Doctoral Thesis

Solution-processed kesterite absorbers for thin film solar cells

Author[s]:
Sutter-Fella, Carolin M.

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Solution-processed kesterite absorbers for thin film solar cells

A thesis submitted to attain the degree of
DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

presented by
CAROLIN MARIA SUTTER-FELLA
Dipl.-Phys. Univ.
Friedrich-Alexander-Universität Erlangen-Nürnberg
born on 29.11.1982
citizen of Germany

accepted on the recommendation of
Prof. Dr. A. N. Tiwari, examiner
Prof. Dr. R. Nesper, co-examiner
Dr. P. J. Dale, co-examiner
Dr. Y. E. Romanyuk, co-examiner

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Abstract

The direct conversion of sunlight into electricity by photovoltaic (PV) devices as a sustainable and clean energy source has a very high potential to cover a big share of the world's electricity demand. Most of the currently installed PV systems are based on crystalline silicon solar cells. However, there exists a large variety of other PV technologies based for example on organic dyes or inorganic materials, such as Cu(In,Ga)Se$_2$ (CIGS), CdTe, amorphous silicon, and CH$_3$NH$_3$PbI$_3$ (perovskite). All mentioned materials belong to the category of thin film solar cells which can be about 100 times thinner than crystalline silicon wafers, to efficiently absorb most of the sun light because of their higher absorption coefficient. The CIGS technology reaches conversion efficiencies above 20 % that are comparable with the market-leading crystalline silicon technology. However, due to the use of non-abundant and costly In and Ga the search for alternative, cheaper and more abundant materials for thin film PV continues.

In this thesis, the alternative chalcogenide material Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe), called kesterite according to its crystal structure, is investigated. This material has attracted enormous research interest in recent years because it consists only of earth-abundant or readily available and non-toxic elements. Recently, CZTSSe solar cells with efficiencies of 12.6 % were reported by IBM employing a non-vacuum deposition process. The main drawback of this approach is the use of highly toxic and explosive hydrazine as solvent. Although non-vacuum solution processes already exhibit low equipment cost, high material utilization and high throughput, the development of simple deposition techniques using only non-toxic chemicals is desirable.

Consequently, the goal of this thesis is to establish a robust non-vacuum process from non-toxic precursor solutions omitting the use of explosive or toxic H$_2$Se or H$_2$S gases. Deposition methods should be simple and potentially scalable to large areas. To address these challenges, two different precursor chemistries are studied: (A) precursor...
solutions containing metal salts and binder material, and (B) precursor solutions with metal salts and thiourea as sulfur source but without organic binder. The precursor is knife- or spin-coated onto the substrate and then crystallized into $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) or $\text{Cu}_2\text{ZnSn(S,Se)}_4$ at temperatures between $\sim 400$-$550^\circ \text{C}$. On the way towards highly efficient CZTSSe cells several challenges have to be overcome: suppression of secondary phase formation during growth of CZTSSe, minimization of recombination losses, controlled doping, avoiding the formation of voids, rough morphology, and poor crystallinity when using non-toxic organic solvents.

To grow kesterite absorbers for the first time in our laboratory, alcohol solvent with metal salts and organic binder material (A) is used, where the binder material helps to adjust the rheology of the precursor solution and to avoid film cracking. The CZTSe formation is kinetically driven and starts with the fast formation of Cu-Se and subsequent incorporation of Sn and Zn. Despite a high surface roughness and a residual carbon-rich layer between the back contact and the absorber, working devices with conversion efficiency up to 4.3 % are demonstrated, which represented at that time (2011) a new approach with one of the highest efficiencies achieved with a non-hydrazine solution precursor. The intermediate carbon-rich layer however, is not desirable for efficient carrier collection and therefore should be avoided.

In order to prevent the formation of the carbon-rich layer, the precursor chemistry is changed to metal salt solutions in dimethyl sulfoxide without binder material, and with thiourea as sulfur source (B). The precursor layer already contains fine-grained CZTS phase with randomly distributed cations and transforms into crystalline CZTS at $\sim 500^\circ \text{C}$. In absence of sulfur it decomposes into CuS, ZnS, Sn$_x$S$_y$, and MoS$_2$. The unambiguous identification and quantification of secondary phases such as ZnSe in CZTSe is very challenging. It is demonstrated that ZnSe can be detected and quantified by the use of synchrotron radiation techniques. This study indicates that plotting the total absorber bulk composition into the ternary $\text{Cu}_2\text{Se} - \text{SnSe}_2 - \text{ZnSe}$ phase diagram can provide a reliable estimate for the presence of ZnSe.

One drawback of non-vacuum solution processing is poor crystallinity, very high surface roughness, high porosity, and the presence of microscopic voids in sintered layers. Two different sintering approaches are explored to circumvent this obstacle. Large grains can be obtained when the precursor composition is initially Sn-rich (i.e. Zn/Sn < 1) and if the annealing atmosphere does not suppress Sn loss. A possible mechanism responsible for massive grain growth involves the mobile and low melting element Sn.
which acts as a flux for example along the grain boundaries while moving out of the CZTS layer. The solar cell performance of such devices is however, limited by poor carrier collection.

To overcome low crystallinity and poor carrier collection, a novel approach for controlled grain growth is presented, where a NaF top-coating of the precursor is applied prior to the selenization. The proposed fluxing mechanism involves three steps: i) enhanced chemisorption of Se molecules, ii) formation of a liquid or quasi-liquid Na$_2$Se$_x$ phase, and iii) crystallization of solid CZTSSe. Besides the massively improved sintering of kesterite layers, the electronic properties are modified by the presence of Na depending on its concentration and location in the absorber. A decrease in the defect activation energy upon Na doping could explain open-circuit voltage and fill factor improvements in solar cells. There are several ways in which Na could influence the electronic properties of CZTSSe. It can either accumulate at grain boundaries or in the CZTSSe bulk to passivate recombination centers, as well as donors and deep defects.

A highest conversion efficiency of 6.04 % is achieved through this thesis work. The device performance is limited by different recombination mechanisms. One of them is the interface recombination, which seems to be a major obstacle and therefore, future efforts should be directed at the elimination of the buffer/absorber interface recombination. Controlling the surface composition by the annealing atmosphere or tailoring the conduction band for example by the surface Sn content could improve the electron transport across the pn-junction. To avoid the surface kesterite decomposition, annealing in a closed system, for example in a graphite box or in a rapid thermal annealing furnace, should be beneficial. Furthermore, intentional Na impurity doping can be directly applied via the precursor solution to remove or introduce electronically active defect states. These developments should lead to further efficiency improvements that would ultimately translate into low-cost, non-vacuum processed kesterite thin film solar cells.
Zusammenfassung (In German)

Die direkte Umwandlung von Sonnenlicht in elektrischen Strom durch Photovoltaik (PV) als eine nachhaltige und saubere Energiequelle hat ein hohes Potential einen grossen Anteil des weltweiten Strombedarfs zu decken. Die Mehrheit der gegenwärtig installierten PV Anlagen basiert auf kristallinen Silizium Solarzellen. Daneben gibt es eine grosse Vielfalt anderer PV Technologien, z.B. aus organischen Farbstoffen oder aus anorganischen Materialien wie z.B. Cu(In,Ga)Se\textsubscript{2} (CIGS), CdTe, amorphes Silizium und CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} (Perowskit). Alle genannten Materialien gehören zur Kategorie der Dünnfilm Solarzellen, die ungefähr 100 mal dünner als kristalline Silizium Wafer sind, und wegen ihres hohen Absorptionskoeffizienten trotzdem einen Grossteil des Sonnenlichts absorbieren können. Die CIGS Technologie erreicht Wirkungsgrade von über 20 % und ist damit vergleichbar mit der marktbeherrschenden kristallinen Silizium Technologie. Wegen der Verwendung von seltenen und teuren Elementen wie In und Ga geht die Suche nach alternativen, günstigeren und weniger seltenen Materialien für Dünnfilm PV weiter.

Das Ziel dieser Arbeit ist es deshalb, einen robusten vakuumfreien Prozess, basierend auf ungiftigen Präkursorscheinen unter Vermeidung von explosiven oder toxischen Gasen wie $\text{H}_2\text{Se}$ oder $\text{H}_2\text{S}$, zu entwickeln. Die Beschichtungsverfahren sollten einfach und potentiell auf große Flächen skalierbar sein. Um diese Herausforderungen anzugehen, werden zwei verschiedene Präkursorchemien untersucht: Chemische Präkursorscheine mit (A) Metallsalzen und Bindematerial, und (B) Metallsalzen und Thiokarbalsstoff als Schwefellieferant aber ohne organisches Bindematerial. Der chemische Präkursor wird mittels Rakel- oder Schleuderbeschichtung auf dem Substrat aufgebracht und dann bei Temperaturen zwischen $\sim 400-550 \, ^\circ\text{C}$ zu $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) oder $\text{Cu}_2\text{ZnSn(S,Se)}_4$ (CZTSSe) gesintert. Um hocheffiziente CZTSSe Solarzellen herzustellen, müssen einige Herausforderungen überwunden werden: Unterdrückung sekundärer Phasen während des Wachstums von CZTSSe, Verminderung von Rekombinationsverlusten, kontrolliertes Dotieren, Verhinderung der Hohlraumbildung, rauher Kristallmorphologie und schlechter Kristallinität, wenn ungiftige organische Lösungsmittel verwendet werden.


Um die Bildung dieser Schicht zu vermeiden, wird eine Präkursorscheiche basierend auf metallsalzhaltigen Lösungen in Dimethylsulfoxid ohne Bindematerial, und mit Thiokarbalsstoff als Schwefellieferant, benutzt (B). Die Präkursorscheiche enthält bereits feinkörniges CZTS mit zufälliger Kationenverteilung, welche sich bei $\sim 500 \, ^\circ\text{C}$ zu CZTS auskristallisiert. In Abwesenheit von Schwefel zersetzt sich die Schicht in CuS, ZnS, $\text{Sn}_x\text{S}_y$ und MoS$_2$. Die eindeutige Identifizierung und Quantifizierung von


Die höchste erzielte Umwandlungseffizienz, die während dieser Arbeit erreicht wurde, ist 6.04 %. Die Leistung der Solarzelle ist limitiert durch verschiedene Rekombinationsmechanismen. Einer davon ist die Grenzflächenrekombination, welche ein wesentliches Hindernis darstellt. Zukünftige Bemühungen sollten deshalb darauf gerichtet werden Rekombination an der Puffer/Absorber Grenzfläche zu unterdrücken. Die Beeinflussung der Oberflächenkomposition durch die Sinteratmosphäre oder An-
List of abbreviations

APT  Atom probe tomography
AS   Admittance spectroscopy
BSG  Borosilicate glass
CBD  Chemical bath deposition
CIGS Cu(In,Ga)Se₂
CZTS Cu₂ZnSnSe₄
CZTSe Cu₂ZnSnSe₄
CZTSSe Cu₂ZnSn(S,Se)₄
CTS  Cu₂SnS₃
CTSe Cu₂SnSe₃
Eₐ   Activation energy for the dominant recombination mechanism
Eₑ   Conduction band energy
E₉   Fermi level energy
Eₑ   Band gap energy
Eₜ   Activation energy for the trap level
Eᵥ   Valence band energy
EBIC Electron beam induced current
EC   Ethyl cellulose
EDX  Energy dispersive X-ray spectroscopy
EQE  External quantum efficiency
η    Efficiency
EtOH Ethanol
FF   Fill factor
FIB  Focused ion beam
FWHM  Full width at half maximum
GB   Grain boundary
ICP-MS Inductively coupled plasma mass spectrometry
i-ZnO  Intrinsic ZnO
J_{sc}  Short circuit current density
JV   Current density voltage
PL  Photoluminescence
ProD  1,2-propanediol
PV  Photovoltaic
SCR  Space charge region
SEM  Scanning electron microscopy
SIMS Secondary ion mass spectrometry
SLG  Soda lime glass (float glass)
TCO  Transparent conductive oxide
T_{sub}  Substrate temperature
TR-PL Time resolved photoluminescence
T-JV Temperature dependent current density voltage
UPS Ultraviolet photoelectron spectroscopy
UV  Ultraviolet
V_{oc}  Open-circuit voltage
XANES X-ray absorption near edge structure
XPS  X-ray photoelectron spectroscopy
XRD  X-ray diffraction
XRF  X-ray fluorescence
Chapter 1

Introduction

1.1 Photovoltaics as a renewable energy source

The photovoltaic (PV) technology, which is the direct conversion of sunlight into electricity, has a very high potential to cover the world's electricity demand. Only 90 minutes of sunlight arriving at the Earth are enough to generate the whole world's energy demand for one year [1]. Still, PV electricity generation contributes only about 0.5 % to the world's electricity consumption [2]. The obstacle for further expansion of the PV share is related to cost when compared to conventional carbon-based technologies. Over 80 % of the installed PV is based on the silicon technology [3]. Silicon-based devices show very stable performance with record efficiencies of 20 and 25 % reported for multicrystalline and large crystalline laboratory-scale cells, respectively [4]. From the physics point of view, silicon is not the first choice as absorber material in solar cells because of its indirect band gap, requiring a thick layer (\( \sim 200 \mu m \)) for absorption of a major part of the incident solar irradiation. Additionally, the nature of the grain boundaries in silicon-based devices demands very high purity of the crystalline material [5] which leads in turn to higher production costs.

1.2 Thin film chalcogenide solar cells

Thin film PV technologies rely on direct band gap (\( E_g \)) semiconductors with high absorption coefficient, where the absorber layer thickness can be reduced to about 2 \( \mu m \),
making them suitable for the application in flexible solar cells on nonrigid substrates as illustrated in Figure 1.1a and thus enabling high throughput roll-to-roll processing. Furthermore, the grain boundaries are more benign, reducing the need for high crystal quality.

Chalcogenide based thin film solar cells are highly attractive for power generation reaching grid parity while at the same time being very energy efficient in manufacturing. Lab cell efficiencies as high as 20.8 % and 19.6 % are reported for the most efficient technologies Cu(In,Ga)Se$_2$ (CIGS) and CdTe, respectively [4,6]. Both materials contain elements which are either toxic (Cd) or rare (In and Te) in the Earth crust. Those two issues could ultimately limit the production capacity because of material shortage or restrictions on heavy metals (Cd).

![Fig. 1.1: a) Flexible CIGS thin film solar module from Flisom company. b) Schematic of a solar cell stack with Mo back contact, chalcogen absorber, CdS buffer and ZnO window layer.](image)

The requirements for thin film semiconductor absorber materials are: $i$) direct band gap between 1 - 1.5 eV and high absorption coefficient $\alpha > 10^4$ cm$^{-1}$, $ii$) composed of abundant and non-toxic elements, $iii$) suitable defect properties and $iv$) high device performance. The emerging compound kesterite - Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) - consisting of earth abundant, and lower priced materials than the reported CIGS system has attracted a lot of research interest in the last years. Up to date the highest conversion efficiency of 12.6 % has been achieved for CZTSSe deposited by a non-vacuum process [7].

The typical device stack of a kesterite thin film solar cell is adapted from the efficient CIGS heterojunction device and is depicted in Figure 1.1b. Incident light enters from the
n-type ZnO semiconductor into the p-type CZTSSe absorber, where photons of energy $h\nu > E_g$ can be absorbed by generating electron-hole pairs. The n-type CdS buffer layer together with the p-type CZTSSe form a pn-heterojunction where the electron-hole pairs can be separated by the built-in electric field and transported to the respective contacts. Usually a very thin CdS layer as well as a thin intrinsic ZnO layer are used as buffers between the CZTSSe absorber and the wide band gap Aluminum doped ZnO front contact. The role of the intrinsic ZnO is to cover pinholes in the CdS layer to avoid leakage currents along the pn-junction. Mo is used as back contact. A very thin MoS(e)$_2$ layer provides a quasi ohmic contact between Mo and the CZTSSe absorber.

### 1.3 Kesterite based solar cells

The optoelectronic properties of Cu$_2$ZnSnS$_4$ (CZTS) were first investigated by Ito et al. [8]. They reported the growth of 112 oriented polycrystalline stannite CZTS films with p-type conductivity, absorption coefficient $> 10^4$ cm$^{-1}$ and a direct optical band gap of 1.45 eV. Consequently, it was recognized to be a suitable material for thin film solar cells. A first heterojunction diode showed a $V_{oc}$ of 165 mV [8]. The first solar cell device yielding an efficiency of 0.66 % was reported in 1996 by Katagiri et al. [9]. The challenges encountered with kesterite based solar cells will be discussed in this section and an overview of state of the art efficiencies will be given.

### 1.3.1 Material properties

#### Structural properties

The kesterite crystal structure can be derived from the cubic zinc-blende (sphalerite) structure [10]. Starting with the zinc-blende (group II-VI) one obtains the tetragonal chalcopyrite-structure by cross-substitution and maintaining the octet rule (see Figure 1.2): Zn(II) is substituted by Cu(I) and Ga(III) and by doubling the unit cell. Further substitution of Ga(III) by Zn(II) and Sn(IV) results in the kesterite structure [11]. In the kesterite structure, the Cu-Zn and Cu-Sn atoms alternate on $z = 0$ and $1/2$ and on $z = 1/4$ and $3/4$ positions, respectively [12]. While there was an initial disagreement whether CZTSSe adopts kesterite or stannite structure, it became accepted that it crystallizes in the kesterite structure (space group $I\overline{4}$) [13] which is energetically more favorable [14].
The zinc-blende as the super-lattice of kesterites [10] creates some challenges in structural crystal analysis. Due to very similar lattice constants of ZnS(e), Cu$_2$SnS$_3$ (CTS(e)) and Cu$_2$ZnSnS$_4$ they cannot be easily distinguished by diffraction methods. To illustrate XRD peak overlap in CZTSe and CZTS the reference diffraction patterns of ZnSe, CTSe, ZnS, and CTS are shown in Figure 1.3. The monoclinic CTS was reported to be the most probable polymorph for the ternary phase [15].

One possibility to verify the presence of kesterite is to analyze diffraction peaks at small angles. CZTS(e) exhibits three peaks between 15° < 2θ < 25°. The cubic phase has no peaks at such low angles while the monoclinic phase exhibits either different intensity distributions or other peak positions. Moreover, the presence of the 103 peak at 28.4° and 29.7° can be ascribed unambiguously to kesterite CZTSe and CZTS, respectively. However, the presence of ZnS(e) and CTS(e) cannot be excluded by XRD characterization. Although kesterite is a crystal structure, it is used in the research community as general term to refer to CZTS, CZTSe or CZTSSe and will be also used as such throughout this thesis.
1.3. Kesterite based solar cells

Fig. 1.3: XRD powder reference patterns for kesterite and related secondary phases for a) selenide and b) sulfide chalcogen. PDF-numbers from FIZ Karlsruhe for Cu$_2$ZnSnSe$_4$, monoclinic Cu$_2$SnSe$_3$/Cu$_2$SnS$_3$ and cubic ZnSe / ZnS are 01-070-8930, 01-072-8034 / 01-070-6338 and 37-1463 / 01-077-2100, respectively. The Cu$_2$ZnSnS$_4$ pattern was published by Choubrac et al. [16].

Optoelectronic properties

The band gap of kesterite can be tuned by adjusting the S/(S+Se) ratio. For pure CZTSe the band gap is $\sim$ 1.0 eV and for pure CZTS it is $\sim$ 1.5 eV [17, 18]. Band gap engineering via the Sn/Ge ratio was outlined as a measure to widen the band gap [19]. The absorption coefficient of kesterite above $E_g$ is $> 10^4$ cm$^{-1}$ [20].

Kesterite is a p-type semiconductor with reported hole mobilities between 1.6 - 40 cm$^2$/V/s [21, 22]. The carrier density is in the range of $10^{15}$-$10^{18}$ cm$^{-3}$ [21–24] and was reported to increase with decreasing Se content [24]. The resistivity is in the range of 0.13-0.74 $\Omega$cm [21, 22]. The net doping density has strong implications on the solar cell device. It determines the built-in voltage and the space charge region width and thereby the $V_{oc}$ and the collection length of electrons and holes, respectively [25].

Defects

The knowledge of the defects in a semiconductor used as solar cell absorber material is of the utmost importance for efficiency improvements. Density functional theory calculations can help to access potential defect states, and support the interpretation of experimental findings. Chalcopyrites and kesterites are doped by intrinsic defects. The dominant p-type acceptor in kesterite is the Cu$_{Zn}$ antisite defect and not the copper vacancy ($V_{Cu}$) as in CuInSe$_2$ [26]. The defect formation energy for the Cu$_{Zn}$ defect is the lowest [26, 27] and its position in the band gap is 0.10 eV above the valence band.
maximum (VBM), while the $V_{Cu}$ defect is at 0.02 eV above the VBM [26]. Formation of donor defects is rather unlikely due to the high formation energies or the facile formation of compensating acceptors [26,27].

For highest device efficiencies Cu-poor and Zn-rich composition (i.e. Cu/(Zn+Sn) $\sim$ 0.8-0.9 and Zn/Sn $\sim$ 1.1-1.3) is required [24, 28]. The reasons why devices with non-stoichiometric absorbers yield better efficiencies include the suppression of the detrimental Cu$_2$S(e) phase [24] and deep defects acting as recombination centers [29]. In this respect, the formation of electrically neutral defect pairs or compensating defect pairs plays an important role because they can passivate deep defects in the band gap [27]. The lowest formation energy was reported for the defect complex $[Cu_{Zn}^{-}+Zn_{Cu}^{+}]$ [27] which gives rise to the possibility of Cu and Zn disorder [30]. This disorder in the cation sublattice is reported to reduce the band gap [12, 31]. Due to the manifold possibility of the formation of defect complexes, CZTS is assumed to possess an electrically benign character [27].

### 1.3.2 State of the art methods and efficiencies

The IBM word-record cell (see Table 1.1) was fabricated by pure solution processing. Compared to their previously successful hybrid solution-particle approach where Cu and Sn chalcogenides (S or Se) are dissolved in hydrazine (N$_2$H$_4$) and in-situ formation of Zn-chalcogen-hydrazinate particles [32], they recently used a zinc salt to prevent nanoparticle formation [33]. Annealing of the precursor on a hot plate at 540 °C (elemental sulfur vapor is employed to adjust the band gap) yields a well crystallized 2-3 µm thick Cu$_2$ZnSn(S,Se)$_4$ absorber [32]. The slurry approach, however led to microscale non-uniformities which were bypassed by pure solution processing [7, 33]. The advantage of N$_2$H$_4$ is the ability to dissolve several metal chalcogenides via "dimensional reduction" [34], it easily dissociates from the precursor at low temperatures [34] and cleanly decomposes into nitrogen and hydrogen gas [35]. The drawback of this approach is the highly toxic and explosive solvent hydrazine which prevents the use for large scale production.

The majority of the research groups working on kesterite use a two-step deposition approach, i.e. a low temperature deposition combined with a high temperature annealing step in chalcogen containing atmosphere. Device efficiencies $> 8\%$ grown by different
1.3. Kesterite based solar cells

methods together with the corresponding annealing conditions are listed in Table 1.1.

Table 1.1: Selection of state of the art efficiencies ($\eta > 8\%$) for CZTS(e) solar cell devices with respective growth method and annealing condition reported by laboratories and companies as of February 2014.

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>annealing condition</th>
<th>$\eta$ (%)</th>
<th>Institute</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZTSSe</td>
<td>solution</td>
<td>S</td>
<td>12.6</td>
<td>IBM</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>PVD</td>
<td>selenization after sulfurization</td>
<td>10.8</td>
<td>Solar Frontier</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>solution</td>
<td>Se, RTP</td>
<td>10.3</td>
<td>ZSW</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td>co-sputtering</td>
<td>SnS + S$_2$</td>
<td>9.3</td>
<td>Stanford Univ. / AQT Solar</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>nanoparticles</td>
<td>Se, box quartz ampoules</td>
<td>8.5</td>
<td>DuPont</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>monograin solution</td>
<td>Se, vented graphite enclosure</td>
<td>8.4</td>
<td>Crystalsol</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>solution</td>
<td>S, Se and S+Se</td>
<td>8.1</td>
<td>UCLA</td>
<td>[41]</td>
</tr>
<tr>
<td>CZTSe</td>
<td>DC sputtering</td>
<td>10 % H$_2$Se</td>
<td>9.7</td>
<td>imec</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>co-evaporation</td>
<td>Se</td>
<td>9.15</td>
<td>NREL</td>
<td>[43]</td>
</tr>
<tr>
<td>CZTS</td>
<td>co-sputtering</td>
<td>20 vol% H$_2$S</td>
<td>8.5</td>
<td>Toyota</td>
<td>[4,44]</td>
</tr>
<tr>
<td></td>
<td>evaporation</td>
<td>S</td>
<td>8.4</td>
<td>IBM</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>co-sputtering in H$_2$S</td>
<td>S, box, RTA</td>
<td>7.9</td>
<td>Angst. Solar Center</td>
<td>[46]</td>
</tr>
</tbody>
</table>

1.3.3 Challenges of kesterite devices

Figure 1.4a shows a scanning electron microscope picture of a kesterite device. The corresponding band diagram of a ZnO/CdS/CZTSSe/MoS(e)$_2$/Mo solar cell is illustrated in Figure 1.4b. $E_C$, $E_V$ and $E_F$ are the conduction and valence band and the Fermi level energy, respectively. It is emphasized that both, the CdS/CZTSSe and CZTSSe/MoS(e)$_2$ band alignments are still under discussion. The different recombination mechanisms with respect to position in the solar cell according to Ref. [47] are depicted in Figure 1.4b. Recombination can occur at the CdS/CZTSSe interface (path A), in the space-charge-region (SCR, path B), in the neutral region (path C) and at the back contact (path D).
Fig. 1.4: a) Cross-section scanning electron micrograph of a typical device stack and b) Schematic band diagram of a CZTSSe solar cell. A-D denote four different recombination pathways: A - recombination at the CdS/CZTSSe interface, B - in the space-charge-region, C - in the neutral region and D - at the back contact.

The challenges found in kesterite are of chemical and electrical nature. The multitude of elements in the pentenary Cu$_2$ZnSn(S,Se)$_4$ compound, the relatively small single phase region (yellow area in Figure 1.5) and therefore omnipresent formation of secondary phases, make it very complex to grow single phase material.

Fig. 1.5: Cu$_2$S - ZnS - SnS$_2$ quasi-ternary system adapted from [48]. The pink star represents the Cu$_{1.71}$Zn$_{1.18}$Sn$_{0.99}$S$_4$ phase which was proven to exist by Choubrac et al. [16].

The quasi-ternary system Cu$_2$S - ZnS - SnS$_2$ was investigated by Olekseyuk et al. and
is depicted in Figure 1.5 [48]. According to this phase diagram there in no ternary Sn-Zn-S phase while there are three ternary Cu-Sn-S phases indicated along the Cu$_2$S - SnS$_2$ tie-line. The single phase region of Cu$_2$ZnSnS$_4$ together with the quaternary phase Cu$_2$ZnSn$_3$S$_8$ are drawn into the diagram as well. The single phase region of kesterite seems to be small. According to a literature search done by Siebentritt [49] there is a good match of the overall layer composition and the observed secondary phases when drawn into the ternary diagram. However, a careful single-crystal and powder X-ray analysis of Cu$_{1.71}$Zn$_{1.18}$Sn$_{0.99}$S$_4$ (denoted by $\star$ in Figure 1.5) proved the existence of this non-stoichiometric phase [16], leading to the assumption that the single phase region is larger than expected.

Another inherent kesterite property is its thermal instability. Decomposition starts at temperatures above 400 °C yielding metal binaries as expressed in the following equations [50, 51]:

\[
Cu_2ZnSnS(e)_4 \Leftrightarrow Cu_2S(e) (s) + ZnS(e) (s) + SnS(e) (s) + \frac{1}{2} S(e)_2 (g) \uparrow \quad (1.1)
\]

\[
SnSe(s) \Leftrightarrow SnSe(g) \uparrow . \quad (1.2)
\]

The driving force for the decomposition is the reduction - oxidation process between SnS(e) with Sn in oxidation state (II) and CZTS(e) with Sn in oxidation state (IV) [51]. At the same time the oxidation state of S(e) (-II) is changed to (0) in S(e)$_2$. Therefore, the instability of kesterite is caused by the multivalence of Sn [51]. The sulfur influences the oxidation state of Sn since it acts as an oxidizing agent, so that at high partial S pressure, Sn in oxidation state (IV) will be favored [51].

The frequently observed decomposition reaction at the back contact [45, 52] was explained by Scragg et al. [53] by an instable kesterite/Mo interface:

\[
2 Cu_2ZnSnS(e)_4 + Mo \rightarrow 2 Cu_2S(e) + 2 ZnS(e) + 2 SnS(e) + MoS(e)_2. \quad (1.3)
\]

Decomposition at the back interface due to the formation of MoS$_2$ and consecutive formation of secondary phases (SnS, Cu$_2$S, Cu$_2$SnS$_3$) could enhance recombination [53]. Scragg additionally pointed out that the phase segregation is triggered by a crystal defect that exceeded its solubility limit [53]. As consequence, this chemically instable
interface could be avoided with another back contact material.

The next paragraph focuses on challenges related to electronic properties of kesterites. Despite the promise of Cu₂ZnSn(S,Se)₄ based solar cells there are some concerns why they are not as efficient as the close cousin CIGS [49, 53, 54]. Electronically, kesterite devices are limited by several non-ideal recombination paths [49]. A detailed study on the optoelectronic properties of the IBM record CZTSSe device points out high open-circuit voltage (V_{oc}) losses accompanied by fill factor (FF) losses [54] (please see section 2.3.1 for the explanation of the PV parameters). The V_{oc} loss as primary limiting factor in CZTSSe follows the relationship: V_{oc} < E_g/q - 0.6 V [55] while in high efficiency CIGS the V_{oc} = E_g/q - 0.5 V [56]. The V_{oc} deficit in CZTSSe could be explained by a short minority carrier lifetime of 3.1 ns, an activation energy smaller than the band gap indicating interface recombination [54] or band tailing, mainly due to electrostatic potential fluctuations [55]. The CdS/CZTS interface could be responsible for high recombination losses associated with the V_{oc} deficit due to a cliff-like conduction band offset (i.e. E_C of CdS is lower than E_C of CZTS) [57]. Another evidence for a strong (radiative) recombination center is the position of the photoluminescence maximum ∼ 100 meV below the band gap [49,55]. This low energetic position is either caused by a very high defect density, by the presence of secondary phases or by stannite inclusions [49]. The losses in FF were partly explained by a high R_s connected to a possible back contact barrier [54]. The blocking back contact barrier apparent in increasing R_s at low temperatures was reported by some groups [54,58,59].

1.4 Non-vacuum solution processing

Distinct advantages of non-vacuum based methods compared with vacuum based techniques are the low cost equipment, increased material utilization and high throughput processing. Non-vacuum deposition methods can be divided into the following categories: electrodeposition, Spray pyrolysis and "ink" based approaches. The latter category can be subdivided into solution, nanoparticle or mixed solution-nanoparticle precursors. This thesis deals with solution based approaches that are especially attractive because of their simplicity, i.e. there is no need for nanoparticle pre-synthesis, and precursor intermixing happens on the molecular level.

The steps and critical parameters involved in solution deposition for thin films are il-
1.4. Non-vacuum solution processing

Illustrated in Figure 1.6. After obtaining a stable and homogeneous precursor solution which might require utilization of complexing agents, the solution is deposited for example by printing, knife- or spin-coating. The wet film has to be dried resulting in uniform, crack-free and non-oxidized films to be further annealed at high temperature to induce sintering. Several parameters can influence film cracking during the initial stage of precursor deposition. In this respect, the solution concentration and viscosity which impact on film thickness will influence the "critical film thickness" above which cracking will occur [61]. Tensile stress contributes to a low critical thickness and is generated during solvent removal and organic residues from the precursor [61]. Lower vapor pressure solvents can help to increase the critical thickness [61]. Surface forces can cause convection (Bénard) cells mostly due to surface tension gradients that can be reduced by having higher viscosities [62].

The final crystalline film has to be phase pure, should not contain impurities (O, C, Cl etc.), with desired composition, 1-2 μm thick, dense and compact. Each property can be
tuned by various parameters which are discussed in detail for example in Refs. [60,63].
The last step, the high temperature annealing is very crucial and will be subject of
discussions in Chapters 3 and 4.

1.5 Motivation for this investigation

At the thesis start, selenization of metal salts deposited by non-vacuum method was a
novel, not explored pathway.
The objectives of this thesis are

(i) Development of a scalable non-toxic and non-vacuum solution based method for
homogeneous precursor deposition.

(ii) Growth of solar grade material without presence of secondary phases and pre-
vention of organic residuals; 2-3 µm thick with large grains and suitable doping
properties.

(iii) Ultimately, improved device efficiency.

The scientific questions discussed in this thesis are

(i) To investigate the influence of the annealing conditions on the metal bulk and
surface composition, film morphology and solar cell performance.

(ii) To study the formation and decomposition mechanisms of Cu₂ZnSnS₄ and
Cu₂ZnSnSe₄, to define stable growth conditions.

(iii) To identify a fluxing phase to promote grain growth and densification of the ab-
sorber.

(iv) To gain insight into electronic defect properties and dominating loss mechanisms
in solution processed CZTSSe devices to ultimately increase the V_{oc}.
1.6 Structure of this thesis

After an experimental Chapter on layer deposition processes and employed characterization tools, four results Chapters will follow. Chapter 3 deals with the selenization of metal precursors utilizing binder material. In Chapter 4 binder material is avoided and chalcogen is directly added to the precursor solution. The influence of reactive annealing on elemental segregation and formation of secondary phases is discussed in the light of solar cell performance.

The two remaining Chapters investigate the role of Na impurities. Intentional incorporation of Na was seen to influence both, absorber crystallinity and electronic behavior of CZTSSe devices. Chapter 5 deals with the crystallization mechanism and presents a model for massive improvement of crystallization. Chapter 6 discusses the implications of Na concentration and location in the CZTSSe device on the electronic properties.
Chapter 2

Solar cell processing and characterization

2.1 Layer deposition

2.1.1 Mo back contact and diffusion barrier

Mo as electrical back contact was deposited on 1 mm thick soda lime glass (SLG) substrates. Three consecutive Mo layers were deposited by DC sputtering resulting in a total thickness of 500 nm.

Prior to back contact deposition, a Si$_3$N$_4$ alkali metal barrier was deposited in some cases to prevent Na-outdiffusion from the SLG substrate. A SIMS depth profile of the complete solar cell stack illustrates the ability of Si$_3$N$_4$ to suppress Na and K diffusion from the SLG (Figure 2.1).

2.1.2 Precursor formulation and deposition

The precursor solutions for the different approaches were prepared by mixing the chemicals as given in Table 2.1. Throughout Chapter 3 two solutions were prepared: the first one with metal salts dissolved in a mixture of ethanol and 1,2-propanediol (volume ratio = 1:1) and a second solution of higher viscosity with 10 wt% ethyl cellulose (EC) dissolved in 1-pentanol. The two solutions were mixed in a weight ratio of 2:1 to obtain
Chapter 2. Solar cell processing and characterization

![Graph showing SIMS depth profile](image)

**Fig. 2.1:** SIMS depth profile of a finished CZTSSe device with Si$_3$N$_4$ diffusion barrier illustrating the blocking of alkali metals Na and K.

<table>
<thead>
<tr>
<th>Chemicals (if necessary with molarity M)</th>
<th>Purity (%)</th>
<th>Company</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol (EtOH)</td>
<td>ACS</td>
<td>Merck</td>
<td>3</td>
</tr>
<tr>
<td>1,2-propanediol (ProD)</td>
<td>99.5</td>
<td>Sigma-Aldrich</td>
<td></td>
</tr>
<tr>
<td>0.90 M Cu(NO$_3$)$_2$ 2.5 \cdot H$_2$O</td>
<td>99.99+</td>
<td>Sigma-Aldrich</td>
<td></td>
</tr>
<tr>
<td>0.83 M Zn(NO$_3$)$_2$ 6 \cdot H$_2$O</td>
<td>98</td>
<td>Sigma-Aldrich</td>
<td></td>
</tr>
<tr>
<td>0.56 M SnCl$_4$ x \cdot H$_2$O</td>
<td>98</td>
<td>Alfa Aesar</td>
<td></td>
</tr>
<tr>
<td>1-pentanol</td>
<td>99+</td>
<td>Alfa Aesar</td>
<td></td>
</tr>
<tr>
<td>Ethyl cellulose 4 m-Pa-s</td>
<td></td>
<td>Sigma-Aldrich</td>
<td></td>
</tr>
<tr>
<td>Dimethyl sulfoxide (DMSO)</td>
<td>99.9</td>
<td>Alfa Aesar</td>
<td>4, 5, 6</td>
</tr>
<tr>
<td>0.57 M CuCl$_2$ anhyd.</td>
<td>98+</td>
<td>Alfa Aesar</td>
<td></td>
</tr>
<tr>
<td>0.39 M ZnCl$_2$ anhyd.</td>
<td>99.99</td>
<td>Alfa Aesar</td>
<td></td>
</tr>
<tr>
<td>0.53 M SnCl$_2$ 2 H$_2$O</td>
<td>98</td>
<td>Sigma-Aldrich</td>
<td></td>
</tr>
<tr>
<td>1.85 M Thiourea</td>
<td>99+</td>
<td>Sigma-Aldrich</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.1:** Used chemicals, purity, provider and respective chapter.

The final precursor solution with a suitable rheology for knife-coating.

A completely different precursor chemistry was employed for studies presented in Chapters 4, 5 and 6. Dimethyl sulfoxide (DMSO) was used as solvent with metal chlorides and thiourea (TU) as chalcogen source and no binder material (compare Ta-
2.1. Layer deposition

The molecules of DMSO and TU are depicted in Figure 2.2. The properties of the employed solvents are listed in Table 2.2.

![Molecules of a) dimethyl sulfoxide and b) thiourea.](image)

**Fig. 2.2: Molecules of a) dimethyl sulfoxide and b) thiourea.**

<table>
<thead>
<tr>
<th>solvent</th>
<th>chemical formula</th>
<th>polarity and nature of solvent</th>
<th>boiling point (°C)</th>
<th>dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>CH₃-CH₂-OH</td>
<td>polar protic</td>
<td>78</td>
<td>1.69</td>
</tr>
<tr>
<td>1,2-propanediol</td>
<td>C₃H₈O₂</td>
<td>polar protic</td>
<td>188</td>
<td>2.20</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>CH₃-S(=O)-CH₃</td>
<td>polar aprotic</td>
<td>189</td>
<td>3.96</td>
</tr>
</tbody>
</table>

**Table 2.2: Properties of solvents employed for the preparation of precursor solutions according to Ref. [64].**

Knife-coating technique

The precursor deposition in Chapter 3 was done by knife-coating under ambient conditions. To define the substrate-to-knife distance (approximately 50 µm), scotch tape was used resulting in about 1 µm thick crystalline CZTSe films. If not stated differently the film was dried under a lamp at \( \sim 200 \) °C and on a hot plate at \( \sim 230 \) °C, each for 1.5 minutes in air.

Spin-coating technique

The precursor deposition in Chapters 4, 5 and 6 was performed by spin-coating. Spin-coating was typically performed on 5 x 5 cm² Mo-coated SLG substrates with a SÜSS Microtec spin-coater. The layers were spin-coated at 500 rpm (5 seconds) before ramping up to 1600 rpm for 30 seconds. Repeated cycles (10 - 20) of spin-coating and drying were employed to build up the final film thickness. Drying was done for 1 minute at 320 °C under ambient conditions (in air) on a hot plate. It is optimized to a temperature as high as possible to maximize solvent evaporation and carbon removal but is limited to a temperature avoiding oxidation of the precursor metals as well as the Mo substrate.
2.1.3 Reactive annealing of precursor films

In the final step of the absorber processing, the precursor films were sintered at high substrate temperature into crystalline CZTSe, CZTS or CZTSSe kesterite layers. Annealing was conducted in a constantly pumped two zone furnace with independent control of substrate ($T_{\text{sub}}$) and chalcogen temperature (see Figure 2.3). Elemental sulfur, selenium or inert $\text{N}_2$ atmospheres were used for reactive sintering. The chalcogen was placed in the first zone while the sample was placed in the second zone. Chalcogen vapors were transported to the substrate with $\text{N}_2$ carrier gas at an operating pressure of 11 mbar (otherwise it is noted). The $\text{N}_2$ flow was kept at 25 sccm/min. The typical annealing duration at high substrate temperature was 25 minutes after a 10 minutes holding at 140 $^\circ$C to allow for the chalcogen to evaporate before the sample was heated up. The heating ramp to the final temperature was 40 $^\circ$C/min and the temperature was measured by a thermocouple embedded in the quartz tube $\sim 2$ cm above the sample. After annealing, the sample was cooled naturally to room temperature. It is noted that the open reactor design is far from equilibrium growth and does not allow for a saturated chalcogen pressure.

![Fig. 2.3: Constantly pumped two-zone annealing furnace with $\text{N}_2$ carrier gas.](image)

2.1.4 Buffer layer and front contact

Prior to CdS buffer layer deposition, the absorbers were KCN etched (10 wt% solution in water) for 30 seconds. Chemical bath deposition (CBD) at a bath temperature of 70 $^\circ$C with cadmium acetate, thiourea and ammonium hydroxide as precursor chemicals were
used for the CdS deposition. Typical immersion time was 22 minutes resulting in a CdS layer thickness of $< 50$ nm.

The solar cells were finished by a transparent bi-layer of RF magnetron sputtered i-ZnO (80 nm) and Al:ZnO (600 nm). Individual cells with an area of 0.09 cm$^2$ were defined by mechanical scribing. The cells were directly contacted via the window layer for electronic characterization.

### 2.2 Material characterization

#### 2.2.1 Thermogravimetric analysis (TGA)

To investigate evaporation and thermal decomposition of the precursor solution, thermogravimetric analysis (TGA) was performed with a STA 409 CD thermal balance coupled to a QMS 403C Aeolos mass spectrometer (both Netzsch). The measurement was carried out from room temperature to 650 °C in steps of 5 °C/min at atmospheric pressure with 30 ml/min N$_2$ carrier gas.

#### 2.2.2 Secondary electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

The microstructure of precursor and annealed layers was analyzed by secondary electron microscopy (SEM) using a Nova NanoSEM 230 or a Hitachi S-4800. The acceleration voltage for top-views was set to 20 kV (interaction volume of electron beam with sample $\sim 1.2$ µm) and for cross-sections to 7 kV (interaction volume $\sim 300$ nm). The cross-sections were prepared by mechanical cleaving and making electric contacts to the sample holder. Elemental quantification by energy dispersive X-ray spectroscopy (EDX) was usually done from the top at 20 kV, otherwise it is noted. The following X-ray emission lines were used in EDX: Cu ($K_{\alpha} = 8.05$ keV), Zn ($K_{\alpha} = 8.64$ keV), Sn ($L_{\alpha} = 3.44$ keV), S ($K_{\alpha} = 2.31$ keV), Se ($K_{\alpha} = 11.22$ keV), and Mo ($L_{\alpha} = 2.29$ keV).
2.2.3 X-ray diffraction (XRD) and in-situ XRD

Crystal structure information by X-ray diffraction (XRD) was obtained on a Siemens D5000 in Bragg-Brentano geometry using a Cu anode (with Cu K$_\alpha$ radiation at $\lambda = 1.542$ Å) and Ni filter. The Ni filter was not sufficient to block the Cu K$_\beta$ radiation ($\lambda = 1.392$ Å) completely, thus the Cu K$_\beta$ peaks of Mo or kesterite could often be detected. The X-ray tube was operated at 40 kV and 37 mA.

In situ XRD was carried out in detector scan mode with fixed incident angle of 10° with a PANalytical X'Pert Pro MPD system. Substrate heating at 20 °C/min was applied from room temperature to 550 °C. XRD patterns were recorded from $2\theta = 10$-60° with step size of 0.1° every 10 °C, so that one pattern took about 13 min (one experiment took ~15 hours). Chalcogenization without excessive metal losses was ensured by a Se top capping layer on the precursor, and additional surrounding Se or S pellets placed inside a graphite dome with volume $\sim$ 4.2 cm$^3$ (see schematic 2.4). The graphite dome led however, to carbon reflections in the diffractograms (PDF-number 26-1079). Technically it was not possible to completely close the dome so that chalcogen could successively evaporate.

![Schematic of the in-situ XRD setup.](image)

**Fig. 2.4:** Schematic of the in-situ XRD setup.

2.2.4 Raman spectroscopy

Raman spectroscopy is sensitive to the local chemical environment of the atoms in a crystal, meaning slight compositional changes can cause Raman peaks to shift in fre-
2.2. Material characterization

Raman spectroscopy was performed on Renishaw systems (Ramascope 2000 and inVia) with 633 (HeNe), 325 (HeCd) and 515 (Ar ion) nm excitation wavelengths. The probing depth of Raman spectroscopy depends on the absorption coefficient ($\alpha$) of the material for the respective wavelength of the excitation source, and is roughly given by $d \approx 1/\alpha$ (or $d \approx 1/(2\alpha)$ in the case of backscattering configuration). For CZTSSe with an absorption coefficient $> 10^4$ cm$^{-1}$, this results in a probing depth of around 100 nm. The spot size was $> 30$ µm in diameter.

2.2.5 Secondary ion mass spectrometry (SIMS)

Depth dependent elemental distribution was investigated by Secondary ion mass spectrometry (SIMS) in dual beam profiling mode on a TOF-SIMS$^5$ from ION-TOF. Depth profiles were sputtered on an area of 300 x 300 µm$^2$ using either O$^+_2$ (2 keV, 400 nA) or Cs$^+$ (2 keV, 120 nA) primary ions when investigating electropositive or electronegative elements, respectively. An area of 100 x 100 µm$^2$ was analyzed using Bi$^+$ ions with 25 keV ion energy.

2.2.6 Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) was used for elemental quantification of KCN etched CZTSSe absorbers. For that purpose the CZTSSe thin films were carefully scratched from the Mo-coated SLG. The scratched samples were dissolved in concentrated HNO$_3$ in gas tight polyethylene vessels heated to 85 °C to oxidize the chalcogenide elements (SO$_4^{2-}$ and SeO$_4^{2-}$) and prevent losses via gaseous H$_2$S(e). An Agilent 7500ce ICP-MS apparatus was used, and external calibration from certified single elemental standards was performed. An error of relative ± 10% is assumed.

In case of S not only sample preparation but also quantification at trace element level is challenging when using ICP-MS. S suffers from severe polyatomic interferences ($^{16}$O$^{2+}$ on $^{32}$S$^+$) and thus using a quadrupole ICP-MS (unfortunately no Xe as collision gas or access to a HR ICP-MS was available to overcome this problem) the less abundant and less interfered sulfur isotopes ($^{33}$S$^+$ or $^{34}$S$^+$) have to be measured resulting in poor detection limits and larger analysis errors when measuring concentrations near
2.2.7 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was performed on a Quantum 2000 Scanning ESCA Microprobe spectrometer (Physical Electronics) which employs monochromatic Al K\(\alpha\) (1486.6 eV) radiation. The analysis spot was 150 µm in diameter, and low energy Ar\(^+\) sputtering was done at 200 eV to prevent sputter damage on an area of 1 x 1 mm\(^2\). The total sputter depth is estimated to be less than 30 nm. The absorbers were KCN etched prior to analysis to have the absorber surface in a similar condition as later on in the solar cell device, where KCN etching was routinely performed on all absorbers before the CdS deposition. Quantification was performed by using relative sensitivity factors provided by the instrument manufacturer. The following binding energy photoemission lines were used for quantification: Cu 2p\(_{3/2}\) at 933 eV, Zn 2p\(_{3/2}\) at 1022 eV and Sn 3d\(_{5/2}\) at 485 eV.

2.2.8 X-ray absorption near edge structure (XANES)

X-ray absorption near edge structure (XANES) measurements were conducted by Justus Just (from Bergische University Wuppertal and HZB Berlin, both Germany) at the selenium K-edge at synchrotron DORIS at HASYLAB (beamline X) in transmission mode. To avoid absorption of the glass substrate, the samples were scratched from the Mo-coated substrate and sandwiched homogeneously between adhesive tape.

The underlying process is absorption of an X-ray photon by an atomic core level and measurement of incident and transmitted X-ray intensity to calculate the absorption by use of the Lambert-Beer law. A X-ray photon can only eject a core electron if it has sufficiently high energy. There is an abrupt absorption edge when X-ray absorption starts. Variation of the X-ray energy around this edge provides information about the chemical environment of the central atom, the crystal structure and the electronic density of unoccupied states [66]. Therefore, XANES spectra provide an unambiguous fingerprint of the material. In order to achieve a high energy resolution, a Si (511) double crystal monochromator was used.
2.3 Device characterization and analysis

2.3.1 Solar cell characteristics

Electronic transport in solar cells can be described by the one-diode model where the current density under illumination is expressed as follows [67]

\[
J(V) = J_0(e^{\frac{q(V - R_s J)/AKT}{T}} - 1) + \frac{V - R_s J}{R_P} - J_{ph} \tag{2.1}
\]

where \(V\) denotes the applied bias voltage, \(J_0\) the dark saturation current density, \(q\) the electron charge, \(k\) the Boltzmann constant, \(T\) the absolute temperature, \(J_{ph}\) the light generated current density, \(A\) the diode ideality factor and the parasitic \(R_s\) (series) and \(R_p\) (parallel) resistances, respectively. The diode ideality factor \(A\) typically has a value between 1 and 2 [67].

![JV characteristic of a solar cell under illumination.](image-url)
The figure of merit of a solar cell is its efficiency $\eta$. It gives the ratio of how much of the solar power can be converted into electricity. The PV parameters describing the performance of a solar cell device can be extracted from current density voltage (JV) measurements (see Figure 2.5): the open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), and the fill factor (FF). The efficiency is defined as

$$\eta = \frac{V_{oc} \cdot J_{sc} \cdot FF}{P_{in}},$$

where $P_{in}$ is the incident solar power. The FF is a measure of the squareness of a JV curve given by

$$FF = \frac{V_{mpp} \cdot J_{mpp}}{V_{oc} \cdot J_{sc}},$$

where $V_{mpp}$ and $J_{mpp}$ are the voltage and current density at the maximum power point (mpp, Figure 2.5).

Recombination losses reduce the conversion efficiency of a solar cell. The main recombination mechanism of electrons and holes in thin film solar cells is the Shockley-Read-Hall recombination via defects in the band gap of the absorber [68, 69]. Recombination paths are at the CdS/CZTSSe interface, in the space-charge-region (SCR), in the neutral region and at the back contact (see also section 1.3.3). Basic equations for each recombination process are summarized and discussed for example in Ref. [47, 70].

Temperature dependent JV measurement is a valuable tool for recombination loss analysis. The activation energy ($E_A$) of the dominant recombination pathway can be extracted from a plot of the $V_{oc}$ versus the temperature, assuming the diode ideality factor $A$ to be only weakly dependent on temperature [70] ($A \sim 1$ if the diode is dominated by recombination in the quasi neutral region; $A \rightarrow 2$ if recombination in the SCR is dominant [67]). If $E_A < E_g$, interface recombination is dominant while recombination in the SCR dominates if $E_A = E_g$ [70]. Interface recombination seems to be limiting CZTSSe based solar cells at the moment [54] while high efficiency CIGS solar cells are dominated by recombination in the SCR [70].
2.3.2 Current density voltage (JV) and external quantum efficiency (EQE)

The performance of the solar cells was analyzed by current density voltage (JV) and external quantum efficiency (EQE) measurements.

**Current density voltage (JV)**

The JV curves were measured in a solar simulator under standard test conditions (25 °C, 1000 W/m², AM1.5G illumination). There is a mismatch between the solar simulator and the AM1.5G spectrum, mainly due to an overestimation of the blue wavelength region while underestimating the IR part of the sun spectrum. This mismatch can lead to variations in the $J_{sc}$ from JV measurements compared to the $J_{sc}$ from EQE measurements.

The dominant recombination mechanism was evaluated by temperature dependent JV (T-JV) measurements in 4-point contacting mode with a Keithley 2400. Therefore, the solar cell is mounted in a cryostat and measured from 120 - 300 K in steps of 20 K.

**External quantum efficiency (EQE)**

In order to correct the spectral mismatch of the solar simulator spectrally resolved EQE was measured. The EQE spectra were recorded using a chopped white light source with a grating monochromator, which was calibrated by certified Si and Ge reference diodes. The solar cell conversion efficiencies were corrected by the $J_{sc}$ obtained from wavelength dispersive EQE measurements.

2.3.3 Admittance spectroscopy

Admittance spectroscopy (AS) measurements were carried out with a LCR-meter from Agilent (E4980A) at an oscillation level of 50 mV. Room temperature capacitance frequency (Cf) measurements were used to extract the SCR width (W) of a solar cell at 0 V bias. This is done by assuming a plate capacitor with capacitance $C = \epsilon_r \epsilon_0 A/W$. Where A is the area, $\epsilon_0$ the vacuum permittivity and $\epsilon_r = 10$ a relative dielectric constant. C was extracted at $\sim 1$ kHz, before the capacitance decay.

Temperature dependent capacitance-frequency spectroscopy (T-Cf) is used to deduce the energy distribution of defects in the band gap. The admittance spectra were col-
Fig. 2.6: a) Schematic band bending with an acceptor defect at position $E_T$ in the band gap (Figure modified from [71]).

lected at zero bias with frequencies ranging from 200 Hz to 2 MHz and in a temperature range from 124 K to 303 K with a small ac-voltage of 50 mV to ensure that the cell stays close to its equilibrium state.

The method to investigate defect levels was proposed by Walter et al. [72]. AS can yield the energetic position of dominant defect bands that are present between the Fermi energy and mid-gap [71]. The differential capacitance $C = \frac{\delta Q}{\delta V}$ originates from the samples response to a small voltage perturbation [71]. The voltage perturbation changes the band bending and causes a change in trap state occupation at the location $x_T$ in the SCR where $E_T = E_F$ (see Figure 2.6) [71].

The basic idea is that defects at an energy level $E_T$ can be charged and discharged accomplished by capture and re-emission of electrons and holes. Depending on the applied frequency $f$ (or temperature) with angular frequency $\omega = 2\pi f$, the occupation of the defect can either follow the ac signal (i.e. $\omega < \omega_0$) and therefore the charging and discharging of the defect contributes to $C$, or not if the ac frequency is too high (i.e. $\omega > \omega_0$) [72]. That means there is a transition between a high and low frequency capacitance at characteristic frequency $\omega_0$ where the derivative of $C$ reaches an extrema. This frequency is often thermally activated and an activation energy $E_T$ can be defined

$$\frac{\omega_0}{T^2} = \xi_0 e^x - \frac{E_T}{k_B T}$$
2.3. Device characterization and analysis

and

\[ E_T = k_B T \ln \frac{\xi_0 T^2}{\omega_0} \]

with the absolute temperature \( T \), the Boltzmann constant \( k_B \), and the parameter \( \xi_0 \) [73]. The activation energy can be extracted from an Arrhenius plot by drawing the logarithm of \( \omega_0/T^2 \) versus \( 1/T \) [73].

2.3.4 Electron beam induced current (EBIC)

EBIC measurements were performed in a FEI Strata 235 Dual Beam focused ion beam (FIB) and SEM. The current was measured with a SR570 preamplifier from SRS at a gain of \( 10^6 \). The samples were prepared by mechanical cleaving and electrically contacting the front and the back with silver paste and indium wires.

Electron beam induced current (EBIC) is a tool to visualize local charge carrier transport. Instead of light, electrons are scanned along the cross section of the solar cell and are used to generate electron-hole pairs. An induced current with respect to the electron beam position is measured when the electron-hole pairs are collected. The EBIC signal is a function of charge carrier collection and generation. The generation function strongly depends on the electron beam energy. An acceleration voltage of 5 keV (without applied bias) was used to be surface sensitive with acceptable local resolution. Therefore, for simplicity it is assumed that the collection function dominates the EBIC signal (for further reading see [74]).
Chapter 3

CZTSe processed from solutions with organic binder

This Chapter describes the pure selenide CZTSe deposited from a metal salt solution with organic binder material. Knife-coating is used to deposit wet precursor films. After presenting the influence of solution viscosity and precursor drying temperature, the phase formation study of reactive selenization by combined in situ and ex situ methods will be discussed in the light of kinetic and thermodynamic predictions. Thereafter the effects of selenization conditions with respect to metal losses will be discussed and possible solutions how to avoid them will be addressed. Finally, solar cell performance and limitations will be outlined.

Sections 3.3.1 and 3.3.2 are based on the publication "Formation mechanism of Cu2ZnSnSe4 absorber layers during selenization of solution deposited metal precursors" by C. M. Fella et al. [75].

Sections 3.3.3 and 3.4 are based on the publications "Cu2ZnSnSe4 absorbers processed from solution deposited metal salt precursors under different selenization conditions" by C. M. Fella et al. [76] and

"Recent trends in direct solution coating of kesterite absorber layers in solar cells" by Romanyuk et al. [63].
3.1 Motivation and prior art

The world record device with 12.6 % was processed by a solution approach employing hydrazine solvent [7]. Less toxic and more environmentally safe solution coatings would rely on organic solvents. An efficiency of 7.5 % was achieved from non-toxic precursors from mixed DMSO and alcohol solutions [77], and the same group reported above 10 % efficiency at the 4th European Kesterite workshop in Berlin, Germany (2013). A recent review by Romanyuk et al. provides a good overview on different non-vacuum approaches, their advantages and disadvantages [63].

Here, a simple non-vacuum paste coating process utilizing ethyl cellulose (EC) as binder material is presented. EC in the precursor solution serves for several purposes: it allows adjusting the paste rheology, prevents the formation of larger crystal precipitations upon evaporation, and therefore helps to increase lateral film stoichiometry, and inhibits evaporation of the precursor salts during drying and selenization [78]. This approach was previously applied by Kaelin et al. for the growth of CIGS. Despite a remaining carbon-rich layer at the CIGS/Mo interface, a conversion efficiency of 6.7 % was achieved [78].

Most successful growth methods for CZTS(Se) include two steps. First, metal containing precursors with or without chalcogen are deposited at low temperature, and second, high temperature annealing in a chalcogen containing atmosphere (see Chapter 1.3.2). In this respect, the knowledge of the formation and conversion reactions that occur during the annealing step is essential for obtaining phase-pure CZTS(Se) absorbers with targeted metal ratios.

The reaction paths during selenization depend on annealing conditions and on the initial precursor, which can be either a stack of Cu, Zn, and Sn-containing layers or a homogeneous mixture of all metals with or without chalcogen elements, respectively. In the case of selenization of sequentially evaporated Sn-Zn-Cu metal stacks, the preferential formation of different binary copper selenides was observed, which were converted into a mixture of CZTSe and ZnSe phases above 370 °C [79]. For mixed hydrazine based precursor inks with ZnS(e)(N₂H₄) nanocrystals and a bimetallic Cu₂Sn(Se,S)ₓ framework, no binary Cu or Sn chalcogenides were detected during the formation of CZTSSe absorbers [80]. For co-electroplated Cu-Zn-Sn precursors two different reaction pathways via binary sulfides were observed for Cu-poor and Cu-rich precursors.
during their sulfurization; both leading to the ternary Cu$_2$SnS$_3$ (CTS) phase that reacted later with ZnS to form CZTS \cite{81}. For CZTS thin films grown by a sol-gel sulfurization of spin-coated metal salt precursors, Cu$_x$S phase was formed first and then it got converted by further sulfurization at more than 450 °C \cite{82}. These studies indicate that the order in which individual metals react with the chalcogen does not depend only on the metal sequence in the initial stack, but strongly depends on the relative reactivity of each metal, and Cu typically exhibits a high reaction rate. Initial formation of Cu-Se phases at the precursor surface was even detected during selenization of CZTS nanoparticle layers \cite{83}.

Although the influence of remaining secondary phases, like Cu$_2$SnSe$_3$ (CTSe), ZnSe or MoSe$_2$, on the performance of kesterite absorber based solar cells is debated, most studies agree that the secondary phases should be avoided \cite{18, 66}. The CTSe phase is the only ternary compound in the Cu$_2$Se-SnSe$_2$ system \cite{84, 85}. Though CTSe is a p-type semiconductor with an optical band gap of 0.84 eV and a high absorption coefficient $\alpha \sim 10^4$ cm$^{-1}$ \cite{86}, its co-existence with CZTSe can lead to a reduced $V_{oc}$ in the finished solar cell device \cite{49}. Presence of ZnSe ($E_g = 2.8$ eV \cite{87}) at the CZTSe/Mo interface is probably the origin of a high series resistance in CZTSSe cells \cite{58}. The presence of its analog ZnS at the back interface is nevertheless not an obstacle for achieving an 8.4 % efficient CZTS cell \cite{45}. Binary copper phases, Cu-Se, can promote the grain growth during the CZTSe evolution but typically result in shunted devices because of their high conductivity \cite{88}.

### 3.2 Precursor characterization

The metal salt precursor solution was knife-coated on Mo-coated SLG substrates and dried under a lamp and on a hot plate at ambient conditions (more experimental details are given in section 2.1.2). The dried precursor exhibited macroscopic crack formation (see Figure 3.1a). To reduce the tensile stress and surface forces which result in film cracking, the rheology of the precursor was adjusted by doubling the content of the more viscous solvent 1,2-propanediol (ProD) which did not significantly reduce film cracking. Since the precursor annealing i.e. heating rate and temperature, can also influence film cracking, a variation of the drying conditions was performed but did not result in crack-free films. Only adding EC (a long chain organic molecule) to the metal
Chapter 3. CZTSe processed from solutions with organic binder

**Fig. 3.1:** a) SEM top views of Cu-Zn-Sn containing precursor layers without EC. b) was coated from a more viscous precursor solution indicated by the ProD/EtOH ratio. c) was coated from a precursor solution with EC.

**Fig. 3.2:** a) XRD patterns of precursors dried at different hot plate temperatures in air and b) SEM cross section of a dried precursor with EC.

Salt precursor solution resulted in crack-free precursor films (Figure 3.1c).

In the following, different drying temperatures for precursor solutions with EC were employed to find the optimum between carbon removal (i.e. burning of EC) and prevention of oxide phase formation. Before drying on a hot plate, the samples were pre-dried for one minute under a lamp at ~ 250 °C. Figure 3.2a illustrates XRD patterns of the precursors dried for two minutes on the hot plate at temperatures ranging from 150 - 350 °C. Up to a drying temperature of 300 °C the precursor is mainly in amorphous state except for some CuCl ($T_{drying} = 150$ °C), elemental Cu ($T_{drying} = 250$ °C) and their mixtures ($T_{drying} = 200$ and 300 °C). The presence of Cu in oxidation states I (CuCl) and 0 (elemental Cu) indicates reduction of Cu$^{2+}$ from the precursor salt possibly by
a redox reaction between Cu(NO$_3$)$_2$ and elemental carbon to form Cu and CO$_2$. Cu and CuCl crystals probably form due to their low solubility in alcohol [78]. The possibility of copper segregations in solution-derived precursor layers for CIGS was reported previously in Ref. [89]. The XRD pattern of the precursor dried at 200 °C but without EC shows some more CuCl and elemental Cu than the comparable sample with EC binder. This reflects the formation of larger crystal precipitation due to the earlier evaporation of the solvent in absence of EC binder. No compositional difference (measured by EDX) was observed between the sample with and without EC, i.e. EC has no stabilizing effect on the precursor with respect to metal losses. Drying of the precursor at temperatures ≥ 350 °C resulted in the formation of undesired oxide phases of Sn, Mo and Cu. The standard routine for precursor drying prior to selenization was set to the following parameters: the film was first dried under a lamp at ~ 200 °C and then on a hotplate at ~ 230 °C, each for 1.5 minutes. The SEM cross section of a precursor with EC dried at 230 °C is shown in Figure 3.2b. It looks dense but quite rough. The roughness is probably caused by the high viscosity of the solution and a rather large wet-film thickness.

3.3 CZTSe absorbers obtained by reactive selenization

Annealing of the metal-containing precursor in elemental selenium atmosphere for 25 minutes was done in a two-zone furnace as described in section 2.1.3. Reactive annealing at $T_{\text{sub}} = 570$ °C resulted in CZTSe layers which are depicted in Figure 3.3. Irrespective of addition of EC binder both samples have a ~ 1.5 µm thick residual carbon layer between Mo and CZTSe. This shows that the thick carbon layer does not necessarily stem from EC but probably stems from metal complex formation with ProD [89].

The aim of the following comparative study was to gain insight into the phase formation processes of CZTSe during the selenization of solution-deposited metal salt precursors.

3.3.1 Phase formation studied by in situ XRD

To study the in situ crystallization of the precursor, it was coated with selenium and placed inside a graphite dome with selenium pellets (see experimental part 2.2.3). The
Chapter 3. CZTSe processed from solutions with organic binder

Fig. 3.3: SEM cross sections of a selenized precursor a) without EC and b) with EC binder.

Fig. 3.4: In situ XRD measurement conducted during selenization of a Cu-Zn-Sn precursor coated with Se top layer. The identified crystal phases are listed on the right Y-axis and are summarized with respect to their temperature range on the top of the graph. The most intense and broadest Bragg reflection stems from the graphite dome at $2\theta \sim 26.5^\circ$. 
3.3. CZTSe absorbers obtained by reactive selenization

As discussed earlier, the precursor contains the CuCl phase. At low temperatures of 100 to 220 °C peaks of the crystalline selenium top layer are visible. Above 220 °C, exactly at its melting point, selenium is molten, and Cu converts into the orthorhombic CuSe$_2$ phase, denoted in Figure 3.4 by ° (PDF-number 01-071-0046), which persists until 300 °C. In parallel, at \( \sim 280 \) °C the overlapping reflections of CZTSe/CTSe/ZnSe evolve at \( 2\theta \sim 27.2^\circ, 45.1^\circ \) and \( 53.6^\circ \). Because of their very similar XRD patterns, it is not possible to distinguish them, and therefore these three phases are denoted with *. The evidence for the tetragonal CZTSe 101 and/or monoclinic CTSe 11 bar phases is the weak reflex at \( 2\theta \sim 17.3^\circ \), which becomes visible at \( 310 \) °C (indicated with an arrow in Figure 3.4). The definitive proof for the presence of CZTSe appears at \( 370 \) °C, when 211 and 114 reflections evolve at \( 2\theta \sim 36.2^\circ \) and \( \sim 38.9^\circ \), respectively. These reflections are absent for the ternary CTSe and binary ZnSe phases. The formation of MoSe$_2$ starts above \( 420 \) °C. The sample is held at \( 550 \) °C for 60 min and cooled down afterward without any phase changes (not shown).

3.3.2 Phase formation studied by ex situ measurements

Ex situ experiments were performed in a constantly pumped two-zone tube furnace where elemental selenium vapors were transported by nitrogen carrier gas into the substrate zone. The standard heating program with a ramp of 40 °C/min was interrupted 2 minutes after reaching the desired substrate temperature in order to obtain individual samples, which were naturally cooled.

XRD

The precursor layer exhibits only cubic Cu peaks (PDF-number 4-836, see Figure 3.5) while Zn and Sn are embedded in an amorphous carbon matrix probably in the form of organo-metallic complexes. Ex situ XRD measurements show preferential selenization of copper, confirming the in situ XRD results. At low substrate temperatures of 230 to 320 °C, ex situ XRD mainly shows a hexagonal CuSe phase (PDF-number 01-072-8417) and some CuSe$_2$ phase observed at \( T_{\text{sub}} = 320 \) °C. A very similar temperature window for the appearance of CuSe was found by Ref. [83]. The small temperature existence range of the selenium-rich CuSe$_2$ phase can be explained by the
Chapter 3. CZTSe processed from solutions with organic binder

Fig. 3.5: Ex situ XRD with elemental selenium from interrupted selenization processes.

lower Se supply in the ex situ experiment as compared to the in situ XRD, where a large excess of selenium is ensured. It is worth mentioning that Cu$_{2-x}$Se with expected XRD peaks at 2θ $\sim$ 44.5° and 26.8° (PDF-number 01-071-0044) was not seen. Cu$_2$ZnSnSe$_4$/Cu$_2$SnSe$_3$/ZnSe phases evolve from 340 °C on.

Raman

More conclusive information on the phase formation can be obtained from Raman measurements (Figure 3.6). Raman spectroscopy is sensitive to the local chemical environment of the atoms in a crystal, meaning that slight compositional changes can cause Raman peaks to shift in frequency [65]. Therefore Raman analysis can help to distinguish for example CZTSe and CTSe (supported by several complimentary elemental EDX point analysis, see next paragraph). For a low annealing temperature of 230 °C, the dominating Raman peak at 262 cm$^{-1}$ can be attributed to binary Cu-Se phase i.e. CuSe, due to a Se-Se stretching mode [90] and Cu$_2$Se [91]. In combination with the XRD results it was assigned to the CuSe phase. Additionally, a peak at 242 cm$^{-1}$, belonging to elemental Se, is observed [92]. Elemental Se probably stems from Se vapor condensation on the samples’ surface after interrupting the annealing process. At $T_{sub}$ = 320 °C, a multiphase structure is observed. At this temperature, the CuSe
Fig. 3.6: *Ex situ* Raman measurements at 633 nm excitation wavelength.

Intensity is seen to decrease, whilst a broad peak at around 193 cm$^{-1}$, and a second weak peak at 233 cm$^{-1}$ evolve. The major peak in the CZTSe Raman spectra at 194 cm$^{-1}$ is the vibrational A mode, which stems from Se vibrations [93, 94]. Thus, the broad peak at 193 cm$^{-1}$ is the first indication of CZTSe crystallization, where the peak broadening may arise from a high defect density and local compositional fluctuations, that is disorder in the cation sub-lattice [65]. Similar Raman spectra were also reported by Volobujeva *et al.* [79]. The weak Raman mode at 233 cm$^{-1}$ most likely belongs to CZTSe [94]. A temperature increase $>320^\circ$C shows the sharpening of the vibrational A mode of CZTSe. A broad shoulder at 180 cm$^{-1}$, next to the main CZTSe peak could indicate the ternary CTSe phase in the temperature region of $T_{sub} = 320 - 370^\circ$C (see inset). Since the peak at 180 cm$^{-1}$ is hidden between the main CZTSe modes at 194 and 172 cm$^{-1}$ no unambiguous conclusion can be drawn. Supporting evidence for the presence of ternary CTSe were numerous point EDX measurements as described in the next section, pointing out a very low Zn content in the crystalline material of the selenized surface layer. The inset of Figure 3.6 highlights the transition from mixed CZTSe and CTSe to an apparently more phase pure CZTSe material. At higher substrate temperatures $\geq 420^\circ$C the shoulder at 180 cm$^{-1}$ significantly decreases, resulting in the typical footprint of kesterite (i.e. Raman peaks at 172 cm$^{-1}$, 194 cm$^{-1}$ and
233 cm$^{-1}$ [95]). Raman spectra at $\lambda = 633$ nm (and 515 nm, not shown) do not indicate presence of ZnSe phase, characterized by a main Raman mode at 250 cm$^{-1}$ [96]. Measurements with shorter excitation wavelength ($\lambda \sim 458$ nm, resonant Raman condition) will significantly improve a potential response from ZnSe [96] with a relatively high band gap of 2.8 eV [87]. Possibly ZnSe is segregated towards the Mo contact away from the layer surface, out of probing depth.

**SEM & EDX**

Fig. 3.7: a-d) SEM images of samples obtained after interrupting the selenization processes at $T_{\text{sub}} = 320$ °C, 340 °C, 420 °C and 510 °C with EDX point measurements.

The insights gained so far are supported by direct quantitative elemental analyses from point EDX measurements at low acceleration voltage of 7 keV (see Figure 3.7a-d). The SEM top view images show the samples obtained after interrupting the selenization processes at $T_{\text{sub}} = 320$ °C, 340 °C, 420 °C and 510 °C, respectively. Hexagonal crystals assigned to the klockmannite CuSe phase with composition of 55 at% Cu and 45 at% Se are visible for $T_{\text{sub}} = 320$ °C. At $T_{\text{sub}} = 340$ °C the crystals are very Zn-poor and have composition close to the CTSe phase: 40 at% Cu, 16 at% Sn and 42 at% Se resulting in an empirical formula $\text{Cu}_{2.45}\text{Sn}_{0.98}\text{Se}_{2.57}$. The Cu-rich composition can
be understood when assuming that Sn is continuously incorporated into the slightly copper-rich Cu-Se phase which was observed at $T_{\text{sub}} = 320 \, ^\circ\text{C}$. A similar observation was made by Mainz et al. [83] where first Cu$_{2-\delta}$Se evolved followed by the formation of CTSe. The main incorporation of Zn occurs $\sim T_{\text{sub}} = 420 \, ^\circ\text{C}$ resulting in an empirical formula Cu$_{2.56}$Zn$_{1.04}$Sn$_{0.88}$Se$_{3.52}$, which is still Cu-rich and there is not yet enough Se available for the full conversion into CZTSe. Small charging crystallites with Zn-rich composition are detected at $T_{\text{sub}} = 510 \, ^\circ\text{C}$. These findings suggest initial Cu-rich growth followed by subsequent transformation into CZTSe. Growth under intermediate Cu-rich conditions is usually employed during co-evaporation of CIGS absorbers to obtain large grained material [97, 98]. Also in CZTSSe Cu-rich growth was associated with the formation of large grains [43]. In the final layer however, Cu-Se is undesired since it can lead to shunt paths [99]. In this study, the initial precursor was very Cu-poor (Cu/(Zn+Sn) = 0.6), resulting in final Cu-poor CZTSe phase with an intermediate Cu-rich growth window which could enhance grain growth.

Table 3.1 summarizes XRD, Raman and SEM/EDX results. Depending on the Se vapor pressure, CuSe$_2$ or CuSe phases are formed first and persist until 320 °C. There is probably a co-existence of Cu$_2$SnSe$_3$ and Cu$_2$ZnSnSe$_4$ between 340 and 370 °C. The main CZTSe phase gets dominant above 420 °C. The temperature offset between in and ex situ measurements for the evolution of different phases can be explained by the different experimental setups, so that crystal phases in in situ XRD are observed at somewhat lower temperatures than in ex situ experiments where the selenization is interrupted two minutes after reaching the desired substrate temperature. The phase evolution during annealing in elemental Se can be written in the following sequence:

$$
\text{Cu, Zn, Sn precursor in carbon matrix } \xrightarrow{\sim 190^\circ\text{C}} \text{CuSe}_x \xrightarrow{\sim 340^\circ\text{C}} \text{Cu}_2\text{SnSe}_3 + \text{Cu}_2\text{ZnSnSe}_4 \xrightarrow{\sim 420^\circ\text{C}} \text{Cu}_2\text{ZnSnSe}_4
$$

Looking at the standard enthalpies of formation $\Delta_fH_{298K}^0$ for binary metal selenides, they are increasing as follows: MoSe$_2$ (-196 kJ/mol) $<$ ZnSe (-159 kJ/mol) $<$ SnSe$_2$ (-121.3 kJ/mol) $<$ SnSe (-88.7 kJ/mol) $<$ Cu$_2$Se (-65.3 kJ/mol) $<$ CuSe$_2$ (-48.1 kJ/mol) $<$ CuSe (-41.8 kJ/mol) [100]. A more rigorous approach is to consider the Gibbs enthalpy $\Delta G = \Delta H - T\Delta S$. Since $\Delta S$ is small for solid state reactions and it is assumed that no phase transition occurs, therefore $\Delta G \approx \Delta H$. $\Delta H$ clearly indicates
Table 3.1: Evolving phases with respective characterization method and temperature range.

<table>
<thead>
<tr>
<th>Method</th>
<th>Phases</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>in situ XRD</td>
<td>CuCl</td>
<td>RT - 210</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>RT - 220</td>
</tr>
<tr>
<td></td>
<td>CuSe</td>
<td>190 - 300</td>
</tr>
<tr>
<td></td>
<td>ZnSe/CZTSe/CTSe</td>
<td>280 - 550</td>
</tr>
<tr>
<td></td>
<td>CZTSe 101/CTSe 11\text{\textbar}1</td>
<td>310 - 550</td>
</tr>
<tr>
<td></td>
<td>CZTSe 211, 114</td>
<td>370 - 550</td>
</tr>
<tr>
<td>ex situ XRD</td>
<td>Cu</td>
<td>RT - 280</td>
</tr>
<tr>
<td></td>
<td>CuSe</td>
<td>230 - 320</td>
</tr>
<tr>
<td></td>
<td>CuSe</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>ZnSe/CZTSe/CTSe</td>
<td>340 - 510</td>
</tr>
<tr>
<td></td>
<td>CZTSe 101/CTSe 11\text{\textbar}1</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td>CZTSe 211</td>
<td>420</td>
</tr>
<tr>
<td>Raman 633 nm</td>
<td>Se</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>CuSe</td>
<td>230 - 320</td>
</tr>
<tr>
<td></td>
<td>CTSe</td>
<td>320 - 370</td>
</tr>
<tr>
<td></td>
<td>CZTSe</td>
<td>320 - 510</td>
</tr>
<tr>
<td>SEM &amp; EDX</td>
<td>CuSe</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>CTSe</td>
<td>340</td>
</tr>
<tr>
<td></td>
<td>CZTSe</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td>ZnSe?</td>
<td>510</td>
</tr>
</tbody>
</table>

that binaries like MoSe$_2$ and ZnSe are more thermodynamically stable than any copper selenides. Whether a reaction is governed by thermodynamic or kinetic reactions depends on the activation needed to obtain a final product. Here, the reaction pathway is clearly governed by kinetic factors, such as the fast reaction of copper with selenium at low temperatures, probably due to a small activation energy for the initial reaction and a high diffusion of copper atoms from the precursor layer to the surface where Se molecules impinge.
3.3.3 Compositional control: Zinc and Tin loss

Zinc loss

Each thermal step can lead to elemental losses. In order to trace metal losses during drying or selenization the metal compositions were measured by EDX after each thermal treatment (see Table 3.2). The metal ratios in the solution are identical to the dried precursor. After selenization at $T_{\text{sub}} = 470 \, ^\circ\text{C}$ for 25 minutes however, significant losses of Zn and also Sn are observed. These losses can be due to evaporation or appear as an artifact due to elemental segregation. However, Zn and Sn might still be unreacted in the carbon-rich layer (compare Figure 3.3).

Annealing of the precursor at $T_{\text{sub}} = 600 \, ^\circ\text{C}$ for 25 minutes in inert $\text{N}_2$ atmosphere without Se results in a total Zn loss. Zn can evaporate as element (Zn has the highest vapor pressure of the metal elements of $\sim 22 \, \text{mbar} \text{ at } 600 \, ^\circ\text{C}$ [64]) or via metal-organic compounds such as diethylzinc, via the reaction of Zn with a functional ethyl group of the EC molecule ($B_p$ of Zn(C$_2$H$_5$)$_2 = 118 \, ^\circ\text{C}$ [64]).

<table>
<thead>
<tr>
<th></th>
<th>Cu/Zn</th>
<th>Cu/Sn</th>
<th>Zn/Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution</td>
<td>1.1</td>
<td>1.6</td>
<td>1.5</td>
</tr>
<tr>
<td>precursor</td>
<td>1.1</td>
<td>1.6</td>
<td>1.5</td>
</tr>
<tr>
<td>annealed with Se</td>
<td>1.6</td>
<td>1.9</td>
<td>1.2</td>
</tr>
<tr>
<td>annealed without Se</td>
<td>-</td>
<td>2.4</td>
<td>0</td>
</tr>
</tbody>
</table>

Loss of elemental Zn can be reduced when first providing Se in the annealing atmosphere before heating up the substrate. The standard annealing routine therefore, contains a first pre-heating step of the chalcogen source to ensure the presence of Se in the annealing atmosphere before heating up the substrate to its final temperature.

Tin loss

The substrate temperature in combination with chalcogen pressure is one of the main parameters determining the final elemental composition of selenized CZTSe layers [51, 101]. The absorber selenization was carried out at increasing substrate temperatures at a chamber pressure of 5 mbar with $\text{N}_2$ background gas. To ensure comparable results, the amount of evaporated selenium for each selenization run was kept constant at around 150 mg by adjusting the selenium zone temperature near 360 $^\circ\text{C}$. The evolu-
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Fig. 3.8: a) Elemental concentrations as obtained from EDX measurements for increasing \( T_{\text{sub}} \) at nominal chamber pressure of 5 mbar. The points are connected as a guide for the eye. The open symbols represent elemental concentrations when annealing at a nominal chamber pressure of 10 mbar. b) Corresponding XRD patterns.

The elemental compositions measured by EDX as a function of \( T_{\text{sub}} \) is presented in Figure 3.8a. High substrate temperatures are beneficial for recrystallization, as well as to drive out the organics, however, a significant Sn loss was observed for \( T_{\text{sub}} > 600 \, ^\circ \text{C} \), while other elemental compositions remained constant. The Se content above 55 at% is explained by the evolving MoSe\(_2\) phase which is probably within the probing depth of the 20 kV electron beam. It is noted that the sample annealed at 660 \( ^\circ \text{C} \) was grown on a 3 mm thick SLG to avoid extensive glass softening.

XRD patterns of films annealed at \( T_{\text{sub}} < 610 \, ^\circ \text{C} \) show characteristic reflections of CZTSe phase already for selenization temperatures as low as 370 \( ^\circ \text{C} \) (Figure 3.8b). The presence of secondary phases, in particular ZnSe and Cu\(_2\)SnSe\(_3\), cannot be excluded because they have almost identical diffraction patterns as CZTSe outlined in section 1.3.1 and Refs. [102, 103]. To discriminate CZTSe from ZnSe and CTSe, smaller peaks such as the 103 peak of CZTSe at 28.4° in combination with the 101 peak at 17.4° can help. The 103 peak is neither present in ZnSe nor in CTSe and its appearance simultaneously with the 101 peak is interpreted as CZTSe phase which is evolving already at 370 \( ^\circ \text{C} \) and remains until \( T_{\text{sub}} = 585 \, ^\circ \text{C} \). As soon as \( T_{\text{sub}} > 600 \, ^\circ \text{C} \), the Sn content is drastically reduced, yielding a mixture of binary Cu\(_{2-x}\)Se (PDF-number 6-680) and ZnSe (PDF-number 37-1463) phases. Alongside this decomposition, MoSe\(_2\) starts to grow. It is only faintly visible by the broad peak at \( \sim 31.5^\circ \) and 32.2° (PDF-
3.3. CZTSe absorbers obtained by reactive selenization

Fig. 3.9: SEM images of a) CZTSe film selenized at $T_{\text{sub}} = 470 \degree C$ and b) decomposed film containing $\text{Cu}_{2-x}\text{Se}$ and $\text{ZnSe}$ selenized at $T_{\text{sub}} = 610 \degree C$.

Figure 3.9a+b show a presumably "single phase" CZTSe layer and a decomposed layer with 1 at% Sn (EDX measurement) exhibiting $\text{Cu}_{2-x}\text{Se}$ and $\text{ZnSe}$ phases. Point EDX measurements at a low acceleration voltage of 7 kV (penetration depth $\sim 300$ nm) is a direct experimental evidence of the co-existence of individual $\text{Cu}_{2-x}\text{Se}$ and $\text{ZnSe}$ grains as indicated by the arrows in Figure 3.9b.

Fig. 3.10: Elemental concentrations as obtained from EDX measurements for increasing selenium zone temperatures. The right Y-axis depicts the ratio of XRD intensities of $100\text{MoSe}_2$ over $110\text{Mo}$. 
Another way to control incorporation of Sn is by means of the selenium partial pressure (Figure 3.10). This parameter can be investigated by increasing the selenium zone temperature, resulting in a higher selenium vapor pressure, whilst maintaining a constant $T_{\text{sub}}$ of 610 °C and a total chamber pressure of 5 mbar. At the lowest selenium zone temperature of 360 °C which corresponds to a selenium evaporation of 170 mg, a significant loss of Sn was observed (see also measurements presented in Figure 3.8). As the selenium zone temperature was elevated from 360 to 380 °C (\textasciitilde saturated Se vapor pressures 2-4 mbar), corresponding to an increase in evaporated amount of selenium from 170 to 3410 mg, the Sn content reaches its targeted value of 11 at%. It is noted that the annealing takes place under non-equilibrium conditions because the furnace is constantly pumped leading to a lower Se pressure than the given saturated pressures.

High selenium vapor pressure promotes the selenization of the molybdenum back contact into MoSe$_2$, see Figure 3.10. There is a rapid increase in MoSe$_2$ formation for Se zone temperatures of 370 °C and higher which is consistent with Ref. [104]. Although the interface MoSe$_2$ layer is needed to provide a necessary quasi-ohmic contact to CIGS [105], and even a 300 nm thick MoSe$_2$ layer is reported for a 9.7% efficient CZTSSe solar cell by Todorov et al. [32], there is a certain risk that the conductivity of the Mo contact is deteriorated and therefore $R_s$ is increased [18, 106]. Therefore, excessive MoSe$_2$ formation has to be avoided.

The decomposition of kesterites above 400 °C resulting in ZnSe, Cu$_2$Se, SnSe and Se$_2$ was already described in section 1.3.3. Here, the decomposition reaction 1.1 becomes significant under annealing conditions at temperatures higher than 600 °C in combination with selenium zone temperature $< 370$ °C. According to the Le Chatelier principle, the chemical equilibrium equation 1.1 can be shifted to the left, the CZTSe side, by suppressing the formation of volatile species, SnSe and Se. The interplay between the critical temperature and partial pressure of volatile products was described by Scragg et al. [51]. Since no additional SnSe is provided during selenization, the decomposition reaction can be suppressed by using either low $T_{\text{sub}}$ or high $T_{\text{sub}}$ in combination with increased Se partial pressure via elevated Se zone temperature (see Figures 3.10 and 3.8a).

Generally, high $T_{\text{sub}}$ combined with high partial Se pressure is beneficial for the recrystallization of CZTSe layers, but it also results in thick MoSe$_2$ layers. In order to find a compromise between the MoSe$_2$ thickness and the CZTSe grain growth, the total
chamber pressure was increased to 10 mbar by partially closing the valve between the reactor and the pump (while the N₂ flow remained constant). At the same time, the Se zone temperature was increased to evaporate the same amount of selenium as at 5 mbar. These measures result in an elevated effective Se pressure because the constant pump volume/time was reduced, and hence the tailored Sn content can be preserved even for samples selenized at T_{sub} > 600 °C, which is depicted as open symbols in Figure 3.8a. The background pressure is not expected to change the chemical equilibrium described in equation 1.1 however, it significantly influences the convection and transport speed of volatile species away from the substrates' surface, that is the rate of desorption. N₂ could also change the surface temperature. An increase in background pressure could lower it, and therefore the decomposition rate and subsequent Sn loss. In an open reactor, the higher N₂ background pressure may retard CZTSe decomposition by slowing down desorption of gaseous SnSe, which according to equation 1.2 is not immediately released from the kesterite into the gas phase, but as solid SnSe which is in equilibrium with its gas phase. From this experiment it was concluded that N₂ is a third important parameter in controlling the absorber composition. It is noted that the oven design substantially influences critical parameters.

The annealing of the precursor without Se atmosphere (compare Table 3.2) indicates Sn loss via evaporation of SnSe with a high vapor pressure of ∼ 1.3 · 10⁻² mbar at 600 °C [107] and not via any volatile organo-metallic Sn compounds, Sn salts, or in its elemental form (vapor pressure of Sn is ∼ 1.1 · 10⁻⁹ mbar at 600 °C [64]).

### 3.3.4 Absorber characterization

By using the optimized selenization conditions with a total chamber pressure of 10 mbar and T_{sub} = 470 °C, crack-free absorber layers with overall metal ratios of Cu/(Zn + Sn) = 0.9 and Zn/Sn = 1.2 (EDX data) were obtained. The SEM cross-section image in Figure 3.11 shows a ∼ 800 nm thick CZTSe absorber layer with compact morphology, rather rough surface, and a ∼ 1.5 µm thick carbon-rich layer between Mo and CZTSe absorber. This carbon layer stems from the incomplete decomposition of ethyl cellulose binder and organic solvents, and consists primarily of carbon with metal impurities [78,89] and selenium (seen in EDX line scans, not shown). The roughness was caused by the high solution viscosity and the large wet film thickness of ∼ 30 µm.
Chapter 3. CZTSe processed from solutions with organic binder

Fig. 3.11: SEM cross section of a Cu-poor and Zn-rich CZTSe absorber with residual carbon layer between CZTSe and Mo.

Fig. 3.12: a) Typical Raman spectrum (\(\lambda = 633\) nm) for a Cu-poor and Zn-rich CZTSe layer. Main CZTSe Raman peaks are indicated by the numbers. b) Normalized and smoothed (by Savitzky-Golay filter) SIMS depth profile of the absorber shown in Figure 3.11.

A typical Raman spectrum of the absorber layer at excitation wavelength \(\lambda = 633\) nm exhibits peaks at 192, 170, and 232 cm\(^{-1}\), in agreement with those reported for CZTSe [95] (see Figure 3.12a). The presence of secondary phases cannot be excluded under the given sensitivity of the Raman measurement, that is penetration depth < 100 nm and poor Raman yield for example for ZnSe with large optical band gap of 2.7 eV due to non-resonant excitation conditions [96]. The normalized SIMS depth profile of
the absorber depicted in Figure 3.12b exhibits a strong Zn gradient with increasing Zn content towards the backside of the absorber. This profile could be a hint for ZnSe formation at the CZTSe/Mo interface. Cu seems to be depleted at the surface. From the metal counts in the absorber it might be suggested that metals accumulate in the carbon layer. It is noted that the sample roughness is very high. By reducing the analyzed area to 20 x 20 µm$^2$ it was tried to reduce the effect of the morphology. Still, the SIMS profile is smeared out because of locally not homogeneous interfaces, therefore it is difficult to clearly draw the line between absorber and carbon layer.

### 3.4 Solar cell performance

![Graph](image)

**Fig. 3.13:** a) JV and b) EQE curves of the record sample illustrated in Figure 3.11 processed with EC. The inset depicts the cut off wavelength to extract the band gap.

Despite the presence of the residual carbon layer, a conversion efficiency of 4.28% on a total area of 0.09 cm$^2$ was obtained. The homogeneity on the 2.5 x 2.5 cm$^2$ sample was reasonable good; 80% of the cells exhibited efficiencies $\geq$ 3.8%. Figure 3.13a shows the JV curves of the record cell under dark and illuminated conditions and Figure 3.13b illustrates the external quantum efficiency (EQE($\lambda$)) of the best cell. The carrier collection is low especially in the long wavelength region. A small minority carrier lifetime and/or too narrow space charge region, which was experimentally verified by EQE($\lambda$) measurements with and without applied bias voltage, can be suggested as the main reasons for the low red response. An extrapolation of the EQE data (inset in
Figure 3.13b) results in a band gap of about 0.93 eV. Although the EQE curve is not ideally rectangular in shape, which makes the extraction of the band gap questionable because a short electron lifetime can shift the apparent EQE cutoff [108], the $E_g$ value is in accordance to literature values [58, 109]. A high doping and consequently small space charge region (SCR) width and poor electronic quality could be responsible for overall low carrier collection.

The room temperature time-resolved photoluminescence (TR-PL) measurement was performed on a photoluminescence life time spectrometer Hamamatsu C12132-12 with 532 nm excitation wavelength. The TR-PL near the band edge emission wavelength 1310 nm (0.95 eV) of the finished solar cell device reveals a short minority carrier lifetime $\tau$ of only 0.44 ns (determined by a single exponential fit to the spectrum, red curve in Figure 3.14). A high $V_{oc}$ is correlated with long minority carrier lifetimes due to a reduction of the reverse saturation current [67, 110]. The inset of Figure 3.14 shows the PL signal with emission at 0.95 eV, which is consistent with the band gap of the CZTSe absorber extracted from the EQE data presented in Figure 3.13b. A small minority carrier lifetime in combination with a narrow SCR width are likely the limiting factors of the device.

**Fig. 3.14: Time resolved PL of the 4.28 % efficient CZTSe device measured at 300 K with 532 nm excitation wavelength. The inset depicts the PL signal with emission at 0.95 eV.**

The influence of the carbon layer on the solar cell performance is not completely clear.
3.5. Summary

Since the carbon layer contains metals and Se, it could act as a "reservoir" helping to suppress decomposition at the back contact reported by Ref. [46]. Cao et al. reported on selenization of binary and ternary metal sulfide nanoparticles with a remaining fine-grained sublayer between Mo and CZTSSe [111]. This fine-grained layer is carbon-rich and contains CZTSSe as well as binary and ternary nanoparticles. The small-grained layer in combination with MoSe₂ is suggested to increase the series resistance and reduce the solar cell performance [111]. Haug et al. [112] reported on a beneficial effect of the carbon layer for thin CIGS absorber films (d ≤ 800 nm). The most beneficial effect was observed for a 230 nm thick CIGS absorber with strong increase of Vₜₜ in presence of the carbon layer. According to their discussion, the back contact recombination is changed by the carbon layer leading to improved Vₜₜ.

3.5 Summary

In conclusion, a novel solution approach with non-toxic solvents, metal salts and organic EC binder was investigated for the growth of kesterite CZTSe. EC in the precursor solution prevents crack formation and increases the lateral compositional homogeneity due to reduced formation of Cu and CuCl crystals. It was shown that CZTSe growth starts with the fast formation of binary Cu-Se phases that are present between 190 °C and 320 °C. Overlapping diffraction patterns of CZTSe/Cu₂SnSe₃/ZnSe phases evolve from 280 °C onwards and remain until a final temperature of 550 °C. The ternary Cu₂SnSe₃ phase probably co-exists with CZTSe between 340 °C and 370 °C. No individual Zn or Sn binary phases were detected (the reason for not detecting ZnSe is possibly due to a not available resonant Raman excitation source). A kinetically driven formation mechanism, which starts with the selenization of Cu requiring the lowest activation energy for reaction, followed by gradual incorporation of Sn and Zn to yield the final CZTSe phase is proposed. Sn loss during selenization is a function of Tₘₚ and Se partial pressure; significant losses can be prevented by adjusting either of them. Sn loss triggers the decomposition of kesterite into ZnSe and Cu₂₋ₓSe. Tₘₚ > 600 °C or high Se partial pressure lead to selenization of the Mo back contact resulting in MoSe₂ formation. Despite a thick residual carbon layer this method gives working solar cell devices with 4.3 % efficiency. The main device limitations are likely a small minority carrier lifetime in combination with a narrow SCR width.
Chapter 4

CZTS and CZTSSe processed from binder-free solutions with chalcogen

In the previous Chapter metal salts were dissolved in alcohols with binder material. The presented approach can be used to grow CZTSe absorbers but it is limited by a small minority carrier lifetime, the absorber layer roughness and formation of a carbon-rich layer [111,112] at the CZTSe/Mo interface.

This Chapter deals with precursor solutions based on dimethyl sulfoxide (DMSO) which shows weak complexing behavior and at the same time can dissolve thiourea that acts as sulfur source and effective metal complexing agent. Therefore, no additional stabilizing agent is needed. The precursor deposition method is changed from knife-coating to spin-coating in order to reduce surface roughness. The focus is on the understanding of the precursor transformation into crystalline kesterite layers by analyzing the effect of annealing on the final phase composition. A growth model will be developed to explain different layer morphologies. This is followed by a discussion on the influence of the absorber surface on solar cell properties. While the first parts of this Chapter concentrate on pure CZTS, the remainder is about CZTSSe. The formation of secondary phases with respect to initial precursor composition is studied by both, lab-based methods and advanced synchrotron techniques. A method based on X-ray absorption near edge measurements is developed to enable ZnSe quantification.

Section 4.2.2 is based on "Reaction Pathways for the Formation of Cu$_2$ZnSn(S,Se)$_4$ Absorbers from Metal Salt Precursors Annealed under Selenium Atmosphere" by C. M. Fella et al. [113].
Chapter 4. CZTS and CZTSSe processed from binder-free solutions with chalcogen

The first part of section 4.3.3 is based on "Large-grained Cu$_2$ZnSnS$_4$ layers sintered from Sn-rich solution-deposited precursors" by C. M. Sutter-Fella et al. [114].

4.1 Motivation and prior art

There are several advantages of incorporating the chalcogen already into the precursor solution: it can improve the spatial homogeneity, avoid poor adhesion due to volume expansion when the chalcogen is incorporated during high temperature annealing, it may be beneficial to suppress Zn loss (vapor pressure of Zn is $\sim 7.4 \cdot 10^{-3}$ mbar at 330 °C [64]) and could prevent demixing of metals and metal salt segregation.

The precursor solutions used for this and the next two Chapters are prepared following the approach reported first by Ki and Hillhouse [115]. The highest efficiency demonstrated by this group was 8.3 % [40]. Schnabel et al. modified their process and yielded 7.5 % [77]. Recently they reported above 10 % efficiency at the 4th European Kesterite workshop in Berlin, Germany (2013). Here, in contrast to the precursor used by the Hillhouse group, thiourea (TU) with metal chlorides instead of mixed acetate and chloride anions dissolved in dimethyl sulfoxide (DMSO) were used. TU is a frequently used sulfur source in non-vacuum processing [116, 117] that can form metal complexes, for example with Cu, Zn and Sn [118]. A redox reaction between Cu$^{2+}$ and Sn$^{2+}$ ions takes place in DMSO and is facilitated by ZnCl$_2$ [40]. The reduction of Cu$^{2+}$ to Cu$^{+}$ ions and oxidation of Sn$^{2+}$ to Sn$^{4+}$ ions is enhanced by complexation of metal ions with TU resulting in a nearly colorless solution [40].

4.2 Precursor characterization

4.2.1 Precursor solution with chalcogen source

An ideal solvent should coordinate metal cations by forming soluble metal complexes, which at the same time should fully decompose at moderate temperatures ($T_{max} \sim 300$ °C), without leaving residual impurities in the layer. Thermogravimetric analysis (TGA) is used to track mass losses during heating of precursor solutions. To study metal complexation in solution, ZnCl$_2$ dissolved in DMSO with and without TU was
in order to study the detailed decomposition products of DMSO with ZnCl$_2$ and TU (indicated by * in Figure 4.1), a TGA-MS measurement was performed. Decomposition of DMSO yields the following main volatile products in order of decreasing yield:
4.2.2 Precursor layer

Precursor solutions were prepared with the recipe given in Table 2.1 and spin-coated onto Mo coated SLG substrates. In order to build up the film thickness spin-coating and drying cycles at $T_{\text{sub}} = 320 \, ^\circ\text{C}$ were repeated (15 times). The copper-zinc-tin-sulfur con-
4.2. Precursor characterization

Fig. 4.3: Characterization of the Cu-Zn-Sn-S precursor: a) SEM cross section b) XRD pattern, c) Raman spectra with expected Raman shifts of CZTS and ZnS and d) SIMS depth profile of a precursor film.

The precursor layers are typically 1.5 – 2 µm thick, where thickness variations are caused by the spin-coating technique. It exhibits a compact and dense film morphology (see Figure 4.3a). The precursor composition according to ICP-MS was Cu-poor: Cu/(Zn+Sn) = 0.8, Zn-stoichiometric: Zn/Sn = 1.0 and S-deficient: S/metals = 0.8-0.9. Note that the precursor is Zn-stoichiometric to compensate for subsequent Sn loss during precursor annealing at high temperatures to finally yield Zn-rich composition. XRD of the precursor yields three broad peaks around $2\theta \sim 28^\circ$, $47^\circ$ and $56^\circ$ which can be attributed to disordered cubic CZTS because no phase separation is expected since the absorber was dried at relatively low temperature of 320 °C (Figure 4.3b). However,
ZnS and CTS have very similar XRD patterns and cannot be discerned from CZTS. Raman scattering at an excitation wavelength of 633 nm reveals a broad main peak around 330-340 cm$^{-1}$ and shoulders at 290 cm$^{-1}$ and 370 cm$^{-1}$ (see Figure 4.3c), which are fingerprints for weakly crystallized or disordered CZTS [95]. Raman spectra at 325 nm (UV) excitation wavelength were also recorded to analyze whether ZnS phase is present in the precursor. Under UV excitation high intensity of the vibrational mode of ZnS is expected at 348 cm$^{-1}$ (696 cm$^{-1}$ and 1045 cm$^{-1}$, second- and third order peaks, respectively), even if small amounts are present [121]. The UV spectrum does not show a strong contribution at 348 cm$^{-1}$. Considering that the precursor composition is Zn-stoichiometric this is not surprising. The elemental depth profile of the precursor (measured by SIMS, Figure 4.3d) is very homogeneous, no elemental segregations or gradients were observed, only Na is accumulating at the absorber surface. In summary, it is suggested that the precursor exhibits fine-grained cubic CZTS phase with randomly distributed cations in the absence of ZnS.

### 4.3 CZTS-based absorbers

#### 4.3.1 Absorbers from solutions with and without sulfur source

![SEM cross sections of CZTS layers annealed at $T_{\text{sub}} = 500$ °C. a) Sample without TU, annealed in S atmosphere and b) sample with TU in the precursor solution, annealed in $N_2$ atmosphere.](image)

The need for TU as S source is evident when annealing precursors, deposited from solutions without and with TU, for 25 minutes at $T_{\text{sub}} = 500$ °C (see Figure 4.4). When TU
was not added to the precursor solution but elemental S was provided during annealing, a very thin and rough layer with disk-like crystal features was obtained, while the addition of TU leads to a thick and compact layer. Although the number of the spin-coated layers was the same, the viscosity in the solution with TU was much higher resulting in a thicker precursor layer compared to the sample from the solution without TU. The XRD patterns for those two layers are depicted in Figure 4.5. The layer without TU basically shows only one clear peak at 28.5° besides the Mo peak while the layer grown with TU shows all typical kesterite CZTS features.

This experiment shows that TU is not only needed as S source but also to form metal complexes resulting in homogeneous absorber layers and for viscosity adjustments. The following precursors were prepared from solutions containing always TU.

![XRD patterns of CZTS layers](image)

**Fig. 4.5:** XRD patterns of CZTS layers annealed at $T_{\text{sub}} = 500^\circ C$. The sample without TU was annealed in S atmosphere and the sample with TU in the precursor solution was annealed in $N_2$ atmosphere.

4.3.2 In situ investigation of reactive sintering in sulfur atmosphere

The fine-grained CZTS precursor (as described in section 4.2.2) was converted into crystalline kesterite CZTS by high temperature annealing. For an in situ study of the
crystallization and decomposition by means of XRD, the precursor was placed with sulfur powder inside a graphite dome and heated from room temperature to 600 °C (experimental details were described in section 2.2.3).

The in situ XRD measurement depicted in Figure 4.6 can be divided into three temperature regions: i) from room temperature to 400 °C, where the precursor is saturated with sulfur from the atmosphere and slowly starts to crystallize, ii) from 400 - 490 °C, where the precursor is transformed to kesterite CZTS and iii) \( T_{\text{sub}} > 490 \) °C, where sulfur evaporates and kesterite is decomposed. The recorded XRD patterns in region i) correspond to XRD patterns shown in Figure 4.3b, reflecting cubic CZTS phase with randomly distributed cations (seen by broad peaks at \( 2\theta \sim 28°, 47° \) and \( 56° \) which overlap with main peaks of cubic ZnS and monoclinic CTS, compare also Figure 1.3). Since the precursor does not contain sufficient S to bound all cations \( (S/\text{metals} = 0.8-0.9 \) as measured by ICP-MS) it can uptake sulfur from the saturated atmosphere while excess sulfur will evaporate (note that the setup is not completely closed).

In region ii), the intensity of the 112 kesterite peak is rapidly increasing until \( T_{\text{sub}} = 490 \) °C (see also Figure 4.7a). An unambiguous identification of kesterite CZTS is possible by the appearance of 002, 101 and 110 reflexes at \( 2\theta < 25° \) and the 103 reflex at \( 29.7° \) which do not appear for the cubic ZnS and monoclinic CTS phases. In this measurement, only the tetragonal 101 reflex at \( 18.1° \) and the 103 reflex were observed, which support the formation of kesterite CZTS. By evaluation of the XRD intensities it was seen that the 112 reflex of kesterite CZTS rapidly increases within a narrow temperature range of \( 460 - 490 \) °C (see Figure 4.7a) when additionally two clear tetragonal signals appear around \( \sim 18.3° \) and \( \sim 32.9° \) (see Figure 4.6).

In region iii), there is no sulfur vapor pressure anymore and kesterite is no longer stable, thus decomposes, as shown by equation 1.1, resulting in the decomposition products ZnS, \( \text{Cu}_2\text{S} \) and SnS. Several observations were made at \( T_{\text{sub}} > 490 \) °C: the decrease of the 112 and tetragonal 101 reflexes goes along with the appearance of a secondary phase at \( 31.5° \) (compare Figure 4.7a) and a sharpening of the 112, 220/204, and 312/116 reflexes at \( 2\theta \sim 28.5°, 47.3° \) and \( 56.0° \), respectively. For a closer look at evolving and disappearing phases, single XRD patterns for \( 400 \leq T_{\text{sub}} \leq 600 \) °C are depicted in Figure 4.7b. As soon as the main CZTS peak at \( 2\theta \sim 28.5° \) decreases, the other tetragonal CZTS peaks at 29.7, 32.9 and 37.8° disappeared at 550 °C. Only peaks at positions of 28.5° and 31.5° remained. The most probable phases which can be assigned to the peak at 31.5 are \( \text{Sn}_2\text{S}_3 \), CuS and SnS. Above \( T_{\text{sub}} = 550 \) °C this
4.3. CZTS-based absorbers

Fig. 4.6: In situ XRD patterns recorded during annealing of a CZTS precursor. The white dotted line at 490 °C indicates highest XRD intensity for CZTS phase. The red arrows indicate a peak sharpening of 2θ ∼ 28.5°, 47.3° and 56.0° representing a shift from CZTS to ZnS phase. The graphite dome led to additional signals at ∼ 26.2° and ∼ 42.8° in the XRD patterns. The peaks at the * positions could be assigned to CuS, Sn₂S₃ or SnS (see also Figure 4.7b)

peak disappears which can either be explained by Sn evaporation via SnS (Sn₂S₃(s) transforms to SnS which has a high vapor pressures of ∼ 1.4·10⁻² mbar at 600 °C [122]) and/or melting of CuS (M_p = 507 °C, [123]). Cubic ZnS is the most probable candidate for the remaining peak at 2θ ∼ 28.5°, which was confirmed by surface sensitive Raman measurements, taken after the in situ annealing experiment with UV laser excitation where ZnS is in pre-resonant Raman condition [121] (see Figure 4.8a). The intensity of the 112 reflex at 600 °C is almost close to the intensity at the beginning of the annealing which leads to the conclusion that most of the CZTS is decomposed supported by the disappearance of tetragonal reflexes. At least surface sensitive Raman measurements do not show any peaks belonging to the CZTS phase (Figure 4.8b). It is noted, that
in presence of both, CZTS and ZnS, it is not possible to distinguish between them. Here, however, the peak sharpening at $2\theta \sim 28.5^\circ, 47.3^\circ$ and $56.0^\circ$, along with the Raman spectroscopy data suggest the transition from CZTS to ZnS. What is interesting to notice is that the 112 CZTS intensity increase is accompanied by the increase of the peak at $31.5^\circ$. This observation indicates that S loss and therefore decomposition at the surface already started or CZTS is formed via binary metal sulfides.

![Figure 4.7](image1)

**Fig. 4.7:** a) XRD intensities of peaks at $28.5^\circ, 18.3^\circ$ and $31.5^\circ$. b) Single XRD patterns with reference peak positions for CuS, Sn$_2$S$_3$, MoS$_2$, SnS and CZTS, indicated at the bottom.

![Figure 4.8](image2)

**Fig. 4.8:** Raman measurements of the investigated sample after the in situ annealing experiment measured at excitation wavelengths of a) 325 nm and b) 633 nm.
4.3. CZTS-based absorbers

Formation of MoS$_2$ was not observed in the XRD patterns but is clearly visible in the Raman spectrum obtained with 633 nm excitation wavelength which is the resonant Raman condition of MoS$_2$ phase [124] (see Figure 4.8b). Raman spectroscopy is a surface sensitive measurement which is not expected to probe MoS$_2$. However, it was shown earlier that Sn loss leads to phase separation into Cu$_{2-x}$Se and ZnSe, accompanied by uncovered spots where the laser beam can penetrate into the underlying MoS$_2$ layer (compare Figure 3.9). The decomposition at the CZTS/Mo as given in equation 1.3 is thermodynamically favorable, resulting in a mixture of Cu$_2$S, ZnS and SnS at the back contact [46,125].

EDX measurements taken after the in situ annealing experiment at magnification of 250 confirmed only presence of Zn and S. While EDX measurements on morphological features, for example "balls" at higher magnifications of 5k and 50k, respectively, revealed mostly Cu and Sn.

To conclude, it was shown that CZTS rapidly decomposed around 500 °C in absence of S atmosphere into ZnS, Sn$_x$S$_y$, CuS, and MoS$_2$.

4.3.3 Influence of annealing atmosphere

The sintering of solution deposited precursors in chalcogen containing atmosphere can influence the grain growth, metal distribution, formation of secondary phases and therefore the electronic properties of CZTS solar cells. Of special interest in the following sections is the evolution of different layer morphologies, as well as the bulk and surface composition when the precursor is annealed in inert atmosphere or chalcogen containing atmosphere.

Layer morphology and bulk composition

The precursor layers (described in section 4.2.2) with S/metals = 0.8-0.9 (as measured by ICP-MS) were annealed at 530 °C for 25 minutes in N$_2$ or S atmosphere (experimental details are described in section 2.1.3). The SEM cross sections illustrated in Figure 4.9 show a compact and dense layer morphology, with grains larger than 1 µm, and a poorly crystallized layer with larger grains only at the surface when the precursors were annealed in N$_2$ or S atmosphere, respectively.

The corresponding XRD patterns are depicted in Figure 4.10a and show a perfect match with the kesterite reference pattern if the precursor was annealed in N$_2$. All
Fig. 4.9: SEM cross sections of CZTS precursors annealed in a) N₂ atmosphere and b) in elemental S atmosphere at T_{sub} = 530 °C.

Fig. 4.10: a) XRD patterns of samples annealed in N₂ and elemental S atmosphere and b) SIMS depth profile of samples annealed in N₂ (dotted lines) and S (solid lines) atmosphere. The sample annealed in N₂ was measured with enhancement of electronegative elements, therefore, ³⁴S is shown but ⁶⁴Zn is not included due to overlap with ³²S.

minor reflexes below 2θ = 25° ascribed unambiguously to kesterite CZTS are clearly visible, as well as the 103 peak at 29.7°. The pattern for the sample annealed in S contains most tetragonal CZTS reflexes with low intensity but no 103 reflex. It should be noted that the presence of cubic ZnS and monoclinic CTS cannot be excluded (see also section 1.3).

The bulk compositions of the samples are listed in Table 4.1. Both samples are Cu-poor (Cu/(Zn+Sn) < 1). The Zn/Sn and Cu/Sn ratios indicate Sn loss when compared to the precursor. The Sn loss however, is higher for the sample annealed in N₂ atmosphere,
Table 4.1: *Bulk composition of the precursor and the samples annealed in N\textsubscript{2} and S atmosphere as measured by EDX from the top. The S content is not given due to the peak overlap of the X-ray emission lines of S and Mo.*

<table>
<thead>
<tr>
<th>sample name</th>
<th>Cu/Zn</th>
<th>Cu/Sn</th>
<th>Zn/Sn</th>
<th>Cu/(Zn+Sn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>precursor</td>
<td>1.5</td>
<td>1.3</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>1.5</td>
<td>2.0</td>
<td>1.4</td>
<td>0.8</td>
</tr>
<tr>
<td>S</td>
<td>1.5</td>
<td>1.6</td>
<td>1.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

which is expected according to the chemical equilibrium equation [50].

To analyse if there are elemental gradients throughout the CZTS layer thickness, SIMS depth profiles were recorded for precursors annealed in N\textsubscript{2} and S atmosphere which are shown in Figure 4.10b. Both depth profiles exhibit constant metal distributions throughout the layer thickness. The sample annealed in S atmosphere exhibits a slight increase of Zn towards the front of the CZTS layer. Both measurements indicate that there is no excessive cation diffusion or phase separation taking place during the growth.

Cu-rich growth accompanied by the formation of a liquid or quasi-liquid Cu-S(e) phase, is typically responsible for large grains in chalcogenides [43, 97, 126]. Recently it was reported that the Zn-rich growth of co-evaporated CZTSe has a similar effect on grain size as the Cu-rich growth [127]. Large grains were observed even under Cu-poor and Zn-rich growth conditions [127]. It was shown that the delayed reaction with ZnSe automatically leads to the existence of Cu\textsubscript{x}Se\textsubscript{y} which might assist the grain growth [127]. An improved crystallinity with increasing Cu/(Zn+Sn) ratio but no dependency on the Zn/Sn ratio was reported in Ref. [128].

The Sn-rich precursor composition with Zn/Sn < 1 results in large grains when annealing in chalcogen-free inert atmosphere. The final layer composition is, however, Sn-poor (i.e. Zn/Sn > 1) indicating Sn loss during the sintering. This is because the Sn content is above the stoichiometric value, and also due to the thermal decomposition of CZTS (see chemical equilibrium equations 1.1 and 1.2).

An exact mechanism of the densification is unclear but it probably involves the liquid-phase as a medium for material transport [126]. The liquid phase sintering starts with rearrangement of the grains, and in the second step small dissolved grains are re-precipitated at larger grains leading to grain growth and densification. The last step comprises neck growth, when two grains are in contact and merge together by dissolv-
ing parts of the grains and re-depositing it at the neck [126]. Taking into account that the fluxing is observed only for initially Sn-rich compositions in our DMSO approach, it is speculated that either a low-melting Sn-containing phase should exist, or a low-temperature eutectic might be formed in the multi-compound mixture. The motion of Sn is suppressed if S is provided in the annealing atmosphere, which results in more porous layers. The S vapors bind the Sn excess and also counteract the thermal decomposition of CZTS [50], which is in agreement with a lower Zn/Sn ratio of 1.0 for the absorber annealed in S as compared to the Zn/Sn ratio of 1.4 for the N2-annealed sample (Table 4.1). Another densification mechanism described in literature is the capillary contraction which can lead to a structural collapse and densification of the layer upon removal of residual organics [61]. Only if the densification is completed before the onset of nucleation and grain growth very dense material can be obtained [61]. The porosity observed in the S annealed sample could stem from organic residuals, since the decomposition of metal-thiourea complexes might be retarded in the presence of S vapors.

**Surface composition**

The annealing atmosphere influences not only the crystal structure of the film but also its composition with respect to secondary phases and elemental surface gradients. During annealing, the front surface is in equilibrium with the gas phase and therefore prone to decomposition (according to the chemical equilibrium equation 1.1). In this section, the near surface region is analyzed by Raman spectroscopy and XPS, with probing depths < 100 nm and < 30 nm, respectively. XPS sputtering with Ar+ was done at low energy to prevent sample damage and compositional modifications (experimental details are given in section 2.2.7). It is noted that absorbers were KCN etched prior to the XPS measurement. In order to obtain different compositional samples, four identical precursors were prepared under the annealing conditions listed in Table 4.2.

When annealing the precursor in N2 (sample I), the chemical equilibrium (equation 1.1) shifts to the decomposition products, accompanied by Sn loss. The Raman measurements shown in Figure 4.11a proof that surface decomposition yields not only ZnS phase (measured at 325 nm excitation wavelength) but also Cu_xS_y, SnS and Sn_2S_3 (measured at 633 nm excitation wavelength). The corresponding XPS profile (Figure 4.11b) of the surface region shows a very Zn-rich and Cu-poor surface, reflecting probably the presence of ZnS phase which was seen by Raman spectroscopy. It also shows Sn accumulation at the surface, which was contributed to various Sn_xS_y phases fol-
Table 4.2: Annealing conditions (always with flowing \(N_2\) background gas) and bulk compositions measured by EDX of the samples under discussion.

<table>
<thead>
<tr>
<th>sample name</th>
<th>annealing atmosphere</th>
<th>(T_{\text{sub, max}}) (°C)</th>
<th>Cu/Zn</th>
<th>Cu/Sn</th>
<th>Zn/Sn</th>
<th>Cu/(Zn+Sn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>(N_2)</td>
<td>530</td>
<td>1.5</td>
<td>2.0</td>
<td>1.4</td>
<td>0.9</td>
</tr>
<tr>
<td>II</td>
<td>S</td>
<td>590</td>
<td>1.6</td>
<td>1.9</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td>III</td>
<td>NaF cap + (N_2)</td>
<td>550</td>
<td>1.5</td>
<td>1.6</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td>IV</td>
<td>NaF cap + S</td>
<td>550</td>
<td>1.6</td>
<td>1.6</td>
<td>1.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Followed by a rapid Sn decrease to an average level of \(\sim 11\) at\%. Surface Sn accumulation might be explained by Sn loss via vaporization of \(\text{SnS}_2(s)\), which occurs according to the following equations:

\[
\text{SnS}_2(s) \rightarrow \frac{1}{2} \text{Sn}_2\text{S}_3(s) + \frac{1}{4} \text{S}_2(g); \quad \text{Sn}_2\text{S}_3(s) \rightarrow 2 \text{SnS}(s) + \frac{1}{2} \text{S}_2(g); \quad \text{and SnS}(s) \rightarrow \text{SnS}(g) [122].
\]

Another explanation for the surface Sn accumulation refers to different KCN etching rates for Cu and Sn resulting in a possible Sn-rich CuSn\(_{3.75}\)S\(_8\) phase at the surface [129].

Sample II which was annealed in S atmosphere (Figure 4.12) shows, as expected significantly reduced surface decomposition seen by the absence of clear Raman shifts corresponding to \(\text{Cu}_x\text{S}_y\), SnS and \(\text{Sn}_2\text{S}_3\). The Raman spectrum at 633 nm excitation wavelength mainly consists of peaks corresponding to CZTS phase. The strongest peak however, is at 332 cm\(^{-1}\) instead of 337 cm\(^{-1}\) which was related to the existence of local structural inhomogeneities i.e. disordered kesterite [30, 130]. Raman shifts of ZnS phase detected by Raman spectroscopy at 325 nm excitation wavelength exhibit apparently higher intensities. The intensity however, can be strongly influenced by the measurement spot on the sample and thus can only be interpreted qualitatively. The XPS sputter profile corroborates the reduced surface decomposition. The surface is not as strongly Zn-rich and Cu-poor in comparison to sample I. Moreover, the Sn content is \(\sim 13\) at\%, and higher as seen before, under \(N_2\) annealing (Figure 4.11b).

The motivation for processing samples III and IV was to coat the surface with a "capping layer" which does not contain elements of CZTS (as for example SnSe\(_2\) [131]) but protects the surface from possible decomposition. Thus, these samples were coated with 10 nm NaF followed by annealing in \(N_2\) and S atmosphere, respectively. The NaF layer possibly acts as a capping layer preventing surface decomposition. Figure 4.13a illustrates the metal depth profiles measured by XPS of sample III. The surface is only
Fig. 4.11: a) Raman measurements of sample I and b) XPS depth profile of the surface region (< 30 nm).

Fig. 4.12: a) Raman measurements of sample II and b) XPS depth profile of the surface region (< 30 nm).

slightly Zn-rich when compared to the XPS profiles of samples without NaF layer (Figures 4.11b and 4.12b). Sample IV with NaF and annealing in S atmosphere is the only sample with Cu-rich surface (Figure 4.13b). The average Sn content is ∼ 14 at% for both samples, revealing a beneficial effect of the NaF cap due to reduced Sn loss. In both samples, however, there are still secondary phases such as Cu$_x$S$_y$ and Sn$_2$S$_3$ at the surface (see Figure 4.13c) leading to the assumption that the NaF capping layer is not fully covering or comes off during annealing. More about the influence of a precursor coating with NaF is discussed in Chapters 5 and 6.
4.3. CZTS-based absorbers

Fig. 4.13: a+b) XPS depth profiles of the surface region (< 30 nm) of samples III and IV. c) corresponding Raman measurements.

It was mentioned earlier, that KCN preferentially etches Cu [129], usually bound in Cu-chalcogenides. Sample IV however, was also KCN etched but does not show a Cu-poor surface. It is assumed that the precursor annealing and possible surface decomposition is responsible for the observed surface metal gradients and to a lesser extend the KCN etching.

Figure 4.14 gives an overview of the XPS surface composition in comparison to the bulk composition (measured by EDX at 20 kV). There is a clear trade-off between surface and bulk composition raising the question how useful the statement, Cu-poor (Cu/(Zn+Sn)<1) and Zn-rich (Zn/Sn>1) absorber composition, as required for high conversion efficiency, really is.

Although, the CZTS absorber surface composition analyzed by Raman spectroscopy was often addressed in literature [131–133] a deviation between bulk and surface composition was seldomly discussed. Bär et al. for example also found a Cu-poor CZTS surface structure by XPS [134]. The surface was interpreted by presence of ZnSnS$_3$ or ZnS and SnS$_2$ phases. This study, however, leaves open questions concerning the direct measurement of surface phases and the impact on PV characteristics. It becomes evident in the next section, that the near surface composition has strong influences on the PV parameters.
Fig. 4.14: Relative XPS and EDX derived cation compositions for samples I-IV. The XPS composition represents the average of the surface (< 30 nm).

### 4.3.4 Solar cell performance

To elucidate the effect of absorber (surface) composition on solar cell performance, the JV and EQE curves of samples I-IV are depicted in Figure 4.15 and the corresponding PV parameters are summarized in Table 4.3. Although all samples are Zn-rich and Cu-poor (bulk composition, see Table 4.2), as reported to be substantial for good kesterite devices [24, 28] the surface composition seems to influence the final device quality as well.

Samples III and IV are excluded from this discussion because Na strongly influences the electronic properties of the CZTS device as outlined in Chapter 6. Therefore, the effect of Na and of the surface composition on the PV characteristics cannot be distinguished and is not further discussed here.

Samples I and II show basically, a trade-off between either high $V_{oc}$ or $J_{sc}$. Moreover, the apparent band gaps of samples I and II ($\sim 1.5$ eV and $\sim 1.4$ eV, respectively) from the EQE cutoff seen in Figure 4.15b differs by $\sim 100$ meV. A similar behavior was also reported in Ref. [46]. It is noted that the sample quality is not sufficient to reliably extract the absorber band gap. The appearing band gap difference might be caused by the presence of secondary phases, band gap fluctuations or a very high density of states.
Table 4.3: Summary of photovoltaic parameters for pure sulfide Cu$_2$ZnSnS$_4$ cells annealed under different conditions (listed in Table 4.2). The $J_{sc}$ was extracted from spectrally resolved EQE measurements.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Annealing atmosphere</th>
<th>Eff (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>Remarks / Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>N$_2$</td>
<td>2.38</td>
<td>567</td>
<td>7.3</td>
<td>57.5</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>S</td>
<td>3.05</td>
<td>372</td>
<td>13.9</td>
<td>59.0</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>N$_2$</td>
<td>4.53</td>
<td>423</td>
<td>18.1</td>
<td>59.2</td>
<td>with NaF</td>
</tr>
<tr>
<td>IV</td>
<td>S</td>
<td>3.35</td>
<td>565</td>
<td>11.3</td>
<td>52.9</td>
<td>with NaF</td>
</tr>
<tr>
<td>Best vacuum</td>
<td>−</td>
<td>9.19</td>
<td>708</td>
<td>21.6</td>
<td>60.0</td>
<td>[135]</td>
</tr>
<tr>
<td>Best non-vacuum</td>
<td>S</td>
<td>7.3</td>
<td>567</td>
<td>22.0</td>
<td>58.1</td>
<td>[136]</td>
</tr>
</tbody>
</table>

Fig. 4.15: a) JV and b) EQE measurements for Cu$_2$ZnSnS$_4$ samples annealed in N$_2$ and S. Please note that the $J_{sc}$ deduced from JV measurements deviates from the $J_{sc}$ extracted from EQE measurements and is caused by a spectral mismatch of the solar simulator.

at this energy which would also limit the $V_{oc}$. Sample I has an EQE below 40% and a corresponding $J_{sc}$ of 7.3 mA/cm$^2$ which can be significantly increased to $\sim$ 55% and corresponding $J_{sc}$ of 13.9 mA/cm$^2$ when annealing in S atmosphere (sample II). Several mechanisms might be responsible for low quantum efficiency and therefore low $J_{sc}$: first, current blocking due to presence of ZnS phase at the CZTS/CdS interface. A low EQE in the range of 60% caused by ZnSe acting as current blocker at the pn-junction was reported by Wätjen et al. [137]. Second, high recombination losses because of enhanced recombination at boundaries of different phases or due to presence of deep defects such as V$_S$. And third, Cu-rich CZTS with very high charge carrier density and
consequently small space charge region (SCR) width \( W \) (\( W \propto \sqrt{V_{bi} - V \over qN_A} \), where \( V_{bi} \) is the built-in voltage, \( V \) the applied voltage, \( q \) the elementary charge and \( N_A \) the number of acceptors). The latter argument could lead to a poor charge carrier collection if the minority carrier diffusion length is short.

The first case, current blocking by ZnS, is expected to happen if the surface is mostly covered by ZnS. In that case, a ZnS/CZTS interface could lead to an unfavorable conduction band alignment which is often referred to as a "spike" (i.e. positive offset between ZnS and absorber) with a height \( > 1.3 \text{ eV} \) acting as a barrier for electrons (determined by first principle calculations [138]). Experimental data for ZnS on CZTSSe resulted in a spike-like conduction band offset of \( 1.1 \text{ eV} \) [139]. Wätjen et al. [137] estimated a spike of \( 0.9 \text{ eV} \) at the ZnSe/CZTSe interface.

Electron beam induced current (EBIC) is a useful tool to visualize charge carrier collection along the absorber thickness. In good solar cell devices collection is observed across the whole absorber thickness. The EBIC signal (red) as a convolution of SCR width and minority carrier diffusion length of sample I is overlaid with the SEM cross-section image, as shown in Figure 4.16. Sample I exhibits charge carrier collection only close to the pn-junction. If covering ZnS would be responsible for the current blocking no EBIC signal would be expected, or dark grains which do not contribute to charge carrier collection.

![EBIC image](image)

**Fig. 4.16:** EBIC measurement on a CZTS solar cell (sample I). The EBIC signal is overlaid with the SEM picture to illustrate the location of the charge carrier collection.

On the other hand, sample I with low \( J_{sc} \) exhibited one of the highest \( V_{oc} \)'s amongst the samples compared here. For argument two, increased recombination, it is expected to result also in a smaller \( V_{oc} \). The third argument, Cu-rich CZTS, can result in a low \( J_{sc} \) if a small SCR is caused due to very high \( N_A \) and at the same time this would explain the high \( V_{oc} \). Upon high acceptor doping, the quasi-Fermi level splitting is increased.
4.4. CZTSSe-based absorbers

relating to a higher $V_{oc}$ [140].

The initially Sn-rich precursor can result in good sintering if annealing is done in N$_2$ atmosphere (sample I, compare Figure 4.9a). A Sn loss in the ternary phase diagram translates simultaneously in a Cu enrichment. This explanation would be in agreement with argument three, Cu-rich CZTS. Cu-rich CZTS might exhibit a higher number of Cu$_{2n}$ antisites which is the dominant p-type acceptor in CZTS (see section 1.3.1) and responsible for a Fermi level shift closer to the valence band.

Following up this argumentation, sample II is less Cu-rich than sample I (compare Cu/Sn ratio in Table 4.2), and therefore might have a lower doping concentration N$_A$, which correlates to a larger SCR and therefore better collection and higher $J_{sc}$. A lower doping concentration is also responsible for a smaller quasi-Fermi level splitting which reflects in a smaller $V_{oc}$. The $V_{oc}$ is not only influenced by the doping but also by recombination which could depend on the interface alignment or elemental surface termination.

In literature, the electronic surface structure of Cu-poor and Cu-rich CZTS was investigated by ultraviolet and inverse photoelectron spectroscopy to analyze the valence band maximum and the conduction band minimum [129]. The surface band gap for KCN etched absorbers were found to be $\sim 1.9$ eV (Cu-poor absorber) and $\sim 2.5$ eV (Cu-rich absorber). In that study however, phase composition probed for example by Raman spectroscopy, and the consequence for the CB offset at the CdS/CZTS interface were not mentioned and leaves questions yet to be answered. A comprehensive study on the chemical and electronic surface (and phase) structure of CZTS(e) and a correlation to PV characteristics, likely reveals insights into electron transport and recombination losses at the CdS/CZTS(e) interface.

4.4 CZTSSe-based absorbers

The first part of Chapter 4 concentrated only on the sulfide CZTS. It was demonstrated that initially Sn-rich precursor solutions can lead to large-grained layers, which however contain secondary phases and exhibit poor charge carrier collection. To suppress on one hand, surface decomposition and on the other hand enhance grain growth, selenization of the precursor will be used throughout this section. The intention was
that large Se atoms which substitute smaller S atoms increase the unit cell volume from 317.1 Å³ (pure CZTS) to 351.5 Å³ (pure CZTSe) [115] and thus, increase grain growth and densification. Furthermore, the anion exchange might induce some elemental fluctuations or movement in the absorber, which might be beneficial for grain growth. Also the world record is based on a sulfo-selenide absorber with high selenium amount leading to the assumption that the intrinsic defects in CZTSe are less harmful than in CZTS [141]. The fine-grained precursor (described in section 4.2.2) is converted to crystalline CZTSSe during a high temperature annealing at $T_{\text{sub}} = 560 \degree C$ for 25 minutes in elemental Se atmosphere where S is (partially) substituted by Se. Although the growth of CZTSe was observed to start around 420 °C (section 3.3.2), significantly higher substrate temperatures were needed, due to the substitution reaction of S and Se in CZTSSe.

The goal of this section is to develop a method based on synchrotron radiation techniques to determine the formation of secondary phases in dependency of the absorber composition along the CTSe-ZnSe tie-line. The challenges encountered when growing kesterites were described in section 1.3, including a small single phase region, and the unambiguous detection and quantification of secondary phases. Beyond MoSe$_2$, ZnSe is the thermodynamically most stable binary secondary phase. It is demonstrated in the following, that ZnSe can be detected and quantified by use of synchrotron radiation techniques. This was done in collaboration with Justus Just from Bergische University Wuppertal and HZB Berlin, both Germany. Prior art on the quantification of ZnS in CZTS and correlation of the ZnS amount to the electronic properties of the solar cell device was reported by Just et al. [66].

### 4.4.1 Absorber characterization

#### Total absorber bulk composition

Precursor samples were prepared by variation of the Zn concentration with $0.5 < \text{Zn/Sn-ratio} < 3.8$ (samples A - E, compare Table 4.4). The overall absorber composition measured by EDX from the top is also given in Table 4.4. By comparing the Zn/Sn ratio in the precursor with the Zn/Sn ratio in the selenized absorber a Sn loss is observed in samples A and B, while samples C-E apparently exhibit a Zn loss. Since the penetration depth of a 20 keV electron beam in CZTSe is about 1.2 µm this could point towards a
4.4. CZTSSe-based absorbers

Zn-gradient in the absorber layer with possible ZnS(e) accumulation at the back, and therefore reduced Zn signal. The Cu/Zn ratio is steadily decreasing upon increasing the Zn content while the Cu/Sn ratio is nearly constant.

Table 4.4: Zn/Sn composition in the precursor solution and metal ratios in the selenized absorbers (measured by EDX from the top) prepared for XANES measurements. Last column: vol% ZnSe as determined by XANES, assuming an error of less than 5%.

<table>
<thead>
<tr>
<th>sample name</th>
<th>Zn/Sn precursor solution</th>
<th>Zn/Sn selenized</th>
<th>Cu/Zn selenized</th>
<th>Cu/Sn selenized</th>
<th>vol% ZnSe (XANES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5</td>
<td>0.9</td>
<td>2.1</td>
<td>1.9</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>0.7</td>
<td>1.1</td>
<td>1.6</td>
<td>1.9</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td>1.7</td>
<td>1.6</td>
<td>1.1</td>
<td>1.8</td>
<td>14</td>
</tr>
<tr>
<td>D</td>
<td>2.1</td>
<td>1.9</td>
<td>0.9</td>
<td>1.8</td>
<td>13</td>
</tr>
<tr>
<td>E</td>
<td>3.8</td>
<td>3.1</td>
<td>0.6</td>
<td>1.8</td>
<td>35</td>
</tr>
</tbody>
</table>

Layer morphology

Figure 4.17 illustrates the influence of the initial Zn concentration in the precursor on the layer morphology after selenization. The SEM top views reveal an increasingly compact morphology the higher the Zn/Sn ratio is. For samples A and B with Zn/Sn ~ 1 it seems, as if there is a very porous crystalline overlayer. When looking at the cross sections, the picture is completely different. The higher is the Zn concentration, the worse is the morphology. In other words, Zn excess seems to inhibit the sintering along the thickness of the absorber, or, by increasing Zn simultaneously the amount of Cu is decreased, however, Cu-rich composition facilitates fluxing and might be needed to enhance sintering (in analogy to CIGS [142,143]). The sample with Zn-poor composition, Zn/Sn < 1, is completely sintered with large grains extending from the top to the bottom. As soon as the composition is Zn-rich the layers only crystallize on the top while the bottom part remains in precursor-like morphology. The last sample with Zn/Sn = 3.1 seems to be better crystallized but this is only caused by a thinner precursor layer and therefore facilitated penetration of selenium.

Crystal structure

XRD measurements of those samples are presented in Figure 4.18 and reveal the following trends: The sample with Zn-poor composition (sample A) exhibits the highest crystal quality with a symmetric 112 peak while other peaks get more asymmetric
Fig. 4.17: SEM top view and cross section images of samples summarized in Table 4.4. The Zn/Sn ratios of the selenized films are given at the right with increasing zinc concentration from the top to the bottom (determined by EDX).
towards higher angles. The most noticeable asymmetric 112 peaks are observed for the samples C and D. The asymmetry i.e. shoulder towards higher angles is probably caused by remaining sulfur, likely in the unsintered underlayer. Another consideration is that S is bonded in ZnS and ZnS is more difficult to selenize due to its lower formation enthalpy \[100\] (assuming more ZnS phase the higher the Zn/Sn ratio). Sample E also exhibits a symmetric 112 peak but this can be explained because of a comparably thinner precursor layer and therefore improved Se incorporation.

![XRD patterns for samples with different Zn/Sn ratio.](image)

**Fig. 4.18: XRD patterns for samples with different Zn/Sn ratio.**

**Phase composition**

Raman spectra at excitation wavelengths of 633 and 515 nm, respectively, are recorded to reveal presence of secondary phases which are not detectable with XRD (see also section 1.3.1). The spectra measured at 633 nm (see Figure 4.19a) show the typically observed main peaks for CZTSe at 196 and 173 cm\(^{-1}\), respectively, and a weak peak around 232 cm\(^{-1}\) [95]. The Raman spectra recorded with 515 nm excitation wavelength reveal some more features (compare Figure 4.19b). The CZTSe main mode at 196 cm\(^{-1}\) is observed for all samples while the peak at 173 cm\(^{-1}\) is masked by the main mode. All samples with Zn/Sn < 3 show an additional peak at 325 cm\(^{-1}\) which is slightly below the main CZTS mode at 339 cm\(^{-1}\) [144]. Presence of this peak reflects the remaining S in the absorber and therefore a mixed CZTSSe phase. The main CZTS mode is already weakly visible in the measurement at 633 nm but is in better
excitation condition at 515 nm. Both main modes (A modes) for CZTSe and CZTS are pure anion modes corresponding to Se and S vibrations, respectively [93, 145]. For the Raman spectra measured at excitation wavelength of 515 nm both main modes follow the two-mode behavior [144], that is a shift of the A modes: from 197 cm$^{-1}$ to 207 cm$^{-1}$ (CZTSe) and from 322 cm$^{-1}$ to 327 cm$^{-1}$ (CZTS) for the samples A-D, representing increasing S content in CZTSSe [144]. This shift is not observed for sample E because Se incorporation was facilitated by using a thinner precursor layer. Two additional peaks around 377 cm$^{-1}$ and 402 cm$^{-1}$ might be attributed to MoS$_2$ phase. The peak around 260 cm$^{-1}$ probably stems from CuSe$_x$ [90, 91] and not ZnSe phase. The main peak corresponding to the ZnSe phase is expected at 250 cm$^{-1}$ [96] but is not observed with excitation wavelengths $\lambda = 633$ nm and 515 nm. Resonant Raman scattering of ZnSe is expected close to its optical band gap $\sim 458$ nm [96]. It is still possible to detect ZnSe with excitation wavelength 515 nm [96] however, the probing depth of Raman is limited to $< 100$ nm and possible ZnSe accumulation close to the back contact may not be detected. This would be another indication for ZnSe accumulation close to the back contact. If Zn is bound to S, UV Raman excitation with 325 nm excitation wavelength would be needed for resonant Raman measurement due to its higher optical band gap than ZnSe [132]. Presence of Cu$_2$SnSe$_3$ with main Raman peak around 180 cm$^{-1}$ cannot be excluded [146], although the ternary phase diagram (Figure 4.20) does not suggest its existence in samples B-E (see next paragraph).

![Raman spectra](image)

**Fig. 4.19:** Raman measurements on samples from Table 4.4 at a) 633 nm and b) 515 nm excitation wavelength.
4.4.2 Quantification of ZnSe with XANES

The ternary diagram depicted in Figure 4.20a can be addressed to estimate the presence of secondary phases with respect to absorber composition. The star represents single phase CZTSe [48]. The CTSe-ZnSe tie-line indicates a binary phase region where CZTSe is expected to co-exist with either CTSe or ZnSe, respectively [48]. The total composition of the samples under investigation along this CTSe-ZnSe tie-line is illustrated in Figure 4.20a (see also Table 4.4).

Measurements of the X-ray absorption near edge (XANES) were performed by Justus Just at the K-edge of Se (edge energy 12666 keV [147]) at HASYLAB beamline X of the DORIS synchrotron in transmission mode. The ZnSe and CZTSe reference samples were produced by solid state reactions of the pure elements in evacuated and sealed ampoules at a maximum temperature of 750 °C with cooling rate of 1 °C/h [148]. The CZTSe reference sample is assumed to be single phase due to the equilibrium growth. The XANES of CZTSe and ZnSe at the K-edge of Se exhibit different features, seen in Figure 4.21a by the $\Delta E$ difference of 1.8 eV. XANES investigation at the Se absorption edge spectra is used because the Zn K-edge does not differ substantially for those two phases [66]. Similar features were observed at the K-edge of S in ZnS and CZTS [66]. The energy resolution at the K-edge of Se however, is lower than at the K-edge of S because of a shorter core hole lifetime. The absolute error depends on the fitting details and the quality of the reference samples and is estimated to be $< \pm 5 \%$ absolut. The volume fraction of ZnSe is determined by least-square fits of the spectra with a linear combination analysis of the reference CZTSe and ZnSe spectra (see the example in Figure 4.21b). The volume of CZTSe and ZnSe is given by the anion lattice which is the same for both phases; therefore, the number of anions divided by the volume is equal and the fit data directly give the volume fraction of ZnSe.

Quantification of ZnSe by XANES revealed an increasing ZnSe content for increasing Zn/Sn ratios, see Table 4.4. Sample E with Zn/Sn = 3.1 contains 35 vol% ZnSe. Only the sample with Zn-poor composition contains no ZnSe phase. In literature, highest efficiencies have been observed for Zn-rich and Cu-poor compositions [28]. Sample B, however, with Zn/Sn = 1.1 contains 5 vol% of ZnSe.

In literature it is debated how the presence of ZnS(e) influences the device properties. It may act as "dark" matter without negative influence on device properties [45]. At the same time it was reported to reduce device efficiency [66] and block the current...
Fig. 4.20: a) Total composition of the samples along the Cu$_2$SnSe$_3$-ZnSe tie-line. The different areas in the diagram correspond to the following phase compositions: * = single phase CZTSe, (1) CZTSe + Cu$_2$Se + ZnSe, (2) CZTSe + ZnSe + SnSe$_2$, (3) CZTSe + SnSe$_2$ + CTSe, (4) CZTSe + CTSe + Cu$_2$Se. The tie-lines indicate binary phase regions where CZTSe and one other phase is present. b) Real composition of the CZTSe phase after subtracting the amount of Zn bound in ZnSe determined by XANES.
4.4. CZTSSe-based absorbers

![Graphs showing absorption spectra and XANES measurements.]

**Fig. 4.21:** a) Measurement of XANES at Se K-edge of the CZTSe and ZnSe reference samples and b) example for the quantification of ZnSe in CZTSe by linear combination analysis.

If present at the interfaces [137]. The presence of ~5 vol% ZnSe (bearing in mind an inaccuracy of <5%) at the considered "optimum" Zn/Sn ratio raises the question on the reported single phase region of CZTS(e) [48]. It could be explained by a slight expansion of the single phase region towards the ZnSe side as also proposed by Ref. [16]. This speculation seems plausible, when considering the quantified amount of ZnSe and subtracting this fraction of Zn bound in ZnSe (instead of bound in CZTSe). All sample compositions are found in or close to the reported single phase region of CZTSe with slight shift to the ZnSe region (see Figure 4.20b).

In comparison to absorber characterization with XRD and Raman, there was no clear indication for presence of ZnSe phase even for sample E with 35 vol% ZnSe. This discrepancy might be explained by ZnSe accumulation at the back, and therefore out of probing depth of the Raman measurements (measured from the top of the absorber) or insufficient laser excitation energy.

### 4.4.3 Solar cell performance

During the annealing studies it was found that sintering is improved when the absorber is sulfurized prior to selenization. Therefore, CZTS precursor films were first sulfurized for 25 minutes at 520 °C followed by selenization for 25 minutes at 550 °C. The resulting absorber layer is completely crystallized, however not very dense, containing pin holes.
Chapter 4. CZTS and CZTSSe processed from binder-free solutions with chalcogen (inset Figure 4.22a).

The best cell efficiency achieved was 4.70% ($V_{oc} = 312$ mV, FF = 56.0% and $J_{sc} = 26.9$ mA/cm$^2$). Light and dark JV and EQE curves are illustrated in Figure 4.22. The cells typically lack in $J_{sc}$ seen in a very poor collection of long wavelength photons (Figure 4.22b).

![Graph showing JV and EQE of a CZTSSe device with inset SEM cross section.](image)

**Fig. 4.22**: a) JV and b) EQE of a CZTSSe device. The inset in a) illustrates the SEM cross section.

### 4.5 Summary

No residual carbon layer was observed when utilizing short chain and low temperature degradable precursor chemicals. TGA analysis showed that S is donated by TU, not by the solvent DMSO due to the stronger complexing nature of TU.

The absorber layer morphology is strongly influenced by the annealing condition as well as the precursor composition. Well crystallized absorbers were obtained for annealing initially Sn-rich precursors in N$_2$ atmosphere, or selenization of Sn-rich precursors. During annealing, the surface degrades very fast in absence of S atmosphere, resulting in Sn loss and remaining ZnS, CuS, Sn$_x$S$_y$ and MoS$_2$ phases. Sn loss accompanied by Cu enrichment might lead to a low EQE due to a high N$_A$ doping density and consequently small SCR, reflected in a poor charge carrier collection (under the assumption that the minority carrier diffusion length is short). A discrepancy of absorber bulk and surface
composition was found, giving evidence that appropriate bulk composition alone does not lead to good device performance. A comprehensive study on the chemical and electronic surface (and phase) structure of CZTS(e) and a correlation to PV characteristics, might increase the understanding of electron transport and recombination losses at the CdS/CZTS(e) interface.

A method based on synchrotron radiation techniques was developed in collaboration with Justus Just, to demonstrate that ZnSe can be detected and quantified by XANES. This is possible because of distinct absorption features of CZTSe and ZnSe. With the help of quantified ZnSe phase inclusions, a cross check of absorber phase composition (XANES) with overall elemental composition (EDX), was feasible. The presented results indicate that ZnSe is present as soon as the composition drawn into the ternary diagram is on the Zn-rich side of the CZTSe-ZnSe tie-line. Even absorber layers with "ideal" Zn-rich composition of Zn/Sn = 1.1 can contain small amounts of ZnSe.
Chapter 5

Sodium assisted crystallization of solution processed CZTSSe

A massive improvement in crystallization of non-vacuum deposited precursors in presence of sodium is presented. In this and the following Chapter, Na is supplied via a NaF layer evaporated onto the fine-grained CZTS precursor in order to conduct a quantitative study on the effect of Na on crystallization. A literature overview on the effects of Na on crystallinity during sintering of CIGS and CZTSSe is given at the beginning (effects on electronic properties are preserved for Chapter 6). Thereafter, the influence of Na on microstructure and texture is presented, and a possible fluxing mechanism leading to massive improvement in grain growth is proposed.

The following sections are based on the publication "Sodium Assisted Sintering of Chalcogenides and its Application to Solution Processed Cu$_2$ZnSn(S,Se)$_4$ Thin Film Solar Cells" by C. M. Sutter-Fella et al. [149].

Parts of the results of this Chapter were obtained during the Master thesis of Josua Stückelberger.
5.1 Motivation and prior art

The main drawbacks in solution and nanoparticle processing remain poor crystallinity, high surface roughness and the presence of microscopic voids in sintered chalcogenide layers [150, 151]. Therefore, a controlled grain growth is one of the key challenges for further efficiency improvement. Several strategies can be employed to enhance the grain growth. Well crystallized material can be achieved by taking advantage of liquid copper-rich selenide phases acting as fluxing agent as demonstrated for CIGS [97, 142, 143, 152]. Another strategy and easier to employ for non-vacuum deposition, is the use of impurity elements promoting crystallization and grain growth. As such, sodium, potassium, cesium, antimony and bismuth have been tested [153–156].

Na in CIGS

In CIGS, the influence of Na on crystallinity is debated. While some groups observe enhancement in crystallinity [153, 157] others observed decreasing crystallinity [158]. Besides its influence on crystallinity, sodium is essential for high efficiency CIGS solar cells which is discussed in Chapter 6.

The chemical environment of Na was explored by several groups. Niles et al., [159] identified Na-Se bonds by a detailed XPS study which are oxidized to Na$_2$SeO$_3$ or NaOH. Also in Ref. [160] the formation of Na$_2$Se was deduced from soft XPS measurements. Braunger et al. [161, 162] investigated the role of Na during CIGS growth. The main conclusions are summarized here: i) presence of Na increases the selenium activity under high Se partial pressure; ii) within the CIGS Na is preferentially bonded to Se via sodium-polyselenide; iii) oxidation of sodium-polyselenides leads to an increased availability of elemental Se via

$$Na_2Se_x + \frac{3}{2}O_2 \rightarrow Na_2SeO_3 + (x - 1)Se.$$  \hspace{1cm} (5.1)

It is worth mentioning, that in those experiments Na was present due to out-diffusion from the soda lime glass (SLG).

Na in CZTSSe

When it comes to kesterites, the effects of Na are assumed to be similar as in CIGS,
5.2 Influence of top NaF layer on morphology

however, only a few studies are available. Repins et al. [43] showed that the out-diffusion of Na from the SLG during growth of CZTSe by co-evaporation was not sufficient for good device properties, and an additional NaF layer on the Mo coated substrate led to improvements in all photovoltaic parameters. No effect on grain growth was noted which is not surprising because a two-stage process with Cu-rich growth period was employed which enhances grain growth [43].

For growth processes without Cu-rich period, grain growth induced by presence of Na was observed by several groups. Oo et al. [163] concluded that both, the substrate temperature and Na enhance grain growth. Promoted grain growth and 112 texture upon Na diffusion from the SLG substrate was also found for spray-deposited CZTS [164]. Improved grain growth and even a significant band gap increase was reported for a sol-gel process with NaSCN as Na source directly included in the chemical precursor [165].

Na incorporation methods

The most frequently employed method for Na incorporation is via out-diffusion from the SLG substrate during a high temperature deposition process. This results in typical amounts of ~ 0.1 – 0.5 at% Na found in CIGS and is considered to be optimum [159, 161, 166].

A more controlled supply of Na via sodium-containing precursors in combination with Na-diffusion barriers or Na-free substrates can be provided before, during or after the growth process [154, 167, 168]. NaF is commonly used as Na precursor [167, 169]. Other precursors such as Na$_2$S [170], Na$_2$Se [171], solution deposited NaOH [172] or a simple absorber soak in aqueous NaCl [157] can also be used. However, NaF is preferred due to lower hygroscopy compared to Na$_2$S and Na$_2$Se and its congruent evaporation [173].

5.2 Influence of top NaF layer on morphology

The effect of Na was investigated by applying a thermally evaporated NaF layer on top of the CZTS precursor, thus enabling quantitative studies on the influence of the NaF thickness. The precursor for all experiments was the same (see Figure 5.2a) and is described in detail in section 4.2.2. NaF top coatings with layer thicknesses from
0 - 300 nm were deposited by thermal evaporation prior to selenization in a two zone furnace at 550 °C for 25 minutes (note: there is always sodium out-diffusion from the SLG). Figure 5.1 schematically depicts the Na supply a) from the SLG substrate, and b) from a combination of NaF top layer and SLG. Diffusion is always in the opposite direction of the concentration gradient which is indicated by the arrows.

**Fig. 5.1:** a) Na diffusion from the SLG and b) from both, SLG and NaF top layer. The direction of Na diffusion is indicated by arrows.

A poorly sintered CZTSSe material is obtained after selenization of the precursor with 0, 10 and 20 nm NaF (Figure 5.2b-d). The absorbers are denoted by CZTSSe since S is not completely substituted by Se. Grain growth is only seen at the top of the absorber, while the bottom part remains in a precursor-like morphology. With increasing NaF layer thickness, selenized CZTSSe films exhibit a massive increase in grain size and reduced surface roughness. Some crystals even extend over the full layer thickness (Figure 5.2e-h) when a NaF coating of ≥ 50 nm was deposited. The grain size again is decreased for NaF layers > 100 nm (see Figure 5.2g-h).

The latter observation could be explained by a reduced interdiffusion of constituent elements in presence of excess Na, similar to CIGS [174, 175]. Simultaneously, the formation of NaCl phase (see Figure 5.5a) was observed, which could hinder further crystal growth. For NaF > 100 nm additionally bubbles appeared (Figure 5.10b) that caused poor adhesion and delamination during further processing. Bubble formation is generally explained by compressive stress due to volume expansion or formation of a gaseous phase which could be linked to formation of NaCl or volatile SO$_x$ species upon sintering.

To exclude the influence of Na out-diffusion from the glass substrate on crystallinity, the precursor layers were deposited on SLG coated with Si$_3$N$_4$ as Na diffusion barrier. This
5.2. Influence of top NaF layer on morphology

Fig. 5.2: SEM cross section images of absorber layers illustrating the enhanced grain growth in the presence of NaF. a) fine-grained CZTS precursor, b) the layer after selenization with 0 nm NaF, and c-h) CZTSSe layers selenized with a NaF top layer with thicknesses from 10 - 300 nm.
approach was chosen to avoid mismatch of the thermal expansion coefficients when using Na free substrates such as borosilicate glass or alumina (both have expansion coefficients which are smaller than for CIS [153] and CZTS [176] (tensile stress); while when using SLG the thermally induced stress is compressive). The efficient suppression of Na diffusion by the Si$_3$N$_4$ barrier layer was confirmed by SIMS depth profiles (see Figure 2.1). A direct comparison of absorbers grown with 0 and 200 nm NaF with Si$_3$N$_4$ barrier and without barrier reveals identical improvements in sintering (Figure 5.3). From this control experiment it is concluded that the enhanced grain growth can be attributed to the NaF top layer. In this case significant amounts of Na are readily available at the surface to react with arriving Se molecules while Na from the SLG first needs to diffuse via Mo into the CZTSSe layer.

Fig. 5.3: SEM cross section micrographs of samples annealed with 0 and 200 nm NaF. Direct comparison of samples with Na diffusion barrier (Si$_3$N$_4$) on the left (a+c) to samples without diffusion barrier on the right (b+d).
5.3. Effect of Na on absorber crystallinity

Fig. 5.4: Direct comparison between cleaved (left) and FIB polished (right) SEM cross section illustrating the formation of voids in the CZTSSe bulk and at the back interface between Mo and CZTSSe. The FIB cut was done on the sample with 200 nm NaF.

Although the grain size is massively improved by additional Na, the layer morphology is not completely satisfying due to the formation of voids at the back interface between Mo and CZTSSe but also in the CZTSSe bulk (illustrated in the right part of Figure 5.4). Independent of the deposition method, voids have been observed in CZTSSe [177, 178]. Several mechanisms can lead here to void formation: first, this sample had inclusions of NaCl phase which could be preferentially removed during focused ion beam (FIB) preparation, however other samples without NaCl phase also showed voids. Second, the voids can be formed due to different elemental diffusion rates and phase segregation during annealing, a mechanism called Kirkendall effect [179]. Third, void formation at the back is obvious when considering the instability of the Mo/CZTSSe interface where the chalcogen out-diffuses to form MoS(e) [46]. Voids can act as recombination centers and at the Mo back contact could cause a higher series resistance, and therefore should be eliminated [151].

5.3 Effect of Na on absorber crystallinity

Figure 5.5 illustrates the XRD patterns for samples with increasing NaF thickness. All minor peaks below $2\theta = 25^\circ$, which are a clear fingerprint of CZTSSe, are distinctly visible when adding $\geq 50$ nm NaF. The 112 and 220/204 reflexes of the samples with 0 - 100 nm NaF gradually shift to smaller angles (Figure 5.5b) representing a complete substitution of S by Se because of an increase of the lattice constant $a$ from 5.419 Å (CZTS) to 5.695 Å (CZTSe) [180]. The peak shift towards smaller angles (pure CZTSe) is in agreement with the ICP-MS quantification of incorporated selenium, expressed by
the increasing Se/(S+Se) ratio (compare Table 5.1). When applying \( \geq 200 \text{ nm NaF} \) a NaCl peak at 31.6° was seen. In the presence of NaCl, as seen for samples with 200 and 300 nm NaF, the 112 and 220/204 peak positions shift back to higher angles, although the Se content of the samples measured by ICP was the highest in the sample with 200 nm NaF (Table 5.1). One possibility for this observation is strain in the layer which resulted in bubble formation (see Figure 5.10b).

![XRD patterns of CZTSSe samples with increasing NaF thickness. Expected NaCl peak positions are marked by dotted lines. b) Magnification around 112 and 220/204 reflexes. The arrows indicate a shift due to an increase of the lattice constant.](image-url)

Fig. 5.5: XRD patterns of CZTSSe samples with increasing NaF thickness. Expected NaCl peak positions are marked by dotted lines. b) Magnification around 112 and 220/204 reflexes. The arrows indicate a shift due to an increase of the lattice constant.

The observation made by SEM morphological inspections (Figure 5.2) are in agreement with the full width at half maximum (FWHM) of the 112 reflex extracted from XRD measurements after stripping the Cu K\(_{\alpha2}\) line (Figure 5.6). Information on the crystallite size (more precisely the average coherent domain length) can be obtained from the FWHM. According to the Scherrer equation, the crystallite size is inversely proportional to the FWHM. The FWHM is decreasing, indicating an increase of the domain size until 100 nm NaF and is increasing again for thicker NaF layers. A rapid decrease in grain size with excess Na (\( \sim 3 \text{ at\%} \)) was also found for CIGS [170]. Peak broadening of the 112 reflex due to mixed sulfo-selenide composition is assumed to be negligible because there is a clear correlation with the grain size observed in SEM and the FWHM. Additionally, the shifts of the 112 and 220/204 reflexes towards smaller angles follow a clear trend with the incorporated amount of Se.

In CIGS a pronounced preferential 112 texture was reported with increasing amount of NaF [181]. An evaluation of the peak height intensities of the 112 reflex over the
5.4. Effect of Na on absorber composition

Elemental quantification of CZTSSe absorbers was done by ICP-MS measurements. The results for different samples with and without NaF and Si₃N₄ barrier are listed in Table 5.1. All samples were KCN etched prior to ICP preparation and measurement, in order to analyze the absorber under similar conditions as it is in the actual solar cell device. Sample 1 with Si₃N₄ barrier and 0 nm NaF (i.e. no intentional Na supply) is a reference sample to determine the "impurity" Na content from precursor contamination and handling under atmospheric conditions. It contained 0.2 at% Na which equals the amount of Na in sample 2, where apparently no detectable increase of Na due to out-diffusion from the SLG was measured. Therefore, it is assumed that the Na diffusion from the SLG into the CZTSSe absorber is slow. The precursor coating with 10 nm NaF (samples 3 and 4) resulted in the highest Na content of 0.4 at% while sample 5 with SLG and 200 nm NaF had the lowest content of 0.1 at%.

Fig. 5.6: a) FWHM of the 112 reflex versus NaF thickness and b) intensity ratio of 112 over 220/204 reflexes versus the NaF thickness.

220/204 reflex is used to illustrate any influence on preferential orientation of CZTSSe with increasing NaF thicknesses (Figure 5.6b). No change of preferential orientation was found. The ratio 112 over 220/204 is constant between 3 and 3.5 regardless the NaF layer thicknesses (the calculated ratio of 112 over 220/204 from ICPDS (PDF-number 01-070-8930) data is 1.5).
Table 5.1: Elemental quantification of selenized CZTSSe absorbers either grown on SLG/Mo (denoted by SLG) or SLG/Si$_3$N$_4$/Mo (denoted by Si$_3$N$_4$) by ICP-MS measurements. The NaF layer thicknesses are 0, 10 or 200 nm. All samples were KCN etched prior to ICP preparation and analysis. The error of the ICP quantification is ± 10 %.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na</th>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
<th>S</th>
<th>Se</th>
<th>S+Se</th>
<th>Se/(S+Se)</th>
<th>Cu/Zn</th>
<th>Cu/Sn</th>
<th>Zn/Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - Si$_3$N$_4$ 0 nm NaF</td>
<td>0.2</td>
<td>20.5</td>
<td>11.3</td>
<td>9.8</td>
<td>13.7</td>
<td>44.7</td>
<td>58.3</td>
<td>0.8</td>
<td>1.8</td>
<td>2.1</td>
<td>1.2</td>
</tr>
<tr>
<td>2 - SLG 0 nm NaF</td>
<td>0.2</td>
<td>21.1</td>
<td>12.0</td>
<td>10.8</td>
<td>20.3</td>
<td>35.9</td>
<td>56.2</td>
<td>0.6</td>
<td>1.8</td>
<td>2.0</td>
<td>1.1</td>
</tr>
<tr>
<td>3 - Si$_3$N$_4$ 10 nm NaF</td>
<td>0.4</td>
<td>21.0</td>
<td>12.0</td>
<td>10.7</td>
<td>16.8</td>
<td>39.5</td>
<td>56.3</td>
<td>0.7</td>
<td>1.8</td>
<td>2.0</td>
<td>1.1</td>
</tr>
<tr>
<td>4 - SLG 10 nm NaF</td>
<td>0.4</td>
<td>21.2</td>
<td>11.7</td>
<td>10.8</td>
<td>15.5</td>
<td>40.7</td>
<td>56.2</td>
<td>0.7</td>
<td>1.8</td>
<td>2.0</td>
<td>1.1</td>
</tr>
<tr>
<td>5 - SLG 200 nm NaF</td>
<td>0.1</td>
<td>20.0</td>
<td>10.8</td>
<td>10.2</td>
<td>3.8</td>
<td>55.2</td>
<td>59.0</td>
<td>0.9</td>
<td>1.9</td>
<td>2.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Since the absorber composition is very crucial for working CZTSSe devices, the metal ratios of Cu/Zn, Cu/Sn and Zn/Sn are given as well in Table 5.1. While the metal ratios are very similar, there is a clear trend of the incorporated amount of Se with increasing NaF thickness. The Se/(Se+S) ratio is steadily increasing for samples 2 - 5. The latter finding suggests, the thicker the NaF top layer the more Se is incorporated into the film. This is interpreted as an enhanced reactivity of Se triggering efficient S substitution. Sample 1 seems to be an outlier.

All samples have a total chalcogen concentration higher than 50 at%. Possible reasons for that are a relatively high uncertainty in the quantified amount of sulfur (as described in the experimental section 2.2.6), formation of secondary phases with chalcogen content > 50 %, for example Na$_2$Se$_x$ (x > 2), SnS(e)$_2$, CuS(e)$_2$ or scratching off of MoS(e)$_2$ during ICP-MS sample preparation. Although XRD measurements do not indicate presence of secondary phases they cannot be excluded since they are frequently observed at the surface or at the back contact interface [46,52,132,177].

In CIGS Na was reported to enhance the formation of MoSe$_2$ [182], which cannot be clearly confirmed by the experiments presented here. The SIMS profiles presented in Figure 5.8 show a higher S signal towards the back interface which could be associated
with MoS$_2$ formation. Since the Zn signal, however also increases towards the back it might as well indicate the formation of ZnS phase. According to the formation enthalpies ($\Delta fH_{298K}^0$ in kJ/mol), MoS$_2$ (-235) is thermodynamically more stable than MoSe$_2$ (-167) [64, 100], therefore the former would be expected to form. A detailed TEM study could clarify this issue and helpful to estimate the MoS(e)$_2$ thickness.

5.5 Na diffusion and distribution in CZTSSe

A few remarks on diffusion are made in the beginning of this section to support the experimental findings. Diffusion between two different materials describes their tendency to intermix and is driven by a lowering of the free energy of the system [183]. Diffusion is measured in terms of diffusion coefficient $D$, which is defined by Fick’s first law of diffusion (1 dimensional):

$$J = -D \frac{\partial c(x,t)}{\partial x}$$

(5.2)

where $J$ and $c$ denote the flux and concentration of diffusing species. The concentration $c$ is a function of position $x$ in the sample and diffusion time $t$. $D$ determines the extent of diffusion and depends on the melting point, structure, defect type and content of the materials as well as the temperature [183]. The minus expresses the flow direction of the diffusing species which is always in the opposite direction of the concentration gradient.

To elucidate Na diffusion either from the SLG substrate or a NaF top layer into the CZTSSe absorber, different layer stacks were investigated by SIMS depth profiling. Si$_3$N$_4$ barriers on top of the SLG are used as Na diffusion barriers. Three samples were prepared: first SLG without NaF coating; second SLG with Si$_3$N$_4$ barrier and without NaF coating (i.e. without external Na source); and third SLG with Si$_3$N$_4$ barrier and with 10 nm NaF. All samples were annealed in elemental selenium atmosphere at $T_{sub} = 550 \degree C$ for 25 minutes. The corresponding Na depth profiles are depicted in Figure 5.7 (arrows indicate the Na diffusion direction). The profile of the precursor (deposited on Mo coated SLG) indicates presence of Na impurities stemming from the precursor chemicals and handling under atmospheric conditions. Na accumulation at the surface and homogeneous distribution in the bulk material is shown. It is noteworthy to men-
tion that SIMS intensities from different samples might not be compared, especially if they have a different microstructure and chemical bonding, where the matrix effect on ionization is not negligible (CZTS precursor layer versus sintered CZTSSe layer).

Fig. 5.7: Na SIMS depth profiles of a precursor and CZTSSe samples on SLG, SLG with Si$_3$N$_4$ barrier without NaF, and SLG with Si$_3$N$_4$ coated with 10 nm NaF.

The SLG sample where Na out-diffused from the substrate exhibits a strong decreasing Na gradient from the back to the front part of the absorber and reflects the nature of diffusion. The Na profile of the Si$_3$N$_4$ – 0 nm NaF sample follows the same trend but with reduced overall intensity. Since the Na distribution in the precursor was constant, a driving force other than concentration might lead to such characteristic profiles. It is assumed that the accumulation of Na is dominated by the layer morphology which is similar to the one depicted in Figures 5.2b-d (bigger grains are only present at the surface and very small grains make up more than half of the layer thickness). Finally, when a Si$_3$N$_4$ barrier and 10 nm NaF top coating were applied, the Na profile is very similar again, however, contains some more Na at the absorber surface than the SLG sample. Such Na gradients are usually not observed in high efficiency CIGS devices [184].

When it comes to the location of Na, there are two options: it can either segregate along the GBs or it is incorporated into the bulk. In CIGS Na was found to accumulate at GBs by SIMS mapping [153] and by atom probe tomography (APT) [185]. The Na
5.5. Na diffusion and distribution in CZTSSe

Fig. 5.8: SIMS depth profiles of finished CZTSSe devices with a) 0 nm, b) 10 nm, c) 20 nm and d) 200 nm NaF.

concentration in the GB is $0.1 - 0.3$ at% while in the bulk $< 0.1$ at% [185]. An APT study on CZTSe by T. Schwarz et al. [186] reported on up to 0.03 at% Na impurities at the CZTSe/ZnSe interface. It was even speculated that Na enrichment could affect the formation of ZnSe domains [186]. The Na dose found in the study of Schwarz is one order of magnitude lower than in CIGS, leading to the assumption that Na diffusion in CZTSSe is not the same as in CIGS (and is also a function of temperature). Here, the SEM cross sections revealed that the CZTSSe bottom part remains fine-grained ($0 \text{ nm} \leq \text{NaF} \leq 20 \text{ nm}$) while the upper part exhibits grain growth (Figure 5.2). In agreement with literature, it is assumed that Na can mainly accumulate at GB and thus, the Na profiles observed by SIMS correlate to the changing layer morphology. An APT measurement on our samples is planned to clarify this issue.
Fig. 5.9: SIMS depth profile of a finished CZTSSe device with 200 nm NaF showing the F, Cl, O and C distribution in the absorber.

After investigating Na diffusion from individual Na sources, combined samples with Na diffusion from both sides (SLG and NaF top layer) were prepared. Elemental depth profiles of four fully processed ZnO:Al/i-ZnO/CdS/CZTSSe/Mo/SLG devices were analyzed (Figure 5.8a-d). The sample with 0 nm NaF (Figure 5.8a) was used as reference where Na diffusion only stems from the SLG. The samples depicted in Figures 5.8b-d were additionally coated with 10, 20 and 200 nm NaF, respectively. The SLG sample shows again the typical Na profile described before. The Na concentration at the pn-junction is clearly reduced with respect to the bulk content following the typical diffusion profile away from high concentrations. When NaF is additionally in-diffusing from the top, the Na profile is leveling out (compare Figures 5.8b-d). According to diffusion theory, diffusion is slowed down when two opposite elemental fluxes are present. All samples with NaF layer have a more homogeneous Na profile and Na is present at the CdS/CZTSSe interface. Apparent Na accumulation at interfaces is a typical feature found in SIMS measurements. The increased intensity can either be contributed to matrix effects, apparent accumulation or a mixture of both.

The sample with 200 nm NaF exhibits a strong sodium out-diffusion from the CZTSSe into the ZnO:Al layer (Figure 5.8d). It also has the lowest Na counts of all four samples which is in accordance to quantitative ICP-MS measurements (see Table 5.1). Comparing the SEM cross section pictures, this sample has comparably large grains (Figure
5.5. Na diffusion and distribution in CZTSSe

Fig. 5.10: a) SEM cross section micrograph of a sample annealed with 200 nm NaF. b) formation of bubbles, c-h) SEM picture overlaid with elemental EDX maps of Na, Cl, Cu, Zn, S and Se.

5.2g). The small incorporation of Na in combination with large grains indicates preferential Na accumulation at grain boundaries (in accordance to Na behavior in CIGS). The apparent increase of the Cu and Sn profiles along the absorber thickness (Figures 5.8a-c) can be explained by the decreasing film porosity i.e. it represents a density effect. All samples exhibit Zn accumulation close to the back contact pointing towards
the formation of Zn(S,Se). Also sulfur is accumulating at the CZTSSe/Mo interface. It is assumed that it forms ZnS and/or MoS$_2$. SIMS depth profiling in negative mode revealed F, O, C as well as Cl throughout the absorber with preferential accumulation at interfaces (Figure 5.9).

Elemental EDX maps (obtained on the sample with 200 nm NaF, at 5 kV acceleration voltage) of Na, Cl, Cu, Zn, S and Se are overlaid with the SEM picture to illustrate their distribution along the cross section (Figures 5.10c-h). Caution has to be taken, when evaluating the mapping: since it was done on a non-polished cross-section, topological artifacts might influence the signal intensity and further, peak overlaps of elemental X-ray emission lines, that is overlap of Mo (L$_\alpha$ = 2.29 keV) and S (K$_\alpha$ = 2.31 keV), and Na (K$_\alpha$ = 1.04 keV) and Zn (L$_\alpha$ = 1.01 keV). At the white spots it seems that Na, Cl and Zn accumulate while Cu and Se are depleted. The high count rate of Na is dominated by the Zn overlap. The overall count rate for S is low because it was mainly substituted by Se. The apparent S accumulation at the back is caused by the overlap with the Mo X-ray emission line. The EDX mapping in combination with the NaCl phase detected by XRD measurements suggests that the bright spots consist of NaCl.

### 5.6 Crystallization mechanism

For a true sintering of a precursor layer going along with grain growth and densification, an annealing has to be done either close to the melting temperature (termed solid state sintering) or at substantially lower temperatures in presence of a liquid phase or flux [126]. A liquid phase can help to facilitate material transport under the conditions that the solubility of the solid in the liquid phase is sufficiently high. The liquid also should wet the solid particles to be sintered resulting in a thin shell of the liquid phase surrounding the solid particles [126]. Consequently, the liquid phase can improve the mass transport leading to large grains.

Grain growth in chalcogenide thin films can be driven by liquid-phase sintering where either atomistic transport at the grain boundaries is enhanced or a fluxing agent serves as medium to dissolve all constituent elements helping to recrystallize the material [143]. There are several fluxing or sintering agents which were successfully used in chalcogenide thin films. In CdTe for example, sintering of screen printed Cd and Te pastes was done with the aid of CdCl$_2$ as a flux [187]. For CIGS sintering, elemental sele-
nium, CuCl, CuSe+Se and Cu$_2$Se+Se were tested. In the latter study, CuCl led to grain growth but no densification and rearrangement was observed [126]. It was concluded, that good sintering requires presence of Cu$_2$Se which in combination with CuCl exhibits the following exchange reaction [126]

$$3CuCl + CuInSe_2 \leftrightarrow 2Cu_2Se + InCl_3 \uparrow.$$ 

Even though the melting point of Cu$_2$Se is above 1100 °C and therefore it does not fit into the category of liquid phase sintering, it promotes grain growth via solid state sintering [126]. It was verified several times that liquid or quasi-liquid copper rich Cu-Se phase enhances growth of large grained CIS and CIGS [97, 143, 152]. For Cu-rich CIS, CuSe was also reported to aid sintering as liquid flux [188].

Possible phases that could form in the multinary CZTSSe system include Cu$_2$S(e), SnS(e)$_2$, ZnS(e), NaF ($T_m = 996$ °C [64]), NaCl ($T_m = 801$ °C [64]), Na$_2$S(e)$_x$, CuCl$_2$ ($T_m = 598$ °C [64]), ZnCl$_2$ ($T_m = 290$ °C [64]) and SnCl$_4$ ($T_m = -34$ °C [64]). Based on the evaluation of phase diagrams for low melting eutectics or compounds with melting points $T_m < 550$ °C several phases could act as liquid fluxing agents: both, the Cu-Se and Cu-S phase diagrams exhibit several mixtures of Cu-S(e) phases in equilibrium with liquid S(e) at low temperatures [123, 189]. Due to the low melting point of Sn ($T_m = 232$ °C [64]) the Sn-Se and Sn-S phase diagrams exhibit liquid tin without the need for high chalcogen availability [190, 191].

Considering the fact that the enhanced grain growth was only found when NaF precursors with thicknesses $\geq 50$ nm were deposited prior to selenization, it is assumed, that the formation of a liquid phase most probably involves Na, or Na influences the chemistry/reactivity of constituent elements. In CdTe something similar was observed: The addition of 12 nm NaF before the CdCl$_2$ treatment massively improved grain growth and let to excessive CdS/CdTe intermixing [192]. The fact that only a small amount of NaF is needed in that case indicates that Na activates or catalyzes the CdCl$_2$ recrystallization and possibly is not participating itself. In our study however, significantly more NaF is needed to observe improved sintering leading to the assumption that Na is directly involved in the liquid phase sintering as possible fluxing agent: elemental Na, NaCl or Na$_2$Se$_x$ are considered. The phase diagram of Na-Se contains several liquid phases with low temperature melting point (see Figure 5.11, [193]) and it was reported in section 5.4, that more Se is incorporated with a thicker NaF layer. Therefore, in the
Chapter 5. Sodium assisted crystallization of solution processed CZTSSe

following, Na$_2$Se$_x$ as possible fluxing agent will be discussed.

5.6.1 Considerations for the formation of Na$_2$Se$_x$

Experimental proof for Na-Se bonds found in CIGS was given by [159, 161, 162]. In their experiments, however Na was out-diffusing from the SLG and not bound in a stable compound. Here, it is still questionable how NaF reacts. Although NaF is a thermodynamically stable compound, it forms ionic bonds and can dissociate upon traces of water and thus might be available in ionic form. Surface Na$^+$ ions can readily react with arriving Se molecules due to the high affinity between Na and Se [162].

In agreement with the Na-Se phase diagram [193] and experimental findings by other groups [159, 161, 162], liquid Na$_2$Se$_x$ is suggested to enhance crystallization. The Na-Se phase diagram exhibits many low temperature phases over a large compositional range (50 at% $\leq$ Se $\leq$ 100 at%) for temperatures around 300 °C (see phase diagram in Figure 5.11 adopted from Ref. [193]).

5.6.2 Na$_2$Se$_x$ fluxing

A liquid Na$_2$Se$_x$ mediated mechanism (schematically depicted in Figure 5.12) is proposed in order to explain the enhanced grain growth in the presence of sodium. The mechanism involves three steps: i) vapors of elemental Se are chemisorbed at the NaF surface, ii) formation of liquid sodium polyselenide phases Na$_2$Se$_x$ at the surface of the precursor, and iii) crystallization of solid CZTSSe by the reaction of the metal-containing precursor with the reactive Se provided via liquid Na$_2$Se$_x$.

The sticking coefficient of Se on the surface is increased by the presence of sodium due to their high affinity [162], which means sodium enhances Se chemisorption and therefore increases the availability of Se. Considering the open reactor design, it is realistic to assume a low Se vapor pressure. Step i) is very important because the sticking of Se on the surface is enhanced and consequently the availability of Se species at the precursor surface for further reactions is increased. Depending on the availability of Se, different liquid phases of sodium polyselenide form already at low temperatures (T $\sim$ 300 °C). The resulting liquid or quasi-liquid Na$_2$Se$_x$ phase possibly aids the CZTSSe growth, similar to the copper-selenide assisted fluxing in CuInSe$_2$ [97, 193]. Also for-
5.6. Crystallization mechanism

Fig. 5.11: Na-Se phase diagram published in Ref [193].

Fig. 5.12: Proposed liquid mediated mechanism for enhanced crystallization: i) vapors of elemental Se are chemisorbed at the NaF surface, ii) liquid sodium polyselenide phases $\text{Na}_2\text{Se}_x$ are formed, and iii) solid CZTSSe is crystallized by the reaction of the metal-containing precursor with the reactive Se provided through the liquid $\text{Na}_2\text{Se}_x$ phase.
formation of a liquid Se phase under a peritectic decomposition is possible. Assuming a low availability of Se, Na$_2$Se$_x$ ($x = 2, 3$) forms and a peritectic transformation into Na$_2$Se and liquid Se, or Na$_2$Se$_2$ and liquid Se occurs at 495 and 313 °C, respectively (see phase diagram Figure 5.11). In both cases, the liquid Se or Na$_2$Se$_x$ phases can help to recrystallize the CZTSSe material. During selenization of the precursor, oxidation of Na$_2$Se$_x$ ($1 < x \leq 6$ and $x \neq 5$, reaction 5.1) can constantly provide elemental Se [162] directly for selenization of metals and sulfur replacement. The availability of oxygen for the formation of Na$_2$SeO$_3$ and consequent Se release (see equation 5.1) throughout the absorber was seen in the SIMS measurement shown in Figure 5.9.

Following up the assumption of the Na$_2$Se$_x$ formation, the formation enthalpies $\Delta_f H^0_{298K}$ (kJ/mol) are decreasing with increasing $x$ ($1 < x \leq 6$ and $x \neq 5$): Na$_2$Se (-342.6), Na$_2$Se$_2$ (-388.4), Na$_2$Se$_3$ (-416.4), Na$_2$Se$_4$ (-434.6) [194]. When Se is subsequently lost during sintering, NaCl ($\Delta_f H^0_{298K} = -411.1$ (kJ/mol) [64]) might finally form with available Cl from the precursor salts (as seen in XRD measurements, Figure 5.5).

### 5.7 Alternative ways of supplying Na

So far, the presented experiments comprised employment of a NaF precursor coating before selenization. This section demonstrates that alternative ways can be pursued for external Na supply. Here, only the crystallization is discussed while electronic modifications will be presented in the next Chapter.

In order to supply Na via a non-vacuum method, 0.05 M NaCl was dissolved in DMSO and spin coated (5 times) on top of the precursor before selenization. There are no morphological changes observed when comparing SEM cross sections from the sample with NaCl (see Figure 5.13a) supplied via the solution to samples where NaF (0, 10 and 20 nm) was evaporated on top (see Figure 5.2).

Another way to provide external Na is via the gas phase. The experimental setup is shown in Figure 6.11 where the precursor is placed next to a NaF coated SLG glass during selenization. Remarkable grain growth appeared (Figure 5.13b) but it has to be noted that this method results in a lateral Na gradient and crystallization is the better the closer the precursor substrate was standing to the NaF glass.
5.8 Summary

It was shown that presence of Na significantly enhances the grain growth of selenized Cu-Zn-Sn-S precursor films. Grain growth promotion depends on the Na dose, where largest grains were found for a NaF thickness of 100 nm. Excess sodium impedes grain growth which was attributed to either reduced interdiffusion or the formation of a NaCl phase. The proposed fluxing mechanism leading to large grains involves three steps: i) vapors of elemental Se are chemisorbed at the NaF surface because of a high affinity between Na and Se, ii) liquid sodium polyselenide phases Na$_2$Se$_x$ are formed, and iii) solid CZTSSe is crystallized by the reaction of the metal-containing precursor with the reactive Se provided through the liquid Na$_2$Se$_x$ phase.

Although there was no direct proof for the proposed formation of Na$_2$Se$_x$, there are several experimental evidences:

(i) NaF on the top is needed for improvement in crystallization where Na can readily react with arriving Se molecules, as shown by experiments with and without Si$_3$N$_4$ barrier, to exclude the effect of Na from the SLG.

(ii) Elemental quantification by ICP-MS showed increased Se incorporation with increased NaF top layer thickness.

(iii) Generally, massive improvement in grain size can be explained by a liquid phase. Massive grain growth was only observed in presence of high Na amounts. Therefore, either a liquid Na-Se phase or liquid Se which is released in high amounts
from Na-Se phases (via peritectic decomposition or oxidation of Na$_2$Se$_x$) can act as flux for recrystallization.
Chapter 6

Effects of sodium on electronic properties of CZTSSe solar cells

In the previous Chapter the influence of Na on the crystallization was presented. Since Na exhibits multiple effects, this Chapter deals with the effects of Na on the electronic properties of CZTSSe devices. An overview of the variety of effects of Na in CIGS and CZTSSe is given in the first part. Superior device efficiencies upon additional Na doping are presented afterwards. A comparison of different NaF layer thicknesses which were deposited on the precursor before the selenization with a reference sample where Na is present due to out-diffusion from the SLG is presented and outlined. For a deeper understanding, comparative temperature dependent JV and Cf measurements are analyzed. The location and depth profile of Na in the CZTSSe absorber resulting from different NaF layer thicknesses is correlated to device performance. Alternative ways of including Na in the absorber layer are addressed in the remainder of this Chapter.

The following sections are partially based on the publication "Sodium Assisted Sintering of Chalcogenides and its Application to Solution Processed Cu₂ZnSn(S,Se)₄ Thin Film Solar Cells" by C. M. Sutter-Fella et al. [149].

Parts of the results of this Chapter were obtained during the Master thesis of Josua Stückelberger.
6.1 Prior art and motivation

Na in CIGS

Already in the beginning of the 90s, the beneficial effect of Na on the efficiency of chalcogen thin film solar cells was realized. First publications by Hedström et al. [195], and Bodegård et al. [153] reported on a strong texturing effect observed in CIS and CIGS grown on SLG substrates. It was also found, that Na is essential for high efficiency CIGS solar cells. Many papers on the influence of Na on electronic and structural properties have been published since those early days. Here, only a short summary on the effects of Na will be given. Na can either out-diffuse from the SLG substrate during a high temperature deposition process, or be supplied as Na-containing precursor before, during or after the growth process [154, 167, 168]. The improvements in conversion efficiency are mainly due to increased $V_{oc}$ and FF, while the $J_{sc}$ is not affected [169, 196]. A correlation between $V_{oc}$ and texture was ruled out [196]. Na is also reported to increase the p-type conductivity [154, 171, 172], reduce the donor density $N_D$ [172] and thereby increase the effective hole density, hinder interdiffusion of In and Ga [158], and enlarge the stable $\alpha$-CuInSe$_2$ region [197].

The increase in $V_{oc}$ was explained by Ruckh et al. [196] by an increase in effective acceptor doping concentration (assuming constant carrier mobilities). A possible mechanism was given as follows: due to an enhanced formation of oxides at the surface correlated with Na-species, selenium vacancies $V_{Se}$ (acting as donor-like defects) could be neutralized by oxygen [196]. Reports on the effect of defect neutralization by oxygen go back to an early proposed model by Cahen and Noufi [198]. This model was followed up by Kronik et al. [199] including the catalytic effect of alkali metals to promote surface oxidation, discovered earlier in silicon technology [200]. The alkali metal induces a polarization of the $O_2$ resulting in $O_2^-$ which dissociates easier than $O_2$ into atomic oxygen needed for neutralization of the $V_{Se}$ donors.

As mentioned in Chapter 5, the optimum amount of Na in CIGS is considered to be about 0.1 – 0.5 at%, which is a typical amount of Na out-diffusing during the growth from the SLG substrate [159, 161, 166, 170]. After exceeding an optimum amount of incorporated Na, the device performance deteriorates because of a decrease in all PV parameters [170].

To separate the effect of grain boundaries and effects of Na on the electronic properties
6.1. Prior art and motivation

Schroeder and Rockett investigated epitaxial CIGS films [172]. Their results clearly confirm that Na has an electronic effect on CIGS that is, to increase the hole density and a drastic reduction of compensating donor densities, again, in absence of grain boundaries.

Na in CZTSSe

There are not as many publications available about the effect of Na in CZTSSe as for CIGS. The effects, however, are assumed to be similar. Grain growth and texturing effects have been observed [163, 164]. Recently, a publication on CZTSe showed that sodium enhances the FF and $V_{oc}$ by increasing the hole density and mobility, and shifting the acceptor level closer to the valence band [201]. Hence a superior efficiency was observed. It also slightly reduces the minority carrier lifetime [201]. In the same study it was reported that Na reduces the SCR and therefore lowers the $J_{sc}$ [201].

For sol-gel deposited CZTSe films it was found that Na increases the carrier concentration and at the same time reduces the resistivity of the absorber however, too much Na reduces the mobility [165]. In non-vacuum CZTSSe devices it was reported, that Na leads to more than twice higher minority carrier lifetime and higher carrier density [202].

Role of Na on grain boundaries in CIGS and CZTSSe

Generally for CIGS, GB are found to be rather benign, which is reflected in more efficient polycrystalline devices compared to single crystalline ones [25].

The current understanding of GBs in CIGS is reviewed in Refs. [203] and [25]. Here it is briefly summarized without going deeply into primary literature. In the review of Rau et al. [203], the various GB models are distinguished as follows: crystallographic orientation, intrinsic GB passivation, extrinsic GB passivation and change of band structure along GBs. The latter model is based on surface reconstruction which implies formation of stable Cu-poor surfaces accompanied by a down shift of the valence band maximum providing a barrier for majority carriers (holes). Experimental proof for a significant reduction of Cu at the GBs was reported in Ref. [185]. The authors explain improved device properties by occupation of $V_{Cu}^-$ with Na$^+$. Na$^{0}_{Cu}$ defects are considered to be electronically inactive. Additionally, a recent study by Li et al. [204] on the role of GBs in CZTSSe showed that there is a higher positive potential at the GBs which can lead to minority carrier (electrons in p-type semiconductors) attraction while holes are re-
Chapter 6. Effects of sodium on electronic properties of CZTSSe solar cells

In contrast, the extrinsic GB passivation based on a chemical defect model was proposed by Cahen and Noufi [198]. According to this model, Se vacancies existing at the GBs which act as donor defects can be neutralized by oxygen. This oxygenation has the following effects: it passivates GB Se deficiencies thereby increases the effective p-type doping level, eliminates recombination centers, and improves inter-grain transport [206]. The beneficial presence of Na was explained by its catalytic effect on the previously described oxygenation [199].

6.2 Solar cell performance for different Na contents

The absorber fabrication and characterization was outlined in sections 5.2 - 5.5. Identically processed precursor films were coated with NaF prior to selenization. The discussed set comprises 7 samples with NaF thicknesses of 0, 5, 10, 20, 50, 200 and 300 nm. Solar cells were processed with the standard configuration ZnO:Al/i-ZnO/CdS/CZTSSe/Mo/SLG including an absorber etch in 10 wt% KCN for 30 s before CdS deposition. During KCN etching and final water rinsing remaining NaF on the surface of the CZTSSe absorber layer is washed away (solubility of NaF in water at 20 °C is 40g/l and 100 nm NaF ≈ 0.2 µg).

In the previous Chapter, the influence of Na on grain growth was discussed. The largest grain size was found for the sample with 100 nm NaF while the optimum for highest efficiency is one order of magnitude lower. The coming sections are intended to illuminate this discrepancy.

Figure 6.1 summarizes device performance versus NaF thickness for the whole data set. The standard deviation for the sample with 50 nm NaF is comparably large which is caused by a partial delamination of the absorber. In this study the highest conversion efficiency of 6.04 % was achieved for the absorber with 10 nm NaF without antireflection coating.

The corresponding JV curves of the best samples are shown in Figure 6.2 (the PV parameters are listed in Table 6.1). An increase of the NaF layer thickness from 0-10 nm led to a gradual increase of $V_{oc}$ and FF. Further thickness increase of the NaF layer (20 - 300 nm) resulted in $V_{oc}$ and FF decrease. All light and dark (dotted lines) JV
6.2. Solar cell performance for different Na contents

![Graph](image)

**Fig. 6.1:** Solar cell efficiency versus NaF top layer thickness for the best cell of each substrate, average of five best cells and corresponding standard deviation. The points are connected as a guide for the eye.

Curves show a cross-over behavior (Figure 6.2, indicated by cycles; dark measurement of the sample with 50 nm is not available). A cross-over was also observed for high quality CZTSSe based devices with efficiency > 10% [54, 178]. In the samples with 10 and 20 nm NaF, the cross-over point is comparably higher and occurs at about 50 mA/cm². The cross-over illustrates the non superposition principle of dark and light JV and can be correlated to a barrier, either at the buffer-absorber interface or at the back contact [207, 208]. A higher cross-over point in correlation with improved FF, as found for the samples with 10 and 20 nm NaF was observed by Todorov et al. [178] in combination with lower ideality factor.

For more conclusive interpretation of the PV parameters, the dark, the dark shifted by $J_{sc}$ and the illuminated JV curves are plotted for the samples with 0, 10 and 200 nm NaF to analyze voltage dependent collection (see Figure 6.3). Generally, in crystalline solar cells it is assumed that the photo current density under illumination is independent of voltage. The principle of superposition requires the light and shifted dark JV to be the same, but this is only observed in Si (due to long diffusion lengths) and III-V based solar cells with small $R_s$ [209]. A difference between light and shifted dark JV is due to voltage dependent collection [209]. The dark current density is not influenced by voltage dependent collection since there is no collection, only injection. Voltage dependent
Chapter 6. Effects of sodium on electronic properties of CZTSSe solar cells

Fig. 6.2: a) Light (solid line) and dark (dotted line) JV curves of samples with increasing NaF thickness (0-10 nm) showing an improvement in PV parameters and b) deteriorating PV parameters for NaF thicknesses of 20-300 nm. The cross-over points between light and dark JV curves are indicated by circles (no dark curve for the sample with 50 nm NaF is displayed since it got destroyed during T-JV measurement).

Table 6.1: Na content if available (measured by ICP-MS) and PV parameters for samples either with different NaF thicknesses, with NaCl coating or with Na supply via the gas phase. The * indicates a modified precursor solution with 10 % less Cu. The error of the ICP-MS quantification is ±10%.

<table>
<thead>
<tr>
<th>Na source</th>
<th>Na (at%)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (mV)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF (%)</th>
<th>Eff. (%)</th>
<th>SCR (nm)</th>
<th>E&lt;sub&gt;r&lt;/sub&gt; (T-Cf)</th>
<th>eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 nm NaF / SLG ref.</td>
<td>0.2</td>
<td>267</td>
<td>29.7</td>
<td>42.7</td>
<td>3.39</td>
<td>80</td>
<td>366</td>
<td></td>
</tr>
<tr>
<td>5 nm NaF</td>
<td>-</td>
<td>325</td>
<td>31.5</td>
<td>45.5</td>
<td>4.64</td>
<td>50</td>
<td>311</td>
<td></td>
</tr>
<tr>
<td>10 nm NaF</td>
<td>0.4</td>
<td>335</td>
<td>30.4</td>
<td>59.2</td>
<td>6.04</td>
<td>60</td>
<td>177</td>
<td></td>
</tr>
<tr>
<td>20 nm NaF</td>
<td>-</td>
<td>324</td>
<td>27.9</td>
<td>55.1</td>
<td>4.98</td>
<td>60</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>50 nm NaF</td>
<td>-</td>
<td>307</td>
<td>33.3</td>
<td>48.3</td>
<td>4.93</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>200 nm NaF</td>
<td>0.1</td>
<td>259</td>
<td>25.7</td>
<td>30.6</td>
<td>2.04</td>
<td>100</td>
<td>284</td>
<td></td>
</tr>
<tr>
<td>300 nm NaF</td>
<td>-</td>
<td>253</td>
<td>27.9</td>
<td>33.4</td>
<td>2.36</td>
<td>90</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>-</td>
<td>357</td>
<td>27.2</td>
<td>57.3</td>
<td>5.56</td>
<td>40</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>gas phase (200 nm)</td>
<td>-</td>
<td>334</td>
<td>31.7</td>
<td>45.5</td>
<td>4.81</td>
<td>50</td>
<td>294</td>
<td></td>
</tr>
<tr>
<td>gas phase* (200 nm)</td>
<td>-</td>
<td>360</td>
<td>32.6</td>
<td>47.2</td>
<td>5.55</td>
<td>50</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
6.3. Effect of Na on carrier collection

To analyze carrier collection, the EQEs of the samples with 0, 10, 50 and 200 nm NaF are plotted with and without external reverse bias in Figure 6.4. For a spectrally resolved analysis, the light spectrum is divided into three regions, I: 350 - 550 nm, II: 550 - 1150 nm, and III: 1150 - 1400 nm. The EQEs were measured with 300 mV externally applied reverse bias (i.e. \( V = -300 \text{ mV} \)) which increases the SCR width \( W \) (because of \( W \propto \sqrt{V_{bi} - V} \) where \( V_{bi} \) is the built-in voltage), thereby enhancing the collection of photogenerated charge carriers, especially if the minority carrier diffusion

---

**Fig. 6.3:** a-c) JV curves of dark, dark shifted by \( J_{sc} \) and illuminated for samples with 0, 10 and 200 nm NaF.

collection can be caused by interface recombination, poor minority carrier mobility or short diffusion length [209, 210]. A shunt (i.e. alternate current path) would affect the dark current density in the same way as the light current density. That means, under illumination, \( J(V) \) is a superposition of voltage dependent diode current density and the photo-generated current density. The dark curves of samples with 0 and 10 nm NaF show a linear increase in dark current density with increasing reverse bias, representing typical shunt losses leading primarily to FF losses. While the dark current density of the sample with 200 nm NaF is flat, and the illuminated \( J(V) \) is gradually increasing with increasing reverse bias. It can be seen in Figure 6.3c that voltage dependent collection causes significant losses in \( V_{oc} \) and FF, and finally efficiency. The same behavior was observed for the sample with 300 nm NaF which in both cases might be explained by NaCl inclusions (discussed in section 5.2) acting as high recombination centers leading to strong voltage dependent collection.
length is small. It is noted that the samples are not uniform and deviations in the EQE curves were observed.

The blue response (region I) is determined by parasitic absorption of the window-, buffer layer and secondary phases with $E_g \geq 2.25$ eV, as well as front surface recombination. A characteristic feature in the spectral response around 410 nm was reported as indicative for the presence of surface ZnSe phase [211]. It remains unclear, if the observed difference in the EQE response in region I is caused by reduced surface ZnSe content or if it stems from modified CdS properties, for example due to Na in-diffusion. Upon reverse bias application, only the sample with 200 nm NaF showed a gain in EQE. This could be correlated either to the presence of excessive Na in the CdS (compare Figure 6.5c), at the pn-junction, or to a very defective CZTSSe surface, leading to very high collection losses. In regions II and III, generally high losses are observed for the samples with 0, 10 and 200 nm NaF. Poor red response can be attributed either to too thin absorber layers, recombination at the backside of the absorber or low minority carrier diffusion length. Overall, the $J_{sc}$ gains with reverse bias were 7.5 % (0 nm NaF), 3.8 % (10 nm NaF), 3.7 % (50 nm NaF) and 18.1 % (200 nm NaF). The sample with 200 nm NaF is different from the other samples in two ways: first, NaCl was detected by XRD measurements acting as possible recombination center and second, the device is limited by voltage dependent collection (see Figure 6.3c). Those properties can explain the high EQE gain under reverse bias. The long wavelength losses for the samples with 0 and 10 nm NaF can be associated to the poor microstructure towards the back observed by SEM (Figure 5.2).

Large grains without detectable NaCl inclusions obtained for the sample with 50 nm (Figure 5.2e and 5.5a) led to the highest and almost rectangular EQE. Therefore, it is likely, that large grains significantly improve the overall EQE response. Due to the rectangular EQE shape, region III can be used to extract the band gap by linear extrapolation and is found to be 0.96 eV, corresponding to the band gap of pure CZTSe [58,109].

Electron beam induced current (EBIC) measurements together with the corresponding SIMS depth profiles of complete solar cells are depicted in Figure 6.5. For direct comparison of samples with 0, 10 and 200 nm NaF, the SEM pictures are overlaid with the EBIC signal and the normalized collection function (integrated EBIC signal along the X-axis) with scaling factor is given. Most efficient charge carrier collection was observed for the sample with 10 nm NaF (red colored region in Figure 6.5b), where
6.3. Effect of Na on carrier collection

The collection expands over approximately $\frac{2}{3}$ of the absorber thickness. The collection in the samples with 0 and 200 nm NaF is more limited to the pn-junction i.e. the SCR width. The very weak collection for the latter sample was already seen in the low EQE and indicated by voltage dependent collection as a measure for high recombination losses (Figure 6.2b).

The collection efficiency is a convolution of SCR width and minority carrier diffusion length (as well as the interaction volume of the electron beam with the absorber; this is, however, neglected because an acceleration voltage of 5 kV was chosen). Since the SCR width (see Table 6.1) does not show a significant change for the presented samples, it is assumed that the carrier diffusion length can be improved when an optimum amount of Na is added to the absorber layer (as seen for the sample with 10 nm NaF). It was recently reported, that an improvement of the diffusion length of the minority carriers could open the pathway to efficiencies $> 13\%$ [7]. It is noted, that the EBIC signals of the samples with 0 and 10 nm NaF are different while the EQEs of those samples look similar. The individual samples show however, some inhomogeneities in EQE. It is not clear if the observed difference in the collection function might be influenced by topological artifacts for example due to surface recombination.

The quality of the pn-heterojunction is of utmost importance for good solar cell devices. The following discussion outlines the critical influence of the location and concentration of Na on the CZTSSe device. SIMS depth profiles illustrate the Na distribution in the
Chapter 6. Effects of sodium on electronic properties of CZTSSe solar cells

Fig. 6.5: a-c) EBIC signals (red area) overlaid with the SEM cross-section pictures of finished CZTSSe solar cells devices with 0, 10 and 200 nm NaF top layers. The collection function (yellow line) is the integrated EBIC signal in x-direction. d-f) Corresponding elemental SIMS depth profiles of finished CZTSSe devices. The sputter time corresponds to the depth into the solar cell stack.

CZTSSe devices (see Figures 6.5d-f). As discussed in detail in section 5.5 the Na diffusion from the SLG into the CZTSSe absorber is slow, thus, the Na concentration at the pn-junction of the sample with 0 nm NaF is low and is likely responsible for the poor PV parameters. In contrast, distinct accumulation of Na at the CdS/CZTSSe interface in the sample with 200 nm NaF again could negatively affect the carrier collection.

ICP-MS measurements after KCN etching revealed the highest amount of Na (0.4 at% corresponding to \( \sim 15.5 \cdot 10^{19} \text{ atoms/cm}^3 \)) in the sample with 10 nm NaF and the lowest amount (0.1 at% corresponding to \( \sim 3.7 \cdot 10^{19} \text{ atoms/cm}^3 \)) in the sample with 200 nm NaF. By a correlation of the measured Na concentration with the observed grain sizes and in agreement with literature [185, 186] it appears reasonable to assume that Na resides at the CZTSSe GBs. The GB density in the sample with 200 nm NaF is the smallest and therefore contains the least amount of Na. The amount of Na which out-diffuses from the SLG substrate depends on the composition of the SLG as well as the density and thickness of the Mo layer.
6.4. Effect of Na on energy distribution of defect levels

There are several ways in which Na could influence the electronic quality of the absorber and solar cell efficiency, respectively. If Na is preferentially located at the GBs it can remove or introduce electronically active defect states. Na at the GBs in CIGS can passivate donors and deep defects, thereby making the acceptor shallower or reduce recombination (manifested by an increase in $V_{oc}$ and FF, in agreement with our measurements, Figure 6.2) [199, 212]. Li et al. showed that there is a higher positive potential at the GBs of CZTSSe which can lead to minority carrier attraction while holes are repelled [204,205]. Consequently, accumulation of Na at the GBs could explain the enhanced overall PV parameters of the sample with 10 nm NaF (Table 6.1). The above arguments suggest that the location of Na seems to be very important for good device properties.

6.4 Effect of Na on energy distribution of defect levels

The defect properties of a semiconductor used in solar cells is of importance for the understanding of device limitations and further efficiency improvements. For the following discussions, a fourth sample is included to clearly corroborate the observed trends. The presented results comprise samples with 0, 5, 10 and 200 nm NaF.

Temperature dependent capacitance-frequency (T-Cf) spectroscopy from 123 – 300 K in steps of 20 K was used to gain insights into the energetic position of defect levels. The T-Cf spectra in Figure 6.6 reveal some interesting features. The capacitance converges for high frequencies at all temperatures, as seen for the samples with 0 and 200 nm NaF. The sample with 10 nm NaF shows a slight deviation from this convergence for $T > 240$ K and the sample with 5 nm NaF reflects something in between. This converging behavior at low frequencies is different from the one typically observed in CIGS [213, 214]. The anomaly however, was also observed by Gunawan et al. [215] in hydrazine processed CZTSSe devices. At the dielectric freeze-out capacitance (= geometric capacitance), the absorber behaves like an insulator because it cannot respond to the high frequency AC excitation [216]. This freeze-out is observed at frequencies around 2 MHz while in CIGS solar cells it appears at 10 times higher frequencies implying that CIGS has a higher conductivity. The dielectric freeze-out capacitance can be used to extract the dielectric constant $\epsilon$ of the absorber ($C = \epsilon \cdot A/t$ where $A$ is the area and $t$ the film thickness) [216]. $\epsilon$ calculated for the samples with 0 and 10 nm NaF is
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Fig. 6.6: Temperature dependent Cf measurements of samples with a) 0 nm, b) 5 nm, c) 10 nm and d) 200 nm NaF top layer.

10 and 15, respectively. For the former, the dielectric constant is close to the one reported in literature for CZTSSe, varying from 6.7 to 8.6 depending on the S/(S+Se) ratio [20,215]. For the sample with 10 nm NaF, however, the deviation between calculated and reported dielectric constant by a factor of two stems probably from a freeze-out at higher frequencies i.e. the capacitance plateau was not reached during the measurement. The low frequency for the capacitance freeze-out is possibly caused by not as shallow acceptor states as they were found in CIGS [216].

Another observation is the gradual capacitance decay for the sample with 0 nm NaF while the other measurements show a capacitance step. The non-step like decrease over the whole frequency range as observed in Figure 6.6a can be explained by a band of deep acceptor states in the depletion region [213]. A capacitance step in contrary can be interpreted by donor type interface states at the CIGS/CdS interface, an energetically
continuous but locally discrete density of states e.g. interface states or a back contact barrier [213, 217, 218]. The capacitance step in CZTSSe was related to the dielectric freeze-out induced by low conductivity in the CZTSSe absorber [215].

The following values for the SCR width were extracted from room temperature Cf measurements at frequencies \( \sim 1 \) kHz (before the capacitance decay): 100 nm (200 nm NaF - 0.1 at% Na), 80 nm (0 nm NaF - 0.2 at% Na), 60 nm (10 nm NaF - 0.4 at% Na, Table 6.1). Comparing these values with the Na concentration in the absorber, it is concluded that the SCR width slightly decreases with the Na content (note: a thick NaF layer does not necessarily result in a high amount of incorporated Na). This finding is in agreement with literature [201].

![Arrhenius diagram deduced from T-Cf measurements to extract the defect activation energies for samples with 0, 5, 10 and 200 nm NaF top layer.](image)

The activation energy of the trap levels \( (E_T) \) can be extracted from an Arrhenius plot of \( \ln(\omega_i/T^2) \) versus \( 1/T \) where \( \omega_i \) is the inflection frequency of the capacitance (see Figure 6.7). \( E_T \) of the main defect are 366 (0 nm NaF), 311 (5 nm), 177 (10 nm) and 284 meV (200 nm). In literature, only few values for the defect activation energy have been reported for kesterite. Gunawan et al. [215] reported for up to 10 % efficient CZTSSe \( E_T \sim 130 - 200 \) meV. A recent publication by Weiss et al. [59] points out the influence of an increasing series resistance with decreasing temperature can model the capacitance step in the T-Cf measurement. Therefore, caution has to be taken when interpreting the
low temperature capacitance step. Complementary measurements of ICP-MS, SIMS and JV show a clear trend with respect to varying Na concentration and location. Thus it is assumed that the trend of the extracted activation energies is plausible.

It is noteworthy to mention, that the role of chlorine stemming from the metal chlorides used as precursors could also influence the defect formation. Cl might form a deep acceptor state which was found in CdTe [219].

### 6.5 Dominant recombination mechanism

In order to study recombination losses in the Na containing CZTSSe devices, temperature dependent JV (T-JV) under dark (dotted lines) and light (solid lines) conditions were carried out and are presented for the samples with 0, 5, 10 and 200 nm NaF in Figure 6.8. All samples exhibit a FF quenching for decreasing temperatures. Additionally, a strong current blocking in forward bias at low temperatures was observed for samples with 0, 5 and 200 nm NaF. The current blocking is accompanied by a heavily increasing dark $R_s$ with decreasing temperature. The current blocking is however, effectively reduced in the sample with 10 nm NaF, as well as the spreading of the temperature dependent $J_{sc}$. As expected, the $V_{oc}$ is increasing with decreasing temperature ($V_{oc} \propto \frac{E_A}{q} - \frac{A k T}{p}$, where $E_A$ is the activation energy of the dominant recombination path and $A$ the diode ideality factor). Redinger et al. [58] observed suppression of the photo current due to high $R_s$ with decreasing temperatures for mixed CZTSSe devices, while $R_s$ is almost constant in pure CZTSe. Therefore, they concluded, that the barrier that is responsible for high $R_s$ is absent in the CZTSe sample.

The presence of a barrier indicated by T-JV due to increasing $R_s$ and the cross-over of light and dark JV is normally associated to a blocking MoS(e)$_2$ back contact which can suppress the hole transport [18, 106]. However, this previous hypothesis was revised by Gunawan et al. [215]. Instead, the $R_s$ increase was correlated with the CZTSSe bulk properties that is, a low bulk conductivity limits the $R_s$ [215]. Considering the well known fact that a lot of secondary phases can form in CZTSSe the above explanation seems reasonable. TEM measurements would be useful to evaluate the presence and thickness of MoS(e)$_2$.

The dominant recombination mechanisms which can lead to $V_{oc}$ losses can be evalu-
6.5. Dominant recombination mechanism

Fig. 6.8: Dark (dotted line) and illuminated (solid line) T-JV measurements of samples with a) 0 nm, b) 5 nm, c) 10 nm and d) 200 nm NaF top layer.

ated by T-JV measurements by extrapolation of $V_{oc}$ to 0 K: $q \cdot V_{oc} = E_A$ for $T \to 0$ K. The $V_{oc}$ deficit is a crucial problem in CZTSSe solar cell devices as outlined in section 1.3.3. The samples with 10 and 200 nm NaF could not be evaluated by this method because the former got shunted during the measurement and the latter has a too poor diode quality.

If the activation energy $E_A$ of the dominant recombination mechanism is smaller than $E_g$, interface recombination is dominant [220]. For $E_A = E_g$ bulk recombination is dominant (see also section 2.3.1). The band gap of the absorber material can be extracted from the EQE cutoff (Figure 6.9a). However, in the presented samples, band gap extraction is difficult due to the non-ideal EQE form, that is, recombination losses in the bulk and back part of the absorber due to short minority carrier lifetime and/or diffusion length, which led to triangular instead of rectangular EQE shape. The EQE fit resulted
in 1.03 eV and 1.06 eV for the sample with 0 and 5 nm NaF (Figure 6.9a). Due to the non-ideal EQE shape, there is a certain error in this evaluation. The influence of interface recombination velocity, minority carrier diffusion length or carrier lifetime on the EQE shape and cutoff is discussed for example in Refs. [108, 210]. Since the band gap in CZTSSe absorbers varies with the Se/(Se+S) ratio and therefore the lattice parameter, the position of the XRD 112 peak can also be used to estimate the band gap. For the sample with 0 and 5 nm NaF, the 112 positions are at 27.28° and 27.27°, respectively (in pure CZTSe: 112 position at 27.18° and $E_g \sim 1.0$ eV). The presence of secondary phases such as ZnSe can however, also influence the XRD peak position. It is concluded that the $E_g$ in both cases is slightly larger than 1.0 eV due to the presence of additional S.

The extraction of $E_A$ is only allowed if the ideality factor is only weakly temperature dependent [70], therefore $A$ is shown on the right Y-axis in Figure 6.9b. For the sample with 0 nm NaF, $A$ is temperature dependent for $T < 150$ K and larger than two which may be observed in devices with high doping concentration [70]. Moreover, a temperature dependent ideality factor is an indication for tunneling enhanced recombination [70]. For the sample with 5 nm NaF, $A$ is only weakly temperature dependent, so that the $V_{oc}$ extrapolation can be used to extract $E_A$. $E_A$ for the sample with 5 nm NaF is 0.91 eV (illustrated in Figure 6.9b). Because of $E_A < E_g$ the device is limited by interface recombination which leads to substantial $V_{oc}$ losses. Other groups reported as well on dominant interface recombination [18, 58]. It could occur due to surface traps at the CZTSSe/CdS interface, or a cliff like band alignment [18]. The conduction band offset between kesterite absorber and CdS is still under discussion. A cliff at the CZTS/CdS interface was reported in Ref. [57] while a spike was proposed for the interfaces of CZTSe, CZTS and CZTSSe with CdS in Ref. [221].

### 6.6 Alternative ways of supplying Na

In order to prove the universal nature of the presented effects of the NaF top layer onto structural and electronic properties of CZTSSe layers, alternative ways of Na incorporation are demonstrated in the last part of this Chapter. The direct incorporation of Na into the precursor solution has not been studied excessively in the course of this thesis but is worth analyzing in the future.
6.6. Alternative ways of supplying Na

Fig. 6.9: a) Band gap extraction by fitting of the EQE data and b) Temperature dependence of the $V_{oc}$ and the diode ideality factor for the samples with 0 and 5 nm NaF. The linear fits to $T = 0\, \text{K}$ are included.

### 6.6.1 Na incorporation via NaCl top layer

As a proof of concept for Na supply by solution method, 0.05 M NaCl was dissolved in DMSO and spin coated (5 times) on top of the precursor. The structural and electronic results obtained are comparable to a precursor coating with 10 nm NaF, corresponding J-V and EQE curves are presented in Figure 6.10 and the PV parameters are listed in Table 6.1. This cell exhibited the highest observed $V_{oc}$ (357 mV) throughout all Na experiments. The efficiency obtained with NaCl top layer was 5.56 % compared to the 6.04 % with 10 nm NaF top layer. The main difference was found in the $J_{sc}$, possibly caused by a reduced charge carrier collection or current blocking due to ZnSe [211] in the NaCl sample seen by an overall slightly lower EQE curve.

### 6.6.2 Na incorporation via gas phase

The motivation of these experiments was driven by the question how Na is incorporated. The following model experiment was designed where the precursor was placed in the two zone furnace next to a SLG substrate which was coated with NaF (schematic 6.11). The intention was that arriving Se molecules react with NaF to form a volatile phase which is transported via the $N_2$ flux towards the precursor sample. The discussed absorbers are referred to as "gas phase" samples.
Chapter 6. Effects of sodium on electronic properties of CZTSSe solar cells

Fig. 6.10: a) JV and b) EQE of the absorber prepared by spin-coating NaCl dissolved in DMSO on top of the precursor.

![Graphs showing JV and EQE](image)

Fig. 6.11: Experimental configuration for the gas phase samples where a SLG substrate coated with NaF is placed next to the absorber. The proposed mechanism for Na supply via the gas phase is illustrated as well.

![Diagram showing gas phase configuration](image)

The selenization was carried out at $T_{sub} = 550 \degree C$ for 25 minutes with the SLG next to the precursor coated with 200 nm NaF. The samples with * were prepared from precursor solutions with 10 % less Cu. By reduction of Cu in the precursor the Cu/(Zn+Sn) ratio in the absorber is decreased from 0.9 with the standard precursor solution to 0.8 (measured by EDX). The JV curves of the gas phase samples together with the sample with 0 nm NaF are presented in Figure 6.12 and Table 6.1. Improvements in $V_{oc}$ and...
FF were observed compared to the 0 nm NaF sample. A maximum efficiency of 5.55 % was measured for the gas phase sample with less Cu in the precursor. The increased $V_{oc}$ and FF possibly stem from increased Na concentration in the absorber supplied via the gas phase.

![Graph showing JV measurements](image)

**Fig. 6.12:** JV measurements for samples grown with Na in the gas phase, including the reference sample which was grown on SLG without additional Na source. The * indicates a precursor solution with 10 % less Cu.

**Fig. 6.13:** EBIC measurements of samples grown with 200 nm NaF on the SLG. a) with standard precursor and b) with reduced Cu content in the precursor.

A comparison of the EBIC measurements on samples with standard precursor and the precursor with 10 % less Cu is illustrated in Figure 6.13. It reveals improved charge carrier collection if a Cu-poor precursor is employed (Figure 6.13b). Assuming that less Cu reduces the formation of the p-type Cu$_{Zn}$ antisite defect, this would lead to
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a lower p-type doping and therefore enlarged SCR width which was however not observed (compare Table 6.1). Since the collection efficiency is a convolution of SCR width and minority carrier diffusion length, it is assumed that a Cu-poor precursor can increase the minority carrier diffusion length. EQE and SIMS of the gas phase sample with standard precursor are depicted in Figure 6.14. The EQE shows better collection in the long wavelength region compared to the sample with 10 nm NaF manifested in a $J_{sc}$ of 31.7 mA/cm$^2$. The SIMS profile is very similar to the one previously shown for the 10 nm NaF sample (compare Figure 6.5e), where Na is present at the CZTSSe/CdS interface which was absent in the sample with 0 nm NaF (Figure 6.5d) and the Na distribution is more homogeneous as compared to the 0 nm NaF sample.

Fig. 6.14: a) EQE and b) SIMS of selected elements for the gas phase sample.

For a further understanding of the above presented results, two samples of borosilicate glass (BSG, substrate without Na) coated with a Mo trilayer were annealed next to a NaF coated glass (see schematic 6.11) under the same conditions as before, with and without elemental Se vapor. The Na distribution in the Mo was measured after the annealing by SIMS and is depicted in Figure 6.15. An untreated Mo/BSG sample, used as reference sample, is also shown. The Na content in the reference sample could stem from the sputtering target or handling under ambient conditions. The Mo sample annealed without Se (denoted by NaF in Figure 6.15) contains a significant amount of Na compared to the Mo reference sample (two orders of magnitude higher Na counts, measured by SIMS). Considering the low vapor pressure of NaF (\(\sim 10^{-6}\) mbar at 550 °C [222]) it is assumed that little NaF could be transported via the gas phase to the Mo/BSG sample. Traces of remaining Se in the furnace could assist Na transport via Na$_2$Se$_x$ or
elemental Na dissociated from NaF upon traces of water might be transported to the Mo/BSG sample. When additionally Se vapors strike the NaF layer the Na counts in the Mo are higher (sample denoted by NaF & Se) leading to the assumption that some volatile Na$_2$Se$_x$ compounds form to facilitate the transport of Na.

![Graph showing Na counts over sputter time for Mo, NaF, and NaF & Se](image)

**Fig. 6.15:** SIMS measurements on Mo/BSG samples annealed with a NaF coated substrate next to the sample with and without Se vapor (denoted by NaF & Se and NaF, respectively) and the not annealed reference sample (Mo).

### 6.7 Summary

Na incorporation into CZTSSe was successfully done by NaF and NaCl coating of the precursor, and via Na in the gas phase. Additional Na supply from the absorber surface led to more homogeneous Na depth profiles as revealed by SIMS. For the CZTSSe devices, additional Na incorporation from the top of the absorber enhanced FF and $V_{oc}$, thus superior device performance was achieved. The highest device performance was observed for 10 nm NaF mainly due to increased $V_{oc}$ and FF while the SCR was slightly decreased. It appears that the location of Na in CZTSSe is very important and has to be tuned by external Na supply because of slow Na diffusion from the SLG substrate into the CZTSSe absorber.
It was found that Na has a profound effect on several electronic properties that are summarized here:

(i) Na enhances \(V_{oc}\) and FF and therefore improves the PV device performance.

(ii) Na reduces current blocking at low temperatures possibly by reduction of a blocking back contact barrier.

(iii) Na shifts the carrier freeze out to smaller activation energy levels.

Still, higher \(V_{oc}\) should be possible and is currently limited by dominant interface recombination irrespective of Na concentration.

Na supply via the gas phase is possible, indicated by the increased presence of Na atoms on the sample. In the presence of Se, the Na transport is enhanced. This finding is used to back up the proposed formation of \(\text{Na}_2\text{Se}_x\) in section 5.6. It would be very useful to do TR-PL measurements on solar cells with different amounts of Na to directly access the minority carrier lifetime. Additionally, XPS and UPS could provide valuable insights into the chemical and electronic properties of the buffer/absorber interface with different deposited amounts of Na.
Chapter 7

Conclusions and Outlook

This thesis presented the growth and characterization of Cu$_2$ZnSnS$_4$, Cu$_2$ZnSnSe$_4$, and Cu$_2$ZnSn(S,Se)$_4$ absorber layers, which were deposited by non-vacuum solution processing followed by high temperature annealing, omitting the use of toxic or explosive reagents and process gases. Two different precursor solution chemistries were studied: (A) precursor solutions containing metal salts and binder material, and (B) precursor solutions with metal salts and thiourea as sulfur source but without organic binder material.

In study (A) metal salt precursor solution with the organic binder material ethyl cellulose were employed to successfully grow CZTSe absorbers after annealing in reactive selenium atmosphere. CZTSe growth was found to be kinetically driven as seen by a fast selenization of Cu followed by subsequent incorporation of Sn to form CTSe, and finally the incorporation of Zn. The CZTSe formation started at $\sim 400$ °C. If T$_{sub}$ $>$ 600 °C or the Se vapor pressure was not sufficient, complete Sn loss was observed resulting in the decomposition products ZnSe and Cu$_{2-x}$Se. Despite a high surface roughness and a thick residual carbon-rich layer between the back contact and the absorber, working devices with up to 4.3 % efficiency were demonstrated. Yet, the intermediate carbon-rich layer is not desirable for efficient carrier collection.

By changing the precursor chemistry to low temperature degradable chemicals with lower carbon content and weaker metal complexation (B) and simultaneous addition of thiourea, carbon layer free absorbers were obtained. Formation of CZTS required T$_{sub}$ $\sim 500$ °C, which is 100 °C higher than the temperature needed to form CZTSe. To identify and quantify secondary phases in CZTSe the use of synchrotron radiation
techniques was helpful. The different absorption features at the K-edge of Se allowed for unambiguous detection and quantification of ZnSe in CZTSe. Those measurements enabled a correlation of elemental and phase composition by utilization of the ternary Cu$_2$Se - SnSe$_2$ - ZnSe diagram. This correlation allows reliable estimation of secondary phases using EDX/XRF methods.

The drawback of poor crystallinity and high surface roughness, frequently observed in non-vacuum processed absorbers was circumvented by two different sintering approaches. By starting with an initially Sn-rich precursor (i.e. Zn/Sn < 1) and allowing for excess Sn to leave the layer during annealing, large grains were obtained. The mobile and low melting element Sn was assumed to be involved in this sinter mechanism. The solar cell devices, however, were limited by poor carrier collection. This was explained by a more Cu-rich absorber composition with increased p-type doping due to the possible formation of Cu$_{1-z}$ antisite acceptor defects. The high p-type doping, on the one hand, reduces the SCR width and therefore limits charge carrier collection, but on the other hand can increase the quasi-Fermi level splitting, and consequently enhance the $V_{oc}$.

To combine grain growth with suitable electronic absorber properties a second, novel process for grain growth was developed, which involved the quasi-liquid assisted sintering in the presence of a top NaF layer. The proposed fluxing mechanism involves three steps: i) enhanced chemisorption of Se molecules at the NaF coated precursor surface, ii) formation of liquid or quasi-liquid Na$_2$Se$_x$ phases at the surface, and iii) crystallization of solid CZTSSe by the reaction of the metal-containing precursor with the reactive Se provided via Na$_2$Se$_x$. Although no direct proof for the formation of the Na$_2$Se$_x$ phases could be found, the proposed mechanism was supported by the enhanced substitution of S by Se in presence of Na, which was confirmed by ICP-MS measurements, and by a shift of the CZTSSe XRD peaks to smaller angles caused by an increase of the lattice constant upon Se incorporation.

It was found that Na not only influences the grain growth but also significantly modifies the electronic properties of CZTSSe absorbers. By varying the NaF top layer thickness deposited on the precursor before selenization, the Na position and profile throughout the absorber was changed. The highest device efficiency of 6.04% was achieved at an optimum of 10 nm NaF corresponding to $\sim$ 0.4 at% Na in the absorber, while the optimum for grain growth was found at 100 nm NaF. Upon Na doping the defect activation energy was shifted from 370 meV to 180 meV which can explain improved
$V_{oc}$ and FF. Na can influence the electronic properties of CZTSSe: if it is preferentially located at the GBs, it could passivate surface recombination states, or donors and deep defects located in the bulk, resulting in an increased effective p-type doping and thereby improved $V_{oc}$. The main limitations were related to the detrimental recombination at the CdS/CZTSSe interface and probably the formation of a back contact barrier.

The results obtained in this thesis yield some recommendations for further experiments. To prevent surface decomposition of CZTSSe, annealing in a closed graphite reactor or rapid thermal processing can be done, whereas an additional tin-containing source could be added during annealing to provide gaseous SnS(e). In order to overcome the device limiting interface recombination it is important to do a detailed study on the buffer/absorber interface using XPS and UPS to characterize its chemical and electronic properties. Tailoring of the metal composition will allow to optimize the band gap offset and therefore the electron transport across the pn-junction.

Intentional Na doping can be directly applied by including Na in the precursor solution. Although it was demonstrated that presence of Na massively enhances the crystallization because of the proposed formation of liquid $\text{Na}_2\text{Se}_x$ phases, the role of Na as a fluxing agent is not completely understood. Further insights on the formation of $\text{Na}_2\text{Se}_x$ might be obtained by an in situ XRD investigation. Since Na can form various $\text{Na}_2\text{Se}_x$ molecules with $x = 1, 2, 3, 4, 6$, which exhibit melting points between 255 °C and $\sim 1000$ °C, variation of the Se vapor pressure could give further indications on the formation of a liquid phase. To prove the location and segregation of Na in CZTSSe an atom probe tomography investigation is planned.

In analogy to CIGS, Na seems to play an important role in CZTSSe and therefore, the controlled incorporation of Na is desirable. The developed NaF approach can be transferred to other deposition methods such as electrodeposition, nanoparticle coating and also vacuum based sputter deposition since most approaches use a two step formation route where our NaF precursor top-coating can be used to promote the grain growth.

Once an acceptable efficiency level is reached, the focus can be shifted towards deposition methods for large area absorber coating. The clear advantages of this solution based approach compared to other methods is the use of non-toxic and off the shelf chemicals. Thus, a focus can be set on adaption of deposition methods rather than solution chemistry. In this respect the application of industry relevant methods such as curtain coating or printing can be investigated in the future for low-cost and high
throughput manufacturing of kesterite thin film solar cells.
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