_4$ was found to be 3 mol.% along the triangulated section Cu$_2$SnSe$_3$–ZnSe, which was established according to the investigation of 20 additional alloys allocated in three sections crossing the equimolar composition of the quaternary compound.

L.V. Piskach et al. have investigated the phase equilibria in the Cu$_2$S–ZnS–SnS$_2$ system [37]. The vertical section Cu$_2$S–A (A-50 mol% ZnS, 50 mol% SnS$_2$) is shown in Figure 6. The liquidus consists of three lines that limit the fields of primary crystallization of the $\alpha$-solid solution range of Cu$_2$S and $\beta'$- and $\beta$-solid solution range of the two polymorphic modifications of ZnS.
Figure 6. Phase diagram of the Cu2S–A section: (1) L, (2) L+α, (3) L+β', (4) L+β+β', (5) L+β, (6) L+α+β', (7) L+β'+δ, (8) L+β'+γ, (9) α, (10) α+δ, (11) δ, (12) β'+δ, (13) β'+γ+δ, (14) β'+γ, (15) β'+δ+Cu2ZnSn3S8, (16) β'+Cu2ZnSn3S8, (17) β'+γ+Cu2ZnSn3S8 [37].

The lines of 1153 and 1063K correspond to ternary peritectic reactions L+β'↔δ+α and L+β'↔δ+γ, respectively. At these temperatures the secondary crystallization of the binary peritectics: L+β'↔α, L+β'↔δ and the binary eutectic L↔β'+γ terminated. The Cu2S–Cu2ZnSnS4 part of the section is quasi-binary in the subsolidus region. Therefore the single-phase region δ is limited by the three-phase region L+β'+δ, and the line between them is two-phase β'+δ. The homogeneity region of the α-solid solution at the annealing temperature contains approximately 1 mol% of A and tends to increase with temperatures reaching a maximum at the ternary peritectic temperature. Also, the homogeneity region of the δ-solid solution (Cu2ZnSnS4) has a tendency to increase slightly with temperature. At the annealing point the solubility of the δ-solid solution consists of up to 2 mol% of the initial components on either side of the stoichiometric composition of the quaternary compound.
1.2.2 Formation of Cu$_2$ZnSn(S,Se)$_4$

There are only few publications describing in detail the formation of Cu$_2$ZnSnS$_4$ or Cu$_2$ZnSnSe$_4$ [38,39,40]. A. Weber et al. [38] studied the phase formation during the annealing/sulfurization step of co-electroplated Cu–Zn–Sn precursors using in-situ Energy Dispersive X-ray Diffraction (EDXRD). At room temperature (RT) there were diffraction peaks which could be assigned to ZnS, CuS and also weak diffraction peaks of Cu. Only at about 150°C they found CuS. Further heating led to the rapid crystallization of Sn$_2$S$_3$ at approximately 200°C. The diffraction intensity of this phase remained constant until 400°C. At about 300°C the CuS-$\text{Cu}_{2-x}$S transformation began. Further heating led to the abrupt phase transition from the Sn$_2$S$_3$ to the SnS phase. This SnS phase was not stable and above 400°C decomposed gradually while strong, broad peaks appeared in the EDXRD spectra, which can be related to Cu$_2$ZnSnS$_4$. They found also Cu$_2$SnS$_3$ together with the quaternary compound. Further heating to 550°C led to a reduction of the Cu$_2$SnS$_3$ phase. S.Schorr et al. [39] found that using the mixture of 2CuS+SnS+ZnS the formation of Cu$_2$ZnSnS$_4$ starts just below 300°C, accompanied by a decrease of the fraction of CuS and SnS, whereas the fraction of the ZnS phase remained.

Results by R.Schurr et al. [40] showed that the crystallization of kesterite Cu$_2$ZnSnS$_4$ was completed by the solid state reaction of Cu$_2$SnS$_3$ and ZnS. The formation mechanism of Cu$_2$SnS$_3$ was dependant on the binary precursor phases. In the case of sulfurization of copper-rich metal films they found at RT Cu$_3$Sn and CuZn phases. The formation of SnS$_2$ and Cu$_{2-x}$S began at 387°C. Further annealing led to the formation of ZnS (500°C). At the annealing temperature of 540°C the formation of Cu$_2$SnS$_3$ began from the binary sulphides Cu$_{2-x}$S and SnS$_2$. The crystallization of kesterite Cu$_2$ZnSnS$_4$ was completed by the solid state reaction of Cu$_2$SnS$_3$ and ZnS, starting approximately at 565°C.

In copper-poor near stoichiometric precursors in addition to Cu$_3$Sn and CuZn phases Cu$_6$Sn$_5$ was detected [40]. The presence of Cu$_6$Sn$_5$ led to the preferred formation of Cu$_2$SnS$_3$ via the reaction educts Cu$_{2-x}$S and SnS$_2$ in the presence of SnS$_2$ (Cu$_4$SnS$_6$) melt, which is the result of the decay of the Cu$_4$SnS$_6$ phase. The formation of SnS$_2$ began at 180°C, induced by the transformation of Cu$_6$Sn$_5$. The further increase of the annealing temperature led to the formation of Cu$_2$S. The Cu$_3$Sn phase occurred at 300°C as a result of the transformation of Cu$_6$Sn$_5$. The formation of the Cu$_4$SnS$_6$ phase took place at 387°C out of the binary educts Cu$_2$S and SnS$_2$ in the sulphur atmosphere. The evolved phase Cu$_4$SnS$_6$ was stable up to 540°C and decomposed into the Cu$_{2-x}$S and SnS$_2$ (melt). This was also the formation temperature of ZnS and Cu$_2$SnS$_3$. The crystallization of kesterite Cu$_2$ZnSnS$_4$ was completed by the solid state reaction between ZnS and Cu$_2$SnS$_3$, starting at 565°C.
1.3 **Monograin powder growth**

The isothermal growth of II-VI, I-III-VI and I-II-IV-VI polycrystalline powders in the presence of the liquid phase of a suitable solvent material (flux) in an amount sufficient for repelling initial crystallites leads to the formation of semiconductive materials with single-crystalline grain structure and narrow-disperse granularity, so called monograin powders [41]. Thus, it is possible to form many little perfect single crystals in one process. The driving force in this process is the difference of the surface energy of crystals of different sizes. The criterion of single grain growth is a sufficient amount of flux for filling the whole free space between initial particles. Otherwise there can occur molten or gaseous phase sintering. The sintering is determined by capillary forces in the solid-liquid phase boundary.

The analogous processes - crystal growth and sintering - proceed also during the heat treatment of semiconductor thin films for solar cells and they are essential for the production of dense and well-oriented crystalline thin films. The presence of the liquid phase of a fluxing agent enables the fast recrystallization and sintering of primary crystals during the heat treatment of films due to the fast diffusion of components through the molten phase [42]. In dense and well recrystallized films a high concentration of inherent defects, particularly in the intergrain region, where a considerable part of photogenerated charge carriers is lost due to the recombination, is reduced.

On the other hand, the liquid phase of the flux represents a source of doping impurities which are easily incorporated into the crystal during the growth process. The level of doping depends on the time and temperature of heating and is limited by the solubility of impurities [43]. The growth of monocrystalline powder grains can proceed at temperatures higher than the melting point of the used flux materials and at lower temperatures than the phase transition or the melting point of the synthesized semiconductor compound. Once the powder grains have the desired size, quenching stops the growth and the fluxing agent has to be removed.

Research directed to the development of CuIn(S,Se)\textsubscript{2} monograin powder technology for solar cell application began at TUT in the Laboratory of Semiconductor Materials in 1994. Already the first results indicated to a possibility of producing CISe monograin powders by the recrystallization of polycrystalline powders in isothermal ampoules in the presence of liquid selenium [44]. Afterwards the recrystallization of polycrystalline powders was replaced by a similar process where the synthesis of the compound and the growth process were combined and proceeded in the CuSe-Se liquid phase [45]. From the technological point of view, the process of flux removal is also of great importance. Due to this Se and CuSe-Se as flux materials were later substituted by water soluble potassium iodide.

The developed monograin powder technology [41-45] appears to be a relatively simple, inexpensive and convenient method to produce powder materials for monograin layer solar cell applications. The advantages of the powder crystals growth in a liquid flux are: single-crystalline structure of every grain, uniform
distribution of doping impurities and the homogeneous composition of grains in the whole patch. 

As the large scale production of copper-indium chalcopyrite based solar cells for terrestrial use in future is limited due to the high price and lack of indium, the replacement of In in CuIn(Se,S)₂ by equal parts of Zn and Sn atoms is preferred. Starting from 2005 the investigations have mainly been directed to the Cu₂ZnSnSe₄, Cu₂ZnSnS₄ and their solid solutions as possible absorber materials.

1.4 Effect of sodium on the properties of CuInSe₂

In the case of vacuum deposited Cu(In,Ga)Se₂ thin film solar cells, the presence of Na in the absorber correlates with numerous changes in the material and device quality. In most cases Na diffuses from the glass substrate into the absorber, but there are also approaches where Na is incorporated by the use of Na-containing precursors such as Na₂Se, Na₂O₂, NaF and Na₂S [46]. The most obvious effects of Na incorporation are improvements in the open-circuit voltage [47,48], preferential grain orientation [48], increased grain size and carrier concentration [49,50]. Using the photoluminescence (PL) measurements, Kimura et al. [51] found that the self compensation of CuInSe₂ was reduced by Na incorporation due to the suppression of donor-type defects.

The addition of 0.1-0.2 at.% sodium has been found to extend the region of single phase existence of polycrystalline α-CuInSe₂ by 2 % towards the Cu₂Se side in the quasibinary phase diagram [32]. A widening of the existence region is beneficial because the synthesis of the single phase semiconductor material is simplified if the product compound tolerates slight deviations from stoichiometry.

1.5 Surface modification by chemical treatments

The active interface of the p-type absorber and the n-type buffer layer plays a key role in solar cell performance. Different research groups have studied the influence of various chemical etchants on CuInSe₂, but detailed surface analytical studies have not been carried out to understand the surface modifications and chemical changes occuring on the Cu₂ZnSn(S,Se)₄ monograins surface. Due to the segregation of Cu-Se binaries, it is necessary to remove these phases with strongly selective etchant that only attacks Cu-Se and does not harm CuInSe₂. The only chemical etchants, which are presently known to fulfil this condition, are cyanide containing solutions such as potassium cyanide (KCN) [52,53,54,55] or sodium cyanide (NaCN) [56]. It has been found that efficient removal of surface oxides can be achieved by NH₃ treatment [57]. Bromine etching is an oxidative etching and leaves elemental Se on crystal surfaces [58,59]. The influence of HCl treatment on CISe surface was investigated by Nelson et al. [59]. They found that after HCl etching the surfaces appeared to be unoxidized and Se rich. At the same time it does not affect the surface morfology significantly.
1.6 Summary of the literature review and the aim of the study

Monograin layers are perspective for the development of inexpencive solar cells. Monograin powders of CuInSe$_2$ can be applied as absorber materials in monograin layer solar cells. The isothermal growth of CuInSe$_2$ monograin powders takes place in the presence of the liquid phase of a suitable solvent material (flux). In this process the chemical nature of the liquid (molten) phase of the used solute material influences certain properties of the obtained absorber material. The system CuInSe$_2$-KI had not been studied yet.

Chalcopyrite-type semiconductors like Cu(In,Ga)$_2$S$_2$ or Cu(In,Ga)Se$_2$ have very beneficial properties for photovoltaic applications [2,3,4], which in turn have led to a strong scientific interest in thin film solar cells based on these materials. Obtained efficiencies are remarkably high, up to 20.3% [5] however, gallium and indium used for the preparation of the active layer are very rare and expensive elements. This could lead to a shortage in the supply of these elements and would inhibit a cost-effective large-scale production. To overcome these limitations, alternative materials are intensively researched in order to substitute the expensive elements In and Ga. Among these materials, Cu$_2$ZnSnSe$_4$ (CZTSe) is one of the most promising materials, as it consists of abundant and relatively cheap elements. The formation of Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ solid solutions has not been investigated yet.

Neither has the behaviour of Cu$_2$ZnSn(S,Se)$_4$ in different etching solutions been studied.

The objectives of the present doctoral thesis were:

- To study the growth process of CuInSe$_2$ in potassium iodide.
- To study the effect of sodium doping on the electrical and photoluminescence properties of CuInSe$_2$ monograin powders with nearly stoichiometric composition in order to clarify the influence of sodium on the parameters of CuInSe$_2$ monograin layer devices.
- To study the effect of chemical treatments on the surface composition of Cu$_2$ZnSn(S,Se)$_4$ monograin powders.
- To study the formation of Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ solid solutions with the aim to find out the best composition of an absorber material for monograin layer solar cells.
2 EXPERIMENTAL

The main experimental features are briefly presented in this section. For details of the experiments, see publications I-VI.

2.1 Preparation of CuInSe₂ and Cu₂ZnSn(S,Se)₄ monograin powders

The initial Cu-In alloys (in molar ratio 1:1.1) were synthesized from the elemental metal precursors of 5N purity in carbon-coated quartz ampoules for synthesis growth of CuInSe₂. The syntheses of Cu-In alloys were made in dynamic vacuum (continuous pumping) at the temperature of 1070K. Cu-In alloy ingots were triturated in the agate mortar and sieved through the 100 µm sieve. Ground Cu-In alloy (1:1.1) and elemental Se in proportions providing stoichiometry of CuInSe₂ were mixed with KI. The amount of components for CuInSe₂ and the amount of KI were nearly equal to provide a sufficient liquid phase for the monograin growth (V₅=V₉). Samples were sealed into evacuated quartz ampoules, annealed isothermally at various temperatures and annealing times and quenched to room temperature. The minimum growth temperature was limited by the melting temperature of the used flux material KI (953-959K) [60] and the maximum growth temperature was limited by the temperature of the phase transition of CuInSe₂ (1083K) [31]. The flux material was removed by leaching with deionized water. Finally, the well-dried powders were sieved into narrow fractions from 38µm to 112µm.

The Cu₂ZnSn(S,Se)₄ powder materials were synthesized from binaries Cu(S,Se), Zn(S,Se), Sn(S,Se) and KI as flux material. The binary precursor compounds for synthesis of Cu₂ZnSn(S,Se)₄ and KI were mixed and ground in planetary ball mill. The mixture was degassed and sealed into quartz ampoules. The recrystallization temperature was 1000K. More detailed description of the procedure of materials preparation is presented in papers [IV,V,VI].

2.2 Doping with sodium

The CuInSe₂ monograin powder used for doping with sodium was synthesized in the molten phase of CuSe to avoid the contamination of material with K and Na from KI. The synthesized material was subdivided into several portions and placed into the quartz ampoules. The doping solution of NaI as a source of Na-dopant was added to each portion directly into the quartz ampoules. Solution of NaI in deionized water was dosed in controlled amounts in the range of 5×10¹⁶ – 1×10²⁰ atoms of Na per cm³ of CuInSe₂. The amount of doping solution was kept constant by sequential diluting. The materials were dried, InI as flux was added and ampoules were vacuum-sealed and heated at 800 K for 48 hours. The materials recrystallized in the presence of molten InI that provided an homogeneous redistribution of Na.
After annealing, the ampoules were quenched to room temperature in water. The flux was removed by 3.7% aqueous solution of HCl [III].

2.3 Chemical treatment

The grown Cu$_2$ZnSn(S,Se)$_4$ monograin powders were divided into several parts and each of them passed through different etching procedures. Concentrated HCl, 10% aqueous solution of KCN, 1% Br$_2$-MeOH (bromine in methanol) solution and 2M NH$_4$OH solution were used as etchants. All the chemical etchings were performed at room temperature. After etching the powders were washed in deionized water and dried [IV].

2.4 Preparation of monograin layer solar cells

To form a monograin layer (see Figure 7) of nearly unisize CuInSe$_2$ or Cu$_2$ZnSn(S,Se)$_4$ powder crystals preliminarily covered with chemically deposited CdS are poured onto a thin layer of epoxy resin so that the upper part of crystals remains untouched with epoxy. After the polymerization of epoxy, i-ZnO and conductive ZnO:Al are deposited by RF-sputtering. The solar cell structure is completed by the evaporation of 1-2 µm thick In grid contacts onto the ZnO window layer. After glueing the structures on glass substrates, the back contact area of

Figure 7. Schematic illustration of the standard structure of monograin layer solar cell.
crystals that was still covered with epoxy is opened by etching epoxy off with concentrated H₂SO₄ (see Figure 8) and by additional abrasive treatment of absorber crystals. The back contact is made using graphite paste.

Figure 8. SEM photos of monograin layer (MGL) solar cells: a) surface of front contact side before glueing on glass and b) cross-section of MGL on glass (upper dark layer) and with graphite back contact (lower dark layer).

### 2.5 Current-voltage characterization of solar cells

The most important parameters that describe the performance of a solar cell - efficiency \( \eta \), open circuit voltage \( V_{oc} \), short circuit current density \( jsc \) and fill factor \( FF \) - can be derived from the I-V curve measured under standard test conditions (AM 1.5, 100 mW/cm²).

The efficiency of a solar cell is defined as the ratio of maximum (electrical) power density delivered by the cell to the power density of the illuminating light source. It is the most important characteristic of a solar cell, given by Eq. (2.5.1.)

\[
\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{j_{sc} \cdot V_{oc} \cdot FF}{P_{\text{in}}}, \quad (2.5.1)
\]

where \( P_{in} \) is the power of the standard illumination of AM 1.5 (100 mW/cm²). The fill factor (\( FF \)) is often used to characterize the quality of a solar cell junction, calculated by Eq. (2.5.2).

\[
FF = \frac{j_m \cdot V_m}{j_{sc} \cdot V_{oc}}, \quad (2.5.2)
\]

where \( j_m \) is current density at maximum power output and \( V_m \) is voltage at maximum power output.
2.5.1 Characterization techniques

The analytical techniques used for the characterization of monograin powders and monograin layer solar cells are summarized in Table 1. More detailed information about the instrumentation and measurements can be found in the experimental sections of References I-VI.

Table 1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Used techniques</th>
<th>Apparatus</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>composition</td>
<td>POL</td>
<td>Metrhom polarograph</td>
<td>[I,II,IV]</td>
</tr>
<tr>
<td>elemental composition</td>
<td>EDS</td>
<td>ZEISS ULTRA 55</td>
<td>[II,IV-VI]</td>
</tr>
<tr>
<td>morphology</td>
<td>SEM</td>
<td>ZEISS ULTRA 55</td>
<td>[I-VI]</td>
</tr>
<tr>
<td>phase composition</td>
<td>Raman</td>
<td>Horiba LabRam HR</td>
<td>[IV-V]</td>
</tr>
<tr>
<td>elemental composition</td>
<td>XPS</td>
<td>Kratos Axis Ultra DLD Al Kα</td>
<td>[IV]</td>
</tr>
<tr>
<td>optical properties</td>
<td>PL</td>
<td>Photoluminescence measurement system</td>
<td>[II,III,V]</td>
</tr>
<tr>
<td>phase composition</td>
<td>XRD</td>
<td>Bruker AXS D5005</td>
<td>[I,II,IV,VI]</td>
</tr>
<tr>
<td>SC output parameters</td>
<td>I-V</td>
<td>Keithley 2400</td>
<td>[II-VI]</td>
</tr>
<tr>
<td>SC quality</td>
<td>QE</td>
<td>Autolab PGSTAT 30</td>
<td>[V,VI]</td>
</tr>
<tr>
<td>carrier concentration</td>
<td>C-V</td>
<td>Autolab PGSTAT 30</td>
<td>[III]</td>
</tr>
<tr>
<td>barrier height</td>
<td>$V_{oc}$ vs. T</td>
<td>Autolab PGSTAT 30</td>
<td>[VI]</td>
</tr>
</tbody>
</table>
3 RESULTS AND DISCUSSION (CISe, CZTSSe)

3.1 CuInSe$_2$ monograin growth in the liquid phase of potassium iodide

In high performance solar cells slightly In-rich CuInSe$_2$ is used as an absorber material. Cu-rich CuInSe$_2$ displays the segregation of a secondary Cu$_x$Se ($y<$2) phase preferably at the material surface. Even after removal of the Cu containing phase from the surface by etching the absorber in KCN, the use of this material for photovoltaic applications is limited, most probably due to the high doping density in the bulk [46]. The growth of CuInSe$_2$ MGP-s in CuSe-Se flux results in near-stoichiometric compositions of material grains [45]. This is in accordance with the Cu-side borderline of CuInSe$_2$ phase existence range of Cu$_2$Se-In$_2$Se$_3$ phase diagram [31]. The use of Se as a flux material allows us to grow the MGP in the large range of deviations from stoichiometric composition. The technological difficulty is the removal of Se flux from powder batch. Therefore, in order to obtain In-rich compositions of MGP-s in a shorter time consuming process, the growth of MGP-s in KI as a flux material that is easily removable by leaching with DI water was studied. CuInSe$_2$ was synthesized from high-purity elements Cu, In and Se (Cu and In were prior melted and used as the CuIn alloy as precursor of metals for the CISe synthesis) [I, II].

3.1.1 Growth parameters of CuInSe$_2$ in the KI flux

The regularities of growth and formation parameters of CuInSe$_2$ monograins in the KI flux are presented in paper [I]. The formation of CuInSe$_2$ monograins takes place in the amount of liquid phase of a flux that exceeds the limit of sintering of initial crystals [61]. The formed liquid phase consists of the molten salt used as a flux material and the product of synthesis dissolved in it. It means that in order to determine the amount of added KI and the volume of liquid phase in the recrystallization process we have to know the solubility of CISe in KI. Therefore, we determined the solubility of CISe in KI at the growth temperature by the weight loss method. Large pieces of polycrystalline CuInSe$_2$ were weighed and sealed with 5 times larger amount of dried KI into quartz ampoules. The ampoules were annealed at 990 K for 120 hours and then quenched in water. The undissolved CuInSe$_2$ was gathered and weighed. From the weight loss we found the solubility of CuInSe$_2$ in KI. For comparison the data of CISe solubilities in Se and CuSe-Se are given in Table 2.
Table 2. Solubility of CuInSe$_2$ in different fluxes: Se, CuSe-Se and KI.

<table>
<thead>
<tr>
<th>Flux material</th>
<th>Se [62]</th>
<th>CuSe-Se [45]</th>
<th>KI (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, K</td>
<td>970</td>
<td>800</td>
<td>990</td>
</tr>
<tr>
<td>Solubility, wt. %</td>
<td>28.5 ± 0.5</td>
<td>8.8 ± 0.5</td>
<td>0.17 ± 0.05</td>
</tr>
</tbody>
</table>

Considering the low solubility of CuInSe$_2$ in KI and the densities of KI (3.12 g/cm$^3$) [63] and ClSe (3.0 g/cm$^3$) [64] we found that the equal masses of both materials guarantee the ratio of $V_S/V_L \geq 0.6$, satisfying the condition for single crystalline growth of grains [61]. The dissolution of KI revealed uniform, nonaggregated microcrystals of tetragonal shape with smooth surfaces and sharp edges (Figure 9), indicating their growth from individual seed crystals rather than from the aggregates of crystallization nuclei.

Figure 9. SEM photos of CuInSe$_2$ monograin powder crystals grown in KI at 990 K for 76 hours.

The X-ray diffraction (XRD) spectra of the formed CuInSe$_2$ monograin powder (Figure 10) showed only the peaks of chalcopyrite CuInSe$_2$.

Figure 10. The X-ray diffraction pattern of CuInSe$_2$ monograin powder grown in KI at 990 K for 76 hours.
In order to find out the growth parameters of CuInSe₂ in KI, the precursors for synthesis of CISe (Cu-In, Se) and KI were ground and sealed into evacuated quartz ampoules and annealed isothermally at various temperatures (970, 990, 1010 and 1050K) and for different annealing times (30, 76, 270 and 334 h). The sieve analysis method was used to determine the particle size distribution. The median particle size was found graphically from the particle size distribution data on the log-normal probability graph [65].

The composition of CuInSe₂ powder materials grown at various temperatures and for different times was analysed polarographically. The composition of CuInSe₂ monograin powder materials was Cu:In:Se = 23.3:25.5:51.2 ([Cu]/[In] = 0.91). The results revealed that the composition remained unchanged by changing the growth temperature and duration. The solubility of potassium and iodine in CuInSe₂ at 990 K was 0.094 wt. %, and 0.0086 wt. %, respectively (results of ICP-MS). All the as-grown monograin powders had p-type conductivity.

The particle size distribution of samples grown at 1010 K for different recrystallization durations is shown in Figure 11. The particle size distribution of all the samples depending on the process duration follows a log-normal distribution.

![Figure 11. Particle size distribution of CuInSe₂ monograin powders grown in KI at 1010 K for different time periods.](image)

It allows the use of the median particle size $d_m$ to describe the grain growth according to the equation:

$$d_m = A t^{1/n} \exp(-E_d/kT), \quad (3.1.1.1)$$

where $A$ is a constant for a given flux and compound, $k$ is the Boltzman constant, $T$ is the growth temperature (K), $E_d$ is the activation energy for linear crystal growth and $n$ is the geometric factor of growth mechanism [42].
From the Arrhenius plot of the median grain diameter $d_m$ the activation energy for the linear crystal growth $E_d = 0.25 \pm 0.05$ eV was determined. If the growth is controlled by one growth mechanism (diffusion), then $n = 3$. The power of the time dependence of crystal growth $l/n = 0.25 \pm 0.06$, $n = 3.9 \pm 0.93$ was found from the time dependencies of $d_m$. The value of $n = 3.9 \pm 0.93$ indicates that the growth process of CuInSe$_2$ particles in KI flux is limited by diffusion processes on the surfaces of sintered grains [66].

### 3.1.2 Growth of CuInSe$_2$ monograin powders with different Cu/In ratio

The aim of this part of experiments was to clarify the limits for the single-phase growth of CuInSe$_2$ in flux materials of different chemical nature and to study the possibilities to tailor CISe properties in the growth process. In order to grow CuInSe$_2$ MGP-s with different compositions, precursor Cu-In alloys with different Cu/In concentration ratios (0.5 - 1.1) were prepared and annealed with Se in sealed ampoules in KI flux. It was found that KI as a flux material allows the growth of In-rich CuInSe$_2$ monograin powders. The obtained results show that the single-phase powder crystals can be grown from precursor Cu-In alloys with Cu/In concentration ratio values between 1>Cu/In>0.7. The powders from precursor Cu-In alloys with Cu/In<0.67 were found to consist of crystals with two different compositions: Cu/In = 0.92 and Cu/In = 0.66. This indicates that this precursor composition is in the region of the multiphase area of CuInSe$_2$ phase diagram (see Figure 3). Selenium content in the grown powders increases almost linearly with the decreasing Cu/In ratio of the materials.

The samples with nearly stoichiometric or slightly In-rich compositions showed $p$-type conductivity and exhibited PL spectrum with dominant peak at 0.93 eV. In contrast, the samples with Cu/In<0.7 had n-type conductivity and exhibited two broad bands in PL spectra with the peak positions at 0.86 eV and 0.93 eV. Results of this research of modifying CISe monograin powder growth in the KI flux in the single-phase region of CISe phase diagram are described in more detail in paper [II].

### 3.2 The influence of sodium doping on CuInSe$_2$ monograin powder properties

The results of the research in this field have been published and are described in paper [III]. Sodium has been found to improve the performance of Cu(In,Ga)Se$_2$ solar cells [48-51]. As the monograin powder growth takes place in the liquid phase of potassium iodide the question arises: if the effect of K on the solar cell output parameters is similar to the effect of Na.

The best results of I-V measurements of solar cells made from powders synthesized in the liquid phase of InI and in the liquid phase of mixture of KI and InI are
presented in Table 3. It can be seen that the presence of KI in the flux improves solar cell parameters.

Table 3. Comparison of solar cell parameters for CuInSe$_2$ synthesized in the InI flux and in the InI/KI flux material.

<table>
<thead>
<tr>
<th>Flux material</th>
<th>$V_{oc}$, (mV)</th>
<th>$J_{sc}$, (mA)</th>
<th>FF, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>InI/KI</td>
<td>481</td>
<td>0.43</td>
<td>45</td>
</tr>
<tr>
<td>InI</td>
<td>357</td>
<td>0.22</td>
<td>38</td>
</tr>
</tbody>
</table>

Results of ICP-MS analysis showed that the concentration of sodium in CuInSe$_2$ synthesized at 990 K in KI was about 6 times higher than the concentration of potassium. The used potassium iodide contains sodium as impurity at a high level and sodium can dissolve in CuInSe$_2$ at the saturation concentration. The explanation can be in the difference of ionic radii of K and Na [49]. The ionic radii of K (see Table 4) is much larger than the ionic radii of Na and sodium fits very well on Cu site.

Table 4. Ionic radii of elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>In</th>
<th>I</th>
<th>Se</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å (charge)</td>
<td>0.96 (+1)</td>
<td>0.81 (+3)</td>
<td>2.16 (-1)</td>
<td>1.91 (-2)</td>
<td>0.97 (+1)</td>
<td>1.33 (+1)</td>
</tr>
</tbody>
</table>

A.Rockett et al. [67] found that there is an optimal concentration of sodium that improves solar cell output parameters. Following our previous results a serie of experiments was planned to determine the optimal sodium concentration in monograin CISe powders. To study the effect of doping we varied sodium concentration (5x10$^{16}$-1x10$^{20}$ at/cm$^3$) in the absorber by adding the solutions of NaI of different sodium concentrations as a source of Na.

3.2.1 Photoluminescence study of sodium doped CuInSe$_2$ powders

The photoluminescence spectra (T = 10 K) of all monograin materials show a broad band with its maximum around 0.99 eV (Figure 12). The peak position of the PL band at 0.99 eV depends on the dosed sodium doping level, as shown in Figure 13. The peak position shifts to higher energy values with increasing sodium concentration up to 1x10$^{19}$ cm$^{-3}$. With further increase in the level of sodium doping, a sharp decrease of the PL peak energy values was observed.
It was found in [47] that Na does not create shallow acceptor levels in CuInSe$_2$. Na incorporation could result in the formation of a solid solution with CuInSe$_2$ in the form of Na$_x$Cu$_{1-x}$InSe$_2$ with higher bandgap energy than CuInSe$_2$. For CuGaSe$_2$, in [68] the formation of a quaternary Na-Cu-Ga-Se compound on the base of defect-chalcopyrite structure in which Cu vacancies are partially filled by Na atoms was proposed. To explain the obtained results we can follow a presumption similar to the abovementioned concerning the formation of a solid solution of CuInSe$_2$ with Na. The formed new Na containing phase locates on the surface of our crystals and has slightly higher bandgap energy as compared to CISe. SEM image (Figure 14)
indicates to the segregation of a phase in our sodium doped samples and supports this presumption.

Figure 14. SEM image of a broken CuInSe$_2$ crystal with a dosed sodium content $10^{19}$cm$^{-3}$.

The bandgap energy of a quaternary Na$_x$Cu$_{1-x}$InSe$_2$ solid solution increases with the increasing sodium doping level. At doping concentrations higher than $10^{19}$cm$^{-3}$, the PL peak position shifts to lower values of energies. More detail analysis are needed to explain this behaviour.

### 3.2.2 Solar cell parameters

The solar cells on the base of undoped and doped with sodium up to $3 \times 10^{17}$cm$^{-3}$ absorber materials had low value of shunt resistance (Figure 15). These materials were etched with 10% KCN aqueous solution. After KCN etching the solar cells showed better diode behaviour. The KCN solution is known as a selective etchant for Cu-Se binary phases [69]. Starting from $3 \times 10^{17}$cm$^{-3}$ and higher concentrations of sodium there was no need to etch CuInSe$_2$ materials with KCN. Therefore we suppose that the segregation of the Cu-Se phase occurs in powders with added Na concentration less than $3 \times 10^{17}$cm$^{-3}$. It is known that sodium incorporation widens the area of the $\alpha$-(CuInSe$_2$) phase existance in the phase diagram [31]. In our case, starting from the doping level of $3 \times 10^{17}$cm$^{-3}$ the increase of sodium content in CuInSe$_2$ widens the single phase area of CuInSe$_2$ towards Cu-rich composition. In undoped materials or in materials with Na concentration up to $3 \times 10^{17}$cm$^{-3}$, the Cu-Se phase segregation is possible.
The values of the open-circuit voltage of solar cells (Figure 16) increase with dosed sodium concentration from $5 \times 10^{16} \text{cm}^{-3}$ to $3 \times 10^{18} \text{cm}^{-3}$. At Na concentrations higher than $3 \times 10^{18} \text{cm}^{-3}$ the open-circuit voltage decreases down to a constant value. Solar cells on the base of absorber material with the doped sodium concentration $3 \times 10^{18} \text{cm}^{-3}$ were found to result in the highest open-circuit voltage values. Wei et al. [47] found theoretically that Na on Cu site does not create levels in the band gap, while Na on In site creates acceptor levels that are shallower than CuIn. The major effect of Na is the elimination of the InCu defects and the resulting increase of the effective hole densities. The theoretical assumption was supported by the experimental work of Kimura et al. [51]. However, as the Na concentration increases to the level where most of the InCu defects have been eliminated, it starts to fill in vacant lattice places in Cu sublattice and diminishing the concentration of the acceptor defect VCu. This process reduces the hole density [47] and leads to the reduction in the solar cell performance at Na contents higher than dosed $3 \times 10^{18} \text{cm}^{-3}$. 

Figure 15. I-V curves of CuInSe2 solar cells without sodium and low sodium concentrations before and after KCN etching.
3.2.3 Carrier concentration

Sodium incorporation enhances the carrier concentration [70]. The carrier concentration in our monograin materials was determined by room-temperature capacitance-voltage measurements (Figure 17). We found that the maximum carrier concentration $2 \times 10^{17}$ cm$^{-3}$ was in materials with the doped sodium concentration of $1 \times 10^{19}$ cm$^{-3}$. Further increase in sodium concentration resulted in the decreased carrier concentration. As seen in Figure 16, a similar tendency was observed in the values of open-circuit voltage.
In conclusion, solubility of CuInSe$_2$ in KI at 720ºC was found to be 0.17 weight %. Crystals of CuInSe$_2$ grown in KI flux have a shape of polyhedrons. The facets of the crystals are smooth. The single-phase powder crystals can be synthesized from precursor Cu-In alloys with the Cu/In ratio values between 1 > Cu/In > 0.7. From the Arrhenius plot of the median grain diameter $d_m$ the activation energy for the linear crystal growth $E_d = 0.25(\pm 0.05)$ eV was obtained. From the time dependencies of $d_m$ the power of the time dependence of crystal growth $l/n = 0.25(\pm 0.06), n = 3.9(\pm 0.93)$ was found.

It was shown that the output parameters of the solar cells are dependent on the Na doping level of the absorber material. Sodium concentration $3 \times 10^{18}$ at/cm$^3$ was found to result in the best open-circuit voltage and fill factor values. The PL spectra of Na doped CISe powders showed that the peak position of the PL band shifted depending on the Na doping level. The peak position of the PL band with maximum energy was observed when sodium concentration was $1 \times 10^{19}$ at/cm$^3$. The same material had the highest carrier concentration $2 \times 10^{17}$ cm$^{-3}$. 
3.3 Cu$_2$ZnSn(S,Se)$_4$ monograin growth in the liquid phase of potassium iodide

The Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ (CZTSSe) powder materials with different x values were synthesized from CuSe(S), ZnSe(S) and SnSe(S) in appropriate relations as precursors for CZTSSe in molten KI, as it was described in section 2.1. The recrystallization temperature was 1000 K. The crystal size was controlled by the duration of the crystallization process. The results of studies on chemical etching and the formation of solid solution of Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ in the form of monograin powders are presented in [IV,V,VI].

3.3.1 Process description

In the process of monograin growth, monograins of a semiconductor compound are formed in the liquid phase of the used flux material. The criteria for the monograin growth is the following: the volume of the molten phase $V_L$ between grains has to exceed the limit of sintering - $V_L \geq 0.6 \ V_S$, where $V_S$ is the volume of solid phase. In this case the liquid phase separates the initial solid particles from each other and the individual single crystals grow [61]. Due to solubility, the precursors and the formed CZTSSe dissolve in the molten flux salt at the used recrystallization temperature and some part of it can re-precipitate on the surface of the formed crystals during the cooling period. These precipitations change the surface morphology and the composition of the crystal surface. On the other hand, it is well known that the active interface of a $p$-type absorber and a $n$-type buffer layer plays a key role in solar cell performance. Therefore, an in-depth understanding of the chemical treatment of CZTSSe monograin powder crystals’ surfaces with different etchants is very important for tailoring the absorber crystal’s surface composition and finally the parameters of solar cells on their base.

The results of chemical treatment of Cu$_2$ZnSn(S,Se)$_4$ are presented in paper [IV].

3.3.1.1 The morphology and surface composition of asgrown Cu$_2$ZnSn(S,Se)$_4$

Cu$_2$ZnSn(S,Se)$_4$ monograin powder crystals had tetragonal shape with rounded grain edges (see Figure 18) and homogeneous chemical composition of crystals bulk through the whole patches.
Figure 18. SEM micrograph of Cu₂ZnSn(S,Se)₄ monograin powder.

Figure 19. SE SEM images (left) and EsB SEM images (right) of a crystal surface of Cu₂ZnSn(S,Se)₄ as-grown monograin powder.

SE and EsB SEM images exposed the inhomogeneity of crystal’s surface of as-grown Cu₂ZnSn(S,Se)₄ monograin powders (see Figure 19). The comparison of the crystal’s surface composition with the bulk by using EDS revealed that the surface of as-grown CZTSSe crystals is Sn-rich while the bulk of crystals is Zn-rich (see Table 5).

Table 5. Compositions of chemically untreated CZTSSe crystals’ surfaces and their bulk (polished cross-section of powder crystals) as determined by EDS.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cu/Zn+Sn</th>
<th>Zn/Sn</th>
<th>Se+S/Met</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal’s surface</td>
<td>0.94</td>
<td>0.86</td>
<td>1.01</td>
</tr>
<tr>
<td>Crystal’s bulk</td>
<td>0.88</td>
<td>1.03</td>
<td>1.03</td>
</tr>
</tbody>
</table>

The difference in the surface and the bulk compositions can be taken as a hint of material precipitation from components dissolved in the flux at the growth-temperature onto the surface of the grown crystals during cooling. After the removal of the flux the remaining solid phase consists of well formed crystallites of CZTSSe and an amorphous material that was originally dissolved in KI at the recrystallization temperature. Some part of the material dissolved in KI at the growth
temperature could precipitate onto the surface of crystals during the cooling period. The composition of the amorphous deposit was analysed by EDS and it was Cu : Zn : Sn : S+Se = 25 : 3 : 20 : 53. This Zn poor elemental composition of the amorphous phase could be a source for formation of compounds like Cu$_2$Sn(S,Se)$_3$ and Sn(S,Se)$_2$ on the surface of monograins. The surfaces of CZTSSe monograins were locally covered with islands (Figure 20). EDS spot measurements revealed the composition of the islands as Sn$_x$(S,Se)$_y$ with elemental ratio Sn : Se/S = 40 : 60.

Figure 20. SEM images of CZTSSe monograins surfaces.

3.3.1.2 **Raman study of Cu$_2$ZnSnSe$_4$ monograins**

The phase composition of as-grown Cu$_2$ZnSnSe$_4$ monograins powders was additionally studied by room temperature micro-Raman spectroscopy. As Raman spectra of CZTSSe materials have the bimodal behaviour and show the Raman peaks of both components (Cu$_2$ZnSnSe$_4$ and Cu$_2$ZnSnS$_4$) we used for Raman studies only Cu$_2$ZnSnSe$_4$ materials. Figure 21 shows normalized RT Raman spectra taken from the surface of powder crystals and Raman spectra of the bulk of Cu$_2$ZnSnSe$_4$ monograins taken from polished samples, together with a normalized Raman spectrum of precipitated amorphous material. The polished cross-sections of Cu$_2$ZnSnSe$_4$ monograins were used to measure Raman spectra of the bulk material.
Two dominating modes of Cu$_2$ZnSnSe$_4$ [V] can be found at 195 and 171 cm$^{-1}$ in the Raman spectra of the bulk of crystals. These modes can also be found in the spectra of the surface of monograins. However, there are some additional modes around 188 cm$^{-1}$ and 175 cm$^{-1}$ in the Raman spectra of the crystal’s surface, indicating the presence of other phases on the crystal’s surface. These additional peaks are also present in the Raman spectra of the precipitate, which confirms our assumption that the material that was dissolved in the molten phase precipitates onto the crystal’s surface in the cooling process. The Sn-rich chemical composition of the crystal’s surface and a Raman peak around 188 cm$^{-1}$ led to an assumption that SnSe$_2$ (A$_1$ mode at 186 cm$^{-1}$ [71]) is a main component of the precipitate [IV]. In the Raman spectra of as-grown CZTSe monograin powders (Raman modes at 173 cm$^{-1}$, 196 cm$^{-1}$ and 231 cm$^{-1}$) the presence of an additional Cu$_2$SnSe$_3$ phase was also detected (Raman peak at 180 cm$^{-1}$) [72]. The frequencies of the A1 Raman modes of Cu$_2$SnSe$_3$ and CZTSe are 180 cm$^{-1}$ and 196 cm$^{-1}$, respectively (see Figure 22) [V]. The conclusion drawn here about the presence of Cu$_2$SnSe$_3$ on the surface is supported also by the results of EDS analysis.
3.3.1.3 Chemical etching of Cu₂ZnSn(S₆Se)₄ powder crystal surfaces

Chemical treatments with several etchants (HCl, KCN, Br₂-MeOH and NH₄OH) were performed in order to remove other phases from the Cu₂ZnSn(SₓSe₆₋ₓ)₄ (x = 0, 0.45) monograins’ surfaces and to improve the active interface of the p-type Cu₂ZnSn(S,Se)₄ solar cell performance.

Figure 23. SEM micrographs of as-grown Cu₂ZnSn(S,Se)₄ monograin powder surfaces (a) and after treatment with b) HCl, c) NH₄OH, d) KCN, e) Br₂-MeOH, and f) Br₂-MeOH+KCN etchants.
SEM micrographs of the CZTSSe surface after treatment with different etchants (see Figure 23 b) show that after etching with HCl the surfaces of Cu$_2$ZnSn(S,Se)$_4$ powder crystals are rough and covered with microparticles. We were unable to determine the elemental composition of these microprecipitates by EDS due to their very small size. The etching with NH$_4$OH resulted in relatively flat surfaces (Figure 23 c). The surfaces of KCN-etched crystals seem to be quite smooth without any precipitates (Figure 23 d). After etching with Br$_2$-MeOH the surfaces of CZTSSe monograins were covered by crater-like areas with microparticles on their edges (Figure 23 e). Additional etching of the Br$_2$-MeOH treated powders with KCN removed these precipitates and resulted in clean crystal surfaces (Figure 23 f).

The polarographic analysis data (see Table 6) of the leaching solutions indicated that preferably Sn and chalcogen have been removed by HCl-etching, probably due to the complexation of tin in HCl solution and formation of [SnCl$_4$]$^{2-}$ [73]. The KCN etching is known as a process to remove preferably Cu-Se binary phases [69]. In our experiments with KCN treatment we found also tin in the leaching solutions of Cu$_2$ZnSnSe$_4$ monograin materials. The used ammonia solution removed selectively Cu and chalcogen in an approximate ratio 1:2.

<table>
<thead>
<tr>
<th>Etchant</th>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCN</td>
<td>1.0</td>
<td>no</td>
<td>0.36</td>
<td>1.5</td>
</tr>
<tr>
<td>HCl</td>
<td>1.0</td>
<td>0.11</td>
<td>5.8</td>
<td>6.5</td>
</tr>
<tr>
<td>NH$_4$OH</td>
<td>1.0</td>
<td>0.17</td>
<td>no</td>
<td>2.2</td>
</tr>
<tr>
<td>Br$_2$-MeOH</td>
<td>1.0</td>
<td>0.83</td>
<td>0.66</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 6. Composition of elements in leaching solution as determined polarographically.

Figure 24 represents XPS spectra of the as-grown and Br$_2$-MeOH-etched Cu$_2$ZnSn(S,Se)$_4$ monograin surfaces. The intensity of Cu2p, CuLMM peaks decreases and the intensity of the Sn and O1s peaks increases after etching materials with Br$_2$-MeOH. Zn2p and ZnLMM peaks are almost undetectable for materials etched with Br$_2$-MeOH. The relative atomic concentrations of zinc, copper, tin and selenium were determined from integrated peak areas of high-resolution XPS core level spectra. The S2p peak area was determined by core level curve-fitting procedures since this peak overlaps with the Se3p core level. The composition of the Cu$_2$ZnSn(S,Se)$_4$ monograin surface etched in Br$_2$-MeOH solution was determined by XPS and it was: Cu: Zn : Sn : S+Se : O = 1.23 : 1.16 : 37.05 : 12.83 : 47.72 at.%. Comparison of the XPS spectra of the as-grown and the Br$_2$-MeOH-etched samples allows us to conclude that Br$_2$-MeOH-etching mainly removes Cu and Zn. This fits well with the results of the polarographic analysis of the leaching solutions.
Figure 24. XPS spectra of the as-grown and Br₂-MeOH etched Cu₂ZnSn(S,Se)₄ monograin surfaces.

I-V dependences of solar cells made from chemically treated Cu₂ZnSn(S,Se)₄ monograin powders are given in Table 7. All the etched powders were post-heat-treated to improve the crystal surface structure.

Table 7. Performance characteristics of Cu₂ZnSn(S,Se)₄ monograin layer solar cells made from nonetched and etched absorber crystals.

<table>
<thead>
<tr>
<th>Etchant</th>
<th>V_{oc}, mV</th>
<th>I_{sc}, mA/cm²</th>
<th>FF, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>300</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Conc. HCl</td>
<td>342</td>
<td>11.5</td>
<td>48</td>
</tr>
<tr>
<td>2M NH₄OH</td>
<td>422</td>
<td>10.5</td>
<td>44</td>
</tr>
<tr>
<td>10% KCN</td>
<td>490</td>
<td>13.5</td>
<td>49</td>
</tr>
<tr>
<td>1% Br₂-MeOH</td>
<td>563</td>
<td>8.5</td>
<td>54</td>
</tr>
<tr>
<td>1% Br₂-MeOH +10% KCN</td>
<td>575</td>
<td>13.75</td>
<td>55</td>
</tr>
</tbody>
</table>

It can be seen that etching of the powder crystals improves the parameters of monograin layer solar cells. Solar cells that were made from combined etched materials have the highest values of V_{oc}, I_{sc} and fill factor. The efficiencies of the best solar cells in etching experiments were in the order of 4%.
3.3.2 Cu$_2$ZnSnSe$_4$ - Cu$_2$ZnSnS$_4$ solid solutions in monograin powder form for solar cells

The first monograin layer solar cells in the structure of ZnO/CdS/Cu$_2$ZnSnSe$_4$/graphite had low output parameters, their conversion efficiency was 1.8% [74] and relatively low value of $V_{oc}$. The results of PL and Raman measurements combined with a detailed analysis of the solar cell parameters enabled us to conclude that Cu$_2$ZnSnSe$_4$ actually has a bandgap much lower than 1.44 eV as it was reported by Matsushita [25]. According to the PL results, it is proposed that the bandgap energy of CZTSe is around 1.02 eV at $T=10K$ [72] that does not allow high values of $V_{oc}$ to be obtained. These considerations led us to the study of the formation of Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ solid solutions in the form of monograin powders to find out the optimal composition for an absorber of monograin layer solar cells.

Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ materials were prepared with the composition $x = 0, 0.25, 0.45, 0.75, 0.85, and 1$. The ratio of Cu to other metals $Cu/(Zn+Sn)$ was 0.925 and the Zn to Sn ratio was kept constant and equal to 1.0.

Monograin growth in molten KI resulted in a homogeneous composition of the Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ powders in the region of sulfur content $x = 0$ to $x = 0.85$ (Figure 25).

![Figure 25. EDS scan over polished individual Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ powder crystal.](image)

This statement was derived from the XRD analyses and from the EDS scan data over polished individual CZTSSe ($0 \leq x \leq 0.85$) powder crystals.
Figure 26. EDS analysis of polished individual crystals of CZTS powder showing existence of different phases.

Figure 27. EDS scanning over a polished multiphase Cu₂ZnSnS₄ powder crystal.

For \( x = 1 \), synthesized powder crystals were multiphase, as can be seen from the SEM photos and from the curves of the distribution of constituent elements (Figure 26, 27). Here, the results of EDS analysis also indicate the presence of separate phases besides the Cu₂ZnSnS₄ phase: Cu₂SnS₃ ([Cu]=32.9 %, [Sn]=17.2 %, [S]=49.8 %), SnS ([Sn]=51.5 %, [S]=48.45 %) and ZnS ([Zn]=50 %, [S]=50 %). The results of XRD investigations confirm that in addition to the dominating CZTS phase, powders contain SnS in small quantities (Figure 28).
Figure 28. X-ray diffraction pattern of the Cu$_2$ZnSnS$_4$ monograin powder.

The XRD pattern did not indicate to the existence of Cu$_2$SnS$_3$ and ZnS. In the system Cu-Zn-Sn-S the diffraction signals of the phases Cu$_2$SnS$_3$ and ZnS cannot be distinguished from the phase Cu$_2$ZnSnS$_4$ due to their structural similarity (the diffraction peaks of these phases can overlap) [75]. One possible explanation for the existence of different phases in synthesized pure CZTS (x=1) is that the homogeneity range of Cu$_2$ZnSnS$_4$ is much narrower than that of Cu$_2$ZnSnSe$_4$ (see Figure 29), resulting therefore in a higher probability for the formation of other phases during the synthesis and the growth process of the Cu$_2$ZnSnS$_4$ (x=1) monograin powders of the same initial composition as the Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ materials with (0 ≤ x ≤ 0.85). Chen et al. [76] demonstrated by the first principles of electronic structure calculations that the chemical potential range for the formation of Cu$_2$ZnSnS$_4$ without secondary phases is very small. This is in agreement with our experimental results.
Figure 29. Change in composition of Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ monograin powders depending on the Se/S concentration ratio.

X-ray diffraction patterns of the monograin powders with different Se/S concentration ratio are presented in Figure 30.

Figure 30. XRD patterns of Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ monograin powders with different x values.
The diffraction peaks were identified as belonging to the Cu$_2$ZnSnS$_4$ compound (x=1) with kesterite structure (space group $I\overline{4}$) and to the Cu$_2$ZnSnSe$_4$ (x=0) with stannite structure (space group $I\overline{4}2m$) [25, 77]. The reflection Miller indexes were assigned according to Matsushita [24]. The ratio of reflection intensities was in correspondence to that measured by Olekseyuk [77]. An exchange of Se with S shifts the peak positions from the stannite structure to the kesterite structure. At a ratio of S to Se of 85 : 15 mole % the XRD pattern shows a splitting of peaks, which could be a sign of existence of two crystal phases at the same time. From the calculated total energy difference $\Delta E_t = E_t$(stannite) - $E_t$(kesterite) the most stable phase is the kesterite structure for both the S-based and the Se-based compounds. This is in accordance with most of the recent experimental data [10,22,27] but it has been suggested that it is possible to grow also the stannite structure [25,77,78]. However, the total energy of the kesterite S-based compounds is only ~1.3 meV/atom lower than the corresponding stannite structure. Similarly, the total energy of the kesterite Se-based compounds is ~3.3 meV/atom lower than their stannite structure. This indicates that kesterite structure should be formed under equilibrium growth conditions, but since the total energy, lattice parameters, and bonds of kesterite and stannite are very similar, both phases may coexist and it should be relatively easy to grow materials with mixed phases depending on the growth method and growth conditions.

### 3.3.2.1 Solar cell characterization

The prepared monograin powders were used as absorber materials in monograin layer (MGL) solar cell structures: ZnO/CdS/CZTSSe/graphite, where every crystal works as an individual solar cell. All the as-grown powders were post-heat-treated to improve the crystal surface structure.

![Figure 31. Distribution of $V_{oc}$ values of two different Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ solar cells with $x=0.75$ and $x=0.85$ over a 1 cm (x-axis) by 1.5 cm (y-axis) cell measured in equal distances. Area of every point is 4 mm$^2$.](image)
Solar cells showed a uniform distribution of solar cell parameters over the whole working area of 1x1.5 cm$^2$ samples (Figure 31).

Open circuit voltages of Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ monograin layer solar cells increased with increasing sulfur content in the monograin powders, from 283 mV for x=0 to 660 mV for x=0.85 (Figure 32).

![Figure 32. Maximum $V_{oc}$ values of Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ monograin layer solar cells in depending on Se displacement by S. Data points describe measurement results from graphite back contacts of 4 mm$^2$ of 1x1.5 cm$^2$ cell.](image)

The pure Cu$_2$ZnSnS$_4$ absorber material resulted in lower $V_{oc}$ (541 mV) probably due to the secondary phases formed. An increase of the open circuit voltage values points to a widening of the bandgap of Cu$_2$ZnSn(Se$_{1-x}$S$_x$) with increasing S concentration. Solar cell structures based on monograin powders with the S/Se concentration ratio of 85 mole % sulfur to 15 mole % selenium yielded in the highest values of the open circuit voltage 660 mV. The Cu$_2$ZnSn(S,Se)$_4$ solid solution with 75 mole % sulfur and 25 mole % selenium gave the best solar cell with parameters: $V_{oc}=622$ mV, $J_{sc}=15.87$ mA/cm$^2$, $FF=60$ %, $\eta=5.9$ %.

The quantum efficiency of solar cell structures was measured as a function of the wavelength of the incident light. The normalized quantum efficiency (QE) spectra of solar cells on the base of Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ monograin powders show the shift of the absorption edge to shorter wavelengths as well as a change in the short wavelengths response with increasing S content in the absorber material, as shown in Figure 33.
It is known that the open-circuit voltage $V_{oc}$ vs $T$ curves are linear at RT and capable of being used to determine the main path of current losses in solar cells. The open circuit voltage can be given by the following equation:

$$V_{oc} = \frac{\Phi_b}{q} - \frac{kT}{q} \ln \left( \frac{q S_p N_v}{j_{sc}} \right),$$  

(3.3.2.1.1)

where $\Phi_b$ is the barrier height for holes, $A$ is the diode ideality factor, $S_p$ is the interface recombination velocity for holes, $j_{sc}$ is the short-circuit current density, $q$ is the elementary charge, and $N_v$ is the effective density of states in the valence band. For bulk recombination, $\Phi_b \approx E_g$ [79]. The temperature dependent open circuit voltage measurements were performed to determine the barrier height of the $p-n$ junction ($\Phi_b$) (Figure 34). The barrier height of the solar cells increases as expected with increasing the S content in Cu$_2$ZnSn(Se$_{1-x}$S$_x$) monograin powders.
Figure 34. $V_{oc}$ vs. $T$ for Cu$_2$ZnSn(Se$_{1-x}$S$_x$)$_4$ monograin layer solar cells with different x values in the monograin powders.

For CZTSe, quite different bandgaps have been reported. Mostly, it is proposed that the bandgap energy lies between 1.4 eV and 1.56 eV. However, it was suggested by our group that the bandgap energy of CZTSe is about 1.02 eV according to PL analysis [72]. Grossberg et al. [80] observed a nearly linear shift of the PL emission towards higher energies with increasing S concentration in Cu$_2$ZnSn(Se$_x$S$_{1-x}$)$_4$ solid solutions up to a total value of 0.4 eV.

Considering the increase in the open circuit voltage values, the linear shift of the PL emission towards higher energies, the quantum efficiency spectra shift to the shorter wavelengths and the increase of barrier height of solar cells with increasing S content in the absorber material gives us an assertion that the published Cu$_2$ZnSnSe$_4$ bandgap energies: 1.44-1.56 eV should be much lower than Cu$_2$ZnSnS$_4$ bandgap energies: 1.45-1.51 eV. During the time of writing this thesis, other groups have obtained similar results [14,81,82]. Ahn et al. [81] proposed that the possible overestimation of the $E_g$ value is caused by the existence of ZnSe in the coevaporated films.

In conclusion, it has been shown that monograin powder technology enables to grow Cu$_2$ZnSn(S,Se)$_4$ materials with homogeneous composition usable for monograin layer solar cells. It has been found that the surface and the bulk compositions of as-grown CZTSSe monograin powder crystals are not identical. The chemical treatments before the deposition of CdS are important to improve the Cu$_2$ZnSn(S,Se)$_4$ monograin layer solar cell performance. The increasing sulfur content in Cu$_2$ZnSnSe$_4$ monograin powder absorber materials improves the values of open circuit voltages of MGL solar cells and shifts the QE curves to the higher energy side. The Cu$_2$ZnSn(S,Se)$_4$ solid solution with 75 mole % sulfur and 25 mole% selenium gave the best solar cell with parameters: $V_{oc}$=622 mV, $j_{sc}$=15.87 mA/cm$^2$, $FF$=60 %, $\eta$=5.9 %. 

50
CONCLUSIONS

CuInSe₂

1. The growth of CuInSe₂ powder crystals in KI results in single crystalline tetragonal particles and the process can be described by the formula:
\[ d_m \sim t^{1/n} \exp(-E_d/kT) \]. From the Arrhenius plot of the median grain diameter \( d_m \) the activation energy for linear crystal growth \( E_d = 0.25 \pm 0.05 \) eV and from the time dependence of the median grain diameter \( d_m \sim t \) at constant temperature the power of the time dependence of crystal growth \( 1/n = 0.25 \pm 0.06 \) and \( n = 3.9 \pm 0.93 \) were determined. \( n \) value is indicating that mass diffusion through the liquid phase and sintering of formed grains by material surface diffusion are dominating in the growth process of monograin powder crystals.

2. The single-phase powder crystals can be synthesized from precursor Cu-In alloys with Cu/In ratio values between 1>Cu/In>0.7. The solubility of CuInSe₂ in KI at 720ºC was found to be 0.17 weight %.

3. In the case of Na doping it was found that the peak position of the PL band of Na doped CISe powders shifted depending on the Na doping level and showed the maximum energy when sodium concentration was \( 1 \times 10^{19} \) at/cm³. The same material had the highest carrier concentration \( 2 \times 10^{17} \) cm³. The Na doping level of the absorber material had strong influence on solar cell parameters and added sodium concentrations \( 3 \times 10^{18} \) at/cm³ resulted in the highest open-circuit voltage and fill factor values.

Cu₂ZnSn(S,Se)₄

1. In the case of Cu₂ZnSn(S,Se)₄ growth in molten KI the bulk and the surface compositions of formed CZTSSe crystals were found to be non-identical. The chemical treatments before the deposition of CdS were found to be important to improve the performance of the Cu₂ZnSn(S,Se)₄ monograin layer solar cell.
   - The analysis of leaching solutions showed that Sn and chalcogen are removed preferably by HCl etching. Leaching solutions after KCN-etching contain Cu, Sn and chalcogen. From XPS measurements we found that etching with 1% Br₂-MeOH resulted in Sn-rich material surfaces.
   - The combination of chemical treatments (1% Br₂-MeOH + 10% KCN) before the deposition of CdS gave the best Cu₂ZnSn(S,Se)₄ monograin layer solar cells with efficiencies in the order of 4 %.

2. Monograin powder technology enables us to grow Cu₂ZnSn(Se₁₋ₓSₓ)₄ materials with homogeneous composition in the region of sulfur content \( x = 0 \) to \( x = 0.85 \) usable for monograin layer solar cells.

3. Increase in the sulfur content in Cu₂ZnSnSe₄ monograin powder absorber materials improves the values of open circuit voltages of MGL solar cells and shifts the QE curves to the higher energy side. The barrier height of solar cells increases also with the increase of S content in Cu₂ZnSn(Se₁₋ₓSₓ)₄ monograin powders.
4. Solar cell structures based on monograin powders with a S/Se concentration ratio of 85 mole% sulfur to 15 mole% selenium yielded in the highest values of open circuit voltage: 660 mV. The Cu$_2$ZnSn(S,Se)$_4$ solid solution with 75 mole % sulfur and 25 mole % selenium gave the highest parameters of solar cell: $V_{oc} = 622$ mV, $j_{sc} = 15.87$ mA/cm$^2$, $FF = 60$ %, $\eta = 5.9$ %. 


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My warmest gratitude belongs to my family.

Tallinn, February 2011

Kristi Timmo
ABSTRACT

Formation of properties of CuInSe$_2$ and Cu$_2$ZnSn(S,Se)$_4$ monograin powders synthesized in molten KI

This thesis is focused on the research of regularities of formation of CuInSe$_2$ (CISe) and Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) monograin powders in liquid potassium iodide (flux). The variation of elemental composition, chemical surface treatment and doping with sodium were used to modify absorber materials properties for monograin layer solar cells (MGL).

The developed CuInSe$_2$ and Cu$_2$ZnSn(S,Se)$_4$ powders were characterized by EDS, SEM, XRD, ICP-MS, XPS, Raman, polarographic analyses and photoluminescence spectroscopy. The monograin powders were used as absorber materials in monograin layer solar cells. The solar cells were characterized by the dark and light current-voltage (I-V), capacitance-voltage, QE and by $V_{oc}$ vs. $T$ measurements.

In the growth process of monograin powders the chemical nature of the liquid (molten) phase of the used flux material impacts the powder crystals growth parameters and properties of the obtained absorber materials. It was found that the growth of powder crystals can be described by the formula: $d_m \sim t^{1/n} \exp(-E_d/kT)$. From the Arrhenius plot of the median grain diameter $d_m$ the activation energy for linear crystal growth $E_d = 0.25 \pm 0.05$ eV and from the time dependence of the median grain diameter $d_m \sim t$ at constant temperature the power of the time dependence of the growth process of monograin powder crystals. Crystals of CuInSe$_2$ grown in KI flux had a shape of polyhedrons with smooth facets. By variation of the Cu/In ratio (0.5 - 1.1) in initial Cu-In alloys the area of single-phase CuInSe$_2$ was determined to be between 1>Cu/In>0.7.

The processes of the synthesis and isothermal growth of CuInSe$_2$ monograin powders proceed at elevated temperatures in KI as a flux material and lead to the doping of the grown materials with iodine and potassium (also with Na as impurity in KI) from the flux. The doping with K and Na influences the surface composition, the defect structure and electrical and optical properties of the materials. The peak position of the PL band of Na doped CISe powders shifted depending on the Na doping level and showed the maximum energy when sodium concentration was $1 \times 10^{19}$ at/cm$^3$. The same material had the highest carrier concentration $2 \times 10^{17}$ cm$^{-3}$. The Na doping level of the absorber material had strong influence on the solar cell parameters and the added sodium concentrations $3 \times 10^{18}$ at/cm$^3$ resulted in the highest open-circuit voltage and fill factor values.
In the case of $\text{Cu}_2\text{ZnSn(S,Se)}_4$ growth in molten KI the bulk and the surface compositions of formed CZTSSe crystals were found to be non-identical. This difference in bulk and surface compositions is caused by the different solubilities of the precursors in the molten flux. As a result, different precursor components precipitate out from the flux during the cooling period onto the surface of the grown crystals. The influence of different chemical treatments of powder crystals on the chemical composition of crystals surface was studied to control the surface composition and to improve the parameters of the $\text{Cu}_2\text{ZnSn(S,Se)}_4$ monograin layer solar cell. The analysis of the leaching solutions showed that tin and chalcogen can be removed preferably by HCl etching. The leaching with KCN leads to the removal of Cu, Sn and chalcogen from the surface. From the XPS measurements we found that etching with 1% Br$_2$ in methanol resulted in Sn-rich material surface. The combination of chemical treatments (1% Br$_2$-MeOH + 10% KCN) resulted in $\text{Cu}_2\text{ZnSn(S,Se)}_4$ monograin layer solar cells with the highest values of parameters.

It was shown that monograin powder technology in the use of KI flux enables us to grow $\text{Cu}_2\text{ZnSn(Se}_{1-x}\text{S}_x)_4$ materials with homogeneous composition in the region of sulfur content $x = 0$ to $x = 0.85$. The increasing of sulfur content in $\text{Cu}_2\text{ZnSn(S,Se)}_4$ monograin powder absorber materials led to the increase of the forbidden band of material and improved the values of open circuit voltages of MGL solar cells. Solar cell structures based on monograin powders with the concentration ratio of 85 mole% sulfur to 15 mole% selenium yielded in the highest values of $V_{oc} = 660\text{mV}$. The $\text{Cu}_2\text{ZnSn(S,Se)}_4$ solid solution with 75 mole % sulfur and 25 mole % selenium gave the highest parameters of solar cell $V_{oc} = 622\text{ mV}$, $I_{sc} = 15.87\text{ mA/cm}^2$, $FF = 60\%$, $\eta = 5.9\%$. 

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KOKKUVÕTE

Kaaliumjodiid-sulandaja keskkonnas kasvatatud CuInSe₂ ja Cu₂ZnSn(S,Se)₄ monoterapulbrite omaduste kujundamine

Käsosolevas töös uuriti CuInSe₂ (CISe) ja Cu₂ZnSn(S,Se)₄ (CZTSSe) monoterade sünteeskasvatust ja nende omaduste kujunemist kaaliumjodiidsulandaja (KI-sulandaja) keskkonnas. Sünteesitud materjali omaduste modifitseerimiseks, eesmärgiga parandada monoteräkihtide baasil valmistatavate päikeseelementide väljundparametreid, kasutati absorbermaterjalide CISe ja CZTSSe lähtefaktori varieerumist, keemilist pinnatöötlust ja legeerimist naatriumiga.

CISe ja CZTSSe monoterade omaduste uurimisel kasutati EDS, SEM, XRD, ICP-MS, XPS ja polarograafilise analüüsi meetodeid, aga ka Raman- ja fotoluminestsents-spektroskoopiat. Monoterapulbrite baasil valmistatud päikeseelementide iseloomustamiseks kasutati valgustundlik spektroskoopiat (QE), Voc vs. T mõõtmisi, mahtuvusspektroskoopiat ja volt-amper kõverate mõõtmisi.

CISe ja CZTSSe monoterad kristallide sünteesis ja seega saadava materjali omadusi mõjutab väga suurel määral prosessis kasutatava KI-sulandaja keemiline koostis. Töös leiti CISe kristallide mediaanse diameetri suurenemist väljendava valemi – 

\[ d_m \sim t^{1/n} \exp(-E_d/kT) \]

- näitajad \( E_d \) ja \( 1/n \) KI-sulandaja puhul alljärgnevalt: kristallide mediaanse diameetri \( d_m \) suurenemise aktivatsioonenergia \( E_d = 0,25 \pm 0,05 \text{ eV} \) ja aja \( t \) astmenäitaja \( 1/n = 0,25 \pm 0,06 \). Mediaanse diameetri asjasõltuvuse astendaja väärustest \( n = 3,9 \pm 0,93 \) järel moodustab, et CISe monoterapulbrite sünteeskasvatusel KI-sulandajas esineb säilinud massidifusioonide läbi sulandaja vedelfaasi ka prekursoor-osakete paakumine koos pinnadifusiooniga. CuInSe₂ lahustuvuseks KI-sulandajas saadi 0,17 kaal %. Kasvanud üksikkristallide tetragonnaalne kuju viitab samuti CuInSe₂ väikesele lahustuvusele KI-sulandajas. Varieerides vase ja indiumi kontsentratsioonide suhet Cu-In prekurorsulamis piirides [Cu]/[In] = 0,5-1,1 Leiti, et ühefaasilise koostisega CISe absorbermaterjale saab sünteesida vähemikus 1>[Cu]/[In]>0,7.

CISe ja CZTSSe kasvatamisel KI-sulandaja keskkonnas toimub kaaliumi ja joodi difusioon moodustuvatesse kristallidesse kuni kasvatustemperatuurile vastava küllastusega. Uuriti ka Na mõju kasvavate kristallide pinnakasvustele, defektstruktuuritele, elektrilistele ja optilistele omadustele. Na mõju uurimiseks CuInSe₂ monoterade omadustele kasvatati CISe monoterapulbrid CuSe sulandajas ja seejärel legeeriti Na-ga kasutades selleks erineva kontsentratsiooniga suhtega NaI vesilahuseid. Fotoluminestsentsspektrofotomeetrist mõõtmisel selgus, et Na kontsentratsiooni suurenemisega toimub PL ribade maksimumi asukohale nihkumine suuremate energiaväärtuste poole. Kõige suurema energiaväärtusega fotoluminestsentsi maksimum oli materjalil, millele oli naatriumit lisatud 1×10¹⁹ at/cm³. Sellise lisatud

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Na koguse juures oli laengukandjate kontsentratsioon CISe absorbermaterjalis $2 \times 10^{17}$ cm$^{-3}$. Päikeseelemendi parim avatud vooluringi pinge saadi CISe absorbermaterjaliga, kus lisatud Na kontsentratsioon oli $3 \times 10^{18}$ at/cm$^3$.


Leiti, et kasutades sünteesiprotsessi sulandajana kaaliumjodiidi, on võimalik kasvata ja (sarnaselt CuInSe$_2$-le) homogeense koostisega CZTSSe tahkeid lahuseid Cu$_2$ZnSn$(Se_{1-x}S_x)_4$ (x = 0, 0.25, 0.45, 0.75, 0.85, 1.0) kuni S sisalduseni $x = 0.85$, mis on sobilikud kasutamiseks $p$-tüüpi absorbermaterjalinia päikeseelementides. Näiditi, et väävli kontsentratsiooni suurrendamine materjalis viib kasvatatud ja uuritud CZTSSe absorbermaterjalide keelutsoonini laienemisele. Väävli kontsentrotsiooni suurrendamine Cu$_2$ZnS$(Se_{1-x}S_x)_4$-s parandas avatud vooluringi pinge väärtusid. Parim avatud vooluringi pinge väärtusid ($V_{oc} = 660$ mV) saadi materjalis, kus $x = 0.85$. Parima päikeseelemendi kasuteguri $\eta = 5.9 \%$ andis materjal, kus väävli ja seleeni sisaldus oli 75 mool% S ja 25 mool% Se ($x = 0.75$). Parima kasuteguriga päikesepatarei teised parameetrid olid: $V_{oc} = 622$ mV, $I_{sc} = 15.87$ mA/cm$^2$, $FF = 60\%$. 
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CuInSe₂ monograin growth in the liquid phase of potassium iodide

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Abstract

The results of monograin CuInSe₂ synthesis from Cu–In alloy and Se in liquid KI are presented. The amounts of CuInSe₂ and KI were nearly equal to fulfill the criterion for the monograin growth (all free volume between the particles has to be filled with liquid). All the grown powder materials with narrow-disperse granularity were chalcopyrite CuInSe₂. The grown crystallites had tetrahedral shapes and homogeneous composition. Particle size distribution was used to describe the growth process. The activation energy of linear growth of crystals was \( E_a = 0.25 \pm 0.05 \text{ eV} \), and the power of time dependence of the crystal growth was \( l/t = 0.26 \pm 0.06 \). The solubility of CuInSe₂ in KI at 990 K was 0.17\% wt. %. The solubility of potassium and iodine in CuInSe₂ at 990 K was 0.094\% wt. %, and 0.0086\% wt. %, respectively. As a result, homogeneous p-type CuInSe₂ monograin materials were synthesised in KI solvent.

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Keywords: Crystallization, CuInSe₂, Halides; Growth mechanism

1. Introduction

Monograin powders of CuInSe₂ have found application as absorber materials in monograin layer solar cells [1]. Till now, monograin layer solar cells with the structure of graphite/CIS/CdS/ZnO have shown open-circuit voltage (Voc) values up to 530 mV and fillfactors up to 65%. The isothermal growth of CuInSe₂ monograin powders in the presence of liquid phase of a suitable solvent material (flux) leads to the formation of semiconductor materials with single-crystalline grain structure and narrow-disperse granularity, so called monograin powders [2]. The growth of CuInSe₂ monograin powders in CuSe-Se flux results in near-stoichiometric compositions of material grains [2]. This is in accordance with the Cu-side borderline of CuInSe₂ phase existence range of Cu₂Se-In₃Se₅ phase diagram [3]. The use of Se as flux material allows to grow the monograin powder in the large range of compositions [4]. The removal of Se from the powder batch is technologically difficult. Therefore, in order to obtain In-rich compositions of monograin powders in a less time consuming process, we studied the growth of monograin powders in different flux materials containing alkali metal compounds that are removable by deionized water. In this study CuInSe₂ compound was synthesized from high-purity elements Cu, In and Se (Cu and In were prior melted and used as Cu–In alloy) and the growth process of CuInSe₂ crystals in the liquid phase of molten potassium iodide (KI) as the flux material is described.

2. Experimental

The initial Cu–In alloys were synthesized from the precursors of 5N purity in quartz ampoules. The synthesis were made in a dynamic vacuum at the temperature of 1070 K. Cu–In alloy ingots were tritutated in the agate mortar and sieved through the 100 μm sieve. Grinded Cu–In alloy (1:1.1) and elemental Se was mixed with KI. The amount of components for CuInSe₂ and the amount of KI were nearly equal for providing enough liquid phase for the monograin growth. The minimum growth temperature was limited by the melting temperature of the used flux material and the maximum growth temperature was limited by the temperature of the phase transition of CuInSe₂. The samples were sealed into evacuated...
quartz ampoules, annealed isothermally at various temperatures (970, 990, 1010 and 1050 K) and annealing times (30, 76, 270, 334 h) and quenched to the room temperature. The flux was removed by deionized water.

The samples were characterized by the X-ray diffraction, the scanning electron microscopy, the photoluminescence and electrical measurements. The X-ray diffraction patterns were recorded by the Bruker AXS D5005 diffractometer with a monochromatic Cu Kα radiation in the 2θ interval of 12–90 deg using the step of 0.04 deg and counting time of 2 s/step.

For the photoluminescence measurements, the excitation source was a He-Cd laser with the wavelength of 441 nm. The powder crystals were mounted inside the closed cycle He cryostat (T=9–300 K). The photoluminescence spectra were recorded with the computer-controlled SPM-2 grating monochromator (λ=0.4 μm). The signal was detected with InGaAs detector using the conventional lock-in technique.

The composition of CuInSe₂ powders was determined polarographically. The solubility of potassium and iodine in CuInSe₂ was determined by the inductively coupled plasma mass spectrometry. The shape and surface morphology were studied by the high-resolution scanning electron microscopy LEO SUPRA 35. The conductivity type was determined by the hot-probe method. The sieve analysis method was used to determine the particle size distribution. The median particle size was determined graphically from sieving analyze data on the log-normal probability graph [5]. Solubility of CuInSe₂ in KI at 990 K was determined by the weight loss method.

3. Results and discussion

The formation of CuInSe₂ monograins take place in the liquid phase of flux that exceeds the limit of sintering of the initial crystals [6]. The flux consists of a molten substance used and the product of syntheses dissolved in it. To find the volume of the liquid phase we need to know the solubility. Therefore, we determined the solubility of CuInSe₂ in KI by the weight loss method. Big pieces of polycrystalline CuInSe₂ were weighed and sealed with 5 times bigger amount of dried KI into quartz ampoules. The ampoules were annealed at 990 K for 120 h and then quenched in water. The undissolved CuInSe₂ was weighed. From the weight loss we found the solubility of CuInSe₂ in KI. Results are presented in Table 1. For a comparison there is also the data of CuInSe₂ solubility in Se [7] and CuSe-Se [2] in Table 1.

Considering the low solubility of CuInSe₂ in KI we used equal amounts of both materials in our growth studies.

The dissolution of the flux revealed uniform, mainly nonaggregated micro crystals of tetragonal shape with smooth surfaces (Fig. 1), indicating their growth from individual seed.

![Fig. 1. The scanning electron microscopy photos of CuInSe₂ monograin powder crystals grown in KI at 990 K for 76 h.](image1)

![Fig. 2. The X-ray diffraction pattern of CuInSe₂ monograin powder grown in KI at 990 K for 76 h.](image2)

![Fig. 3. The photoluminescence spectrum of the CuInSe₂ monograin powder grown in KI at 990 K for 76 h.](image3)
crystals rather than from the aggregates of crystallization nuclei.

The X-ray diffraction spectra of formed CuInSe₂ monograin powder (Fig. 2) showed the peaks of chalcopyrite CuInSe₂ only.

The composition of CuInSe₂ powder materials, which were grown at various temperatures and different times, were analysed polarographically. The results revealed that the composition did not change by changing the growth parameters temperature and time. The composition of CuInSe₂ monograin powder materials were Cu:In:Se = 23.3:25.5:51.2 (Cu/In = 0.91). The inductively coupled plasma mass spectrometry analysis data showed that the solubility of potassium and iodine in CuInSe₂ at 990 K was 0.094 wt. %, and 0.0086 wt. %, respectively. All the asgrown monograin powders had p-type conductivity.

The photoluminescence (PL) spectrum of our CIS crystals grown in liquid KI is shown in Fig. 3. A broad asymmetric band characterizes the typical PL spectrum of In-rich CIS with the maximum around 0.93 eV.

The sieve analysis was used to determine the particle size distribution. Fig. 4 shows the particle size distribution of the samples grown at 1010 K for different periods. The particle size distribution of all the samples follows a log-normal distribution in which the distribution shifts with growth duration t. It allows the use of the median particle size $d_{50}$ to describe the grain growth according to the equation:

$$d_{50} = A t^{1/n} \exp(-E_d/kT),$$  

where $A$ is a constant for a given flux and compound, $k$ is the Boltzmann constant, $T$ is the growth temperature, $E_d$ is the activation energy for linear crystal growth and $n$ is the geometric factor of growth mechanism [8]. If the growth is controlled by one growth mechanism (diffusion) then $n = 3$. From the time dependencies of $d_{50}$, we found the power of the time dependence of crystal growth $1/n = 0.25 \pm 0.06, n = 3.9 \pm 0.93$. From the value of $n = 3.9 \pm 0.93$ we suppose that the growth process of CuInSe₂ particles in KI flux is limited by diffusion processes on the surfaces of sintered grains (compare with [9]).

From the Arrhenius plot of the median grain diameter $d_{50}$, we obtained the activation energy of the linear crystal growth $E_d = 0.25 \pm 0.05$ eV.

4. Conclusions

From Cu-In (1:1.1) alloy, Se and KI it is possible to synthesize and grow p-type CuInSe₂ powder materials with single-crystalline grain structure and narrow-disperse granularity. From the Arrhenius plot of the median grain diameter $d_{50}$ activation energy for linear crystal growth $E_d = 0.25 \pm 0.05$ eV was determined. The power of time dependence of the crystal growth $1/n = 0.26 \pm 0.06, n = 3.9 \pm 0.93$ was determined from the time dependencies of $d_{50}$. Crystals of CuInSe₂ grown in KI flux had mainly tetragonal shapes with smooth surfaces.

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Growth of CuInSe$_2$ monograin powders with different compositions

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ABSTRACT

CuInSe$_2$ monograin powders (MGP) were synthesized from Cu-In alloys of different Cu/In concentration ratios and elemental Se in liquid phase of flux material in evacuated quartz ampoules. The surface morphology, phase structure, and composition of the powder crystals were analyzed by scanning electron microscopy, X-ray diffraction, and energy-dispersive X-ray analysis respectively. Bulk composition was analyzed polarographically. Photoluminescence spectra were measured at 9 K. It was found that the composition of MGP material (Cu/In concentration ratio) can be controlled by the concentration ratio of precursor Cu-In alloys. Single phase CuInSe$_2$ growth is realisable between 0.7\textless Cu/In\textless 1 at the growth temperature of 1000 K. Photoluminescence spectra of near-stoichiometric materials had one dominant peak at 0.93 eV, which is typical to In-rich CuInSe$_2$. Samples with high In content exhibited two broad bands with peak positions at 0.86 and 0.93 eV.

INTRODUCTION

The monograin powders of CuInSe$_2$ (CIS) have found application as absorber material in monograin layer solar cells [1]. The monograin layer consists of one crystal thick layer of grains embedded into an organic resin. The advantages of the developed powder materials are the single-crystalline structure of every grain, the uniform distribution of doping impurities and narrow granulometric composition. Till now, monograin layer solar cells with the structure of graphite/CIS/CdS/ZnO have shown open-circuit voltage ($V_{oc}$) values up to 530 mV and fill factors up to 60% [2]. The growth of CuInSe$_2$ MGP-s in CuSe-Se flux [3] results in near-stoichiometric compositions. This is in accordance with the Cu-side borderline of $\alpha$- (CuInSe$_2$) phase existence range of Cu$_2$Se-In$_2$Se$_3$ phase diagram [4]. Therefore, in order to obtain more In-rich compositions of MGP-s, we studied the growth of MGP-s in different flux materials containing alkali metal compounds.

The structural, morphological, electrical and optical properties of CIS materials depend highly on the composition and the method of preparation. Cu-rich CIS are usually p-type materials. As the material becomes indium rich a conversion to n-type conductivity often occurs. Noufi et al. have shown that the conductivity type depends not only on the Cu/In concentration ratio but also on the Se content of the material [5].

The Cu concentration of absorbers in highly efficient solar cells varies typically between 22 to 24%. At growth temperatures this composition lies within the single-phase region of $\alpha$-phase. However, by cooling to the room temperature, this composition enters the two-phase $\alpha+\beta$ region.
of equilibrium phase diagram. Fortunately, there are some results, where Na incorporation allows to widen the range of the α-(CuInSe₂) phase in the phase diagram [6].

In order to grow CuInSe₂ MGP-s with different compositions we prepared Cu-In alloys with different Cu/In concentration ratios (0.5-1.1) as precursor materials. Our aim was to clarify the limits for the single-phase growth of CuInSe₂ in flux materials of different chemical nature and to study the possibilities to tailor CIS properties in growth conditions.

**EXPERIMENTAL DETAILS**

**Crystals growth**

CuInSe₂ monograin powder growth was proceeded from synthesised Cu-In alloys and elemental selenium. All used precursors had 5N purity. The syntheses of Cu-In alloys were made in carbon-coated quartz tubes under dynamic vacuum (continuous pumping) at temperature of 1070 K. Cu-In alloy ingots were ground in a mortar. Powdery alloys with different Cu/In ratios, Se and flux material for solution growth of CuInSe₂ were loaded into quartz ampoules. Different alkali halides were used as flux materials. As it is shown in Ref. [3], the formation of CuInSe₂ monograins takes place in the amount of liquid phase of flux that exceeds the limit for crystals sintering. The melting temperature of the used flux material limits the minimum growth temperature and the temperature of phase transition of CIS limits the maximum growth temperature. In the present study the samples in sealed evacuated quartz ampoules were annealed isothermally at 1000 K for 96 hours and then quenched to the room temperature. The flux material was removed by dissolution in deionised water.

The X-ray diffraction (XRD) spectra of formed Cu-In alloys showed Cu₁₁In₉ and indium phases. According to Ref. [7, 8] the metallic precursors of Cu-In alloys (with the indium composition of 47.62 at. % - 60 at.%) have been identified as the mixtures of Cu₁₁In₉ compound and indium with the solidus temperature of 153°C. The presence of metallic In in In-rich precursors corresponds also to the equilibrium phase diagram [9]. Above the melting point of In, the equilibrium phases are liquid indium with dissolved Cu and solid Cu-In alloy. It has been observed by several investigators that Cu₁₁In₉ is the most commonly observed phase for Cu-In alloys [10].

**Characterization**

The bulk composition of each powder was determined polarographically and by energy-dispersive X-ray analysis (EDS). The surface morphology and crystalline phases were examined by scanning electron microscopy (SEM) and XRD respectively. For the photoluminescence (PL) measurements the closed-cycle He cryostat (T = 9 - 300 K) and the He-Cd laser were used. The PL signal was detected using a standard lock-in technique, computer-controlled SPM-2 grating monochromator (f = 40 cm) and an InGaAs detector. The signal detected was corrected in conformity with the grating efficiency and detector sensitivity spectra. The grain resistances were determined by pressing the grain between two indium contacts. The ohmic behaviour of indium contacts with CIS has been proven by linearity of I-V measurements. The conductivity type was determined by hot-probe method.
RESULTS AND DISCUSSION

Composition of the grown crystals

The Cu/In concentration ratios of Cu-In alloys, deviation from molecularity ($\Delta m=[\text{Cu}] / [\text{In}] - 1$), and deviation from stochiometry ($\Delta s = (2[\text{Se}] / ([\text{Cu}] + 3[\text{In}]) - 1$), as calculated from the polarographic analysis data of grown powders and the conductivity type of developed powders are presented in Table I. The Cu/In concentration ratios of the grown powders (determined polarographically) versus the one of the Cu-In alloys are shown in Fig. 1. In the case of In-rich precursor alloys ($[\text{Cu}] / [\text{In}] < 1$), Cu/In ratios in the grown powders correspond nearly (or slightly less indium-rich) to the Cu/In ratios of initial Cu-In alloys. Powder materials from the Cu-rich ($[\text{Cu}] / [\text{In}] \geq 1$) initial compositions ‘have lost’ some amount of copper after KCN etching. This indicates the entering of material into multiphase region of phase diagram. Additionally, we determined Cu, In, and Se concentrations in the flux material leaching solutions and found that relative Cu concentrations in leaching solutions were in the range of 25-26% while the corresponding In concentrations were 21-23%. Consequently, in growth conditions some chemical reactions between the flux material and precursor components are going on that result in water-soluble compounds.

The EDS analysis of single powder grains showed that the materials with Cu/In $\geq 0.71$ consisted of the crystals with uniform composition. At the same time, the powder with Cu/In=0.67 consisted of crystals with two different compositions: with Cu/In = 0.92 and with Cu/In=0.66. This indicates that the growth process result in multiphase solid material.

Table I. $[\text{Cu}] / [\text{In}]$ in Cu-In alloy, powder analysis data, $\Delta m$ and $\Delta s$ (calculated from polarographic analysis data) and conductivity type of CuInSe$_2$ monograin powders.

<table>
<thead>
<tr>
<th>$[\text{Cu}] / [\text{In}]$ in Cu-In alloy</th>
<th>Cu, at%</th>
<th>In, at%</th>
<th>Se, at%</th>
<th>$\Delta m$</th>
<th>$\Delta s$</th>
<th>Conductivity type</th>
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<tr>
<td>1.1</td>
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<td>24.9</td>
<td>49.4</td>
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<td>-0.02</td>
<td>p</td>
</tr>
<tr>
<td>1</td>
<td>24.1</td>
<td>25.6</td>
<td>50.4</td>
<td>-0.06</td>
<td>0.00</td>
<td>p</td>
</tr>
<tr>
<td>0.92</td>
<td>23.7</td>
<td>25.6</td>
<td>50.7</td>
<td>-0.07</td>
<td>0.01</td>
<td>p</td>
</tr>
<tr>
<td>0.83</td>
<td>22.7</td>
<td>26.2</td>
<td>51.0</td>
<td>-0.13</td>
<td>0.01</td>
<td>p</td>
</tr>
<tr>
<td>0.71</td>
<td>20.6</td>
<td>27.1</td>
<td>52.3</td>
<td>-0.24</td>
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<td>p</td>
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<tr>
<td>0.66</td>
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<td>n</td>
</tr>
<tr>
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<td>33.1</td>
<td>51.2</td>
<td>-0.52</td>
<td>-0.11</td>
<td>n</td>
</tr>
</tbody>
</table>
Figure 1. The Cu/In ratio versus molecularity $\Delta m$.

The selenium concentration of the synthesized powders, determined polarographically and by EDS, as the function of the molecularity $\Delta m$ is presented in Fig. 2. Selenium content in the powders increases with decreasing molecularity and changes from 49% up to about 54%.

Figure 2. Selenium content in powder as function of molecularity $\Delta m$.

Figure 1. and figure 2. show that there are three regions of Cu/In ratios. Each region is characterized by different crystal growth equilibrium and with the different composition of powders. The approximate borders of those regions are marked with dashed lines in Fig. 1 and Fig. 2. The border of II/III region coincides with the changes of the type of conductivity. According to the polarographic analysis, the bulk composition of powder crystals in the III region indicates that we have a two-phase material containing probably CuInSe$_2$ and In$_2$Se$_3$. Single-phase CuInSe$_2$ monograin powders can be produced in the II region (0.67<Cu/In<1). XRD measurements indicate that in the I region (Cu/In>1) also CuSe phase can be detected.
**PL study of CuInSe$_2$ powders**

Fig. 3 shows the PL spectra of CIS powders with different indium content. The change of In content in CIS influences the shape of PL curve and the positions of peaks in spectra. A broad asymmetric band characterizes the typical PL spectrum of In-rich CIS with the maximum around 0.93 eV. The PL In-rich samples (Cu/In<0.83) exhibit two broad bands with peak positions at ~0.86 and 0.93eV. The broad band at ~ 0.86 eV is probably related to the recombination through deep intrinsic defect levels (~245 meV) that are caused by indium interstitials (In$_i$) or In$_{Cu}$ [12, 13]. The relative intensity of the latter band increases with the increasing indium content, which seems to be a prerequisite for the creation of corresponding defects. The wide PL peak at about 0.99 eV dominates the PL spectra of Cu-rich powders.

![PL spectra of Cu-rich, near stoichiometric and In-rich CuInSe$_2$ at 9K. The Cu/In ratio of precursor Cu-In alloys is shown numerically.](image)

**Electrical resistance and conductivity type**

Fig. 4 shows the electrical resistance of CuInSe$_2$ grains as the function of Cu/In molar ratio of precursor Cu-In alloys. All measured grains were in sizes within 112-150 µm. The measurement data of grains with compositions corresponding to n-type region are represented by solid squares, while p-type ones are shown as open squares. As the Cu/In ratio increases from 0.5 to 1.1, the grain resistance decreases from $2 \times 10^7$ to $8 \times 10^2 \Omega$. Accordingly, the resistance of the materials increases with In content. This is typical for semiconductor materials with high doping levels – the mobility of charge carriers decreases. The change of conductivity type occurs in the region of the Cu/In ratio values of 0.67-0.71. Within this region, the materials consist of crystals with both different types of conductivity. In that region materials selenium content is rather high (about 52 %) and according to EDS analysis, materials consist of crystals with different compositions: with Cu/In=0.92 and Cu/In=0.66. Based on these results the crystal growth takes place in multiphase conditions.
Figure 4. Grain resistance in dependence of Cu/In ratio in material. Sizes of measured grains were within 112-150 μm.

CONCLUSIONS

We determined the preparation conditions for CuInSe₂ monograin powder growth in the molten fluxes of different chemical nature. We found that flux material allows the growth of In-rich CuInSe₂ monograin powders. The single-phase powder crystals can be synthesized from precursor Cu-In alloys with Cu/In ratio values between 1 > Cu/In > 0.7. The powders from initial Cu-In alloy with Cu/In < 0.67 were found to consist of crystals with different compositions: Cu/In = 0.92 and Cu/In = 0.66. Accordingly, we had multiphase growth conditions. Selenium content in the grown powders increases almost linearly with the decreasing Cu/In ratio of the materials.

The samples with nearly stoichiometric or slightly In-rich compositions showed p-type conductivity and exhibited PL spectrum with dominant peak at 0.93 eV. In contrast, the samples with Cu/In < 0.7 had n-type conductivity and exhibited two broad bands in PL curve with the peak positions at 0.86 eV and 0.93 eV.

ACKNOWLEDGEMENTS

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The effect of sodium doping to CuInSe₂ monograin powder properties

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Abstract

The effect of sodium doping to the electrical and photoluminescence properties of CuInSe₂ monograin powders was studied. Sodium was added in controlled amounts from 5 x 10^{16} cm⁻³ to 1 x 10^{20} cm⁻³. The photoluminescence spectra of Na-doped stoichiometric CuInSe₂ powders had two bands with peak positions at 0.97 and 0.99 eV. The photoluminescence bands showed the shift of peak positions depending on the Na doping level. Peak positions with maximum energy were observed if added sodium concentration was 1 x 10^{19} cm⁻³. This material had the highest carrier concentration 2 x 10^{17} cm⁻³. In the case of stoichiometric CuInSe₂ (CuIn:Se=25.7:25.3:49.0), Na doping at concentrations of 3 x 10^{17} cm⁻³ and higher avoided the precipitation of Cu–Se phase. Solar cells output parameters were dependent on the Na doping level. Sodium concentration 3 x 10^{18} cm⁻³ resulted in the best open-circuit voltage.

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Keywords: CuInSe₂; Sodium; Photoluminescence; Solar cells

1. Introduction

Monograin layers are perspective for the development of low priced solar cells. Monograin powders of CuInSe₂ have been applied as absorber material in monograin layer solar cells [1]. The isothermal growth of CuInSe₂ monograin powders in the presence of liquid phase of a suitable solvent material (flux) leads to the formation of semiconductor materials with single-crystalline grain structure and narrow-disperse granularity, so called monograin powders [2]. In this process the chemical nature of the liquid (molten) phase of used solute material impacts certain properties of the obtained absorber material.

In the case of vacuum deposited Cu(In,Ga)Se₂ thin film solar cells, the presence of Na in the absorber correlates with numerous changes in material and device quality. The observed changes include improvements in the open-circuit voltage [3,4], preferential grain orientation [4], increased grain size and carrier concentration [5,6]. Using the photoluminescence (PL) measurements, Kinura et al. [7] found that by Na incorporation the compensation of CuInSe₂ was reduced due to the suppression of donor-type defects.

In this paper we focus on the effects of Na doping on the electrical and photoluminescence properties of CuInSe₂ monograin powders with stoichiometric composition. In order to clarify the influence of sodium doping on the parameters of CuInSe₂ monograin layer devices, the synthesized materials doped with Na were used as absorber materials in solar cells.

2. Experimental

CuInSe₂ monograin powders used in the present study was synthesized from Cu–In alloy and elemental Se in the liquid phase of CuSe as the flux material in evacuated quartz ampoules. The growth processes of CuInSe₂ in CuSe is described in [2]. For doping with Na the synthesized material was heat-treated in the presence of NaI as a flux at 800 K for 48 h in addition of sodium as NaI. Solution of NaI in deionized water was dosed in controlled amounts in the range of 5 x 10^{16}– 1 x 10^{20} cm⁻³. By sequential diluting we kept the amount of doping solution constant. The doped materials were dried and vacuum-sealed into quartz ampoules. After annealing, the ampoules were cooled to room temperature in water. The flux was removed by 3.7% aqueous solution of HCl.

The surface morphology and composition of single powder crystals were analyzed by the scanning electron microscopy (SEM) and the energy dispersive X-ray spectroscopy. Materials were characterised by electrical measurements.

For the photoluminescence measurements, the excitation source was a He–Cd laser with the wavelength of 441 nm. The
powder crystals were mounted inside a closed cycle He cryostat ($T=9$–$300$ K). The PL spectra was recorded with a computer-controlled SPM-2 grating monochromator ($f=0.4$ m). The signal was detected with InGaAs detector using the conventional lock-in technique.

All the as-grown absorber materials were annealed in sulphur vapour at 800 K for 18 h before solar cell production. More processing details could be found in [8]. For monograin layer formation the monolayer of unsize CuInSe$_2$ powder crystals covered with chemically deposited CdS was sedimentated into thin layer of epoxy resin without the contamination of the upper surfaces of crystals. After polymerization of epoxy, i-ZnO and conductive ZnO:Al were deposited by RF-sputtering. The solar cell structure was completed by the evaporation of 1–2 μm thick In grid contacts onto the ZnO window layer. After gluing the structures on glass substrates, the back contact area of crystals covered by epoxy was opened by etching with H$_2$SO$_4$ and by additional abrasive treatment. Graphite paste was used as back contact. Monograin layer solar cells on the basis of Na-doped CuInSe$_2$ monograin powders were characterised with current–voltage and capacitance–voltage measurements.

3. Results and discussion

3.1. Photoluminescence study of CuInSe$_2$ powders

The photoluminescence spectra of all monograin materials show a broad band with its maximum around 0.99 eV (Fig. 1). This band consists of two subbands with peak positions at 0.97 and 0.99 eV. The peak position of the PL band at 0.99 eV depends on the dosed sodium doping level as it is seen in Fig. 2. The peak position shifts to higher energy values with increasing sodium concentration up to $1 \times 10^{19}$ cm$^{-3}$. With further increase in sodium doping level the sharp decrease of the PL peak energy values was observed.

It was found in [3] that Na does not create any shallow acceptor level in CuInSe$_2$, but it can form a solid solution with CuInSe$_2$ in the form of Na$_2$Cu$_{1−x}$In$_x$Se$_2$ with higher bandgap energy than the base material. For CuGaSe$_2$ in [9], there was proposed the formation of a quaternary Na–Cu–Ga–Se compound on the base of defect-chalcopyrite structure in which Cu vacancies are partially filled by Na atoms. To explain the obtained results we propose, analogically to the above mentioned studies, the formation of a solid solution of CuInSe$_2$ with Na with slightly higher bandgap energy on the surface of our crystals. SEM photo indicates to the segregation of an unknown phase in our sodium doped samples (Fig. 3).

The bandgap energy of a quaternary Na$_x$Cu$_{1−x}$In$_x$Se$_2$ solid solution increases with increasing sodium doping level. At doping concentrations higher than $10^{19}$ cm$^{-3}$, the PL peak position sharply shifts to lower values of energies. The bandgap energy of ternary compounds is sensitive to the high concentration of defects [10]. The potential fluctuations due to randomly distributed defects cause the widening of the defect levels and the local perturbation of electron potential. Thus, the peak position of the PL band shifts towards lower energies at higher defect concentrations. The increase in the half-width of the PL bands with Na concentration also indicates to the increase of defect density.

3.2. Solar cell parameters

The solar cells with undoped and doped with sodium up to $1 \times 10^{17}$ cm$^{-3}$ absorber materials had low value of shunt resistance (Fig. 4). These materials were etched with 10% KCN aqueous solution. After KCN etching we were able to measure the solar cell parameters. The solution is known as selective etchant for Cu–Se binary phases [11]. Therefore we suppose that the segregation of the Cu–Se phase occurs in powders with added Na concentration less than $3 \times 10^{17}$ cm$^{-3}$.
It is known that sodium incorporation widens the range of the $\alpha$-(CuInSe$_2$) phase existence in the phase diagram [12]. In our case, the increase of sodium content in CuInSe$_2$ widens the single phase area of CuInSe$_2$ towards Cu-rich compositions starting from the doping level of $3 \times 10^{17}$ cm$^{-3}$. In materials without Na or with low Na concentration levels up to $1 \times 10^{17}$ cm$^{-3}$, the Cu–Se phase segregation is possible.

The values of the open-circuit voltage of solar cells (Fig. 5) increase with increasing doped sodium concentration from $5 \times 10^{16}$ cm$^{-3}$ to $3 \times 10^{18}$ cm$^{-3}$. At higher than $3 \times 10^{18}$ cm$^{-3}$ values of Na concentrations the open-circuit voltage decrease and stay constant. Sodium concentration $3 \times 10^{18}$ cm$^{-3}$ was found to result in the best open-circuit voltage.

At low concentrations, at first Na eliminates the In$_{Cu}$ defects that act as traps for the majority carriers. Thus, the effective hole density increases [3,7]. However, as the Na concentration increases to the level where the most of the In$_{Cu}$ defects have been eliminated, it starts to remove the acceptor $V_{Cu}$. This process reduces the hole density [3]. That may cause a reduction in the cell performances at Na contents higher than $3 \times 10^{18}$ cm$^{-3}$.

### 3.3. Carrier concentration

Carrier concentration was determined by room-temperature capacitance–voltage measurements (Fig. 6). We found that the maximum carrier concentration $2 \times 10^{17}$ cm$^{-3}$ was in materials with doped sodium content of $1 \times 10^{19}$ cm$^{-3}$. Further increase in sodium content resulted in decreased carrier concentration. As seen in Fig. 5, the same tendency can be observed in the values of open-circuit voltage.

### 4. Conclusions

The PL spectra of Na-doped CIS powders showed that the peak position of the PL band shifted depending on the Na doping level. The peak position of the PL band with maximum energy was observed when sodium concentration was $1 \times 10^{19}$ cm$^{-3}$. The material with the same sodium concentration had the highest carrier concentration $2 \times 10^{17}$ cm$^{-3}$. It has been found that in the case of stoichiometric CuInSe$_2$ (Cu: In: Se = 25:7:25:3:49.0) Na doping avoided the precipitation of Cu–Se phase at dosed Na concentration $3 \times 10^{17}$ cm$^{-3}$ and higher. The obtained results were explained by formation of a solid solution of CuInSe$_2$ with Na containing compound with slightly higher bandgap energy on the surface of crystals. Solar cells output parameters were dependent on the Na doping level of the absorber material. Sodium concentration $3 \times 10^{18}$ cm$^{-3}$ was found to result in the best open-circuit voltage.

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CHEMICAL ETCHING OF Cu$_2$ZnSn(S,Se)$_4$ MONOGRAIN POWDER

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ABSTRACT

Cu$_2$ZnSn(S,Se)$_4$ (CZTS,Se) monograin powders were synthesized in the liquid phase of molten KI as flux material from binary compounds in evacuated quartz ampoules. Monograin powders were subjected to various chemical treatments with several etchants (HCl, KCN, NH$_4$OH and Br in methanol (Br$_2$-MeOH)) to modify the crystal surface. Polarographic analyses of leaching solutions showed that Sn and Se were removed preferably by HCl etching. Treatment with 10% KCN dissolved mainly Cu, Sn and chalcogen, and ammonia solution removed selectively Cu and chalcogen in an approximate ratio of 1:2. From XPS measurements we found that after etching with 1% Br$_2$-MeOH the material surfaces were Sn-rich. The prepared monograin powders were used as absorber materials in monograin layer solar cells: ZnO/CdS/CZT(S,Se)/graphite. A combination of chemical treatments before the deposition of CdS led to the best parameters of Cu$_2$ZnSn(S,Se)$_4$ monograin layer solar cells. The here achieved efficiencies of solar cells were above 4%.

INTRODUCTION

The quaternary compounds Cu$_2$ZnSnS$_4$ and Cu$_2$ZnSnSe$_4$ are new interesting semiconductor materials as absorber layer in solar cells. The most of their elemental components are abundant in the earth's crust and they have semiconductor properties such as p-type conductivity, direct band gaps and high absorption coefficients (>10$^5$ cm$^{-1}$) [1]. Typical methods for thin film production, such as sputtering and PVD in the case of Cu$_2$ZnSnSe(S)$_4$ materials, lead to inhomogeneous and multiphase composition of the layer films [2, 3]. Monograin growth in molten fluxes results in a homogeneous composition of the CZTSe powder material [4]. In the process of the monograin growth the formation of monograin of a semiconductor compound takes place in the liquid phase of the used flux material. The criteria for the monograin growth is the following: the volume of the molten phase $V_L$ between grains has to exceed the limit of sintering - $V_L$ $>$ 0.6 $V_S$, where $V_S$ is the volume of solid phase. In this case the liquid phase separates the initial solid phase from each other and the individual single crystals grow [5]. Due to the solubility, the precursors and the formed CZT(S,Se) may partially dissolve in the molten flux salt at the used recrystallization temperature and some part of it can re-precipitate on the surface of the formed crystals during the cooling period. These precipitations change the surface morphology and the composition of the absorber crystal surface. On the other hand, it is well known that the active interface of p-type absorber and n-type buffer layer plays a key role for the solar cell performance. Therefore, an in depth understanding of the chemical treatment of CZT(S,Se) monograin powder crystals' surfaces with different etchants is very important for tailoring the absorber crystal's surface composition and finally the parameters of solar cells on their base.

In this paper we present some results of our studies on chemical etching of CZT(S,Se) monograin powders.

EXPERIMENTAL

Cu$_2$ZnSn(S,Se)$_4$ monograin powders were synthesized from Cu(S,Se), Zn(S,Se) and Sn(S,Se) precursors in molten KI. The ground precursors were sealed in evacuated quartz ampoules and annealed at 1000 K. The growth process was stopped by quenching the ampoules in water. The flux material was removed by leaching with deionized water. These leaching solutions contained also some amorphous phase. The amorphous precipitates were separated, dried and analyzed polarographically and by energy dispersive x-ray analysis (EDX). The grown monograin powders were divided into several parts and each of them passed through different etching procedures. As etchants we used concentrated HCl, 10% aqueous solution of KCN, 1% Br$_2$-MeOH (bromine in methanol) solution and 2M NH$_4$OH solution. All the chemical etchings were performed at room temperature. The composition of the leaching solutions was analyzed polarographically. The surface morphology of the powder crystals before and after etching were studied by high resolution scanning electron microscope (SEM) equipped with an In-Lens SE detector for topographic imaging and energy and angle selective backscattered electron detector (ESB) for compositional contrast. The bulk and surface chemical composition of the monograin was analyzed using EDX. The phase composition was studied by room temperature (RT) micro-Raman spectroscopy. The changes in surface composition of materials was determined using X-ray photoelectron spectroscopy (XPS). The photovoltaic properties of graphite/Cu$_2$ZnSn(S,Se)$_4$/CdS/ ZnO solar cell structures were characterised by current-voltage (I-V) measurements under 100mW/cm$^2$ illumination.

RESULTS

Cu$_2$ZnSn(S,Se)$_4$ monograin powder crystals had tetragonal shape with rounded grain edges (see Fig. 1).
SE and EsB SEM images exposed the inhomogeneity of crystals’ surface of as-grown Cu2ZnSn(S,Se)$_4$ monograins powders (see Fig. 2). The comparison of the crystals’ surface composition with the bulk by using EDX revealed that the surface of as-grown CZT(S,Se) crystals is Sn-rich while the bulk of crystals is Zn-rich (see Table 1).

<table>
<thead>
<tr>
<th>Material</th>
<th>Cu/Zn+Sn</th>
<th>Zn/Se</th>
<th>Se+Se/Met</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystals’ surface</td>
<td>0.94</td>
<td>0.86</td>
<td>1.01</td>
</tr>
<tr>
<td>Crystals bulk</td>
<td>0.88</td>
<td>1.03</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Table 1: Compositions of chemically untreated CZT(S,Se) crystals’ surfaces and their bulk (polished cross-section of powder crystals) as determined by EDX.

The difference in the surface and the bulk compositions can be taken as a hint of material precipitation from components dissolved in the flux at the growth-temperature onto the surface of the grown crystals during cooling.

After the removal of the flux by deionized water the remaining solid phase consists of well formed crystallites of CZT(S,Se) and an amorphous material that was originally dissolved in KI at the recrystallization temperature and then precipitated during cooling. The composition of the amorphous deposit was analysed by EDX as Cu : Zn : Sn : S + Se = 24.74 : 3.02 : 19.83 : 52.82. This elemental composition indicates the existence of surface compounds like Cu$_2$Sn(S,Se)$_3$ and Sn(S,Se)$_3$.

Figure 3 shows normalised RT Raman spectra of the surface and the bulk of Cu$_2$ZnSnSe$_4$ monograins, together with a normalised Raman spectrum of precipitated material. The polished Cu$_2$ZnSnSe$_4$ monograins were used to determine Raman spectra of the bulk material. Two dominating modes of Cu$_2$ZnSnSe$_4$ [6] can be found at 195 and 171 cm$^{-1}$ in the Raman spectra of the bulk of crystals. These modes can also be found in the spectra of the monograins surface. However, there are some additional modes around 188 cm$^{-1}$ and 175 cm$^{-1}$ in the Raman spectra of the crystal's surface, indicating the presence of other phases on the crystals' surface. These additional peaks are also present in the Raman spectra of the precipitate, which confirms our assumption that a part of the material dissolved in the molten phase could precipitate onto the crystals’ surface in the cooling process. The Sn-rich chemical composition of the crystals’ surface and a Raman peak around 188 cm$^{-1}$ give us the base to suppose that SnSe$_2$ (A$_1$ mode at 186 cm$^{-1}$ [7]) is a main component of the precipitate.

In order to remove other phases from the CZT(S,Se) monograins’ surfaces and to improve the active interface of the p-type Cu$_2$ZnSn(S,Se)$_4$ solar cell performance, chemical treatments with several etchants (HCl, KCN, Br$_2$-MeOH and NH$_3$-H$_2$O) were performed.

From SEM micrographs of the CZT(S,Se) surface after treatment with different etchants (see Fig. 4) we found that the Cu$_2$ZnSn(S,Se)$_4$ crystal surfaces are rough and covered with microparticles after etching with HCl. We were unable to determine the elemental composition of these microparticles by EDX due to their very small size. Etching with NH$_3$-H$_2$O results in relatively flat surfaces with some structure. The surfaces of KCN-etched crystals seem to be quite smooth without any precipitates. After
etching with Br₂-MeOH the surfaces of CZT(S,Se) monograins were covered by crater-like areas with microparticles on their edges. Additional etching of the Br₂-MeOH treated powders with KCN removes these precipitates and leads to clean crystal surfaces.

Figure 4 SEM micrographs of as-grown Cu₂ZnSnSe₄ monograin powder surfaces (a) and after treatment with b) HCl, c) NH₄OH, d) KCN, e) Br₂-MeOH, and f) Br₂-MeOH+KCN etchants.

A polarographic analysis (see Table 2) of the leaching solutions indicates that Sn and chalcogen are removed preferably by HCl-etching probably due to complexation of tin as [SnCl₄]⁻. The KCN etching is known as a process to preferably remove Cu-Se binary phases [8]. In our experiments with KCN treatment we also found Sn in the leaching solutions of the Cu₂ZnSn(S,Se)₄ monograin materials. Ammonia solution removes selectively Cu and chalcogen in an approximate ratio 1:2.

<table>
<thead>
<tr>
<th>Etchant</th>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCN</td>
<td>1.0</td>
<td>0.5</td>
<td>0.36</td>
<td>1.5</td>
</tr>
<tr>
<td>HCl</td>
<td>1.0</td>
<td>0.11</td>
<td>5.8</td>
<td>6.5</td>
</tr>
<tr>
<td>NH₄OH</td>
<td>1.0</td>
<td>0.17</td>
<td>no</td>
<td>2.2</td>
</tr>
<tr>
<td>Br₂-MeOH</td>
<td>1.0</td>
<td>0.83</td>
<td>0.66</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 2 Composition of elements in leaching solution as determined polarographically.

Figure 5 shows XPS spectra of the as-grown and Br₂-MeOH-etched Cu₂ZnSn(S,Se)₄ monograin surfaces. We can see that Br₂-MeOH-etching decreases the intensity of Cu2p, CuLMM peaks and increases the intensity of the Sn and O1s peaks. Zn2p and ZnLMM peaks are almost undetectable after etching with Br₂-MeOH. Changes in the monograin surface composition after Br₂-MeOH-etching can be understood using the Zn 2p, Cu 2p, Sn 3d, O1s, S 2p and the Se 3d core levels. The relative atomic concentrations of zinc, copper, tin and selenium were determined from integrated peak areas of high-resolution XPS core level spectra. The S 2p peak area was determined by core level curve-fitting procedures since they overlap with the Se 3p core level. The composition of the Cu₂ZnSn(S,Se)₄ monograin surface after Br₂-MeOH was analysed by XPS as Cu: Zn : Sn : S-Se : O = 1.23 : 1.16 : 37.05 : 12.83 : 47.72 at.%. Comparison of the XPS spectra of as-grown and Br₂-MeOH-etched samples allows to conclude that Br₂-MeOH-etching mainly removes Cu and Zn as was found also from the polarographic analysis of the leaching solutions.

Figure 5 XPS spectra of the as-grown and Br₂-MeOH etched Cu₂ZnSn(S,Se)₄ monograin surfaces.

Some results of I-V measurements of solar cells made from chemically treated Cu₂ZnSn(S,Se)₄ monograin powders are given in Table 3.

<table>
<thead>
<tr>
<th>Etchant</th>
<th>Vₜₖ, mV</th>
<th>Iₜₖ, mA/cm²</th>
<th>FF,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>330</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Conc. HCl</td>
<td>342</td>
<td>11.5</td>
<td>48</td>
</tr>
<tr>
<td>2M NH₄OH</td>
<td>422</td>
<td>10.5</td>
<td>44</td>
</tr>
<tr>
<td>10% KCN</td>
<td>490</td>
<td>13.5</td>
<td>49</td>
</tr>
<tr>
<td>1% Br₂-MeOH</td>
<td>563</td>
<td>8.5</td>
<td>54</td>
</tr>
<tr>
<td>1% Br₂-MeOH</td>
<td>575</td>
<td>13.75</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 3 Performance characteristics of Cu₂ZnSn(S,Se)₄ monograin layer solar cells made from etched absorber crystals.

It can be seen that the parameters of monograin layer solar cells improves by etching the powder crystals. Cells made from materials treated in combined etching procedures showed the highest values of Vₜₖ, Iₜₖ and fill
factor. The here achieved efficiencies of the best solar cells were in the order of 4%. Higher efficiencies were obtained after further optimized surface treatments.

CONCLUSIONS

We found that the surface and the bulk compositions of as-grown CZT(S,Se) monograin powder crystals were not identical. The analysis of leaching solutions showed that Sn and chalcogen are removed preferably by HCl etching. Leaching solutions after KCN-etching contain Cu, Sn and chalcogen. Aqueous ammonia solutions do not remove Sn from CZT(S,Se) surface. The Raman spectra of the surface after etching with HCl and KCN are similar to the spectrum of the bulk material. From XPS measurements we found that etching with 1% Br2-MeOH results in Sn-rich material surfaces. The combination of chemical treatments before the deposition of CdS gave the best Cu2ZnSn(S,Se)4 monograin layer solar cells with efficiencies in the order of 4%.

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Cu$_2$Zn$_{1-x}$Cd$_x$Sn(Se$_{1-y}$S$_y$)$_4$ solid solutions as absorber materials for solar cells

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1 Introduction

Quaternary compounds Cu$_2$ZnSnS$_4$, Cu$_2$ZnSnSe$_4$, and Cu$_2$CdSnS$_4$ are new interesting semiconductor materials for absorber layer in thin film solar cells. The most of their elemental constituents are abundant on the earth’s crust and they have semiconductor properties such as p-type conductivity, direct band gaps and high absorption coefficients (> 10$^4$ cm$^{-1}$) [1]. Almost all investigations on solar cells are based on Cu$_2$ZnSnS$_4$ absorbers. The overview of progress in Cu$_2$ZnSnS$_4$ thin film solar cell development has been given by Katagiri [2]. The highest conversion efficiency of Cu$_2$ZnSnS$_4$ solar cells is till now 5.74% [3]. The methods for thin film production such as sputtering and PVD in the case of quaternary materials lead to inhomogeneous composition of layers [4, 5]. As a rule, monograin growth in molten fluxes results in homogeneous material. In our previous report [6], we showed, that Cu$_2$ZnSnSe$_4$ monograin powders with tailored chemical composition could be prepared by isothermal recrystallization of initial binary compounds in molten fluxes. Cu$_2$ZnSnSe$_4$ powder crystals grown in molten KI had tetragonal shape with rounded grain edges. By XRD analysis the powders had stannite structure (space group I42m).

The ZnO/CdS/Cu$_2$ZnSnS$_4$/graphite monolayer solar cells had low fill factors (25–30) and the barrier height of their p–n junction was around 250 mV [6]. The present research was performed with the aim to gain better understanding of the reasons of low efficiency of Cu$_2$ZnSnS$_4$ monolayer solar cells by comparing the properties of absorber materials on the base of solid solutions Cu$_2$Zn$_{1-x}$Cd$_x$Sn(Se$_{1-y}$S$_y$)$_4$. Therefore Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ monograin materials with $x$ = 0, 0.2, 0.33, 0.5 and Cu$_2$Zn$_{1-x}$Cd$_x$SnSe$_4$ powders with $x$ = 1, 0.5, 0 were prepared and studied.

2 Experimental

2.1 Powder preparation

The Cu$_2$Zn$_{1-x}$Cd$_x$Sn(Se$_{1-y}$S$_y$)$_4$ powder materials were synthesized from CuSe(S), ZnSe(S), CdSe(S) and SnSe(S) precursors in molten KI. The binary compounds in stoichiometric relation of Cu$_2$ZnCdSnSe$_4$ and KI were mixed and ground in planetary ball mill. The mixture was degassed and sealed into quartz ampoules. The recrystallization temperature was 1000 K. Crystallite size was controlled by the temperature and duration of the recrystallization process. Crystals
of the synthesized powders were released from flux by washing with deionized water. More details about this process can be found elsewhere [8]. Polycrystalline Cu$_2$SnS$_2$ was synthesized by melting of CuSe and SnSe in a vacuum ampoule at 1170 K.

2.2 Characterization The bulk composition of powders was determined by energy dispersive spectroscopy (EDS). The shape and surface morphology of crystals were studied with the help of high-resolution scanning electron microscope (SEM) Zeiss ULTRA 55. Photoluminescence (PL) was excited by a He–Cd laser with the wavelength of 441 nm. Powder samples were mounted inside a closed cycle He cryostat (T = 9 – 300 K). The PL spectra were recorded with a computer-controlled SPM-2 grating monochromator (f = 0.4 m). The signal was detected with an InGaAs detector using the conventional lock-in technique. The room temperature (RT) micro-Raman spectra were recorded by using a Horiba LabRam HR high-resolution spectrometer equipped with a multichannel detection system in the backscattering configuration. The incident laser light with the wavelength of 532 nm was focused on samples within a spot of 1 μm in diameter and the spectral resolution of the spectrometer was about 0.5 cm$^{-1}$.

2.3 Solar cell preparation Narrow granometric fractions of the grown powders were used as absorber material in MGL solar cell structures: graphite/Cu$_{2}$Zn$_{1-x}$Cd$_{x}$Sn(S$_{y}$Se$_{1-y}$)$_{2}$/CdS/ZnO [6, 7]. Cu$_{2}$Zn$_{1-x}$Cd$_{x}$Sn(S$_{y}$Se$_{1-y}$)$_{2}$ powder crystals were covered with CdS thin layer by chemical bath deposition. For MGL formation a monolayer of sieved, nearly unsize grains was bound into a thin layer of epoxy resin, so that the contamination of upper surfaces of crystals with epoxy was avoided. After polymerization of epoxy, ZnO window layer was deposited onto front side of MGL by RF-sputtering. Solar cell structures were completed by vacuum evaporation of 1–2 μm thick In grid contacts onto the ZnO window layer. After applying the structures on glass substrates, the back contact area of crystals covered with epoxy was opened by etching epoxy with H$_2$SO$_4$ followed by an additional abrasive treatment. The back contact was made using graphite paste.

3 Results and discussion

3.1 Powder preparation and characterization Cu$_{2}$Zn$_{1-x}$Cd$_{x}$SnS$_{2}$ materials were prepared with x = 0, 0.2, 0.33, 0.5 and Cu$_{2}$Zn$_{1-x}$Cd$_{x}$Sn(S$_{y}$Se$_{1-y}$)$_{2}$ powders with y = 1, 0.5, 0. EDS scanning over polished individual powder crystals showed homogeneous distribution of constituent elements.

The ratio of Cu to other metals Cu/Zn(Cd) + Sn was 0.85–0.9, Zn/Sn = 1.04 and Se/metal ratio ≥ 1. PL spectra of pure Cu$_{2}$ZnSnS$_{2}$ (x = 0) and Cu$_{2}$ZnSnS$_{2}$ (y = 1) are presented in Fig. 1. The PL spectrum of Cu$_{2}$ZnSnS$_{2}$ (see Fig. 1) is similar to that one described by Tanaka et al. [9]. They attributed the detected broad PL band between 1.1–1.45 eV to donor–acceptor pair recombination. The asymmetrical shape of this band and our temperature and excitation power density dependant measurements of this band showed that the PL band might also originate from band-to-tail (BT) recombination as it was observed in ternaries [10]. A blue shift of the PL band of magnitude about 15 meV per decade with excitation power density was detected while in the case of DA pair recombination the shift is usually smaller. Details of these measurements will be published elsewhere. The PL spectrum of Cu$_{2}$ZnSnS$_{2}$ shows one nearly symmetrical band with the band maximum at 0.85 eV. The peak position $h\nu_{\text{max}}$ (see Fig. 2) and the full width at half maximum (FWHM) of the band shifted with increasing Cd content in Cu$_{2}$Zn$_{1-x}$Cd$_{x}$SnS$_{2}$ linearly to lower energy side: from $h\nu_{\text{max}} = 0.85 \text{ eV} \ (x = 0)$ to 0.77 eV (x = 0.5) and from FWHM = 0.09 eV (x = 0) to 0.078 eV (x = 0.5), correspondingly. By Matsushita et al. [11] the band gap value of Cu$_{2}$ZnSnS$_{2}$ is 1.44 eV and observed PL emission at 0.85 eV cannot originate from this compound. We tried to identify the possible source of this band by Raman measurements. RT Raman spectra of Cu$_{2}$Zn$_{1-x}$Cd$_{x}$SnS$_{2}$ revealed two main peaks at 196 cm$^{-1}$ and 173 cm$^{-1}$ (see Fig. 3), which positions did not change noticeably with x, and a third, less intensive peak with varying peak position in the region of 231–253 cm$^{-1}$. In this region there were peaks in all Raman spectra of Cu$_{2}$Zn$_{1-x}$Cd$_{x}$SnS$_{2}$ materials. From initial binary compounds, SnSe does not have Raman peaks.
in this region, but ZnSe has a peak at 253 cm\(^{-1}\) and CuSe at 260 cm\(^{-1}\).

Cu\(_2\)SnSe\(_3\) is the most probable ternary compound in this system. In Cu\(_2\)SnSe\(_3\) spectra there are also Raman peaks in the above-mentioned region (see Fig. 4). At the moment the attribution of the Raman peaks in the region of 231–253 cm\(^{-1}\) remains questionable and Raman spectra do not give base for unambiguous identification of the bright PL emission at 0.85 eV. The PL spectrum of Cu\(_2\)SnSe\(_3\) showed one asymmetrical band at 1.33 eV and so excluded this compound also from the list of probable source of 0.85 eV PL band. The Raman spectra of Cu\(_2\)SnS\(_2\) showed the most intensive peak at 338 cm\(^{-1}\) and the other peaks at 287 cm\(^{-1}\) and 368 cm\(^{-1}\) (see Fig. 4) that are close to the values found in [12].

3.2 Solar cell characterization Quantum efficiency (QE) curves of solar cells on the base of Cd containing Cu\(_2\)Zn\(_{1-x}\)Cd\(_x\)SnSe\(_4\) showed a shift to the longer wavelengths with increasing Cd content as it is seen in Fig. 5. The highest value of open circuit voltage (\(V_{OC} = 422\) mV) was achieved with Cu\(_2\)Zn\(_{1-x}\)Cd\(_x\)SnSe\(_4\) material with \(x = 0.2\) (see Fig. 6). By Matsushita et al. the band gap values of Cu\(_2\)ZnSnSe\(_4\) and Cu\(_2\)CdSnSe\(_4\) are 1.44 eV and 0.96 eV correspondingly [11]. The temperature dependence of \(V_{OC}\) gave the barrier height of the junction \(\Phi = 758\) meV. This value is much lower than that one possible with an absorber material with the band gap value being a little bit lower than 1.44 eV, as it should be for Cu\(_2\)Zn\(_{1-x}\)Cd\(_x\)SnSe\(_4\) with \(x = 0.2\). PL spectra of Cu\(_2\)ZnSnSe\(_4\) (see Fig. 2) showed a band with the band maximum at 0.85 eV. The measured PL spectrum of used SnSe showed the PL band maximum at 0.67 eV. At the same time the QE curves showed a regular shift with increasing Cd content (with increasing \(x\)) to the longer wavelength region and with increasing sulphur content (with increasing \(y\)) to the shorter wavelength side (see Fig. 5). Considering all these facts we assume that a narrow band gap compound or a solid solution formed on the surface of Cu\(_2\)Zn\(_{1-x}\)Cd\(_x\)SnSe\(_4\) limits the efficient work of solar cells at the moment. It is also possible that Cu\(_2\)ZnSnSe\(_4\) itself has smaller than given in [11] band gap value. Further investigations should clarify the origin of the PL band of Cu\(_2\)ZnSnSe\(_4\) at 0.85 eV.

4 Conclusions Cu\(_2\)Zn\(_{1-x}\)Cd\(_x\)SnSe\(_4\) monograin powders were synthesized and characterised by PL and Raman measurements. The results of PL and Raman measurements combined with solar cell parameters enabled to conclude that a narrow band gap compound or a solid solution formed on the surface of Cu\(_2\)Zn\(_{1-x}\)Cd\(_x\)SnSe\(_4\) limits the efficient work of solar cells or Cu\(_2\)ZnSnSe\(_4\) itself has lower than 1.44 eV bandgap.
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Sulfur-containing Cu₂ZnSnSe₄ monograin powders for solar cells


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Cu₂ZnSn(Se₁₋ₓSₓ)₄ monograin powders with different x values were prepared from binary compounds in the liquid phase of flux material (KI) in evacuated quartz ampoules at 1000 K. Narrow granometric fractions of the grown powders were used as absorber materials in monograin layer solar cells: graphite/Cu₂ZnSn(Se₁₋ₓSₓ)₄/EDS/ZnO. The values of Voc increased with increase in content of sulfur in the absorber from 283 mV for x = 0 to 660 mV for x = 0.85.

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1. Introduction

The Cu₂-Ⅱ-Ⅳ-Ⅴ₄ quaternary compounds Cu₂ZnSnSe₄ (CTZS) and Cu₂ZnSnS₄ (CTZS) are novel absorber materials for solar cells, alternatives to CuIn(Se,S)₂ due to their p-type conductivity, high absorption coefficients (> 10⁶ cm⁻¹) and direct band gap close to the optimum value for terrestrial solar energy conversion. Several research groups have found that Cu₂ZnSnSe₄ has band gap energies from 1.44 to 1.56 eV [1-4] and Cu₂ZnSnS₄ from 1.45 to 1.51 eV [5,6]. At present, to our knowledge the best conversion efficiency of the CTZS thin film solar cells reported has been 6.77%, achieved using a three-source co-sputtering system for metal film deposition followed by annealing in sulphur containing atmosphere [7].

In our previous reports [8,9] we showed that monograin powders of Cu₂ZnSnSe₄ and Cu₂ZnSn(Se₁₋ₓSₓ)₄ solid solutions with x = 0.5 can be prepared by isothermal crystallization from initial binary compound precursors in molten potassium iodide. The high temperature (970-1000 K) synthesis and homogenization in molten phase of flux material resulted in uniform composition of powder crystals of these complex multicomponent compounds. Cu₂ZnSnSe₄ powder crystals grown in molten KI have stannite structure (space group \( \text{A2\text{m}} \)). The first monograin layer solar cells with the layer structure of ZnO/CdS/Cu₂ZnSnSe₄/graphite had low values of solar cell parameters and their conversion efficiency was 1.8% [8]. The following research on solid solutions of Cu₂Zn₁₋ₓCdₓSn₄(Se₁₋ₓSₓ)₄ [9] was performed with the aim to gain better understanding of the reasons for the low efficiency of the Cu₂ZnSnSe₄ monograin layer solar cells. The results of PL and Raman measurements combined with a detailed analysis of the solar cell parameters enabled us to conclude that Cu₂ZnSnSe₄ actually has a band gap much lower than 1.44 eV as reported by Matsushita et al. [3]. According to the PL results, it is proposed that the band gap energy of CTZS is around 1.02 eV at \( T = 10 \text{K} \) [10]. In the present paper we report further the results of studies on solid solutions of Cu₂ZnSn(Se₁₋ₓSₓ)₄ in the form of monograin powders.

2. Experimental

Cu₂ZnSn(Se₁₋ₓSₓ)₄ (CTZSSE) monograin powders with different x values were synthesized from CuSe(S), ZnSe(S) and SnSe(S) in appropriate relations as precursors for CTZSSE in molten KI. The ground initial substances were sealed into evacuated quartz ampoules and annealed at 1000 K. The processes of formation and growth of semiconductor compound CTZSSE crystals took place in the liquid phase of KI as flux material. The crystal size was controlled by the temperature and duration of the crystallization process. The growth process was stopped by quenching the ampoules in cold water. Crystals of the synthesized powders were released from KI flux by washing with deionized water. Narrow granometric fractions of the grown powders obtained by sieving were used as absorber material in monograin layer (MGL) solar cell structures: graphite/Cu₂ZnSn(Se₁₋ₓSₓ)₄/CdS/ZnO [11].

The bulk composition of powder crystals was determined by energy dispersive X-ray spectroscopy (EDS). The shape and surface morphology of crystals were studied with the help of a
3. Results

3.1. Composition and structure

Cu₂ZnSn(Se₁₋ₓSₓ)₄ materials were prepared with x = 0, 0.25, 0.45, 0.75, 0.85 and 1. The ratio of Cu to other metals (Cu_{Zn+Sn}) was 0.925 and the Zn to Sn ratio was 1.0.

Monograin growth in molten KI resulted in homogeneous composition of the Cu₂ZnSn(Se₁₋ₓSₓ)₄ powders in the region of sulfur content x = 0 - 0.85. This was concluded from analyzing XRD data and EDS scans over polished individual CZTS/S (0 ≤ x ≤ 0.85) powder crystals. For x = 1, some synthesized powder crystals consisted of several phases, as can be seen from the SEM photos and from the distribution of constituent elements (Fig. 1).

Here, the results of EDS analysis also indicate the presence of separate phases besides the Cu₂ZnSnS₄ phase: Cu₂SnS₃ ([Cu_{Zn} = 32.9%, Sn_{Zn} = 17.2%, Sn_{Cu} = 49.8%], SnS (Sn_{Sn} = 51.6%, Sn_{Sn} = 48.45%) and ZnS (Zn_{Sn} = -50%, Sn_{Sn} = 50%). The results of XRD investigations confirm that in addition to the dominating CZTS phase, powders contain SnS in small quantities (Fig. 2).

The XRD pattern did not confirm the existence of Cu₂SnS₃ and ZnS. It means that the concentrations of Cu₂SnS₃ and ZnS are lower than the sensitivity of the XRD analysis (± 2%) or the distribution of these phases is inhomogeneous in the synthesized material. One possible explanation for the existence of different phases in synthesized pure CZTS (x = 1) is that the homogeneity range of Cu₂ZnSnS₄ is much narrower than that of Cu₂ZnSnSe₄, resulting therefore in a higher probability for the formation of other phases during the synthesis and the growth process of the Cu₂ZnSnS₄ (x = 1) monograin powders of the same initial composition as the other Cu₂ZnSn(Se₁₋ₓSₓ)₄ materials (0 ≤ x ≤ 0.85).

X-ray diffraction patterns of the Cu₂ZnSn(Se₁₋ₓSₓ)₄ monograin powders with different Se/S concentration ratios are shown in Fig. 3.

The diffraction peaks were identified as belonging to the Cu₂ZnSnS₄ compound (x = 1) with kesterite structure (space group I4/m) and to the Cu₂ZnSnSe₄ (x = 0) with stannite structure (space group I4/m). The reflection Miller indexes were assigned according to Matsushita et al. [3]. The ratio of reflections intensities was in correspondence to those measured by Oleksyuk et al. [12]. An exchange of Se with S shifts the peak positions from the stannite structure to the kesterite structure. At a ratio of S to Se of 85:15 mole%, the XRD pattern shows a splitting of peaks, which could be a sign of existence of two crystal phases at the same time. More detailed investigations are necessary to confirm these results.

**Fig. 1.** EDS scanning over polished individual Cu₂ZnSn(Se₁₋ₓSₓ)₄ powder crystal.

**Fig. 2.** X-ray diffraction pattern of the Cu₂ZnSnS₄ monograin powder.

**Fig. 3.** XRD patterns of Cu₂ZnSn(Se₁₋ₓSₓ)₄ monograin powders with different x values.
3.2 Solar cell characterization

The prepared monograin powders were used as absorber materials in monograin layer (ML) solar cell structures: ZnO/Cds/CZTS/Se/graphite, where every crystal works as an individual solar cell. All the as-grown powders were post-heat-treated for improving the crystal surface structure. Solar cells showed uniform distribution of solar cell parameters over the whole working area of the 1 × 1.5 cm² samples (Fig. 4). Open circuit voltages of Cu₂ZnSn (SₓSe₁₋ₓ)₄ monograin layer solar cells increased with increase in sulfur content in the monograin powders, from 283 mV for x=0–680 mV for x=0.85 (Fig. 5). The pure Cu₂ZnSnSe₄ absorber material resulted in lower Voc (541 mV) probably due to secondary phases being formed. An increase of the open circuit voltage values points to a widening of the band gap of Cu₂ZnSn(SₓSe₁₋ₓ)₄ with increase in S concentration. Solar cell structures based on monograin powders with a S/Se concentration ratio of 85 mole% sulfur to 15 mole% selenium yielded the highest values of the open circuit voltage. The Cu₂ZnSn(SₓSe₁₋ₓ)₄ solid solution with 75 mole% sulfur and 25 mole% selenium gave the best solar cell with parameters: Voc=622 mV, Isc=15.87 mA/cm², FF=60%, P=95%.

The normalized quantum efficiency (QE) spectra of solar cells on the base of Cu₂ZnSn(SₓSe₁₋ₓ)₄ monograin powders show the shift of the absorption edge to shorter wavelengths as well a change in the short wavelengths response with increase in S content in the absorber material as shown in Fig. 6.

Temperature-dependent open circuit voltage measurements were performed to determine the barrier height of the p–n junction (qΦB) (Fig. 7). The barrier height of the solar cells increases as expected with increase in the S content in Cu₂ZnSn(SₓSe₁₋ₓ)₄ monograin powders.

As expected from the increase in open circuit voltage values for increasing sulfur content, the quantum efficiency spectra shift to shorter wavelengths. This increase of the barrier height of solar cells with increase in S content in the absorber material gives us a basis to believe that the Cu₂ZnSnSe₄ band gap energy value (in literature 1.44–1.56 eV) should be much lower than the Cu₂ZnSnS₄ band gap energy: 1.45–1.51 eV.

4. Conclusions

Monograin powder technology enables us to grow Cu₂ZnSn(SₓSe₁₋ₓ)₄ materials with homogeneous composition usable for monograin layer solar cells. The increasing sulfur content in Cu₂ZnSnSe₄ monograin powder absorber materials improves the values of open circuit voltages of MGL solar cells and shifts the QE curves to the higher energy side. Solar cell structures based on monograin powders with a S/Se concentration ratio of 85 mole% sulfur to 15 mole% selenium yielded the highest values of open circuit voltage: 600 mV.

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