Doctoral Thesis

Alkali Treatment of Solution Processed Kesterite Solar Cells

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Alkali treatment of solution processed kesterite solar cells

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

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2017
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Abstract

Worldwide increasing energy needs and negative effects of fossil and nuclear power demand environmental friendly and cost-effective alternative energy sources like solar power. Silicon based solar cells dominate the photovoltaic (PV) market thanks to their high efficiency and matured technology. However, alternative absorber materials are desired that offer lower production cost and employ cheap and readily available constituents with little negative environmental impact.

Cu(In,Ga)Se$_2$ (CIGS) and CdTe are chalcogen-based absorber materials with a high absorption coefficient rendering them suitable for the application in thin film solar cells. These thin film technologies offer the advantage of lower material consumption, shorter energy payback time and the possibility of flexible substrates. However, the scarcity, high costs or toxicity of In, Te, Ga and Cd used in these absorber layers demands for alternative materials. Kesterite Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) solar cells present a suitable alternative due to the non-toxicity, abundance of the material’s constituents and similarly high absorption coefficient. Kesterite solar cells exhibit efficiencies of up to 12.6%, demonstrating the high potential of the kesterite material. The relatively low open circuit voltage ($V_{OC}$), which is often described quantitatively as $V_{OC}$-deficit ($V_{OC}$-deficit = $E_g$ - $V_{OC}$), still remains the major problem inhibiting further efficiency improvement.

The major reason for the $V_{OC}$-deficit is still under debate, especially whether the main recombination paths are located in the bulk, grain boundaries or interfaces of the device. A major source for recombination are secondary phases such as binary and ternary copper-, zinc- and tin-selenides and -sulphides, which can exist in the absorber or at its interfaces. The secondary phases can impede the carrier transport and lead to increased
recombination rates. Prevention of the formation of secondary phases is challenging due to a narrow homogeneity region and an incongruent melting of the kesterite phase. Losses in $V_{OC}$ can also be caused by recombination at the absorber interfaces due to a high density of interface states as well as a non-optimal band alignment. The lack of shallow defect states in kesterite is expected to lower mobility, lifetime and therefore decrease the $V_{OC}$. Bandgap fluctuations stemming from structural or compositional inhomogeneities, or potential fluctuations due to a high concentration of charged defects can also lead to a higher $V_{OC}$-deficit.

In this thesis two separate approaches are investigated in order to overcome the aforementioned performance limitations. Both approaches are based on a solution process using dimethyl sulfoxide (DMSO), thiourea and metal-chlorides. The absorber fabrication is comprised of two steps, the precursor synthesis and the annealing in a chalcogen atmosphere. The first approach is aiming to improve the annealing in chalcogen atmosphere, thereby leading to the formation of homogeneous absorber layers, free of detrimental secondary phases and with a large-grained morphology. A detailed study conducted in this thesis on different annealing setups eventually results in a 3-stage annealing process under a controlled selenium atmosphere in a $\text{SiO}_x$ coated graphite box. The improved annealing environment leads to an improved morphology of the absorber layer and the $V_{OC}$-deficit can be reduced to 0.57 V, which appears to be one of the lowest values reported for kesterite solar cells.

The second approach focuses on the understanding of alkali treatments on kesterite solar cells. Sodium treatment has shown significant improvements of bulk properties by enhancing grain growth, increasing doping concentration and passivating grain boundaries. Other alkali elements have also been reported but their impact on electronic properties and device performance is more ambiguous. So far, alkali post deposition treatment of the kesterite absorber has not been thoroughly investigated yet. In the closely related absorber material CIGS, potassium-fluoride post deposition treatment (KF-PDT) of the absorber surface yielded significant improvements in $V_{OC}$ and fill factor leading to record efficiencies above 20 % for this material. In this thesis the KF-PDT and potassium bulk treatment on kesterite absorber layers are investigated. It is shown that KF-PDT improves
the open circuit voltage of kesterite solar cells. However, a severe blocking of the short circuit current and reduction of fill factor reduces the device efficiencies. Furthermore, quantum efficiency measurements indicate that KF-PDT alters the properties of the buffer layer. In contrast to KF-PDT, potassium bulk treatment leads to an enhanced grain growth and to overall improved photovoltaic parameters resulting in device efficiencies close to 10%. The impact of potassium as a fluxing agent is more efficient compared to sodium. Additionally, potassium suppresses incorporation of sodium from the soda lime glass. There are no observable synergetic effects between potassium and sodium but both alkali elements equally improve kesterite solar cell performance.

Finally, a comprehensive study to unveil the discrepancy between published results is presented comparing the effects of alkali treatments on device performance. The hypothesis is that each alkali element requires a different absorber composition to achieve the highest photovoltaic performance and therefore an extensive set of samples with different alkali elements and alkali concentrations as well as various metal ratios is studied. The investigation reveals a complex dependency of metal ratios, alkali elements and alkali concentrations on the device performance in high-efficiency kesterite solar cells. From Li to Cs the nominal Sn concentration ($\frac{Sn}{Cu+Zn+Sn}$) required for best device properties is reduced and the alkali concentration resulting in highest device efficiencies is lower by an order of magnitude for the heavy alkali elements (Rb, Cs) compared to the lighter ones (Li, Na, K). The PV parameters correlate with changes in morphology with best devices exhibiting large grains throughout the whole absorber layer and a low density of grain boundaries. A ranking of best device performances employing alkali treatment resulted in the order of Li > Na > K > Rb > Cs based on the statistics of more than 700 individual cells. A champion device with 11.5% efficiency is presented using a “high” Li concentration in conjunction with an optimized Sn content.

In conclusion, improvements in the annealing environment and alkali treatment of kesterite absorber layers cleared the way for more than 11% conversion efficiency. Further investigations on Li alloying and interface treatments are promising paths to reach anticipated efficiency levels in the future.
Zusammenfassung (Abstract in German)


Cu(In,Ga)Se₂ (CIGS) und CdTe sind Chalkogen basierte Absorbermaterialien mit hohem Absorptionskoeffizienten, und daher für die Anwendung in Dünnschichtsolarzellen geeignet. Die Dünnschicht-Technologie bietet den Vorteil eines geringeren Materialverbrauchs, kürzerer Energie-Amortisationszeiten und die Möglichkeit flexible Substrate zu verwenden. Doch die beschränkte Verfügbarkeit, die damit verbundenen hohen Kosten oder die Toxizität von In, Te, Ga und Cd, die in diesen Absorberschichten verwendet werden, ergeben Probleme, welche durch Kesterit Cu₂ZnSn(S,Se)₄ (CZTSSe) Solarzellen aufgrund der Nicht-Toxizität und hohen Verfügbarkeit der Hauptbestandteile, sowie eines vergleichbar hohen Absorptionskoeffizienten, gelöst werden können.

Effizienzen von bis zu 12,6% zeigen das ausserordentliche Potential von Kesterit Solarzellen und spiegeln sich in einem erhöhten Forschungsinteresse wieder. Weitere Effizienzverbesserungen werden jedoch durch die relativ niedrige Leerlaufspannung (V_{OC}), welche häufig quantitativ als V_{OC}-Defizit (V_{OC}-Defizit = E_g - V_{OC}) bezeichnet wird, erschwert. Die Hauptursachen für das hohe V_{OC}-Defizit sind noch nicht endgültig geklärt, u.a. ist noch offen, ob sich die Hauptrekombinationskanäle im Bulk, den Korngrenzen


Der zweite Ansatz konzentriert sich auf die Untersuchung der Beimischung von Alka-

Zuletzt wird eine umfassende Studie zur Aufklärung der Diskrepanz zwischen veröffentlichten Ergebnissen präsentiert, die die Auswirkungen von Alkali Behandlungen auf die Solarzellen Effizienz untersuchen. Die aufgestellte Hypothese ist, dass jedes Alkalielement eine andere Absorberkomposition benötigt, um die optimale Solarzellen Leistung zu erzielen. Um dies darzulegen wurde ein umfangreicher Satz von Proben mit unterschiedlichen Alkalielementen und Alkalikonzentrationen sowie verschiedenen Absorberkompositionen detailliert untersucht. Die Auswertung zeigt eine komplexe Abhängigkeit von Absorberkom-
Zusammenfassung

### List of abbreviations

<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>A-CVD</td>
<td>Atmospheric chemical vapour deposition</td>
</tr>
<tr>
<td>Al:ZnO</td>
<td>Aluminium doped zinc oxide</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>AR coating</td>
<td>Anti-reflection coating</td>
</tr>
<tr>
<td>AS</td>
<td>Admittance spectroscopy</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>CIGS</td>
<td>Cu(In,Ga)(S,Se)$_2$</td>
</tr>
<tr>
<td>CV</td>
<td>Capacitance-voltage</td>
</tr>
<tr>
<td>CZTS</td>
<td>Cu$_2$ZnSnS$_4$</td>
</tr>
<tr>
<td>CZTSe</td>
<td>Cu$_2$ZnSnSe$_4$</td>
</tr>
<tr>
<td>CZTSSe</td>
<td>Cu$_2$ZnSn(S,Se)$_4$</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>$E_A$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>$E_C$</td>
<td>Conduction band energy</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi level energy</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band gap energy</td>
</tr>
<tr>
<td>$E_T$</td>
<td>Activation energy for the trap level</td>
</tr>
<tr>
<td>$E_V$</td>
<td>Valence band energy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Efficiency</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>GIXRD</td>
<td>Grazing incidence X-ray diffraction</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>i-ZnO</td>
<td>Intrinsic ZnO</td>
</tr>
<tr>
<td>J-V</td>
<td>Current density - voltage</td>
</tr>
<tr>
<td>$J_{SC}$</td>
<td>Short circuit current density</td>
</tr>
<tr>
<td>KF-PDT</td>
<td>Potassium-fluoride post deposition treatment</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>RTP</td>
<td>Rapid thermal processing</td>
</tr>
<tr>
<td>SILAR</td>
<td>Successive ionic layer adsorption and reaction</td>
</tr>
<tr>
<td>SCR</td>
<td>Space charge region</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry</td>
</tr>
<tr>
<td>SLG</td>
<td>Soda lime glass (float glass)</td>
</tr>
<tr>
<td>T-JV</td>
<td>Temperature dependent current density - voltage</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conductive oxide</td>
</tr>
<tr>
<td>TR-PL</td>
<td>Time resolved photoluminescence</td>
</tr>
<tr>
<td>$V_{OC}$</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
</tr>
</tbody>
</table>


1 Introduction

1.1 Renewable energy resources

The Paris climate agreement, declared by 196 member states in December 2015, formulates climate change mitigation and energy policy targets for the upcoming decades [1]. All member states are obliged to take appropriate measures that limit global warming to less than 2°C compared to pre-industrial levels.

![Temperature anomaly graph](image)

**Figure 1.1:** Observed globally averaged combined land and ocean surface temperature anomaly 1850–2012 relative to 1961–1990. Adapted from [2].

The rise of the global temperature, shown in Figure 1.1, poses a significant threat because of the following assumed consequences [2]:

- Increased water restriction
- Increased damages from river and coastal urban floods
• Reduced crop productivity and food security
• Increased damages from extreme heat events and wildfires
• Heat-related human mortality
• Risk for ecosystems

The replacement of the greenhouse gas emitting fossil fuel based energy production to a sustainable and climate neutral energy production plays a key role to achieve the $2^\circ$C target.

![Primary energy consumption](image)

**Figure 1.2:** Worldwide primary energy consumption from the pre-industrial era until today. Adapted from [3].

Since the industrial revolution the energy consumption nearly 10 folded thereby enabling wealth and prosperity in the western world (see Figure 1.2). Throughout the 19th and early 20th century the increase in primary energy consumption is based on coal and after the midst of the 20th century additionally on oil and natural gas. In this perspective fossil fuels make up for more than 3/4 of the primary energy consumption today.  

\footnote{It should be pointed out that the concept of primary energy does not take the conversion efficiency of different energy resources into account, thus generally Figures like 1.2 overstate energy resources exhibiting low conversion efficiency like fossil fuels and understate those accounted for in converted forms like photovoltaic, wind power or hydroelectricity.}
1.2. Solar cells

The major part of global warming results from the burning of fossil fuels and the release of the greenhouse gas CO$_2$. In order to comply with the 2°C target it is imperative to withdraw from fossil fuel dependency and transit to renewable energy resources. Wind and solar power will play a major role in this upcoming energy transition. Although today in some regions solar power became already the cheapest source of energy [4], the cost of energy from solar power is still required to drop further. Therefore continuous research in alternative technologies like kesterite solar cells are needed to provide clean and sustainable energy combined with low costs in the future.

1.2 Solar cells

Solar cells are photovoltaic devices that convert part of the energy stored in the incident sunlight into electric energy. The conversion of sunlight into electric energy requires the absorption of photons and generation of electron hole pairs, followed by the separation of these electron-hole pairs and collection in separate contacts from which the charge carriers can be released into an external circuit to do work.

![Diagram of solar spectrum and Shockley-Queisser limit](image)

**Figure 1.3:** a) Solar spectrum of the sun with (black) and without (red) the influence of the atmosphere. The green area indicates the range of optimal bandgap for a single junction solar cell [5–7]. b) Dependency of the theoretical maximum efficiency for a single-junction solar cell depending on the bandgap. Adapted from [8].

The absorption and utilisation of sunlight requires a semi-conductor with a suitable bandgap. The bandgap determines the part of the sun spectrum that can be absorbed
by the semi-conductor. As shown in Figure 1.3 a) the spectrum of the sun (black curve) is close to the theoretical black body radiation at 5730 K (blue curve). Absorption and reflection in the earth’s atmosphere lead to a reduction of the irradiation on the earth’s surface (red curve).

For a solar cell device with one absorber material (single-junction solar cell) the bandgap defines the theoretical maximum conversion efficiency, which is the so-called Shockley-Queisser limit (SQL), presented in Figure 1.3 b). The bandgap range leading to conversion efficiencies >31% is located between 1.0–1.5 eV.

![Figure 1.4: a) Absorption coefficient $\alpha$ for relevant single junction solar cell absorber materials [9,10]. b) Loss channels for a single junction solar cell with an optimal bandgap. Reproduced with permission [11].](image)

The onset of the absorption coefficient $\alpha$ defines the bandgap and the higher the absorption coefficient is, the more sunlight can be absorbed for a given thickness of the semiconductor material. Figure 1.4 a) presents the energy dependent absorption coefficient for the relevant single junction solar cell absorber materials. Absorber materials with an indirect bandgap, e.g. c-Si, exhibit a comparably low absorption coefficient in the energy range close to their bandgap, and thicker layers of several hundred $\mu$m are required. In contrast, for direct bandgap materials like GaAs, CIGS or kesterite, which possess a high absorption coefficient, a few $\mu$m thick absorber layer is sufficient. The Shockley-Queisser limit of 33.7% appears to be low, because a major part of the power in the sunlight cannot be used in a single-junction solar cell due to thermalization losses, energy loss in the carnot cycle and entropy losses. All relevant loss mechanisms in a
real device are shown in Figure 1.4 b). The loss due to thermalization can be minimized by multi-junction solar cells, which utilize more than one absorber layer with optimized bandgaps [12] and the losses due to angle restriction by using concentrator systems.

The recent progress in the best research-cell efficiencies of all types of solar cell materials is summarized in Figure 1.5 [13].

![Figure 1.5: State of the art (July 2017) conversion efficiencies of solar cells [13].](image)

For single junction solar cells (non-concentrators) GaAs and c-Si based solar cells exhibit highest efficiencies of 28.8% and 26.6% [14]. However, the thin film technologies of CIGS and CdTe surpassed the industrial relevant multi-crystalline Si solar cells with 22.6% [15] and 22.1% [16], respectively. Perovskite solar cells exhibited a spectacular increase to 22.1% since 2013 [17] and the initial stability issues [18, 19] could also be improved [20]. Kesterite solar exhibit 12.6% certified efficiency [21] achieved by a hydrazine based solution process from IBM.
1.3 Kesterite thin film solar cells

Cu$_2$ZnSn(S,Se)$_4$ (CTZSSe) is a quaternary compound that crystallizes in the kesterite structure, hence giving it its name. Sulphur-based kesterite (CZTS) is constituted of only earth abundant, cheap and non-toxic elements. Table 1.1 presents the relative abundance, worldwide production and price of raw materials relevant for the fabrication of solar cells from various technologies [22].

Table 1.1: Cost of raw materials in January 2016 [22], abundance of elements in the earth’s crust in parts per million (ppm) by weight [23] and the worldwide production in 1000 metric tonnes in 2016 [22].

<table>
<thead>
<tr>
<th>Element</th>
<th>Cost ($/kg)</th>
<th>Abundance (ppm)</th>
<th>World Production (1000t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4.4</td>
<td>68</td>
<td>19,400</td>
</tr>
<tr>
<td>Zn</td>
<td>1.6</td>
<td>79</td>
<td>11,900</td>
</tr>
<tr>
<td>Sn</td>
<td>14.3</td>
<td>2.2</td>
<td>280</td>
</tr>
<tr>
<td>S</td>
<td>0.11</td>
<td>420</td>
<td>69,300</td>
</tr>
<tr>
<td>In</td>
<td>255</td>
<td>0.16</td>
<td>655</td>
</tr>
<tr>
<td>Ga</td>
<td>130</td>
<td>19</td>
<td>0.55</td>
</tr>
<tr>
<td>Se</td>
<td>19</td>
<td>0.05</td>
<td>2.2</td>
</tr>
<tr>
<td>Cd</td>
<td>0.94</td>
<td>0.15</td>
<td>23</td>
</tr>
<tr>
<td>Te</td>
<td>34</td>
<td>0.001</td>
<td>0.4</td>
</tr>
</tbody>
</table>

It is assumed that for the production at the Gigawatt scale the scarcity of In and Te will pose a significant problem for the mature chalcogen-based technologies CdTe and CIGS [24]. In this context kesterite solar cells present a promising alternative.

Kesterite exhibits a high absorption coefficient of $>10^4$ cm$^{-1}$, resulting in thin absorber layers of 1–2 µm being sufficient to capture more than 99% of the usable sunlight. Thin film solar cells exhibit advantages as low material consumption, the possibility to use flexible substrates and thus roll-to-roll processing. The bandgap of Cu$_2$ZnSn(S,Se)$_4$ can be varied from 1.0 eV for the pure Se compound to 1.5 eV for the pure S compound. Therefore, bandgap engineering is possible by changing the S/(S+Se) ratio in the Cu$_2$ZnSn(S,Se)$_4$ layer.

**Growth techniques for kesterite absorber layers**
1.3. Kesterite thin film solar cells

Most Cu$_2$ZnSn(S,Se)$_4$ absorber layers are fabricated by a 2-step process. The initial step is the deposition of a precursor layer followed by an annealing at temperatures between 500°C – 600°C in a chalcogen atmosphere. Table 1.2 shows the relevant kesterite solar cells for various process techniques. The devices are separated into non-vacuum and vacuum-based fabrication techniques. Solution processes utilize various solvents like hydrazine [25] or dimethyl sulfoxide (DMSO) [26] in combination with spin-coating. Larramona et al. fabricate the precursor layer via non-pyrolytic spraying of CZTS nanoparticles, dispersed in a water-ethanol mixture [27,28]. Other non-vacuum techniques are electroplating of a metal precursor [29] and nanoparticle synthesis using the hot injection method [30,31].

Vacuum-based processes for the precursor synthesis use either sputtering [32,33], thermal evaporation [34–36] or pulsed laser deposition (PLD) [37]. Various targets can be used for the sputtering approach like pure metal targets, binary metal-sulfide or selenide targets or CZTS compound targets. Layer deposition can be achieved by either co-sputtering or sequential sputtering. Thermal evaporation was successfully applied for a 1-step process by Repins et al. without the necessity of a subsequent annealing step [36], however volatile phases pose great difficulties for process control. The crystal growth during the high temperature annealing step in chalcogenide atmosphere was intensively studied by in-situ XRD analysis revealing the formation of binary phases, ternary phases and eventually the kesterite phase depending on temperature and time [38]. The in-situ analysis shows that the kesterite formation starts with the formation of Cu$_2$Se phases followed by the formation of the ternary Cu$_2$SnSe$_3$ and eventually kesterite phase as described in Equation 1.1.

\[
(Cu, Zn, Sn) \xrightarrow{\sim 190^\circ C} Cu_xSe \xrightarrow{\sim 340^\circ C} Cu_2SnSe_3 + Cu_2ZnSnSe_4 \xrightarrow{\sim 420^\circ C} Cu_2ZnSnSe_4
\]  
(1.1)
### Table 1.2: List of representative kesterite samples fabricated by different non-vacuum and vacuum processes.

<table>
<thead>
<tr>
<th>sample</th>
<th>precursor</th>
<th>deposition technique</th>
<th>annealing</th>
<th>highest $\eta$</th>
</tr>
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<tr>
<td><strong>non-vacuum processed</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBM [21] CZTSSe</td>
<td>hydrazine-based solution</td>
<td>spin-coating</td>
<td>&gt; 500°C, sulfo-selenization</td>
<td>12.6%</td>
</tr>
<tr>
<td>Empa [39] CZTSSe</td>
<td>dimethyl sulfoxide based solution</td>
<td>spin-coating</td>
<td>550°C, selenization with Se$_2$</td>
<td>11.5%</td>
</tr>
<tr>
<td>ZSW [40] CZTSSe</td>
<td>dimethyl sulfoxide based solution</td>
<td>doctor blading</td>
<td>540°C, selenization with Se$_2$ and SnSe$_2$</td>
<td>10.3%</td>
</tr>
<tr>
<td>IMRA [27, 28] CZTSSe</td>
<td>water-ethanol based nanoparticle ink</td>
<td>non-pyrolytic spraying</td>
<td>a) annealing on hotplate at 525°C in N$_2$</td>
<td>10.8%</td>
</tr>
<tr>
<td>NCKU [41] CZTSSe</td>
<td>2-Methoxyethanol based solution</td>
<td>spin-coating</td>
<td>b) sulfo-selenization at 500°C with Se &amp; SnS</td>
<td>10.1%</td>
</tr>
<tr>
<td>PU [30, 31] CZTSe</td>
<td>Nanoparticles by hot-injection method</td>
<td>spin-coating</td>
<td>550°C in selenium atmosphere</td>
<td>9.3%</td>
</tr>
<tr>
<td>AMU/NEXCIS [29] CZTSe</td>
<td>stacked metal precursor Cu / Sn / Zn</td>
<td>sequential electro-deposition of Cu, Sn, Zn</td>
<td>550°C in Se and Sn containing atmosphere</td>
<td>8.2%</td>
</tr>
<tr>
<td><strong>vacuum-processed</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DGIST [33] CZTSSe</td>
<td>stacked metal precursor Cu / Sn / Zn</td>
<td>sequential sputtering from pure metal targets</td>
<td>510°C sulfo-selenization process with S$_2$ and SeS$_2$</td>
<td>12.3%</td>
</tr>
<tr>
<td>AIST [34] CZTGSn</td>
<td>CuZnGeSnSe deposited at 200°C</td>
<td>co-evaporation of elemental Cu, Zn, Ge, Sn, Se</td>
<td>500 – 550°C annealing with GeSe$_2$, SnSe$_2$ and Se</td>
<td>12.3%</td>
</tr>
<tr>
<td>IBM [35] CZTSe</td>
<td>CZTSe precursor grown at 150°C</td>
<td>co-evaporation of elemental Cu, Zn, Sn, Se</td>
<td>590°C in selenium atmosphere</td>
<td>11.6%</td>
</tr>
<tr>
<td>UU [32] CZTSSe</td>
<td>CZTS precursor</td>
<td>sputtering from binary metal-sulphide targets</td>
<td>560°C in selenium atmosphere</td>
<td>9.7%</td>
</tr>
<tr>
<td>NREL [36] CZTSe</td>
<td>co-evaporation of Cu, Zn, Sn, Se</td>
<td>single step co-evaporation 500°C</td>
<td>-</td>
<td>9.15%</td>
</tr>
<tr>
<td>DTU [37] CZTS</td>
<td>CZTS</td>
<td>pulsed laser deposition of CZTS target</td>
<td>560°C in the presence of S and SnS</td>
<td>6.10%</td>
</tr>
</tbody>
</table>
1.3. Kesterite thin film solar cells

Solar cell structure

Kesterite is an intrinsically p-type semiconductor that is employed as the absorber layer in a stack of Mo/CZTSSe/CdS/i-ZnO/Al:ZnO with an Ni-Al grid and an optional AR coating on top, as illustrated in Figure 1.6. The device structure is adopted from the mature CIGS technology and the best kesterite devices are still obtained by this layer structure, although several attempts have been made to replace or modify the back contact and buffer layer materials.

Figure 1.6: a) Coloured scanning electron microscopy image of the cross-section of a CZTSSe solar cell stack constituted of Mo/CZTSSe/CdS/i-ZnO/Al:ZnO (Ni-Al grid not shown). b) Band diagram of the kesterite solar cell under dark conditions.

The molybdenum (Mo) back contact is suitable only to a limited extent due to a reaction between the kesterite phase and Mo [42] at elevated temperatures. The chemical instability of kesterite in the presence of Mo [43] leads to a decomposition reaction in the vicinity of the Mo back contact following Equation 1.2. The decomposition reaction can be partly suppressed by a sufficient chalcogen background pressure during annealing.

\[
2Cu_2ZnSn(S, Se)_4 + Mo \rightarrow 2Cu_2(S, Se) + 2Zn(S, Se) + 2Sn(S, Se) + Mo(S, Se)_2 \quad (1.2)
\]

CdS is the standard buffer layer and all published high-efficiency devices with more than 10% use a CdS buffer layer deposited by CBD. CdS deposited by CBD creates a
comparably defect-poor interface and for CZTSe a suitable band-alignment [44].

Table 1.3: Properties of buffer layers for kesterite solar cells.

<table>
<thead>
<tr>
<th>material</th>
<th>deposition technique</th>
<th>bandgap</th>
<th>best efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>CBD</td>
<td>2.4 eV</td>
<td>12.6% [21]</td>
</tr>
<tr>
<td>CdS+In$_2$S$_3$</td>
<td>CBD</td>
<td>2.4 eV and 2.1 eV</td>
<td>12.3% [45]</td>
</tr>
<tr>
<td>Zn$<em>{0.35}$Cd$</em>{0.65}$S</td>
<td>SILAR</td>
<td>2.7 eV</td>
<td>9.2% [46]</td>
</tr>
<tr>
<td>In$_2$S$_3$</td>
<td>CBD</td>
<td>2.1 eV [47]</td>
<td>7.6% [48]</td>
</tr>
<tr>
<td>ZnO</td>
<td>A-CVD</td>
<td>3.3 eV</td>
<td>5.2% [49]</td>
</tr>
<tr>
<td>Zn(O,S)</td>
<td>ALD</td>
<td>2.8–3.8 eV</td>
<td>4.6% [50]</td>
</tr>
<tr>
<td>ZnS</td>
<td>CBD</td>
<td>3.6 eV</td>
<td>4.5% [52]</td>
</tr>
</tbody>
</table>

However, due to the toxicity of Cd, a low bandgap of 2.4 eV and a cliff-like band-alignment with sulphur-based CZTS absorber layers [51,53] a more suitable buffer layer material is desired. Table 1.3 presents a list of buffer layers, their bandgap and the highest efficiency achieved with the specific buffer layer.

**Crystal structure**

![Figure 1.7: Cation mutations from the zincblende structure of Zn(S,Se) to the kesterite structure adopted by Cu$_2$ZnSn(S,Se)$_4$. Reproduced with permission [54].](image)

The crystal structure of kesterite belongs to the symmetry group $\overline{4}$ [55,56] and can be derived from the zincblende structure by cation mutations as illustrated in Figure 1.7 [54]. Substitution of one half of the Zn(II) atoms with Cu(I) atoms and the other half with
In(III) atoms results in the chalcopyrite structure. In a likewise step, In(III) atoms are substituted by Zn(II) atoms and Sn(IV) atoms to obtain the kesterite structure.

![Diagram of elemental cells of zincblende, chalcopyrite, and kesterite structure.](image)

**Figure 1.8:** Elemental cells of zincblende and kesterite structure. The chalcopyrite structure is a result of cation mutation of the Zn(II) atoms into Cu(I) and In(III). The kesterite structure can be obtained from the chalcopyrite structure by replacing the In(III) atoms with Zn(II) and Sn(IV) likewise.

The crystal structure of the elemental cells of the zincblende, chalcopyrite and kesterite structure are presented in Figure 1.8. The kesterite structure exhibits alternating z-planes with Cu/Zn and Cu/Sn atoms. Because of the similar size of Cu and Zn the Cu/Zn planes are prone to disorder [57, 58]. The Cu/Zn disorder in the synthesized absorber layer depends on the metal ratios, especially Cu/(Zn+Sn) ratio, and the thermal history of the absorber layer [59]. A phase transition from partially ordered to disordered kesterite occurs at 260°C [60] for CZTS and 200°C [61] for the CZTSe compound, which can be described by the order parameter S. Fully disordered kesterite (S=0) exhibits a lower bandgap of approximately 110 meV compared to the more ordered kesterite. It is under discussion if the Cu/Zn disorder is one of the major bottlenecks hindering further efficiency improvements for kesterite solar cells [62–64].

**Phase stability, defects and secondary phases**

The optimal range of matrix compositions for highly efficient kesterite solar cells was experimentally determined to be Cu/(Zn+Sn) = 0.8 and Zn/Sn = 1.2 by Katagiri et al.
One of the reasons that best devices are achieved in this compositional range is the formation of secondary phases. Of the common secondary phases Cuₓ(S,Se), Zn(S,Se), Sn(S,Se), Sn(S,Se)₂ and Cu₂Sn(S,Se)₃ it is only Zn(S,Se) which is comparably benign due to its high bandgap, while the other secondary phases lead to a severe degradation as described in Table 1.4.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Cu₂ZnSn(S,Se)₄ [66]</th>
<th>Zn(S,Se) [67]</th>
<th>Cu₂(S,Se) [68,69]</th>
<th>Sn(S,Se)₂ [70–72]</th>
<th>Cu₂Sn(S,Se)₃ [73,74]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap</td>
<td>1.0–1.5 eV</td>
<td>2.7–3.7 eV</td>
<td>1.2 eV</td>
<td>1.0–2.5 eV</td>
<td>0.8–1.35 eV</td>
</tr>
<tr>
<td>Electrical properties</td>
<td>Semiconductor</td>
<td>Insulator</td>
<td>metal like p-type</td>
<td>n-type</td>
<td>p-type</td>
</tr>
<tr>
<td>Structural properties</td>
<td>p-type, highly defective</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impact on solar cell performance</td>
<td>Kesterite</td>
<td>Sphalerite and wurtzite</td>
<td>Chalcocite</td>
<td>Rhombohedral</td>
<td>Cubic and tetragonal</td>
</tr>
<tr>
<td>Absorber material</td>
<td>Insulating, reduces device active area</td>
<td></td>
<td>Metallic, shortens solar cells</td>
<td>Forms diodes and barriers for carrier collection</td>
<td>Effects carrier collection efficiency</td>
</tr>
</tbody>
</table>

First principal studies by Chen et al. revealed that the chemical potential range for the growth of secondary phase free kesterite is indeed narrow as depicted by the black area in Figure 1.9 a) [75]. Furthermore, thermodynamic calculations by Scragg et al. [43] explain the observed decomposition of the kesterite phase at elevated temperatures. At temperatures above 400 °C [76] the kesterite phase can decompose following Equation 1.3 (for the Se case) because of the multivalent nature of Sn that can exist in both +2 and +4 oxidation states.

\[
Cu_2ZnSnSe_4 \Leftrightarrow Cu_2Se (s) + ZnSe (s) + SnSe (s) + \frac{1}{2}Se_2 (g) \uparrow \tag{1.3}
\]

The equilibrium vapour pressure of SnSe(s) at elevated temperatures of 550 °C reaches comparably high values of 2.5E-3 mbar [77], thus leading to a significant loss of Sn and selenium during the annealing step. It is suggested to provide a chalcogen and SnSe background pressure to avoid the decomposition reaction and/or replace lost Sn and Se [78].
1.3. Kesterite thin film solar cells

![Diagram of energy levels and phase space](image1.png)

**Figure 1.9:** a) Chemical potential phase space for $\mu_{\text{Cu}} = -0.20\, \text{eV}$. The narrow, black area defined by the points PQMN resembles phase pure kesterite. b) Calculated energy position within the CZTSe bandgap of point defects. Figures reproduced with permission [75].

![Ternary phase diagram](image2.png)

**Figure 1.10:** a) Ternary phase diagram with different composition dependent defect types from A to F. b) Same defect types in the planar Zn/Sn vs Cu/(Zn+Sn) diagram. The red region indicates the compositional area that resulted in secondary phase free off-stoichiometric kesterite. Figures reproduced with permission [79].
The composition dependent appearance of secondary phases can be deduced from the ternary phase diagram shown in Figure 1.10 a). The center of the ternary phase diagram coincides with the stoichiometric kesterite phase. The calculated energetic positions of possible point defects in the kesterite lattice are visualized in Figure 1.9 b). $V_{Cu}$, $Cu_{Zn}$ and $Zn_{Sn}$ are the p-type defects not being located too deep inside the bandgap to act as recombination centres, similar to $Zn_{Cu}$ and $Cu_i$ for n-type defects.

Deviations from the stoichiometry result in defect clusters, which are described by the types A, B, C, D, E and F and the corresponding secondary phases. The various types and defect clusters forming in the specific compositional regimes are listed in Table 1.5.

Table 1.5: Off-stoichiometric cation substitution reactions for compositional types A–F [56,80]. Adapted from [79].

<table>
<thead>
<tr>
<th>type</th>
<th>Composition</th>
<th>Cation substitution reaction</th>
<th>Intrinsic point defects</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cu↓/Zn↑/Sn-const.</td>
<td>2Cu$^+$ → Zn$^{2+}$</td>
<td>$V_{Cu}$ + Zn$^{2+}_{Cu}$</td>
<td>Cu$<em>{2-\delta}$Zn$</em>{1+\delta}$Sn(S,Se)$_4$</td>
</tr>
<tr>
<td>B</td>
<td>Cu↓/Zn↑/Sn↓</td>
<td>2Cu$^+$ + Sn$^{4+}$ → 3Zn$^{2+}$</td>
<td>2Zn$^{2+}<em>{Cu}$ + Zn$^{2+}</em>{Sn}$</td>
<td>Cu$<em>{2-\delta}$Zn$</em>{1+\delta}$Sn$_{1-\delta}$(S,Se)$_4$</td>
</tr>
<tr>
<td>C</td>
<td>Cu↑/Zn↓/Sn↑</td>
<td>3Zn$^{3+}$ → 2Cu$^+$ Sn$^{4+}$</td>
<td>2Cu$_2^{2+}$ + Sn$_2^{4+}$</td>
<td>Cu$<em>{2+\delta}$Zn$</em>{1-2\delta}$Sn$_{1+2\delta}$(S,Se)$_4$</td>
</tr>
<tr>
<td>D</td>
<td>Cu↑/Zn↓/Sn-const.</td>
<td>Zn$^{2+}$ → 2Cu$^+$</td>
<td>Cu$<em>{Zn}^{2+}$ + Cu$</em>{^{\delta}}$</td>
<td>Cu$<em>{2+\delta}$Zn$</em>{1-\delta}$Sn(S,Se)$_4$</td>
</tr>
<tr>
<td>E</td>
<td>Cu↓/Zn↓/Sn↑</td>
<td>Zn$^{2+}$ → 2Cu$^+$</td>
<td>2$V_{Cu}$ + Sn$<em>{Zn}^{4+}$ or $Sn</em>{Cu}^{4+}$ + $V_{Cu}$ + $V_{Zn}$</td>
<td>Cu$<em>{2-\delta}$Zn$</em>{1-\delta}$Sn$_{1+\delta}$(S,Se)$_4$</td>
</tr>
<tr>
<td>F</td>
<td>Cu↑/Zn↑/Sn↓</td>
<td>Sn$^{4+}$ → Zn$^{3+}$ + 2Cu$^+$</td>
<td>Zn$^{2+}<em>{Sn}$ + 2Cu$</em>{^{\delta}}$ or Cu$<em>{Sn}^{2+}$ + Cu$</em>{^{\delta}}$ + Zn$_{^{\delta}}^{2+}$</td>
<td>Cu$<em>{2(2-\delta)}$Zn$</em>{2-\delta}$Sn$_{4}$ (S,Se)$_4$</td>
</tr>
</tbody>
</table>

Valle-Rios et al. synthesized off-stoichiometric kesterite via solid state reaction and identified the compositional region of secondary phase free kesterite formation, which is highlighted by the red area in Figure 1.10 b). The experiments have shown that kesterite is capable of self-adapting to both copper rich and copper poor conditions without changes in the underlying crystal structure but solely by changing the cation distribution. In conclusion the optimal absorber layer composition of Zn rich and Cu poor is yielding best results not only due to Zn(S,Se) being a rather benign secondary phase, but also the ascribed point defects $2Zn^{2+}_{Cu}$ + $Zn^{2+}_{Sn}$ result in an improved photovoltaic performance.
1.3. Kesterite thin film solar cells

Alkali treatment

Since the early 1990’s it is known that Na leads to significant improvements of CIGS solar cells [81]. Specifically, Na treatment improves grain growth, alters the preferential crystal orientation and increases the p-type doping concentration [82–85]. Subsequent experiments also encompassed heavier alkali elements and led to numerous new world record efficiencies in recent years [15, 86–88]. The heavier alkali elements are introduced to the absorber layer by a PDT process and modify the CIGS/CdS interface [89]. The modified interface improves the coverage of CdS, thus allowing for a thinner CdS buffer layer, and an overall better junction quality, which results in an improvement of the $V_{OC}$ and $FF$.

Table 1.6: Properties of alkali and kesterite bulk elements [90–92].

<table>
<thead>
<tr>
<th>Property</th>
<th>Li$^{(+)}$</th>
<th>Na$^{(+)}$</th>
<th>K$^{(+)}$</th>
<th>Rb$^{(+)}$</th>
<th>Cs$^{(+)}$</th>
<th>Cu$^{(+)}$</th>
<th>Zn$^{(2+)}$</th>
<th>Sn$^{(4+)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic No.</td>
<td>3</td>
<td>11</td>
<td>19</td>
<td>37</td>
<td>55</td>
<td>29</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Atomic mass</td>
<td>6.94</td>
<td>22.99</td>
<td>39.1</td>
<td>85.47</td>
<td>132.90</td>
<td>63.55</td>
<td>65.39</td>
<td>118.71</td>
</tr>
<tr>
<td>Covalent radii (Å)</td>
<td>1.28</td>
<td>1.66</td>
<td>2.03</td>
<td>2.20</td>
<td>2.44</td>
<td>1.32</td>
<td>1.22</td>
<td>1.39</td>
</tr>
<tr>
<td>Ionic radii (Å)</td>
<td>0.9</td>
<td>1.16</td>
<td>1.52</td>
<td>1.66</td>
<td>1.81</td>
<td>0.91</td>
<td>0.88</td>
<td>0.83</td>
</tr>
</tbody>
</table>

For kesterite solar cells the effects of Na were thoroughly investigated [36, 40, 93, 94]. Similar to CIGS, Na treatment increases grain size and improves the overall absorber layer morphology, increases doping concentration and was shown to yield improved opto-electronic properties of the absorber layer. The increased grain size is attributed to the capability of Na to form low-temperature NaSe$_x$ liquid phases [94] that act as a fluxing agent and facilitate grain growth. The improvements of opto-electronic properties is associated with the passivation of defects at grain boundaries and interfaces, which are the predominant locations for Na inside the absorber layer [95].

Also lithium addition has shown to improve device performance by boosting the electronic quality of the CZTSSe absorber material and grain boundaries [33, 96]. A first principal study by Maeda et al. revealed that the substitution and migration energies for Li are significantly smaller due to the smaller ionic radius of Li (see Table 1.6), thus allowing for an effective incorporation into the kesterite structure in contrast to larger alkali metals like Na and K [95]. Investigations of the solid solution of Cu$_{1-x}$Li$_x$ZnSnS$_4$ demon-
strated that Li can be alloyed over the full range of $x = [0, 1]$ and affects the bandgap and, at higher concentrations, the crystal structure [97].

First studies on the effect of potassium treatment confirmed advantageous effects on kesterite absorber growth and opto-electronic properties similar to Na [98, 99]. Several studies comparing different alkali elements and their effect on solar cell properties and device performance have recently been published [100–103]. However, published results about alkali treatments in kesterite solar cells are not able to give a conclusive picture and partly contradict each other.

1.4 Aim, objectives and structure

The aim of the thesis is to investigate possibilities to overcome the most important challenges kesterite solar cells are facing. These are the high $V_{OC}$-deficit and low $FF$ that all kesterite solar cells exhibit. Figure 1.11 presents the $V_{OC}$-deficits of different solar cell technologies. Bourdais et al. summarized the existing knowledge and identified deep defects and electrically active grain boundaries as the prominent candidates for causing high non-radiative recombination and thus high $V_{OC}$-deficits. Additionally, compositional inhomogeneities and secondary phases have also been reported to deteriorate device properties [104].

For this thesis two main approaches were chosen to tackle the $V_{OC}$-deficit and low $FF$:

1. Detailed investigation about the precursor synthesis and selenization process in order to obtain homogeneous absorber layers without detrimental secondary phases and a large-grained morphology with a low density of grain boundaries.

2. Studying the effects of alkali treatments on the morphological and opto-electronic properties of kesterite solar cells.

Structure of the thesis

In chapter 2 the experimental setups that were used to characterize the precursor and absorber layers as well as finished devices are introduced. Chapter 3 continues by describ-
1.4. Aim, objectives and structure

![Figure 1.11: V<sub>OC</sub> vs bandgap of different technologies. Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> solar cells with bandgaps from 1.0 – 1.5 eV exhibit a comparably low V<sub>OC</sub> of <60% of V<sub>OC max</sub>. Adapted from [63].](image)

ing the synthesis process of all layers of the kesterite solar cell. The following chapters report the main results of this thesis. Chapter 4 is dedicated on the reactor design and selenization process resulting in a reproducible process that yields highly efficient kesterite solar cells. Based on this process several detailed studies about the effect of alkali treatment are presented in Chapter 5. First the effects of potassium, both bulk and PDT treatment are presented, followed by the investigation about Li bulk treatment. Finally, a comprehensive study comparing Li, Na, K, Rb and Cs bulk treatment with different alkali concentrations and absorber compositions is described. The conclusion and outlook are given in Chapter 6.
2 Device and material characterization

This chapter describes the characterization and measurement techniques which are employed to investigate compositional, morphological and structural properties of the absorber layer as well as opto-electronic and photovoltaic parameters of the corresponding solar cells.

2.1 Compositional and structural measurements

2.1.1 X-ray fluorescence (XRF)

In order to measure the composition of the main matrix elements (Cu, Zn, Sn, Se) inside the precursor and absorber layer an XRF setup is used. The XRF setup is an in-house construction using a 45 keV X-ray source (Oxford Instruments, XTF-5011) and a Si pin detector (Amptek, XR-100CR). XRF measurements result in a spectrum with specific peaks for each element as shown in Figure 2.1. For the quantification the Kα emission lines of Cu (Kα 8.040 keV), Zn (Kα 8.637 keV), Se (Kα 11.220 keV) and Sn (Kα 25.359 keV) of a reference sample are correlated to ICP-MS measurement results of the same sample. The obtained correlation factor is used to quantify the composition of samples measured by XRF without the need of destructive ICP-MS measurements.
2.1.2 Secondary ion mass spectrometry (SIMS)

SIMS is a powerful tool to detect concentration variations of constituents locally resolved with a sub-micrometer resolution. Additionally, trace elements can be detected down to the ppm scale. However, the results obtained from SIMS measurements are only qualitative, not quantitative. In this thesis, SIMS is used for depth profiles of complete solar cell stacks as well as imaging to reveal the lateral distribution of trace alkali metals. The measurements were recorded on a TOF-SIMS system from ION-TOF using O$_2^+$ primary ions with 2 keV of ion energy, a current of 400 nA, and a raster size of 400 x 400 µm$^2$. An area of 100 x 100 µm$^2$ in the case of depth profiles and 20 x 20 µm$^2$ for the imaging mode was analysed using Bi$^+$ ions with 25 keV of ion energy.

2.1.3 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS was used to calibrate the XRF setup and to quantify the amount of alkali elements inside the absorber layer of alkali treated samples. For ICP-MS analysis, approximately 1 cm$^2$ of the kesterite solar cells were etched for 60 s in 5 wt% acetic acid solution in order to remove the window layer. Subsequently, the kesterite absorber material was detached from the thin-film solar cell at the Mo/CZTSSe interface, directly transferred into 50 ml
trace metal-free polyethylene tubes and fully dissolved in a mixture of 2.5 mL H$_2$O$_2$ 30\% MERCK suprapure, 4 mL HNO$_3$ 67\% MERCK ultrapure and 2.5 mL HCl 32\% MERCK ultrapure. After filling to 25 ml with 18 MΩ cm deionized water, the sample was diluted 1:10 with 18 MΩ cm deionized water for analysis. Metal determinations were performed on an Agilent 8800 triple quadrupole ICP-MS with different reaction modes such as He and O$_2$ and external calibration using certified metal standards (1000 µg.ml$^{-1}$, Alfa Aesar Specpure). For quality assurance, analysis of reference materials and spiking experiments were performed, with recoveries between 90\% and 110\%.

2.1.4 X-ray diffraction (XRD)

![XRD pattern of relevant phases for the analysis of kesterite absorbers and full solar cells. The Laue-indices are given for the Bragg reflexes that can be identified in XRD pattern presented in this thesis.](image)

Figure 2.2: XRD pattern of relevant phases for the analysis of kesterite absorbers and full solar cells. The Laue-indices are given for the Bragg reflexes that can be identified in XRD pattern presented in this thesis.
XRD was used to derive the S/(S+Se)-ratio using Vegards Law [105], for the identification of secondary phases, for the assessment of the crystal quality and the calculation of the tetragonal distortion of the kesterite structure. The phases identified by XRD in this thesis are presented in Figure 2.2: CZTS [106], CZTSe [107], Mo [108], MoSe$_2$ [109], ZnO [110], Al [111] and SnSe$_2$ [112]. Not all Bragg peaks of the phases are eventually visible because of overlaps or preferential orientation. XRD patterns were recorded in $\Theta/2\Theta$ scan mode using a Bruker D8 diffractometer with CuK$\alpha$ radiation ($\lambda = 1.5418$ Å, beam voltage: 40 kV, beam current: 40 mA, calibrated using Si100 and Si111 single crystals), a step size of 0.04$^\circ$ and a scan rate of 0.5 s/step for the full pattern and a step size of 0.004$^\circ$ and a scan rate of 2 s/step for the detailed XRD pattern.

2.1.5 Scanning electron microscopy (SEM) & Energy dispersive X-ray spectroscopy (EDX)

SEM measurements were used to determine the morphology and layer thicknesses of precursors, absorber layers and full devices including the buffer and window layers. The measurements were performed on a Hitachi S-4800 electron microscope using 20 kV acceleration voltage which results in an interaction volume of $>1$ $\mu$m. Cross section images were taken from mechanically cleaved samples.

EDX compositional measurements were performed only in top-view mode using 20 kV acceleration voltage with 20 $\mu$A current and the following detection energies for the matrix elements were used: Cu (K$\alpha$ 8.040 keV), Sn (L$\alpha$ 3.444 keV) and Zn (K$\alpha$ 8.637 keV).

2.2 Device characterization

2.2.1 Current density - Voltage measurements (J - V)

$J - V$ measurements under dark and illuminated conditions give valuable information about the performance of the solar cell. The following characteristics, shown in Figure 2.3, are obtained from dark and illuminated $J - V$ measurements: efficiency $\eta$, open circuit voltage
2.2. Device characterization

\[ FF = \frac{V_{\text{MPP}} \cdot J_{\text{MPP}}}{V_{\text{OC}} \cdot J_{\text{SC}}} = \frac{A_1}{A_2} \]

Figure 2.3: Illuminated and dark current-voltage (J-V) measurement of a kesterite solar cell device. From the dark curve the parallel resistance \( R_P \), and from the illuminated curve the efficiency \( \eta \), \( V_{\text{OC}} \), \( J_{\text{SC}} \), FF and series resistance \( R_S \) is obtained.

\( V_{\text{OC}} \), short circuit current density \( J_{\text{SC}} \), fill factor \( FF \), series resistance \( R_S \) and the parallel resistance \( R_P \). The \( V_{\text{OC}} \) is the voltage at 0 current density, while the \( J_{\text{SC}} \) is the current density at 0 voltage. The \( FF \) is the ratio of the area span up by the maximum power point (MPP) \( A_1 \) and the area span up by \( V_{\text{OC}} \) and \( J_{\text{SC}} \) (\( A_2 \)). The series resistance \( R_S \) is calculated from the slope \( m \) of the illuminated \( J \cdot V \) curve at around +0.7V with \( R_S = [m^{-1}]_{V=0.7} \) and the parallel resistance \( R_P \) from the slope of the dark \( J \cdot V \) curve around 0V with \( R_P = [m^{-1}]_{V=0V} \).

The \( J \cdot V \) characterization was performed under standard test conditions (100 mWcm\(^{-2}\), 25°C, AM1.5G) using a LOT-QuantumDesign solar simulator calibrated with a certified Si diode. The solar simulator possesses a spectral quality A, a lateral homogeneity quality of B and a temporal stability of A, that is ABA according to the European IEC 60904-9 norm. The electric measurements are performed by a Keithley 2400 in four-terminal sensing mode. All \( J \cdot V \) measurements are based on the designated illumination area, which is defined as the cell including metal grid lines but without the back contact area.
2.2.2 External quantum efficiency (EQE)

Figure 2.4: The EQE (orange) of a typical kesterite solar cell. From the inflection point of the EQE signal in the long-wavelength region the bandgap $E_g$ of the absorber layer is determined. Opto-electronic losses are described by the regions I - III.

EQE measurements reveal the spectral composition of the $J_{SC}$ following Equation 2.1.

$$J_{PH}|_{V=0} = J_{SC} = \int_{0}^{\infty} G(\lambda) \cdot EQE(\lambda) \, d\lambda,$$

(2.1)

with $J_{PH}(V=0)$ the photocurrent at 0 V, and $G(\lambda)$ the incident photon flux [113]. Figure 2.4 shows a typical EQE spectrum of a kesterite solar cell. Optical losses are caused by reflection (I) and parasitic absorption in the buffer and window layer (II). Area (III) describes transmitted photons or photons that are absorbed in the absorber layer, but the generated carriers recombine before reaching the contacts.

From the inflection point of the internal quantum efficiency (IQE) signal ($\frac{d(IQE)}{d\lambda^2} = 0$) in the long-wavelength region the bandgap $E_g$ of the absorber layer is determined [114]. In Figure 2.4 the minimum of the dashed curve ($\frac{d(EQE)}{d\lambda}$) indicates the inflection point and thus the bandgap $E_g$. The IQE is connected to the EQE via $IQE(\lambda) = \frac{EQE(\lambda)}{(1-R(\lambda))}$. The error when using the EQE instead of the IQE is typically less than 10 meV and therefore EQE curves are often used for bandgap determination in this thesis.
The EQE spectra were recorded using a chopped white light source (900W halogen lamp) with a LOT MSH-300 monochromator. The EQE setup was calibrated with certified Si and Ge diodes. The illuminated area on the sample was 0.1 cm$^2$ including metal grid lines.

2.2.3 Temperature dependent J-V (T-JV)

For T-JV measurements the solar cells are placed on a temperature controlled Cu stage inside an evacuated cryostat cooled with liquid nitrogen and illuminated by a 100 W halogen lamp. It should be noted that the lamp spectrum exhibits significant deviations of a standard AM1.5G spectrum, especially lacking intensity in the UV and blue spectral range. From T-JV measurements the temperature dependence of the $V_{OC}$, $J_{SC}$, $FF$, $R_S$, $R_P$ can be obtained.

With the same setup the intensity of the incident light can be varied by two orders of magnitude from approximately 1–142 mW cm$^{-2}$ using neutral density filters. From illumination and temperature dependent $J-V$ measurements the reversed saturation current $J_0$ and the ideality factor $A$ were calculated. Using Equation 2.2, $J_0$ and $A$ are obtained from a semi-logarithmic plot of $J_{SC}$ versus $V_{OC}$ under varying illumination intensities.

$$A(T)ln(J_0) = \frac{E_A}{kBT} + A(T)ln(J_{00})$$  \hspace{1cm} (2.2)

2.2.4 Admittance spectroscopy (AS)

Admittance measurements are used for two separate measurement modes: C-V and C-f. Both measurement modes were carried out with a LCR-meter from Agilent (E4990A) with a level voltage of 30 mV. The solar cell is connected by a four-terminal sensing setup to avoid the influence of parasitic resistance, capacitance and inductance in the cables and contacts. For C-V measurements a voltage sweep from -1.5 V to +0.5 V is conducted while measuring the capacitance $C(V)$ at a frequency of 1 kHz and a level voltage of 30 mV under dark conditions. Equation 2.3 connects the capacitance of a p-n junction with the
doping concentration $N_A$ in the case of a n$^+$p-type junction without the influence of deep defects (Mott-Schottky representation) [115].

$$\frac{1}{C(V)^2} = \frac{2}{q\epsilon_R\epsilon_0 N_A} (V_{bi} - V)$$ (2.3)

The variables $q$ is the electric charge, $\epsilon_R$ the electric permeability of kesterite (8.5 is used throughout the thesis [116]), $\epsilon_0$ the electric permeability of the vacuum and $V_{bi}$ the built-in voltage.

![Mott-Schottky plot following Equation 2.3. Reproduced with permission [117].](image)

Figure 2.5: Mott-Schottky plot following Equation 2.3. Reproduced with permission [117].

From the slope in Figure 2.5 the doping concentration in an ideal device can be calculated. Several non-ideal influences like contributions from the n-side [118], an inhomogeneous doping profile and contributions from deep defects [115, 119] can influence the measured capacitance signal. Therefore the calculated quantity is an “apparent carrier concentration”.

Temperature dependent capacitance-frequency measurements can give information about the energy-depths of defects in an absorber material. For the measurement an alternating voltage in a frequency range from 200 Hz - 2 MHz and a temperature range from 123 K to 323 K is applied to the sample (in dark conditions) while simultaneously recording the capacitance. From the inflection point of each frequency dependent $C(f)$ curve an activation energy $E_A$ via an Arrhenius plot can be calculated,
\[ \omega_0 = 2\xi_0 T^2 e^{\left(\frac{E_A}{kT}\right)} \quad (2.4) \]

with \( \omega_0 = 2\pi f \) the inflection frequency and \( \xi_0 \) the temperature-independent thermal emission prefactor [120]. In an ideal case this activation energy describes the energy-depth of the defect indicated by the capacitance steps. However, barriers at the front or back contact [121,122] or a high series resistance [123] can influence the measurement.

### 2.2.5 Photoluminescence (PL) & time-resolved photoluminescence (TR-PL)

TR-PL and PL spectra were measured on a FT300 fluorescence lifetime spectrometer from PicoQuant with a 639 nm pulsed diode laser as excitation source (pulse width 90 ps, repetition rate 10 MHz) and a thermoelectric cooled Hamamatsu NIR-PMT module H10330A-45 (rise time 0.9 ns, transit time spread 0.4 ns). TR-PL measurements were fitted with a two exponential equation (Equation 2.5), whereas the first exponent describes the separation of holes and electrons due to the built-in potential and the second exponent approximates the minority carrier lifetime [124].

\[ I_{PL}(t) = C_1 e^{-t/\tau_1} + C_2 e^{-t/\tau_2} \quad (2.5) \]

### 2.2.6 UV-Vis

Reflectance measurements were used to calculate the IQE via \( IQE(\lambda) = \frac{EQE(\lambda)}{1-R(\lambda)} \). Reflectance measurements were conducted with a Shimadzu UV-3600 UV-Vis spectrophotometer with an integrating sphere and performed against a BaSO\(_4\) or Spectralon (SRS-99-010, AS-01160-060) reference.
3 Solar cell processing

This chapter covers all fabrication steps starting from the substrate to the final solar cell device. The experimental details for all process steps are described and important preliminary experiments that precede the advanced investigations in Chapter 4 and 5 are presented.

3.1 Substrate and back contact

The conventional substrate for chalcogenide solar cells is soda-lime glass (SLG). SLG contains significant amounts of alkali elements as shown in Table 3.1.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>72.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>14.3</td>
</tr>
<tr>
<td>CaO</td>
<td>6.4</td>
</tr>
<tr>
<td>MgO</td>
<td>4.3</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.03</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Na possesses a high mobility [125] and can diffuse into the absorber layer during high temperature processes [126]. Both for CIGS and CZTSSe it was shown that Na diffusion from SLG has positive effects on absorber morphology and device properties [94,127,128]. SLG exhibits a suitable thermal expansion coefficient to avoid delamination because of stress at the interface after high temperature process steps.
The 1 mm thick SLG was cleaned in three different supersonic baths at a temperature of 80°C. The first bath consisted of salt-free water with soap (Borer Deconex), the second bath consisted of a weak acetic solution (~5%) and the final bath contained only de-ionized water (18 MΩ cm). The residual water was blown off with an N₂ gun and the substrates were dried in vacuum prior to the subsequent layer deposition.

In order to achieve a higher degree of control over alkali content in the absorber layer a 200–300 nm thick SiOₓ diffusion barrier layer was deposited in between the SLG substrate and the subsequent Mo layer. Reactive sputtering in an oxygen containing atmosphere at 200°C substrate temperature of a silicon (Si) target with a power density of 4 W/cm² was used. The diffusion barrier is especially important for the studies in Chapter 5 dealing with alkali treatment of kesterite solar cells.

The back contact material typically utilized for kesterite solar cells is Mo. Here a tri-layer structure for Mo is used that was optimized for adhesion to the SLG substrate as well as to the subsequent absorber layer [129]. The Mo layer is deposited by conventional dc-sputtering with a layer thickness of 0.5 µm or 1 µm. The optimal properties of the tri-layer structure are achieved by variation in the Ar background pressure and the power density (1.7–4.0 W/cm²) applied to the Mo target.

### 3.2 Precursor synthesis for solution processed kesterite solar cells

The precursor synthesis consists of three steps (Figure 3.1):

- Preparation of the precursor solution
- Spin-coating of the precursor solution onto the Mo coated SLG substrate
- Subsequent drying step

Steps 2-3 are repeated between 10 to 15 times leading to the desired film thickness of 1.0–1.5 µm.
3.2. Precursor synthesis for solution processed kesterite solar cells

Figure 3.1: Methodology of the precursor synthesis.

For the solution formulation the metal chlorides are added to the dimethyl sulfoxide (DMSO) solvent in the order of Cu(II)Cl₂·2H₂O, Sn(II)Cl₂·2H₂O and Zn(II)Cl₂. The quantities are specified in Table 3.2.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Conc. mM</th>
<th>Purity (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>-</td>
<td>99.9</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Cu(II)Cl₂·2H₂O</td>
<td>560</td>
<td>≥99.99</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Sn(II)Cl₂·2H₂O</td>
<td>340-560</td>
<td>98</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Zn(II)Cl₂</td>
<td>440</td>
<td>99.99</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Thiourea</td>
<td>1850</td>
<td>99+</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

The sequence is important in order to allow the redox-reaction described in Equation 3.1 to finish [130] before complexation of the metal ions starts to suppress the redox-reaction. Finally, thiourea (CH₄N₂S) is added, which stabilizes the metal ions inside the solution and acts as the sulphur source to form metal sulphide phases in the precursor layer during the drying process.

\[ 2Cu^{2+} + Sn^{2+} = 2Cu^{+} + Sn^{4+} \]  

Equation 3.1

The solution has a transparent, slightly yellowish color and is stable over long periods of
time. For experiments with alkali bulk treatment the alkali elements were added directly to the solution as alkali chlorides. In Chapter 4 NaCl (99.99%, Alfa Aesar) was used and for the alkali treatment experiments in Chapter 5 additionally LiCl anhydrous (99.0%+, Fluka), KCl (99.995%, Alfa Aesar), RbCl (99%, Alfa Aesar) and CsCl (99%, Alfa Aesar) were employed.

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**Figure 3.2**: Thickness variation of a $5 \times 5 \text{cm}^2$ sample. The positions of the 11 measurement points are indicated by the red line in the inset. The layer thickness was measured with a profilometer.

For the process steps two and three 0.75 ml solution is pipetted onto the $5 \times 5 \text{cm}^2$ Mo coated substrate with a subsequent spinning at 1500 rpm for 20 s. The wetted sample is placed on a hotplate at 320°C for 60 s. During the drying step both DMSO and thiourea decompose. The sulphur stemming from thiourea forms ZnS, Cu$_2$SnS$_3$ and Cu$_2$ZnSnS$_4$ phases as nano sized particles [131]. Details of the chemistry during drying of DMSO based precursor layers were thoroughly investigated by C. Sutter-Fella [132].

Each layer is approximately 100 nm thick after the drying step. Therefore the steps two and three are repeated up to 15 times in order to achieve the desired precursor thickness of approximately 1.5 µm. Figure 3.2 shows the thickness variation in a $5 \times 5 \text{cm}^2$ precursor layer (here: 20 layers) measured with a profilometer. The thickness is constant around 2 µm for the central part of sample and gets significantly thicker close to the edge of the
substrate because of the border effect during spin-coating. When pipetting new solution on top of the absorber layer the constituents of the underlying layer get partly dissolved. The effect of different layer thicknesses due to the border effect of the glass substrate and the dissolution of the previous layer leads to an inhomogeneity of the metal ratios in the lateral dimension of the precursor film that also persists into the final absorber layer.

Figure 3.3: Variations in the metal ratios a) Cu/Sn, b) Cu/Zn, c) Cu/(Zn+Sn) and d) Zn/Sn of the precursor layer.

The metal ratios of the precursor layer measured by EDX in the lateral dimension are shown in Figure 3.3. Cu/Sn exhibits a lower value in the center of the sample while Cu/Zn shows a higher ratio. It is assumed that the initial Cu content does not change as there are no volatile Cu compounds and the vapour pressure of Cu is the lowest of all constituents, therefore changes in the Cu/Sn and Cu/Zn ratio are caused by locally different losses in
Sn and Zn, which could be due to laterally varying temperatures during drying on the hotplate. Additionally, during spin-coating of subsequent layers the underlying layer is partly dissolved and spinned off the sample and the remaining composition depends on the differences in solubility of the different metal compounds. Figure 3.3 c) reveals that the Cu/(Zn+Sn) ratio is comparably homogeneous because the Zn and Sn inhomogeneities compensate each other, but in d) for the Zn/Sn ratio a strong radial inhomogeneity can be observed.

![Figure 3.4](image)

**Figure 3.4:** Changes in the morphology of the precursor layer in dependence of the drying temperature. Below 300°C residues from the organic constituents of the solution determine the morphology. At higher temperatures the layer exhibits agglomerations of nano-sized particles.

The drying time and temperature are important parameters that define the morphology and composition of the precursor layer. Figure 3.4 shows the morphology in three different magnifications of precursors dried for 60 s at temperatures varying from 275°C–320°C. With higher temperatures the decomposition and evaporation of organic material originating from DMSO and thiourea is promoted and the morphology shifts to an agglomeration of nano-sized particles. The formation of detrimental metal-oxide phases starts at temperatures of >350°C [132]. Therefore a drying temperature of 320°C is used for the
precursor synthesis throughout this work. The large three-leaved particles, best visible at the medium magnification, are recrystallized NaCl crystals and are homogeneously distributed on the surface in a distance of several $\mu$m of each other.

XRD analysis of the precursor is presented in Figure 3.5 a). The main kesterite Bragg reflexes are present in the precursor layer, however they overlap with the Bragg reflexes of Cu$_2$SnS$_3$ and ZnS. The Bragg reflexes at $14.7^\circ$, $17.1^\circ$ and $22.1^\circ$ that would identify unambiguously the kesterite phase are not visible. Also Bragg reflexes for the SnS or CuS phase are not present, suggesting that the precursor mainly consists of nano-particles of Cu$_2$SnS$_3$, ZnS and Cu$_2$ZnSnS$_4$. Utilizing the Debye-Scherrer formula with the FWHM of the 112 Bragg reflex results in an average size of approximately 6 nm for these particles. The SEM cross section image of a precursor in 3.5 b) reveals a fine grained and porous morphology which is in agreement with the aforementioned particle size.

![XRD pattern and SEM image](image)

**Figure 3.5:** a) XRD pattern of a precursor dried at 320°C. The Bragg reflexes indicated by the red circles at $28.5^\circ$, $47.4^\circ$ and $56.3^\circ$ could similarly stem from CZTS, ZnS or Cu$_2$SnSe$_3$ crystals. Additional Bragg reflexes indicate Mo. b) SEM cross section image of a precursor layer.

### 3.3 High temperature annealing in selenium atmosphere

Following the precursor deposition, a high temperature annealing step in chalcogen atmosphere is conducted to obtain the desired crystal quality and layer morphology. Both S [133, 134] and Se are used [21, 135] as chalcogen source, however in this work only Se
is investigated. In the solution approach with a sulphur based precursor, annealing in Se atmosphere offers the possibility to tailor the bandgap by controlling the replacement of the S in the precursor by Se [136]. Additionally, Se based kesterite solar cells have shown better device properties than their S based counterparts.

The important parameters during the annealing step are the temperature, chalcogen partial pressure and the capability of volatile constituents to escape. Different setups for the annealing step in chalcogen atmosphere are suggested in literature, including tubular furnace, closed graphite box and evacuated quartz ampoules [131,137–140]. The different setups vary in the degree of control over the temperature and partial pressures of gases and volatile constituents.

| + Grain size | + Crystal quality | + Decomposition and loss of organic residuals |
| - Loss of Sn, Se and related compounds | Decomposition of CZTSSe | Mo(S,Se)\(_2\) layer thickness |

Figure 3.6: Effects correlated with increasing temperature during selenization with positive effects (top) and negative effects (bottom).

Figure 3.6 shows the positive (top) and negative (bottom) effects that correlate with the selenization temperature. Apart from the annealing temperature also the annealing time correlates with the effects in Figure 3.6, therefore an optimal compromise is required to achieve high quality absorber layers.

In addition to the annealing temperature and time, the leak tightness of the reactor has to be considered. The expected effects of an increasing leak tightness of the annealing reactor are:

- Higher the Se partial pressure
  → larger grain size, higher crystal quality
- Thicker Mo(S,Se)\(_2\)
- Reduced loss of volatile constituents
In a previous publication by Werner et al. the differences of an open and “semi-open” reactor were described [140]. In the following sections the annealing inside a completely closed reactor (evacuated ampoules) is being compared to the open and semi-open reactors.

### 3.3.1 Open reactor

An open reactor is a system that can exchange gases with the outside. The layout of the open reactor design used here is given in Figure 3.7.

![Figure 3.7: Layout of the open reactor which consists of a quartz tube with an inlet on the left side and exhaust connected to a pump on the right side. Two heating zones allow for careful control over the evaporation rate of the Se source (zone 1) and the sample temperature (zone 2).](image)

The open reactor is a 2-zone furnace with separate temperature controls for each zone. The Se source is placed in zone 1 and the sample in zone 2. The N\textsubscript{2} carrier gas is transporting the Se vapour from zone 1 to the sample in zone 2. The tube is constantly pumped and a zeolite trap between the exhaust and the pump prevents Se from reaching and thus damaging the pump. This 2-zone reactor allows for an independently controlled Se partial pressure and the open design for unhindered evaporation of undesirable components. However, the achievable Se partial pressure in this open system is limited to low values compared to the temperature specific saturated vapour pressure of selenium because of constant pumping, the big volume and the lower temperature in zone 1 compared to zone 2. Additionally, volatile constituents as SnSe\textsubscript{x} and Se are also easily evaporated and lost.

Figure 3.8 shows the temperature profile used for the annealing inside the open furnace with 2 zones. In order to provide a constant Se partial pressure during the high temperature annealing in zone 2, the sample is first kept at 140°C until the Se source in zone
Chapter 3. Solar cell processing

3.3.2 Semi-open reactor

Figure 3.9: Closable graphite reactor with sample and additional Se inside a rapid thermal processing (RTP) unit.

In contrast to the open reactor the semi-open reactor is a system that interacts with the outside on a much lower rate. The semi-open reactor is realized by a closable graphite box within a thermal processing furnace (Annealsys AS-One 150) as illustrated in Figure 3.9. The selenium is placed together with the precursor inside the graphite box, which is closed by six graphite screws and placed within the rapid thermal processing (RTP)
unit. The RTP unit enables a precise temperature control by heating with halogen lamps. Although the graphite box is closed tight, gas can still exchange through miniature gaps between lid and bottom part as well as through the pores of the graphite material itself.

![Temperature profile of the selenization in the RTP unit.](image)

**Figure 3.10:** Temperature profile of the selenization in the RTP unit.

The temperature profile for selenization inside the RTP is shown in Figure 3.10. A 2-stage process with a holding temperature at 300°C and 500°C is used. During the selenization the added Se pellets (∼800 mg) melt and partly evaporate, providing a temperature dependent saturated Se partial pressure (see Figure 3.11). The added Se quantity is much higher than would be required to replace all sulphur in the kesterite and maintain a saturated partial pressure. But because of the leakage from the graphite box the excess Se is used up in dependence of the leakage rate. Additionally, the saturated partial pressure of Se for the given temperature is lower than in a totally closed system. Compared to the open furnace the Se partial pressure is higher both due to the higher temperature of the Se source and using a more closed reactor. In order to reduce leakage from the graphite box further, the background pressure in and around the graphite box is kept at approximately 500 mbar N₂ during the selenization.
Figure 3.11: *Temperature dependence of the Se saturated partial pressure [141].*

3.3.3 Closed reactor

![Diagram of a closed reactor](image)

Figure 3.12: *Evacuated quartz glass ampoule containing the CZTS precursor and additional Se pellets. The internal background pressure is $p_0 = 10^{-2}$ mbar.*

The graph 3.12 shows the selenization setup of a closed reactor realized by an evacuated ampoule, which contains the precursor and additional Se pellets. The ampoule has an internal pressure of approximately $10^{-2}$ mbar. In the closed system the Se partial pressure can be exactly controlled by the added Se quantity and the temperature. The temperature profile used for the selenization of precursors inside the evacuated ampoules, i.e. closed
reactor, is shown in Figure 3.13. It is important to mention that all 3 reactor types use a different geometry and thus the measured temperatures (measured by thermocouples) and the actual sample temperature is varying slightly for each reactor type.

![Figure 3.13: Measured temperature profile used for the selenization of samples in the closed reactor.](image)

### 3.4 Buffer layers

The buffer layer constitutes the first layer in the window layer stack and forms the n-type part of the p-n junction. A suitable buffer layer for kesterite solar cells requires the following characteristics [142] [143]:

- High electron mobility for an effective carrier transport.
- High bandgap in order to avoid parasitic absorption.
- A band alignment of the conduction band to the CZTSSe absorber layer with a small spike $0 < E_C < 300 \text{meV}$.
- Formation of a benign interface with a low density of interface defects which would act as recombination centres.
- High doping concentration for a maximum Fermi-level splitting
In the p-n junction under illumination the photo-generated electrons are collected at the front contact and therefore need to be transported through the buffer layer, which requires a high conductivity and thus mobility inside the buffer layer. An optimal band alignment of the conduction band requires a small so-called “spike” between 0 to 300 meV that reduces interface recombination but does not form a potential barrier for the minority carrier transport. The high recombination rate of photo-generated electron-hole pairs inside the buffer layer demands a high bandgap of the buffer layer material in order to reduce absorption and thus generation of electron-hole pairs inside the buffer layer. Similar to the p-type absorber layer, a high doping concentration increases the quasi-Fermi-level splitting under illumination and thus the open circuit voltage of the solar cell.

The standard buffer layer material for kesterite solar cells is CdS deposited by CBD [144]. 185 ml deionized H₂O are mixed with 35 ml 28% ammonium-hydroxide (NH₃·OH) solution, 0.028 mM Cd-acetate (Cd(CH₃COO)₂) and 0.374 mM thiourea (SC(NH₂)₂) and placed with the immersed samples for 20 min in a 70°C water bath. Following the CdS deposition the samples are rinsed with deionized water and dried under N₂ flow. The growth conditions result in a 50–60 nm thick CdS buffer layer as determined by SEM cross section images.

Variations in the film thickness by changing the CBD time from 19 to 26 min result in CdS layer thicknesses of approximately 45, 55, 65, and 75 nm. In Figure 3.14 a) the effects on the external quantum efficiency are presented. Thicker CdS decreases collection in the short wavelength region up to 520 nm and increases collection in the longer wavelength region.

The decrease in collection in the short wavelength region can be attributed to the thicker CdS with a bandgap of 2.4 eV, which increases the parasitic absorption. The increased collection in the longer wavelength region stems from an improved p-n junction quality. The gain and losses of short circuit current deduced from the EQE spectra result in no significant change and the best cells of the four devices reveal similar PV parameters and thus device performances (see Figure 3.14 b).
3.5 Window layer, metal grid and AR coating

The window layer consists of the intrinsically doped zinc-oxide layer (i–ZnO), the aluminum doped ZnO layer (Al:ZnO) and the optional antireflective (AR) coating. The i–ZnO layer is rf-sputtered using 150 W from a 4 inch target with a resulting layer thickness of 70 nm and the Al:ZnO within the same system at 200 W from a 4 inch target for a layer thickness of 250 nm. The role of the highly resistive i–ZnO layer is to block shunt paths that may occur due to insufficient coverage of CdS on the rough kesterite absorber layer surface [145].

Figure 3.14: a) EQE of four samples with different CdS layer thicknesses varying from 45–75 nm. b) PV parameters of the same devices. Small changes in CdS layer thickness do not affect the overall device performance.

3.5 Window layer, metal grid and AR coating

Figure 3.15: Photograph of a 2.5x2.5 cm² sample with 9 individual cells defined by mechanical scribing. An AR coating is deposited on top of the cell and the exposed Mo back contact is soldered with In in order to obtain an optimal ohmic contact.
The front contact is deposited on top of the Al:ZnO layer by e-beam evaporation of 50nm Ni and 4µm Al. Individual cells are mechanically scribed with a cell size of approximately $0.3 \pm 0.02 \text{cm}^2$. The area covered by the grid fingers is 0.023cm$^2$ resulting in a shadowing over the whole designated illumination area of 7%. All electrical measurements are conducted by contacting the front metal grid pad depicted in Figure 3.15 and an exposed part of the Mo back contact, which is soldered with a thin layer of In. The optional AR coating is deposited by e-beam evaporation of MgF$_2$ and has a thickness of 105nm. With a refractive index of 1.39 for MgF$_2$ the thickness is optimized to minimize reflection of incoming photons with a wavelength of 0.58µm. Figure 3.16 shows the EQE of a kesterite solar cell with and without AR coating.

![EQE of a kesterite solar cell with and without AR coating. The major increase in the current stems from the wavelength region around 0.58µm because of a reduction in reflectance.](image)
4 Development of selenization process

Following the introduction of the open, semi-open and closed reactor in Chapter 3, Chapter 4 discusses the properties of absorber layers and solar cells fabricated in these different annealing environments. Subsequently, the implementation of an improved reactor and the 3-stage temperature profile for the selenization process are presented in section 4.2.

This chapter is based on the following publications:


4.1 Comparison of reactor types

In order to compare the three reactor types, a representative sample from each reactor type is analysed and the advantages and disadvantages of each reactor type are discussed. The precursors used for this comparative study were similarly prepared by the DMSO based solution processed described in Section 3.2 including NaCl. NaCl treatment of solution processed kesterite solar cells was initially established by C. Sutter-Fella and M.
Chapter 4. Development of selenization process

Werner [94,140]. It was shown that NaCl treatment improves grain growth and optoelectronic properties, especially the $V_{OC}$ and $FF$.

### 4.1.1 Open reactor

The open reactor was described in Chapter 3.3.1 and the morphology of the absorber layer obtained after selenization in the open reactor is shown in Figure 4.1 a). The absorber layer exhibits a porous and small grained morphology which is caused by a low Se partial pressure and a high amount of material loss due to the evaporation of the volatile constituents SnSe and Se [43]. The XRD pattern in Figure 4.1 b) exhibits only the most prominent Bragg reflexes of the kesterite phase, which coincide with Zn(S,Se)$_2$ and Cu$_2$Sn(S,Se)$_3$, as well as the Mo Bragg peaks. The main 112 Bragg reflex of kesterite is located at an angle of 27.52°, which corresponds to a S/(S+Se) ratio of approximately 0.25. The S/(S+Se) ratio suggests a bandgap of 1.12 eV. Bragg reflexes around 31.5° and 56.4° caused by Mo(S,Se)$_2$ cannot be identified, implying that only neglectable amounts of Mo(S,Se)$_2$ were formed during selenization.

![Figure 4.1: a) SEM cross section of a complete device showing only the absorber and window layer. b) The XRD pattern of the open reactor sample exhibits only the larger Bragg reflexes of the kesterite phase. Mo(S,Se)$_2$ related Bragg reflexes cannot be identified.](image)

The metal ratios of the matrix elements of the absorber layer before and after the selenization step are shown in Table 4.1. It is assumed that respective changes in the metal ratios of Cu/Zn and Cu/Sn are due to changes in Zn and Sn because Cu does not form
4.1. Comparison of reactor types

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu/Zn</th>
<th>Cu/Sn</th>
<th>Cu/(Zn+Sn)</th>
<th>Zn/Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>precursor</td>
<td>1.69</td>
<td>1.33</td>
<td>0.74</td>
<td>0.79</td>
</tr>
<tr>
<td>selenized</td>
<td>1.73</td>
<td>1.96</td>
<td>0.92</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Table 4.1: Composition of the open reactor sample measured by XRF

any volatile phases and thus the Cu content stays constant. The Cu/Zn ratio is changing from 1.69 to 1.73 indicating a comparably small loss of Zn during the high temperature annealing. Sn exhibits a change from 1.33 to 1.96 meaning that approximately 32% of the initial Sn escaped the absorber layer during selenization.

![Figure 4.2](image)

**Figure 4.2:** Opto-electronic properties of a representative sample from the open reactor. a) EQE reveals a bandgap of 1.14 eV derived from the inflection point in the long-wavelength region. b) Apparent carrier concentration calculated from room-temperature C-V measurements. c) Linear fit of $V_{OC} \cdot T$ to 0 K resulting in an activation energy $E_A = 0.85$ eV d) Dark and light J-V curves. The solar cell exhibits an efficiency of 4.8%.

The high loss of Sn is expected due to the decomposition reaction of kesterite described in Equation 1.3 in conjunction with the low Se and SnSe partial pressure which is caused
Chapter 4. Development of selenization process

The opto-electronic properties of a typical device with an absorber layer selenized in the open reactor are illustrated in Figure 4.2. The EQE in a) indicates a short minority carrier collection length and a bandgap of $E_g = 1.14\text{eV}$ is deduced from the inflection point in the long-wavelength region. The maximum EQE is around 0.8 which suggests a barrier impeding carrier transport or high interface recombination. The apparent carrier concentration is $2.7\text{E16 cm}^{-3}$ with an SCR width of $0.13 \mu\text{m}$ (at 0 V) measured by room temperature C-V. The $V_{OC} - T$ fit results in an intersection voltage of 0.85 V, which is 0.28 V lower than $E_g/q$ and indicates an adverse influence of surface or interface recombination on PV properties [146]. The device results in a conversion efficiency of 4.8% with a $V_{OC}$-deficit of 0.80 V.

In conclusion, the selenization process in the open reactor results in porous absorber layers with small grains. The porosity and small-grained morphology is formed due to the loss of Sn caused by the low Se and SnSe partial pressures. Structural defects at the interface like Se or S vacancies could cause the high surface recombination determined from the $V_{OC} - T$ fit.

4.1.2 Semi-open reactor

The semi-open reactor is described in Chapter 3.3.2 and the characteristics of the absorber layer, the opto-electronic properties as well as PV-parameters are presented in this section. The morphology of the absorber layer obtained from selenization in the semi-open system is shown in Figure 4.3 a). The absorber layer consists of a bi-layer structure with larger grains of up to 1 $\mu\text{m}$ size on top and smaller grains in the vicinity of the back contact. The XRD pattern in Figure 4.3 b) exhibits distinct Bragg reflexes for the kesterite phase and from Bragg reflexes at 31.5° and 56.4° the Mo(S,Se)$_2$ phase can be identified. The main kesterite Bragg reflexes reveal a double peak as shown in the inset of Figure 4.3 b), which is caused by two separate kesterite phases with different $S/(S+Se)$ ratios. The two Bragg reflexes at 45.34° and 45.66° correspond to $S/(S+Se)$ ratios of 0.1 and 0.25 and a bandgap of 1.05 eV and 1.13 eV, respectively. The higher Se containing kesterite phase is
attributed to the larger grains in the upper part of the absorber layer.

![SEM cross section](image1)

**Figure 4.3:** a) SEM cross section of a complete device with Mo back contact, absorber layer and window layer. b) XRD pattern of semi-open reactor sample exhibiting additional Mo(S,Se)$_2$ Bragg reflexes and the main kesterite Bragg reflexes are double peaks indicating two separate kesterite phases with different S/(S+Se) ratios.

In Table 4.2 the metal ratios of the matrix elements of the active layer before and after the selenization step are shown. The Cu/Zn ratio is changing from 1.55 to 1.59 suggesting a small loss of Zn. The loss of Sn is <8% indicated by the change of the Cu/Sn ratio from 1.74 to 1.89.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu/Zn</th>
<th>Cu/Sn</th>
<th>Cu/(Zn+Sn)</th>
<th>Zn/Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>precursor</td>
<td>1.55</td>
<td>1.74</td>
<td>0.82</td>
<td>1.12</td>
</tr>
<tr>
<td>selenized</td>
<td>1.59</td>
<td>1.89</td>
<td>0.86</td>
<td>1.19</td>
</tr>
</tbody>
</table>

The opto-electronic properties are illustrated in Figure 4.4. The EQE exhibits a short minority carrier collection length and it is not possible to derive the inflection point in the long-wavelength region. The bandgaps derived from the S/(S+Se) ratios are depicted in the EQE spectra. The maximum EQE height is 0.9 indicating unimpeded carrier transport. The apparent carrier concentration from room temperature $C-V$ measurements is 1.1E16 cm$^{-3}$ with an SCR width of 0.16 µm. The $V_{OC}-T$ fit results in 1.00 V at 0K, which is still lower by 50-150 meV than the bandgap. A representative sample with 8.3% conversion efficiency and a $V_{OC}$-deficit of 0.6 V – 0.7 V is shown in Figure 4.4 d).
Conclusively, the semi-open reactor realized by a closable graphite box results in a favourable morphology with a dense upper crust of large grains. The improved morphology and higher Se content is attributed to the higher Se partial pressure.

**Figure 4.4:** Opto-electronic properties of a representative sample selenized in the semi-open reactor.

The loss of Sn is greatly reduced and the incorporation of Se increased in comparison to the open reactor. Furthermore, interface recombination derived from the $V_{OC}$ - $T$ fit is reduced.

### 4.1.3 Closed reactor

The closed reactor type realized by evacuated ampoules with additional selenium is described in Chapter 3.3.3. From calculations based on the ideal gas equation the amount of additional Se required to replace all sulphur inside the precursor while maintaining a saturated Se partial pressure is 30 mg Se. Experiments however revealed that this amount is insufficient to replace all sulphur and thus a detailed sample series with varying amounts
of Se inside the evacuated ampoules is conducted.

Figure 4.5: SEM top view images of the samples with 1, 5, 51 and 351 mg Se. With higher Se content the growth of large grains on top of the porous absorber layer is significantly promoted leading to grain sizes larger than 5 µm.

The morphology of the absorber layers obtained from selenization in the closed reactor with increasing Se amount is shown in Figure 4.5 for a) 1 mg, b) 5 mg, c) 51 mg and d) 351 mg Se. Larger kesterite grains with up to 5 µm size are forming on the top of a porous fine grained layer with increasing Se amount (see Figure 4.6).

Figure 4.6: SEM cross section of the absorber layer with large grains on top.

The composition of the large grains (spectrum 1) and the porous bottom layer (spectrum 2) differ in Sn and Zn content as measured by EDX, shown in Table 4.3. The larger grains
Chapter 4. Developement of selenization process

exhibit a higher Sn content and lower Zn content than the porous bottom layer. This is in agreement with the assumption that inside the closed reactor the abnormal grain growth is supported by Se and Sn from the gas phase with Cu and Zn diffusing from the precursor layer [137]. The reason for the small grain size in the bottom layer is that organic residuals from the precursor and sulphur cannot readily escape the absorber layer. The residuals remain at the grain boundaries and restrain further grain growth because of a solute drag effect [147].

<table>
<thead>
<tr>
<th>Metal ratio spectrum 1</th>
<th>spectrum 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Sn 1.67</td>
<td>1.85</td>
</tr>
<tr>
<td>Cu/Zn 2.07</td>
<td>1.78</td>
</tr>
<tr>
<td>Cu/(Zn+Sn) 0.92</td>
<td>0.91</td>
</tr>
<tr>
<td>Zn/Sn 0.81</td>
<td>1.04</td>
</tr>
</tbody>
</table>

The bulk composition in Figure 4.7 in dependence of the added Se amount reveals that with increasing Se inside the evacuated ampoules the losses of Zn and Sn are increasing. A reduction in losses of Sn and Zn is expected for the closed reactor, however residuals on the inner walls of the evacuated ampoules after selenization show precipitations of Sn and Zn which are deposited by vapour transport deposition (VTD) [148]. The VTD is caused by a temperature difference between the quartz glass walls and the sample surface.

Figure 4.7: Metal ratios of the absorber layers in dependence of the added Se amount. The loss of Sn and Zn is increasing with higher Se amount.
4.1. Comparison of reactor types

The XRD pattern of all five samples are shown in Figure 4.8 a). The kesterite main 112 Bragg reflexes shifts to lower angles with increasing amount of Se, indicating a decrease in S/(S+Se) ratio. Additionally, the height of the Bragg reflexes increases and the FWHM decreases with higher Se amount, indicating a higher crystal size and quality (Figure 4.8 b).

![Figure 4.8: a) XRD pattern of closed reactor samples with increasing amount of added Se. The inset shows the evolution of the 112 kesterite main Bragg reflex. b) The change of the FWHM of the 112 Bragg reflex and S/(S+Se) ratio of the kesterite phase with increasing Se amount.]

Although 30mg Se should be sufficient to completely replace all sulphur inside the layer, it is clear from the Bragg peak shifts in the inset of a) that more Se is needed to form pure CZTSe. For 1000mg Se all S is replaced by Se and additionally the formation of Mo(S,Se)$_2$ is confirmed by the specific Bragg reflexes at $31.7^\circ$ and $56.2^\circ$, verifying that a high Se partial pressure leads to an increased growth of Mo(S,Se)$_2$.

The $J$-$V$ and EQE characteristics in Figure 4.9 show a representative cell with 2.4% efficiency and a comparably low $V_{OC}$, resulting in a $V_{OC}$ - deficit of 0.75V and a low $J_{SC}$ of 14.6mAcm$^{-2}$. The low current could originate from the fact that only the large grains on top of the absorber layer (see figure 4.5) contribute to the $J_{SC}$ and only a part of the surface is covered with these large grains.

The EQE reveals an overall low quantum efficiency with <0.8 for the maximum and
Chapter 4. Development of selenization process

Figure 4.9: a) J-V curves of a representative sample with 100 mg Se added into the evacuated ampoule. b) The EQE exhibits a low maximum of <0.8 and a reduced collection from the long-wavelength region. The shape of the EQE in the long-wavelength regions renders determination of the bandgap via inflection point method impossible, therefore the XRD Bragg peak position was used to calculate the bandgap.

reduced collection from the long-wavelength region, leading to a shape that renders determination of the bandgap via inflection point method impossible. The bandgap was therefore approximated by the 112 Bragg reflex position to 1.08 eV. The difference in \( J_{SC} \) from J-V measurement and integrated EQE spectrum could be due to the difference in illumination intensity during both measurements. In the EQE measurement the bias light does not resemble an AM1.5G spectrum and also exhibits a significantly lower power density (approximately 0.1 suns). A possible explanation is that the device exhibits a barrier for the minority carriers and due to a limited thermionic emission current, the comparably small current density of a quantum efficiency measurement can pass the barrier, but the high current density under AM1.5G is blocked [149].

In conclusion the closed reactor type does not result in a favourable morphology because organic residuals and sulphur cannot readily escape the precursor layer. The loss of Sn, Zn and Se is not suppressed but even promoted by a vapour deposition transport reaction that leads to precipitations of these elements on slightly colder parts of the quartz ampoule walls.
4.2 3-stage selenization in the semi-open reactor

The different reactor types and their influence on morphology, composition, opto-electronic properties and PV parameters were discussed and the semi-open system consisting of a closable graphite box in an RTP furnace resulted in the best device properties. Therefore, a detailed study employing an improved semi-open reactor and the 3-stage temperature profile for the selenization process were conducted to further improve device properties and performance.

The focus of this investigation is the comparison of the uncoated graphite box and a standard 2-stage annealing to the 3-stage annealing process under controlled selenium atmosphere in a SiO\textsubscript{x}-coated graphite box. With this novel approach the $V_{OC}$-deficit can be reduced to 0.57 V, which appears to be one of the lowest value reported for any kesterite devices. Systematic electrical characterization of absorbers and finished solar cells with SIMS, TR-PL, $T$-$JV$ and AS are used to identify the reasons of the improved voltage.

![Graph showing temperature profiles](image)

**Figure 4.10:** a) Temperature profile of the 2- and 3-stage selenization process. The additional 3rd step allows for an improved grain growth while keeping elemental losses still at a minimum. b) Design of the closable graphite box with bottom and lid. The cavity in the bottom houses the sample and additional Se pellets.

Figure 4.10 a) shows the temperature profiles of the 2-stage process exhibiting holding temperatures at 300°C and 500°C with a slow ramping speed of 5°Cmin\textsuperscript{-1} and the 3-stage process consisting of three holding temperatures at 300°C, 500°C and 550°C and a faster
ramping speed of 60 °C min⁻¹. The lower holding temperature at 300 °C is intended to out-gas remaining residues of the organic solvent before the dense top crust on the absorber layer starts to form. Additionally, Na₂Seₓ phases with low melting points can form, which act as fluxing agents and improve the grain growth [94]. The higher holding temperature at 500 °C facilitates the crystallization, grain growth and selenium incorporation. The saturated vapour pressures are 0.3 mbar and 55 mbar at 300 °C and 500 °C, respectively [150]. The selenium vapour pressure during the annealing is lower than the saturated vapour pressure for the given temperature due to the porosity of the graphite material and leakage of Se vapour through miniature gaps. The grain growth at 500 °C, which leads to the bi-layer structure, consists of an abnormal grain growth of the large-grained upper layer and a normal grain growth for the small-grained bottom layer [137]. The abnormal grain growth is driven by the surface area and total energy difference, and is also facilitated by volatile Zn-, Sn- and Se-containing species from the gas phase. The third holding temperature at 550 °C exclusively at the end of the 3-stage process accounts for increased grain growth. At this stage none of the added selenium is left in the graphite box and the grain growth is presumably governed by redistribution of grain boundaries. A significant loss channel of Se during the selenization process is the porosity of the graphite itself and therefore a 200 nm thick SiOₓ-coating was applied to the inner side of the graphite box as depicted in Figure 4.10 b). The SiOₓ-coating reduces the effect of the porosity allowing a higher Se partial pressure during the annealing process, which improves crystallization especially in the bottom layer of the absorber. At the same time the system still allows the exchange of gases with the outside which is important to allow undesired constituents to escape the precursor layer.

4.2.1 Morphology and composition

Figure 4.11 shows the SEM cross-section images of the four different CZTSSe absorbers A – D yielding efficiencies from 6.6% to 10.1% (designated illumination area). The annealing conditions are varied from uncoated graphite box (A, B) to SiOₓ-coated graphite box (C, D) and 2-stage temperature profile (A, C) to 3-stage temperature profile (B, D). The
selenization of sample A is conducted in an uncoated graphite box employing a 2-stage temperature profile, and the absorber layer exhibits a distinct bi-layer structure with a thick small-grain bottom layer [140]. A SIMS depth profile of sample A is shown in Figure 4.12 and reveals an increased carbon signal (\(\text{CH}_3^+\)) in the vicinity of the back contact. The accumulation of carbon was not observed in sample B and D indicating that the 3-stage temperature profile helps to remove all organic residuals.

![Figure 4.11: SEM cross-section images of samples A–D illustrating changes in the absorber morphology when switching the selenization process from the uncoated graphite box (A, B) to the SiO\(_x\)-coated graphite box (C, D), and varying the temperature profile from the 2-stage (A, C) to the optimized 3-stage process (B, D).](image)

Sample B was selenized in an uncoated graphite box similar to A but employing a 3-stage temperature profile. The SEM cross-section shows an improved crystallization and grain size in both upper crust and bottom layer. However, the distinct bi-layer structure of the absorber layer remains. The selenization of sample C was conducted in a SiO\(_x\)-coated graphite box using the 2-stage process, and the morphology of the film
Chapter 4. Development of selenization process

Figure 4.12: SIMS depth profile of the absorber layer of sample A. The distribution of the main matrix elements is constant throughout the layer. At the vicinity to the Mo back contact the appearance of \( CH_3^+ \) indicates residuals of carbon at the fine-grained bottom layer of the bi-layer structure.

Exhibits a comparably thin upper layer with small grains, but an improved crystallization in the bottom layer in contrast to sample A. Finally, sample D was selenized in the \( SiO_x \)-coated graphite box with the 3-stage temperature profile and shows an overall improved crystallization with large grains and a significant reduction of the small-grain bottom layer.

Table 4.4: Compositions of the precursor and the samples A–D determined by XRF. The \( SiO_x \)-coated graphite box employed for sample C and D results in no change in the loss of Zn or Sn, but the 3-stage annealing with the higher holding temperature of 550°C increases the loss of Sn.

<table>
<thead>
<tr>
<th>sample</th>
<th>Cu/Zn</th>
<th>Cu/Sn</th>
<th>Cu/(Zn+Sn)</th>
<th>Zn/Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>precursor</td>
<td>1.21</td>
<td>1.60</td>
<td>0.69</td>
<td>1.32</td>
</tr>
<tr>
<td>A (2-stage)</td>
<td>1.24</td>
<td>1.83</td>
<td>0.74</td>
<td>1.48</td>
</tr>
<tr>
<td>B (3-stage)</td>
<td>1.29</td>
<td>1.96</td>
<td>0.78</td>
<td>1.52</td>
</tr>
<tr>
<td>C (2-stage / ( SiO_x ))</td>
<td>1.25</td>
<td>1.83</td>
<td>0.74</td>
<td>1.46</td>
</tr>
<tr>
<td>D (3-stage / ( SiO_x ))</td>
<td>1.28</td>
<td>1.98</td>
<td>0.78</td>
<td>1.55</td>
</tr>
</tbody>
</table>

The composition of sample A–D is shown in Table 4.4 and reveals a substantial loss of Sn after selenization and a minor loss of Zn. Here it is again assumed that all changes in Cu/Zn and Cu/Sn ratios are attributed to loss of Zn and Sn while the Cu content
4.2. 3-stage selenization in the semi-open reactor

stays constant. The change in metal ratios due to the high temperature annealing is proportional to the annealing time and corresponding temperature. The loss of Sn and Zn is more pronounced for the 3-stage process compared to the 2-stage process, because of the higher temperature employed in the 3-stage process [151]. Surprisingly, the change from uncoated to coated graphite box did not affect the final metal ratios. As a result, metal ratios of samples A, C and B, D are quite close and in the compositional range typically yielding high efficiencies [49]. In this off-stoichiometric range, so-called B-type, the presence of defect complexes \(2\text{Zn}^{2+}\text{Cu} + \text{Zn}^{2+}\text{Sn}\) with a formation energy of 0.86 eV is expected [80].

![XRD pattern of samples A–D exhibiting Bragg reflexes of CZTSSe](image)

**Figure 4.13:** a) XRD pattern of samples A–D exhibiting Bragg reflexes of CZTSSe (marked with star *), Mo back contact, Mo(S,Se)\(_2\), and the sample holder (marked with ↓). b) 312/116 Bragg reflex of the CZTSSe phase for samples A–D. The double Bragg peak alters depending on selenization conditions, indicating regions with a different S/(S+Se) ratio.

The XRD patterns in Figure 4.13 show a double kesterite Bragg reflex at 53.4° for all samples, indicating two kesterite phases with a different S/(S+Se) ratio. The reflexes corresponding to the higher S/(S+Se) ratio extenuate with the shift from uncoated to SiO\(_x\)-coated graphite box as well as with the change of the temperature profile from 2-stage to 3-stage process. No secondary phases can be identified from the XRD patterns of the four
samples in Figure 4.13 a), although the presence of Zn(S,Se) and Cu$_2$Sn(S,Se)$_3$ impurity phases cannot be excluded since their Bragg reflexes coincide with those of CZTSSe and therefore, cannot be distinguished by XRD [152]. Bragg Reflexes at 14.7°, 17.4° and 22.1° confirm unambiguously the CZTSSe phase. For all samples additional reflexes appear at 31.6° and 56.5°, indicating the Mo(S,Se)$_2$ phase [153] whose thickness is evident from the SEM cross sections and the Bragg peak size. Both the employment of the SiO$_x$ coated graphite box and the 3-stage temperature profile increase the Mo(S,Se)$_2$ layer thickness.

4.2.2 Opto-electronic properties

The EQE spectra of samples A–D are shown in Figure 4.14 a). The band gap values were extracted from the inflection point of the EQE spectrum in the long-wavelength region (dashed lines). Integration of the EQE spectra yields $J_{SC}$'s of 31.6, 32.8, 28.2 and 35.4 mA cm$^{-2}$ for samples A–D, respectively, which are in good agreement with the $J_{SC}$ values obtained from $J$-$V$ measurements. The extracted bandgaps are similar to the bandgaps estimated from XRD measurements assuming 1.0 and 1.5 eV for CZTSe and CZTS phase, respectively.

Figure 4.14: a) EQE spectra for samples A–D. The minimum in the derivative of the EQE curve from the long-wavelength range is used to estimate the absorber bandgap. b) TR-PL transient of samples A–D measured on complete cells and at room temperature. The inset shows room temperature PL spectra of samples A–D.
Figure 4.14 b) shows the TR-PL decay curves and the PL spectra both acquired at room temperature of the devices A – D. The TR-PL decay curves suggest an increased radiative lifetime for the samples annealed with the 3-stage process. In comparison with the SEM cross-sections the radiative lifetime correlates with the thickness of the large-grain upper layer of the absorber. The TR-PL results are in good agreement with the long-wavelength characteristics of the corresponding EQE spectra, so that a lower EQE is observed for the samples with a faster TR-PL intensity decay. However, new investigations on the interpretation of TR-PL decay curves measured on kesterite absorber layers revealed that the typically extracted decay constants from TR-PL transient curves do not resemble the real minority carrier lifetime [154]. The TR-PL measurements are significantly influenced by minority carrier trapping, surface effects and energetic relaxation of carriers.

Figure 4.15: Temperature-dependent TR-PL measurements from 10K to 300K on a sample equivalent to sample D. The decay time is increasing by several orders of magnitude due to the presence of tail states and/or potential fluctuations in the kesterite absorber layer.

The PL spectra exhibit a broad peak for all samples, and the peak maxima are red-shifted as compared to the bandgap by 0.11 eV, 0.02 eV, 0.06 eV and 0.02 eV for samples A, B, C and D, respectively. In literature, PL maxima red shifts of 110 meV are reported for solution-based methods, whereas vacuum methods can yield values as low as 10–20 meV [35, 155, 156]. The rather broad shape here indicates the presence of tail states
and/or potential fluctuations [157], which are responsible for the increased decay time by several orders of magnitude when performing low-temperature TR-PL measurements, presented in Figure 4.15. The decrease in red shift of the PL maxima with respect to the bandgap values of samples A, C to B and D indicates a reduction in tail states.

### 4.2.3 PV parameters

The $V_{OC}$, $FF$, $J_{SC}$ and efficiency are presented as box-plots consisting of the data of 9 cells for each sample in Figure 4.17 a)–d). The $V_{OC}$ remains similar for all samples, however this does not take the change in bandgap into account. The average $FF$ increases from 41% to more than 55%, the $J_{SC}$ is increasing in accordance with the change in bandgap resulting in lower current values for the higher bandgap. Conclusively, changing the reactor from uncoated to SiO$_x$-coated graphite box leads to a higher $FF$, whereas the change from the 2-stage to the 3-stage temperature profile during selenization improves $FF$, $J_{SC}$ and reduce the $V_{OC}$-deficit. Figure 4.16 shows the $J$-$V$ curves of the best cells from the samples A–D including their PV parameters.

![Figure 4.16: J-V curves of the best cells of sample A–D.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eff.</th>
<th>$V_{OC}$</th>
<th>$J_{SC}$</th>
<th>FF</th>
<th>$V_{OC}$-deficit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.6</td>
<td>481</td>
<td>31.1</td>
<td>44.5</td>
<td>0.67</td>
</tr>
<tr>
<td>B</td>
<td>8.7</td>
<td>469</td>
<td>32.6</td>
<td>57.0</td>
<td>0.55</td>
</tr>
<tr>
<td>C</td>
<td>7.1</td>
<td>458</td>
<td>28.2</td>
<td>55.1</td>
<td>0.65</td>
</tr>
<tr>
<td>D</td>
<td>10.1</td>
<td>472</td>
<td>35.0</td>
<td>61.2</td>
<td>0.57</td>
</tr>
</tbody>
</table>
4.2. 3-stage selenization in the semi-open reactor

Figure 4.17: PV parameters of sample A (2-stage), B (3-stage), C (2-stage / SiO$_x$) and D (3-stage / SiO$_x$).
4.2.4 Advanced characterization of the 11.2% efficient device

Figure 4.18: Characteristics of the best device D_2 obtained with the identical fabrication process as sample D. a) SEM cross section exhibiting large grained morphology. b) Dark and illuminated J-V measurement. c) EQE measured with 0V and -1V bias. The integrated EQE yields the current of 36.5 mA cm\(^{-2}\). A bandgap of 1.05 eV is estimated from the inflection point of the EQE signal in the long-wavelength region. In the upper part the ratio of EQE(-1V)/EQE(0V) is shown. d) PL measurements reveal a broad peak with the maximum located at 1260 nm.

Figure 4.18 shows the properties of the 11.2% efficient device D_2, which was fabricated with an identical process as sample D but in another batch. The SEM cross-section image exhibits a similar structure as sample D with a large-grain upper crust, a rather narrow small-grain bottom layer and a distinct Mo(S,Se)\(_2\)-layer. The J-V curve yields a total-area efficiency of 11.2% for a cell area of 0.29 cm\(^2\), whereas the 10 best cells have an efficiency of 10.6% ± 0.3%. The EQE measurement shows that the major part of additional current, compared to sample D in the previous section, is stemming from the
long-wavelength region, which is manifested by plotting the ratio of reversed bias EQE and zero bias EQE. Further advanced characterization on sample D_2 was conducted using AS and $T$-$J$-$V$ measurements. Figure 4.19 a) shows the $T$-$J$-$V$ curves in darkness and under illumination. The crossover of illuminated and dark curves is becoming more pronounced at lower temperatures, whereas the increasing roll-over of the $J$-$V$ curves leads to a complete blocking of the current at the lowest temperature of 123 K. Possible explanations for this blocking are a barrier at the interface between absorber and the Mo back contact, which facilitates the minority carrier recombination [149], or an increase in bulk resistivity, due to the lack of shallow acceptor states and therefore a freeze out of deeper acceptor states rendering the device fully depleted and exhibiting high resistivity [116].

![Figure 4.19: a) Temperature dependent $J$-$V$ measurement (dark curve-dotted line, light curve-solid line) of device D_2. The inset shows a linear fit of the $V_{OC}$ that can be extrapolated to an intersection value of $E_A=0.99$ eV, which is close to the estimated bandgap of $E_g=1.05$ eV. b) Temperature dependence of the series resistance $R_S$ of sample D_2 obtained from the dark $J$-$V$ curves, which is fitted with a thermal activation energy $E_A=182$ meV using Equation 4.1 (see inset).](image)

The temperature dependence of the $V_{OC}$ extrapolated to $T=0$ K provides an intercept of $E_A (V_{OC} - T) = 0.99$ eV, representing the activation energy for the dominant recombination mechanism. Since this value is very close to the derived bandgap of 1.05 eV, one can conclude that the dominant recombination paths are located within the bulk of the absorber rather than at the interface [158].

In Figure 4.19 b) the temperature dependence of the dark series resistance $R_S$ is shown.
Using the model for a Schottky barrier at the back contact [120] the barrier height can be calculated from Equation 4.1

\[ R_S = R_0 + \frac{k}{q A^* T} e^{-\frac{E_A}{kT}} \]  

(4.1)

where \( A^* \) is the effective Richardson constant, \( R_0 \) is the background series resistance and \( E_A \) the activation energy due to the barrier. The Arrhenius plot in the inset yields an activation energy of \( E_A(R_S - T) = 182 \) meV.

AS measurements in Figure 4.20 show one capacitance step in the frequency range from 200 Hz to 2 MHz. Assuming a point defect, one can utilize Equation 4.2 in order to extract the activation energy:

\[ \omega_0 = 2 \xi_0 T^2 e^{-\frac{E_A}{kT}} \]  

(4.2)

with \( \omega_0 = 2\pi f \) the freeze out frequency and \( \xi_0 \) the temperature independent thermal emission pre-factor. This results in a thermal emission depth \( E_{A,1}(Cf-T) = 108 \) meV with \( \xi_0 = 4694 \) s\(^{-1}\)K\(^{-2}\).

Figure 4.20: a) Temperature-dependent capacitance frequency measurements in the temperature range from 123 K to 323 K and frequencies from 200 Hz to 2 MHz. b) Arrhenius plot of the freeze out frequency yields an activation energy of \( E_A = 108 \) meV with \( \xi_0 = 4694 \) s\(^{-1}\)K\(^{-2}\).

However, the freeze out observed in the AS measurement could also be attributed to a Schottky barrier in the device and a corresponding activation Energy is derived by
4.2. 3-stage selenization in the semi-open reactor

a change in the temperature dependence of the pre-factor from $T^2$ to $T^{3/2}$, yielding an activation energy of $E_{A,2}(Cf-T) = 115 \text{ meV}$ [121]. From the $Cf-T$ measurements the dark series resistance can also be calculated by employing an admittance circuit model of a depletion region in series with the undepleted quasi-neutral region [116]. Comparing these values with the $R_S$ derived from $JV-T$ (Figure 4.21) shows one order of magnitude lower values for $R_S$ obtained from AS, implying that the activation energies $E_A(Cf-T)$ and $E_A(R_S - T)$ are not attributed to the same effect. The drop of the capacitance to the geometric capacitance at high frequencies generally rules out that the capacitance step originates from a barrier. Therefore it hints towards a defect with an activation energy of $E_A(Cf-T) = 108 \text{ meV}$.

![Figure 4.21: $R_S$ from $JV-T$ in comparison to the calculated $R_S$ from $Cf-T$ measurements. The obtained values differ by one order of magnitude and imply that the increase in $R_S$ from $JV-T$ and the observed freeze out of the capacitance signal in $Cf-T$ measurements do not originate from the same source.](image)

In Table 4.5 the current champion devices having efficiencies > 10 % for non-vacuum and vacuum deposition techniques are listed. The record efficiency of 12.6 % is obtained with a pure-solution approach utilizing hydrazine as the solvent [21]. The highest FF with 72.7 % is observed for a Ge containing sample synthesized from a co-evaporated precursor [34]. DMSO-processed cells reach efficiencies of 11.5 % (see Section 5.4.4), 11.8 % (active area measurement) [159] and 10.3 % [40]. Vacuum-based pure selenide absorbers can deliver the highest photocurrents $J_{SC}$ of 40.6 [35] and 39.7 mAcm$^{-2}$ [155] due to their bandgap of 1.0 eV. The 10.8 % mini-module from Solar Frontier features the lowest $V_{OC}$ - deficit of
0.56 V (determined from a linear fit of the transformed EQE curve) [160]. The 11.2\% device of this study exhibits one of the lowest $V_{OC}$-deficits of 0.57 V indicating a low concentration of defects in the absorber bulk and interfaces and the lowest ideality factor of $A = 1.14$ suggesting that the dominant recombination paths are shifting from the space charge region (SCR) to the quasi neutral region (QNR) [149], which is consistent with the fact that the $V_{OC}$ - $T$ fit intersects at $T = 0$ K very close to the bandgap value.

**Table 4.5:** Comparison of PV parameters of published kesterite solar cells with more than 10\% conversion efficiency. All cells use an AR-coating; a) Pure-solution approach utilizing hydrazine as solvent; b) DMSO-based solution approach; c) Non-pyrolytic spraying of water-ethanol-based ink d) Selenization of co-evaporated metal precursors; e) Selenization of sputtered metal precursors; [f] active area; [g] measured under illumination; [h] derived from J-V characteristics; [i] determined from linear fitting the transformed EQE curve;

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eff.</th>
<th>FF</th>
<th>$V_{OC}$</th>
<th>$J_{SC}$</th>
<th>$R_S$</th>
<th>$G_S$</th>
<th>$A$</th>
<th>$J_0$</th>
<th>$E_g$ (eV)</th>
<th>$E_g$ - $V_{OC}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>solution-processed</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>this study D_2b</td>
<td>11.2</td>
<td>63.8</td>
<td>479</td>
<td>36.5</td>
<td>1.0</td>
<td>0.9</td>
<td>1.14</td>
<td>3.16E-06</td>
<td>1.05</td>
<td>0.57</td>
</tr>
<tr>
<td>IBM [21] CZTSSe_a</td>
<td>12.6</td>
<td>69.8</td>
<td>513.4</td>
<td>35.2</td>
<td>0.72[g]</td>
<td>1.61[b]</td>
<td>1.24</td>
<td>7.0E-05</td>
<td>1.13</td>
<td>0.617</td>
</tr>
<tr>
<td>Empa [39] CZTSSe_b</td>
<td>11.5</td>
<td>65.8</td>
<td>496</td>
<td>35.2</td>
<td>0.7</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
<td>1.11</td>
<td>0.61</td>
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<tr>
<td>UW [159] CZTSSe_b</td>
<td>11.8[f]</td>
<td>68.1</td>
<td>449</td>
<td>38.8[f]</td>
<td>0.43</td>
<td>-</td>
<td>1.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IMRA [28] CZTSSe_e</td>
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<td>65</td>
<td>510</td>
<td>32.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.18</td>
<td>0.67</td>
</tr>
<tr>
<td>ZSW [40] CZTSSe_b</td>
<td>10.3</td>
<td>69.6</td>
<td>471</td>
<td>31.6</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.07</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>vacuum-processed</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>DGIST [33] CZTSSe_e</td>
<td>12.3</td>
<td>67.2</td>
<td>521</td>
<td>35.0</td>
<td>0.96</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.10</td>
<td>0.576</td>
</tr>
<tr>
<td>AIST [34] CZTGESe_e</td>
<td>12.3</td>
<td>72.7</td>
<td>527</td>
<td>32.3</td>
<td>0.36</td>
<td>0.9</td>
<td>1.47</td>
<td>3.6E-05</td>
<td>1.11</td>
<td>0.58</td>
</tr>
<tr>
<td>IBM [35] CZTSe_d</td>
<td>11.6</td>
<td>67.3</td>
<td>423</td>
<td>40.6</td>
<td>0.32</td>
<td>1.66</td>
<td>1.57[b]</td>
<td>1.38E-03[b]</td>
<td>1.0</td>
<td>0.58</td>
</tr>
<tr>
<td>Solar Frontier [160] CZTSSe_d</td>
<td>10.8</td>
<td>64</td>
<td>502</td>
<td>33.5</td>
<td>0.92</td>
<td>2.57</td>
<td>1.9</td>
<td>-</td>
<td>1.06[b]</td>
<td>0.56[d]</td>
</tr>
<tr>
<td>IREC [161] CZTSe_e</td>
<td>10.6</td>
<td>65.4</td>
<td>473</td>
<td>34.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.05</td>
<td>0.58</td>
</tr>
<tr>
<td>IMEC [155] CZTSe_e</td>
<td>10.4</td>
<td>66.2</td>
<td>394.9</td>
<td>39.7</td>
<td>0.6</td>
<td>0.93</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

In summary, an 11.2\%-efficient (designated illumination area measurement) CZTSSe solar cell is fabricated using the hydrazine-free DMSO solution approach. The best device features the $V_{OC}$ - deficit of only 0.57 V, which is amongst the lowest for kesterite solar cells.
The open circuit voltage improvement was possible because of the 3-stage annealing process in a silica-coated closed reactor, which enabled an increased incorporation of selenium and a large-grained microstructure. The reduced $V_{OC}$-deficit is attributed to a low diode saturation current and ideality factor, which are signatures of the semiconductor material with a low concentration of recombination centers.
5 Alkali treatment of kesterite solar cells

The development of an efficient absorber synthesis route via an improved selenization process for highly efficient kesterite solar cells including Na bulk treatment was presented in Chapter 4. Nevertheless, the low open circuit voltage remains the major problem inhibiting further efficiency improvements. Alkali treatments of kesterite solar cells is one of the measures to reduce the high $V_{OC}$-deficit, constituting the motivation for the following studies.

Chapter 5 presents investigations on alkali treatments of kesterite solar cells. In Section 5.2 the effects of potassium-fluoride post deposition treatment and potassium bulk treatment are studied. In Section 5.3 the effects of Li bulk treatment and Li alloying are investigated. Finally, a comparison of Li, Na, K, Rb and Cs bulk treatment for different alkali concentrations and Sn contents is conducted in section 5.4.

This Chapter is partly based on the following publications:


5.1 The effects of alkali metals in chalcogenide solar cells

Alkali treatment of kesterite solar cells is one of the measures to reduce the high $V_{OC}$-deficit and most of today's >10% efficient kesterite devices utilize the beneficial effects of alkali elements on absorber layer morphology and opto-electronic properties. So far, the most research attention has been paid to sodium, resulting in many thorough investigations which revealed grain size enhancement, passivation of grain boundaries and an increase in net hole concentration as the major beneficial effects [36, 93, 94, 128]. Also lithium addition has shown to improve device performance by boosting the electronic quality of the CZTSSe absorber material and grain boundaries [96]. First studies on the effect of potassium addition confirmed advantageous effects on kesterite absorber growth and opto-electronic properties similar to Na [98, 99]. Several studies comparing different alkali elements and their effect on solar cell properties and device performance have recently been published [100–103], but the results are often contradictory as will be discussed in Section 5.4.

5.2 Effects of potassium treatments

Potassium treatment of kesterite solar cells is investigated in two separate approaches. The first approach investigates the potassium-fluoride post deposition treatment (KF-PDT) and the second one studies the effects of potassium bulk treatment.

5.2.1 Potassium-fluoride post deposition treatment

KF-PDT has been a major breakthrough for CIGS solar cells yielding world record efficiencies [86, 162]. KF-PDT results in significant improvements in $V_{OC}$, $FF$ and CdS coverage leading to efficiencies above 20% for CIGS solar cells. Here a similar KF-PDT approach for solution processed kesterite solar cells is investigated. The absorber layers are prepared by the dimethyl sulfoxide (DMSO) solution process described in Chapter 3 including 100 mM nominal NaCl content. Kesterite absorber layers with potassium fluoride
5.2. Effects of potassium treatments

(KF) thicknesses of 0, 0.25, 1, 5, 10, 25 and 60 nm, deposited by thermal evaporation, were
prepared and subsequently annealed at 350°C in selenium atmosphere. The parameters
are comparable to the processing parameters for KF-PDT on CIGS absorber layers [86].
A significant difference in the methodology, however, is that in this study the KF evap-
oration is conducted at room temperature in a separate evaporation chamber following a
transfer in ambient atmosphere. In the original CIGS KF-PDT process the KF evapora-
tion takes place at elevated temperatures directly proceeding the absorber layer growth
process without breaking the vacuum.

5.2.1.1 Morphology and composition

Figure 5.1: SEM cross section images of the finished devices processed with 0 nm KF (A)
and 60 nm KF (B). The morphology of both absorber layers is similar and was therefore
not altered by the KF-PDT process. The thin CdS layer thickness was determined to
50 nm–60 nm for both samples indicating no change in CdS growth velocity due to the
KF-PDT.

The KF-PDT treatment is conducted at a temperature of 350°C in Se atmosphere,
which does not cause changes to the morphology or structure of the absorber layer. Figure
5.1 shows two cross sections of the samples with 0 and 60 nm KF. The 0 nm KF was
neither exposed to KF evaporation nor to the annealing at 350°C in Se atmosphere. The
morphology of both samples is identical, confirming that KF-PDT does not alter the
morphology of the absorber layer. Additionally, the CdS thickness of the whole sample
series was investigated by SEM, showing similar thicknesses of 50 nm–60 nm and leading
to the conclusion that, in contrast to CIGS, no measurable effect on CdS growth can be observed in the case of kesterite KF-PDT.

![XRD pattern of all samples from 0.25nm to 60nm KF thickness. All patterns are similar indicating that no morphological or structural changes are caused by the KF-PDT treatment.](image)

**Figure 5.2:** XRD pattern of all samples from 0.25nm to 60nm KF thickness. All patterns are similar indicating that no morphological or structural changes are caused by the KF-PDT treatment.

The XRD patterns of all samples in Figure 5.2 indicate that no structural and morphological changes are caused by KF-PDT and differences in device performance and opto-electronic properties must be attributed to other effects. For the samples with thicker KF layer of 25nm and 60nm two Bragg reflexes appear at 24.8° and 29.5° which may be related to potassium-selenide phases but could not be clearly assigned. The depth distribution of K and Na, measured by SIMS, is presented in Figure 5.3. Figure a)–d) show the depth profiles from samples with 0.25nm, 5nm, 25nm and 60nm KF thickness. The K signal exhibits an accumulation at the front interface and increases after an initial drop towards the back contact. The higher K amount in the part of the absorber layer adjacent to the back contact results from the higher density of grain boundaries in which K is predominantly located. In order to compare the K signal in the different samples correctly, the K signal is divided by the integrated Cu counts in the absorber layer to account for changes in the sensitivity during the SIMS measurements of the 4 different
5.2. Effects of potassium treatments

cells. The K/Cu ratio is shown in Figure 5.3 e) – f) and both in the bulk and at the surface the K/Cu signal is increasing as expected with a thicker initial KF layer.

**Figure 5.3:** SIMS depth profiles of the samples with a) 0.25 nm, b) 5 nm, c) 25 nm and d) 60 nm KF thickness. e) and f) show the distribution of K as a ratio of K/Cu in the absorber layer. K accumulates at the front interface but also diffuses into the absorber layer.
5.2.1.2 Opto-electronic properties

The EQE spectra of all samples are shown in Figure 5.4 and reveal a reduced carrier collection throughout the whole wavelength range for an increasing KF thickness. In the short-wavelength region from 375 nm to 550 nm, which is partly absorbed by the CdS layer due to its bandgap of 2.4 eV, an abnormal behaviour of the EQE signal exceeding unity can be observed for the samples with $\geq 10$ nm KF thickness. It is assumed that this artefact is attributed to the increased photoconductivity of the CdS layer as a result of the incorporation of alkali impurities [163].

![Figure 5.4: EQE of the best cells treated with KF-PDT and KF thicknesses from 0 nm to 60 nm. For KF $\geq 10$ nm the EQE exhibits an abnormal signal peak in the wavelength region from 375 nm to 550 nm which is an artefact that is probably related to the increased photoconductivity of the CdS layer.](image)

During the EQE measurements the incident light, which is modulated by a frequency of 272 Hz, is absorbed in the CdS layer and changes the conductivity of the CdS layer with the same frequency of 272 Hz. The modulated conductivity of the CdS layer consequently modulates part of the photocurrent, which originates from the bias light, and is eventually falsely interpreted by the lock-in amplifier as photocurrent arisen from the chopped light source [149]. The increased EQE signal in this short-wavelength region is therefore a
5.2. Effects of potassium treatments

measurement artefact and does not represent the collection probability of electron-hole pairs. The $J_{SC}$ derived from the integration of the EQE signal over the AM1.5G solar spectrum conclusively does not agree with the $J_{SC}$ from $J-V$ measurements. Without the bias light during the EQE measurements, the abnormal EQE behaviour disappears.

5.2.1.3 PV properties

![Photovoltaic characteristics of KF-PDT treated samples with the KF thickness varying from 0nm to 60nm. a) $J_{SC}$ decreases similar to FF (b) and efficiency $\eta$ (c) with an KF thickness of $\geq 5$nm. d) $V_{OC}$ increase with an KF thickness of $\geq 5$nm.](image)

Figure 5.5: Photovoltaic characteristics of KF-PDT treated samples with the KF thickness varying from 0nm to 60nm. a) $J_{SC}$ decreases similar to FF (b) and efficiency $\eta$ (c) with an KF thickness of $\geq 5$nm. d) $V_{OC}$ increase with an KF thickness of $\geq 5$nm.

Figure 5.5 presents the photovoltaic parameters of all samples with statistics being derived from 9 cells for each KF thickness. In Figure 5.5 a) the $J_{SC}$ remains around 34mAcm$^{-2}$ for the samples with up to 1nm KF thickness and decreases when further
increasing the amount of KF, as expected from the EQE measurements. Additionally, the \( J_{SC} \) values for the same KF thickness start to spread considerably. A qualitatively similar behaviour is observed for the \( FF \) and efficiency. The efficiency reaches up to 9.7% for the baseline with 0 nm KF (no anti reflective coating was applied to the samples). The \( V_{OC} \) exhibits an upwards trend with \( \geq 5 \) nm KF thickness. For the samples with 25 nm and 60 nm KF the spread in the values for each thickness becomes increasingly larger, so only the best cells exhibit a higher \( V_{OC} \).

\[
\text{Figure 5.6: J-V curves of the best cells treated with KF-PDT and varying KF thicknesses from 0 nm to 60 nm. The J-V curves show the blocking of } J_{SC}, \text{ reduction in } FF \text{ and an increase in } V_{OC} \text{ with increasing KF thickness. The shape of the curves indicates that the source of the current blocking behaviour originates from a barrier.}
\]

Representative \( J-V \) curves for each KF thickness are presented in Figure 5.6. The shape of the curves with thicker KF layer indicates that the source of this current blocking behaviour originates from a barrier. This barrier could be caused by an insulating layer formed during the KF-PDT. Alternatively, KF-PDT could alter the electrical properties of the CdS layer, leading to the abnormal EQE behavior. This constitutes a significant difference to the CIGS case that neither exhibits a current blocking behaviour nor a distinct impact on the electrical properties of the CdS layer. Additionally, for CIGS the KF-PDT results in a copper-poor interface layer composed of K, In and Se that reduces interface recombination and improves CdS growth properties [164].
In conclusion, potassium-fluoride post deposition treatment of solution processed kesterite solar cells with various KF thicknesses exhibits a decrease in $J_{SC}$, $FF$ and efficiency with increasing KF thickness, which originates from a severe blocking of the photocurrent. The CdS buffer layer growth is not affected by KF-PDT, but the buffer layer exhibits a photoconductivity effect in EQE measurements. Although KF-PDT improves the $V_{OC}$, it is evident that the different surface chemistry compared to the CIGS case does not yield a comparable beneficial interface layer and thus no performance improvements can be observed.

### 5.2.2 Potassium bulk treatment

It was shown in the previous section that KF-PDT does not yield similar improvements of PV parameters compared to CIGS solar cells. However, potassium is also expected to show beneficial effects as a fluxing agent and dopant in the bulk of the material during selenization [165]. Therefore, an analysis of the impact of K bulk treatment on the kesterite absorber composition, morphology, lattice structure and the photovoltaic parameters of resulting kesterite solar cells is investigated.

The K bulk treatment approach exploits the advantage of solution processing, which enables a controlled and homogeneous incorporation of alkali metals at the precursor stage. Potassium was added to the precursor solution in various concentrations in the form of KCl which has a high solubility in the Dimethyl sulfoxide (DMSO) solvent. The subsequent process steps were conducted equally for all samples (see Chapter 3). It has to be pointed out that for these samples no Na was added and a barrier layer of SiO$_x$ between the soda-lime glass and Mo back contact was used to inhibit the diffusion of Na from the SLG substrate. Nevertheless, due to the long annealing times at high temperatures Na was still present in the absorber layer due to possible transport through the gas phase [128].

Finally, in order to explore any synergetic effects between K and Na, controlled amounts of KCl were added on top of a constant amount NaCl, and results are compared to the samples with only KCl addition. All devices were extensively characterized by XRF, XRD, SIMS and SEM and by $J-V$, voltage dependent EQE and AS. The used nominal
concentrations of KCl are 0, 1, 5, 10, 50 and 100 mM, which correspond to $\frac{K}{Cu+Zn+Sn}$ ratios in percent of 0%, 0.07%, 0.35%, 0.7%, 3.5% and 7%. For simplicity reasons the mM values will be used here.

### 5.2.2.1 Morphology and composition

Figure 5.7 shows the SEM cross section images of full devices with different amounts of KCl. For 0, 1 and 5 mM KCl the absorber layer exhibits a distinct bi-layer structure and an increase in crystal size can be observed. The bi-layer structure vanishes upon further addition of KCl and the grain size increases to up to 1–2 $\mu$m.

![SEM cross section images of full devices with increasing KCl concentrations](image)

**Figure 5.7:** SEM cross section images of full devices with increasing KCl concentrations (no Na addition). The morphology of the CZTSSe absorber layers exhibits a distinct bi-layer structure for 0–5 mM KCl. For higher KCl amount the grain size in the lower part of the absorber is increasing, yielding grains that span over the whole absorber layer thickness.

Potassium can form K$_x$Se phases at temperatures as low as 155°C, which act as a fluxing agent and improve grain growth [166]. The mechanism for an K assisted grain growth improvement is suggested to be similar to the sodium case [94]: Chemisorption
of gaseous Se during the high temperature selenization step and formation of liquid K polyselenide phases. These liquid K based phases act as a fluxing agent, thereby promoting selenium transport into the precursor layer and enhancing diffusion processes of less mobile phases during crystallization, resulting in an increased grain growth and grain size [166]. The formation of a Mo(S,Se)$_2$ layer during the high temperature annealing in chalcogen atmosphere can be estimated from the increase in the Mo/Mo(S,Se)$_2$ layer thickness and the appearance of the characteristic XRD Bragg reflexes. From SEM cross sections a Mo(S,Se)$_2$ thickness of 200–300 nm is deduced, which is not affected by increasing KCl concentrations. The absorber layer thickness is decreasing with higher KCl concentration due to the denser morphology of the absorber layer.

The precursor solution composition for all samples is identical - apart from the KCl concentration. Compositional measurements in Table 5.1 of Cu, Zn and Sn by ICP-MS show a reduced Cu content, which could be attributed to a reduced loss of Sn and Zn during the high temperature annealing. The relatively lower Cu content affects the bandgap and order/disorder of the Cu/Zn sub-lattice and will be discussed later. In order to investigate the depth distribution inside the absorber layer K and Na, SIMS measurements were performed. Traces of Na stem from the SLG substrate, transported via the gas phase during the high-temperature annealing step. Additionally, minor diffusion of Na through the SiO$_x$ blocking layer cannot be ruled out.

Table 5.1: Composition in at% of samples with K bulk treatment measured by ICP-MS

<table>
<thead>
<tr>
<th>sample</th>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>22.4%</td>
<td>15.8%</td>
<td>12.2%</td>
</tr>
<tr>
<td>1 mM KCl</td>
<td>22.4%</td>
<td>15.6%</td>
<td>12.0%</td>
</tr>
<tr>
<td>10 mM KCl</td>
<td>22.2%</td>
<td>16.2%</td>
<td>12.2%</td>
</tr>
<tr>
<td>100 mM KCl</td>
<td>21.5%</td>
<td>16.3%</td>
<td>12.2%</td>
</tr>
</tbody>
</table>

Figure 5.8 a) and b) show the relative amounts of K and Na (the samples with 5 and 50 mM KCl were not measured by ICP-MS). Both measurement techniques show qualitatively the same results. For the SIMS measurements the integrated Na and K counts were divided by the integrated Cu counts inside the absorber layer. Cu is chosen as the reference element because the Cu amount is constant throughout the absorber depth.
and exhibits similar quantities in all samples. A higher nominal KCl concentration leads to an increase in the measured K amount, which demonstrates the successful incorporation of K into the absorber layer by simply adding KCl to the solution. While for the low quantity of 1 mM KCl 85% of the nominal KCl content in the precursor solution is still present in the final absorber layer, for 10 mM 45% and for 100 mM 4% are still present in the final layer. How potassium is lost during the solar cell synthesis was not further investigated in this study.

Figure 5.8: a) Na and K content measured by ICP-MS. b) K/Cu and Na/Cu counts from SIMS measurements integrated over the whole absorber layer. ICP-MS and SIMS measurements exhibit similar results. In c) and d) the distribution of K and Na inside the absorber layer is shown. The CdS/CZTSSe interface is located at the normalized absorber depth of 0 and the CZTSSe/Mo(S,Se)₂ interface at 1.

Interestingly, the amount of Na is first increasing upon incorporation of KCl, however decreasing with subsequently higher KCl concentrations. The reduction of Na concentration upon incorporation of K was also observed in highly efficient CIGS thin film solar cells [86, 164]. The distribution of both alkali metals is depicted in Figure 5.8 c), d) and reveals that for the samples with a distinct bi-layer structure the alkali metal concentrations
are increased in the small-grained, lower part of the absorber layer. The profile flattens for the samples with large grains and no bi-layer structure ($\geq 10 \text{ mM}$). The signal increase in the front of the absorber layer from 0 to 100 mM KCl for both K and Na suggests that the alkali metals accumulate predominantly at the grain boundaries.

Figure 5.9: Lateral SIMS image of the $^{39}\text{K}^+$ signal within the 100 mM KCl containing kesterite absorber. A circular distribution with sizes comparable to the grain size suggest that K accumulates predominantly at the grain boundaries.

SIMS imaging was used to identify the location of K within the kesterite absorber. The lateral resolution of the SIMS setup used here is limited to approximately 500 nm, therefore the sample with the largest grains (100 mM KCl) was used for the measurement. Figure 5.9 reveals that the K signal originates from roundish areas with the size of grains, which is in agreement with the assumption that K accumulates at the grain boundaries. An accumulation of potassium at the interfaces reported by Li et al. [99] cannot be confirmed by this study. Alloying of K within the kesterite lattice is unlikely due to the large size of 1.66 Å of the K ion and thus high migration and substitution energies of $\geq 0.3\text{ eV}$ and 1.53 eV, respectively [95].

Figure 5.10 a) shows the XRD patterns of the full devices including CdS, i-ZnO/Al:ZnO, Ni/Al grid and MgF$_2$. All samples produce equivalent kesterite specific Bragg reflexes at 14.7°, 17.4° and 22.1°. For the sample with 100 mM KCl a Sn(S,Se)$_2$ Bragg reflex at
14.07° [112] can be observed. The FWHM of the main 112 Bragg reflex in Figure 5.10 b) is lower for samples with ≥ 10 mM KCl concentration, implying an increase in grain size and crystal quality which is in agreement with the SEM cross section images in Figure 5.7.

A detailed measurement of the 400/008 Bragg reflex pair [167] is shown in Figure 5.10 c). While the 400 Bragg reflex does not shift due to KCl incorporation, the 008 Bragg reflex shifts to larger angles, which originates from a reduction of the c parameter of the unit cell.

![Figure 5.10:](image)

Figure 5.10: a) shows the XRD patterns of the full devices including CdS, i-ZnO/Al:ZnO, MgF₂ and Ni/Al grid. The FWHM of the main 112 Bragg reflex is presented in b). c) A detailed measurement of the 400/008 Bragg reflex pair.

A reduction of the c parameter in conjunction with a constant a parameter and an increase in bandgap was reported to be connected to an increase in the ordering of Cu and Zn atoms [58, 64]. This increase in ordering correlates with the reduction of the Cu
content that is also known to lead to higher ordering [168].

### 5.2.2.2 Opto-electronic properties

![Chart a)](image1)

**Figure 5.11:** a) IQE of all samples calculated from EQE and reflectance measurements. b) Results of SCAPS simulations upon introducing a back barrier with a height between 0.30–0.36 eV, which can reproduce the observed IQE behavior in a).

The internal quantum efficiency (IQE) patterns of the samples were calculated following Equation 5.1 and are presented in Figure 5.11.

$$IQE(\lambda) = \frac{EQE(\lambda)}{1 - R(\lambda)}$$  \hspace{1cm} (5.1)

$R(\lambda)$ is the reflectance measured on the whole device including metal grid lines. The bandgaps determined by the inflection points in the long-wavelength region are increasing from 1.00 eV for 0 mM KCl up to 1.04 eV for 100 mM KCl. The bandgap increase is connected to the decrease in Cu/(Zn+Sn) ratio leading to an increase in ordering of the Cu/Zn sub-lattice, which leads to a higher bandgap. The shape of the IQE curves in the long wavelength region does not indicate a change in the collection probability with increasing KCl concentration. This implies a constant SCR width, which is in agreement with room-temperature C-V measurements in Figure 5.12, which reveal only a slight
increase in the apparent carrier concentration. A significant decrease of the apparent carrier concentration was measured with decreasing relative Cu content (see Chapter 5.4 or [39]). Therefore, the slight increase in apparent carrier concentration in combination with the decrease in relative Cu content for this sample series suggests that K doping increases the carrier concentration. This result is in agreement with reported effects of K doping in kesterite solar cells by Li et al. and Hsieh et al. [99, 101].

Figure 5.12: Apparent carrier concentrations and SCR widths for samples treated with 0–100 mM KCl concentration, derived from room temperature C-V measurements.

The IQE value is rising from 0.85 to 0.97 in the whole range, which can be explained by a removal of a barrier between the absorber layer and back contact for holes towards the back contact. SCAPS simulations [169] with a barrier height between 0.30 eV–0.36 eV can reproduce the observed IQE behavior (Figure 5.11 b) [170]. In the simulations the focus was solely to investigate the increase in the IQE, therefore no attention was paid to the increase in bandgap. The increase of the IQE value upon KCl incorporation could also stem from other effects, e.g. a spike in the conduction band alignment of the kesterite absorber and CdS buffer layer. However, due to the high series resistance that is reduced and the bi-layer structure that is transformed into a well crystallized absorber layer upon KCl incorporation, a hole barrier stemming from the small grained layer in the vicinity of the back contact is the most likely explanation.
5.2.2.3 PV properties

Figure 5.13 and Figure 5.14 exhibit the photovoltaic parameters for all 6 samples with increasing KCl concentrations. Each sample consists of 9 cells, represented by box plots, with a cell size of $0.30 \pm 0.05 \text{cm}^2$. The series resistance in a) is reduced with higher KCl concentrations, which is in agreement with the improved crystallization of the absorber layer in the vicinity of the back contact.

**Figure 5.13:** a), b) Parallel and series resistance with increasing KCl amount. Up to 5 mM KCl reduces the series resistance. The parallel resistance is decreasing from 50 mM KCl onwards. c) The ideality factor $A$ is increasing with higher KCl content. d) The reversed saturation current $J_0$ shows a minimum for 10 mM and increases with higher KCl concentrations.

The parallel resistance is constant for lower and decreases rapidly for higher KCl concentrations. The sample with 100 mM KCl exhibits average values for the parallel resistance.
below $100 \Omega \text{cm}^2$. The shunting behaviour coincides with the appearance of Sn(S,Se)$_2$ secondary phase identified by XRD in Figure 5.10. The ideality factor $A$ is increasing with higher KCl concentrations and $J_0$ shows a minimum value for the 10 mM sample, indicating that undesirable recombination is lowest in this sample.

![Figure 5.14](image)

**Figure 5.14:** a)–d) PV parameters with increasing KCl content yielding efficiencies of up to 9.7% for 10 mM KCl. Additional experiments in Section 5.4 show that 10mM is the optimal concentration for the metal ratios used for this study, because of Sn(S,Se)$_2$ formation at higher KCl concentrations.

From these parameters it can be assumed that the 10 mM sample is the optimal concentration due to reduced series resistance, favourable morphology and lowest $J_0$ but without the formation of secondary phases that deteriorate the device performance. Figure 5.14 shows the best device with 9.7%, 432 mV $V_{OC}$, 61% $FF$ and 36.7 mA cm$^{-2}$ for 10 mM KCl. Taking the increase in bandgap into account, the $V_{OC}$ - deficit remains similar around 0.62–
5.2. Effects of potassium treatments

0.64 V for all samples with the exception of the sample with 10 mM KCl concentration, which exhibits the lowest $V_{OC}$-deficit of 0.59 V. The higher $J_{SC}$ value of the 10 mM KCl sample is partly due to an overall lower reflectance of the sample as shown in Figure 5.11 c). The improvement of the $FF$ can be attributed predominantly to the reduction of the series resistance $R_S$ (Figure 5.13 a). It should be noted that the comparably high performance of the sample with 100 mM KCl is surprising when taking the low parallel resistance, high $J_0$ and the appearance of Sn(S,Se)$_2$ secondary phase into account. However, additional experiments in Section 5.4 show that indeed 10 mM is the optimal concentration for the metal ratios used for this study, and with higher KCl concentration formation of Sn(S,Se)$_2$ is deteriorating the device performance.

5.2.2.4 Comparison to Na treatment

![Figure 5.15: SEM cross section images of the full devices including the window layer. The added KCl amount is increasing from 0 – 100 mM while the NaCl concentration remains at 100 mM for all samples.](image)

In order to reveal if addition of potassium to CZTSSe exhibits any additional effects on Na-containing samples, a series of samples with different amount of KCl (0–100 mM
KCl) and 100 mM NaCl was studied. Kesterite solar cells grown with 100 mM NaCl added to the precursor solution are described in Chapter 4.2. The morphology of the samples with 100 mM NaCl and different KCl concentrations are shown in the SEM cross sections in Figure 5.15, and they exhibit that NaCl is less effective in promoting grain growth compared to KCl. This may be due to the lower melting point of K$_x$Se phases (160°C) compared to Na$_x$Se phases (255°C) [166, 171], which both act as a fluxing agent and improve grain growth [94, 172].

Figure 5.16 a) and b) show the device performance and $V_{OC}$-deficit for added KCl concentrations varying from 0 to 100 mM. From 0 to 50 mM KCl both efficiency and $V_{OC}$-deficit show a similar trend with average efficiencies of $\geqslant 9\%$ and $V_{OC}$-deficits below 0.6 V. For the 100 mM KCl sample a drop in efficiency below 6% and a high $V_{OC}$-deficit of 0.7 V are observed and connected to a decrease in parallel resistance, similar to the sample with only 100 mM KCl.

Figure 5.16: a)–c) The PV parameters and EQE spectra of samples treated with 100 mM NaCl and 0–100 mM KCl.
5.2. Effects of potassium treatments

The IQE patterns of the 100 mM NaCl samples with various KCl amounts are shown in Figure 5.16 c). In contrast to the sample series without NaCl no reduction of the IQE value can be observed here, suggesting that the presence of Na lowers or removes the back barrier by either improving the morphology of the lower part of the absorber layer or increasing the hole conductivity of the back interface and grain boundaries. A shift to higher bandgaps of up to 1.04 eV can also be observed, similar to the sample series without NaCl.

Finally, Table 5.2 presents a comparison of the best cells for non-treated and alkali-treated samples with only KCl or NaCl. Both alkali treatments essentially can produce high-efficiency devices around 10% with comparable opto-electronic properties. However, a ten times lower concentration of potassium is required compared to sodium in order to achieve similar improvements.

<table>
<thead>
<tr>
<th>sample</th>
<th>Eff. (%)</th>
<th>FF (%)</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$A$</th>
<th>$J_0$ (mA cm$^{-2}$)</th>
<th>$E_g - qV_{OC}$ (eV)</th>
<th>$N_C$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no alkali treatment</td>
<td>6.4</td>
<td>51.6</td>
<td>364</td>
<td>33.8</td>
<td>1.21</td>
<td>4.3E-04</td>
<td>0.63</td>
<td>6.6E15</td>
</tr>
<tr>
<td>10 mM KCl</td>
<td>9.7</td>
<td>61.0</td>
<td>432</td>
<td>36.7</td>
<td>1.24</td>
<td>7.0E-05</td>
<td>0.59</td>
<td>1.6E16</td>
</tr>
<tr>
<td>100 mM NaCl</td>
<td>10.1</td>
<td>65</td>
<td>428</td>
<td>36.5</td>
<td>1.27</td>
<td>1.25E-04</td>
<td>0.57</td>
<td>2.2E16</td>
</tr>
</tbody>
</table>

In summary, the K bulk treatment of kesterite solar cells leads to an enhanced grain growth and improved PV properties resulting in devices close to 10% conversion efficiency. The impact of K as a fluxing agent is more effective compared to Na, and K suppresses incorporation of Na from the soda lime glass. Incorporation of high concentrations of K decrease the loss of Sn which results in a change of order/disorder of the Cu/Zn sub-lattice and thereby additionally widens the bandgap and increases the tetragonal distortion. The reduction of series resistance previously reported [98] is confirmed by this study. Higher nominal Potassium concentrations require an adjustment of the Sn content in the absorber
layer in order to avoid formation of Sn(S,Se)$_2$ secondary phase and thus deterioration of the device performance. Synergetic effects between K and Na are not observed and both alkali elements exhibit similar beneficial effects on the kesterite solar cell performance.

5.3 Li bulk treatment

Addition of Li has been shown to affect the bandgap, lattice parameters, carrier concentration and crystal growth of kesterite thin film solar cells, leading to an improved absorber quality and device efficiency [96,173]. A recent study investigating the effects of Cu substitution by Li in kesterite material synthesized by high temperature annealing in evacuated glass ampoules found that the solid solution of Li$_x$Cu$_{2-x}$ZnSnSe$_4$ for 0 $\leq x \leq$ exists [97].

In this Section the possibility of Li alloying within CZTSSe thin films at temperatures of only 550°C via a solution processing route is investigated. The samples A–E are prepared with an increasing nominal amount from 0 to 300 mM LiCl (300 mM LiCl corresponds to Li$_{(Cu+Zn+Sn)/3}$ = 0.20 or Li$_{Cu+Li}$ = 0.35). For sample F (Li200*) the amount of Cu was reduced by 100 mM and LiCl increased from 100 to 200 mM, aiming to facilitate the incorporation of Li by reducing the chemical potential of Cu during the absorber synthesis.

5.3.1 Morphology and composition

Li forms Li$_x$Se phases that can act as a fluxing agent and promote grain growth equivalent to the heavier alkali elements [94,174]. However, the lowest melting point in the Li$_x$Se system is 350°C, which is significantly higher than of the heavier alkali elements Na, K, Rb and Cs (160°C–255°C). The SEM cross section images of all samples in Figure 5.17 show that with more than 10 mM LiCl the grain size increases, the bi-layer structure vanishes and a dense layer forms. In comparison to the K bulk treatment in Section 5.2.2 a higher LiCl concentration is required in order to obtain a similar increase in grain growth. For sample F the formation of Sn(S,Se)$_2$ secondary phase, shown in Figure 5.18, deteriorates the device performance and shows that reducing the Cu chemical potential did not lead to an increased Li incorporation.
Figure 5.17: SEM cross section images of the samples from low to high LiCl content. Compared to K bulk treatment in Section 5.2.2 a higher concentration of LiCl is required to obtain a comparable increase in grain size.

Figure 5.18: Tilted SEM cross section of sample F showing a high amount of Sn(S,Se)$_2$ secondary phase formed on top of the absorber layer.
The composition of all samples measured by XRF is shown in Table 5.3. The sample composition does not change for the samples from 0 – 300 mM LiCl within the experimental error. Therefore, changes in PV parameters and opto-electronic properties are not due to any compositional changes of the absorber layer. For sample F the reduction in Cu content of 100 mM from 560 mM to 460 mM corresponds to a relative change of 18%. However, Sample F exhibits approximately 19% lower Cu/Zn and 23% lower Cu/Sn ratios compared to the samples A–D, indicating a slight reduction in Sn loss during the absorber synthesis, which is also in agreement with the lower Zn/Sn ratio.

Table 5.3: Compositions of all samples measured by XRF for Cu, Zn, Sn and ICP-MS for Li.

<table>
<thead>
<tr>
<th>sample</th>
<th>Cu/Zn</th>
<th>Cu/Sn</th>
<th>Cu/(Zn+Sn)</th>
<th>Zn/Sn</th>
<th>Li/(Li+Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>1.40</td>
<td>1.64</td>
<td>0.75</td>
<td>1.17</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>1.40</td>
<td>1.67</td>
<td>0.76</td>
<td>1.20</td>
</tr>
<tr>
<td>C</td>
<td>100</td>
<td>1.37</td>
<td>1.72</td>
<td>0.76</td>
<td>1.26</td>
</tr>
<tr>
<td>D</td>
<td>200</td>
<td>1.35</td>
<td>1.61</td>
<td>0.73</td>
<td>1.20</td>
</tr>
<tr>
<td>E</td>
<td>300</td>
<td>1.36</td>
<td>1.68</td>
<td>0.75</td>
<td>1.24</td>
</tr>
<tr>
<td>F</td>
<td>200*</td>
<td>1.10</td>
<td>1.27</td>
<td>0.59</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Figure 5.19: a) XRD patterns of all samples with increasing LiCl content from nominal 0 to 300 mM (A–E) and 200 mM LiCl, but 100 mM less Cu (F). b) Detailed measurement of the 400/008 Bragg reflex pair revealing an increase of the tetragonal distortion for a higher LiCl content.

The XRD patterns are shown in Figure 5.19. For sample F the formation of Sn(S,Se)2 can be deduced from the Bragg reflex at 14.5°, 30.7°, 44.2°, 52.58° and 60.2° [112]. For
the samples A–E no secondary phases can be identified. Analysis of the 400/008 Bragg reflex pair in 5.19 b) reveals a shift of the 400 Bragg reflex towards lower angles with increasing LiCl content, indicating an increase in the lattice constant $a$. The 008 Bragg reflex does not change and thus the $c$ lattice parameter stays constant with increasing LiCl concentration. The tetragonal distortion calculated from $\eta = c/2a$ is decreasing, which is attributed to Li alloying with the kesterite phase [39,97]. The observed changes of the $a$ and $c$ parameter and the change in bandgaps in conjunction with the measured Li content inside the absorber layer can be comprehensively explained by Li alloying following the results of Lafond et al. [97]. The effect of Li alloying on the disorder in the Cu/Zn planes, which also effects the bandgap and tetragonal distortion was not further investigated here.

### 5.3.2 Opto-electronic properties

The EQE spectra of all samples are presented in Figure 5.20 a). The bandgap is increasing from 1.06 eV to 1.15 eV for samples A–E. This increase is predicted from calculations and originates from the alloying of Li with the kesterite structure. Figure 5.20 b) shows the predicted bandgaps in dependency to the nominal LiCl content (squares) in comparison to the actual measurement (stars). The bandgaps were determined by the EQE inflection point and the Li content was measured by ICP-MS. The predictions for the bandgaps are in agreement with the measurement although a significant part of Li is lost during the absorber synthesis.

The CdS deposition was conducted similar for all samples A–F. The parasitic absorption of the CdS layer up to 540 nm, shown in the inset of Figure 5.20 a), indicates that with increasing LiCl concentration the CdS layer becomes thinner. Influence on the growth of CdS was also observed for KF-PDT treated CIGS solar cells [89]. The collection in the long-wavelength region is reduced from low to high LiCl content and sample F exhibits an overall lower EQE. Furthermore, the bandgap of sample F is close to the sample with 200 mM LiCl suggesting that the reduction of the Cu chemical potential did not result in the increased incorporation of Li.

The apparent carrier concentrations measured by room-temperature $C-V$ reveal an in-
Figure 5.20: a) EQE of all devices with increasing LiCl content. Bandgaps were derived from the inflection point of the EQE in the long-wavelength region. The inset shows the normalized EQE in the low-wavelength region and indicates a decrease in thickness of the CdS layer with higher LiCl concentrations. b) Calculated and measured bandgap in dependence of the nominal (squares) and measured (stars) Li content by ICP-MS.

Figure 5.21: Apparent Carrier concentration determined by room-temperature C-V measurements.
crease from $3 \times 10^{15}$ cm$^{-3}$ for sample A up to $5 \times 10^{17}$ cm$^{-3}$ for sample E (Figure 5.21). The higher apparent carrier concentrations result in a reduced space charge region width down to 60 nm and therefore are in agreement with the reduced quantum efficiency in the long-wavelength region in Figure 5.20 a). The increase in carrier concentration was also observed for CZTSSe when increasing the Cu content from a Cu poor to a more stoichiometric composition and thus supports the assumption that Li is located at Cu vacancies in the lattice and exhibits comparable electronic properties [39].

### 5.3.3 PV properties

Figure 5.22: a) $V_{OC}$, b) FF, c) $J_{SC}$ and d) efficiency of samples A–F containing 0 to 300 mM LiCl.

Figure 5.22 shows an increased $V_{OC}$ for a higher LiCl content, which is expected due to
the higher bandgap. Additionally, a $V_{OC}$ increase stems from the increase in the apparent carrier concentration for the higher LiCl concentration. The $V_{OC}$-deficit for the best performing samples C–E is between 0.60 and 0.62 V. The $FF$ improves to approximately 65% with $\geq 100$ mM LiCl. The efficiency shows the highest value for 200 mM LiCl, however all 3 samples with a LiCl content of 100–300 mM exhibit nearly identical performance of $\geq 11\%$ efficiency. The high loss of Li during the absorber synthesis, evident from the difference of nominal LiCl addition and measured Li content by ICP-MS, explains the formation of secondary phases and overall low device performance of sample F. Due to an insufficient amount of Li present in the absorber layer the reduced Cu is not replaced, leading to the formation of Sn(S,Se)$_2$, which deteriorates the device performance.

### 5.3.4 Conclusion

Li alloying is a highly promising route to further boost the device performance of kesterite solar cells. LiCl treatment improves the grain growth leading to a dense and large-grained morphology. The alloying with Cu$_{1-x}$Li$_x$ZnSn(S,Se)$_4$ is verified by the increase in tetragonal distortion of the kesterite lattice and the increase in bandgap, which follows Vegards Law for $x < 0.4$. Li alloying results in a higher apparent carrier concentration, which is associated with Li occupying the V$_{Cu}$ locations inside the kesterite lattice. Less Cu poor kesterite exhibits similarly a higher apparent carrier concentration (see Chapter 5.4). LiCl treatment affects the growth of CdS, which was also observed for KF-PDT in CIGS solar cells and led to significant performance improvements.

### 5.4 Comparison of alkali metals

Several studies comparing different alkali elements and their effect on solar cell properties and device performance have recently been published [100–103]. Table 5.4 compares the effects on device performance by extracting a ranking of the various alkali elements in each publication in the order of their capability to improve device performance. It is important to mention that two of the four publications do not explicitly state to use an
alkali diffusion barrier for their experiments.

**Table 5.4:** List of publications comparing the effects of alkali elements on the device performance of kesterite solar cells.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Order of performance improvement</th>
<th>Alkali barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Effect of different alkali (Li, Na, K, Rb, Cs) metals on Cu2ZnSnSe4 solar cells” [100]</td>
<td>Na &gt; Cs &gt; K &gt; Rb &gt; Li</td>
<td>200 nm SiO2Nₓ</td>
</tr>
<tr>
<td>“Efficiency enhancement of Cu2ZnSn(S,Se)4 solar cells via alkali metals doping” [101]</td>
<td>K &gt; Rb &gt; Na &gt; Li &gt; Cs</td>
<td>-</td>
</tr>
<tr>
<td>“Influence of alkali metals (Na, Li, Rb) on the performance of electrostatic spray-assisted vapour deposited Cu2ZnSn(S,Se)4 solar cells” [102]</td>
<td>Li &gt; Na &gt; Rb</td>
<td>-</td>
</tr>
<tr>
<td>“Alkali doping strategies for flexible and light-weight Cu2ZnSnSe4 solar cells” [103]</td>
<td>K &gt; Na</td>
<td>Cr barrier layer</td>
</tr>
</tbody>
</table>

It is apparent from these rankings that no consistent experimental results have been obtained, which triggers two questions:

i) Why do the published results differ so much?

ii) Which alkali element possesses the highest potential for efficiency improvements?

![Figure 5.23](image_url)

**Figure 5.23:** a) All samples fabricated for this study are presented in dependence of the alkali element, alkali concentration and Sn content. b) The alkali content in total at% in the absorber layer for samples with 3.33 at% (red) and 0.33 at% (green) nominal alkali content, determined by ICP-MS measurements.
The aim of this chapter is to unveil the discrepancy between the recently published results comparing the effects of alkali treatments on device performance. The hypothesis is that each alkali element requires a different absorber composition to achieve the highest PV performance and therefore a comprehensive set of samples was prepared with different alkali elements and alkali concentrations as well as various metal ratios. All samples were thoroughly characterized by SEM, XRD, XRF, ICP-MS as well as $J-V$, $C-V$, TR-PL and EQE measurements.

The methodology used for absorber synthesis is based on the solution process described in Chapter 3, allowing for alkali incorporation by simply adding alkali chlorides to the solution. Figure 5.23 a) illustrates the matrix of sample compositions prepared with five different alkali elements: lithium (Li), sodium (Na), potassium (K), rubidium (Rb) and caesium (Cs). The nominal alkali concentration was varied in three steps of 0, 10 and 100 mM in the precursor solution, which corresponds to 0, 0.33 and 3.33 at% relative to all absorber elements. Variations in the metal ratios were put into effect by changing the Sn concentration in the precursor solution in up to 12 steps yielding overall more than 80 samples and thus >700 individual cells. In the following it will be referred to the nominal values of Sn/(Cu+Zn+Sn) in at% because the step size of variations are smaller than the error margins of the compositional measurements by XRF. Additionally, it will be referred to the 10 mM (0.33 at%) and 100 mM (3.33 at%) alkali containing samples by “low” and “high” alkali content, respectively.

The Alkali content in the absorber layer of the full devices was analysed by ICP-MS and compared to the nominal input. Figure 5.23 b) shows the measured concentration of all five alkali elements in the two nominal concentrations. The concentrations represent the alkali element that was intentionally added to the specific sample (Li in the Li sample and so on). The ICP-MS measurements show that intentionally added alkali elements are successfully incorporated into the absorber layer and a higher nominal alkali concentration corresponds to a higher measured alkali content by ICP-MS. However, the majority of the alkali amount escapes during the processing, which could take place during the spin-coating process (subsequent layers can dissolve preferentially alkali-chloride crystals from the antecedent layer and wash them off), during the chemical bath deposition of the
CdS buffer layer because of the high solubility of alkali compounds in water or by forming volatile compounds that evaporate during the drying and/or annealing step. Furthermore, the results of ICP-MS measurements reveal that heavier alkali elements remain at higher concentrations inside the absorber layer than lighter elements, except for the case of Li. As the alkali elements are preferably located along the grain boundaries [164,175], the overall amount measured by ICP-MS, which does not discriminate between alkali elements inside grains or at the grain boundaries, is expected to be higher for samples with a higher density of grain boundaries.

### 5.4.1 Morphology and composition

![Figure 5.24: SEM cross sections of the full devices including the window layer. a) sample with no alkali treatment, b)–c) samples with “low” and “high” Li treatment and d)–e) samples with “low” and “high” Rb treatment.](image)

In Section 5.3 it was already shown that the improvement in grain growth depends on the concentration of the alkali elements. The SEM cross sections in Figure 5.24 show full devices including the CdS and the i-ZnO/Al:ZnO/MgF$_2$ window layer of representative samples. Figure 5.24 a) shows the cross section of a nominally alkali-free sample, which exhibits a distinct bi-layer structure with large grains on top and small grains in the lower
part. Images b)–e) display the evolution for “low” and “high” Li and Rb concentration. While for Li a “high” alkali content is required in order to grow large grains, in the case of Rb already a “low” alkali content is sufficient. However, upon adding a “high” Rb concentration the morphology changes to a dense, small grained layer that possesses a high density of grain boundaries. Comparing devices with different Sn content confirms that no morphological changes are caused by variations in Sn concentration (Figure 5.25). Therefore, all morphological changes can be attributed to the alkali treatment. As will be shown later, the improvement in the morphology is largely correlated with the device performance.

Figure 5.25: SEM cross sections of devices with no alkali treatment but decreasing amount of nominal Sn content from $\text{Sn}/(\text{Cu}+\text{Zn}+\text{Sn}) = 27.5\%$ in a) to $33.3\%$ in d). Variations in Sn content do not affect the layer morphology and grain size.

The morphology for each alkali element and concentration indicates that the lighter alkali elements require a higher concentration to reach a similar improvement in mor-
5.4. Comparison of alkali metals

Phenology as compared to the heavier alkali elements. This could be due to lower melting points for alkali-polyselenide phases of heavier alkali species as compared to lighter ones [166, 171, 174, 176, 177]. Because of the lower melting points the heavier alkali elements act more efficiently as a fluxing agent and, hence, lower concentrations are required to achieve similar grain size improvements.

Therefore, each alkali element has its own optimal concentration at which it results in favourable morphology improvements and thus highest device performance. The trend of alkali content measured by ICP-MS in Figure 5.23 b) correlates with the increasing density of grain boundaries in the order of Na < K < Rb < Cs that are present in the samples with “high” alkali concentrations. Li does not follow this trend, but exhibits the highest content with 0.76 at%, which could be explained by the existence of a Cu$_{1-x}$Li$_x$ZnSn(S,Se)$_4$ alloy [97, 173].

Figure 5.26: a) Set of XRD pattern for high Na content and different nominal Sn concentrations. Red dots indicate Bragg reflexes for kesterite, black arrows for Al grid, blue triangles for ZnO and green squares for Sn(S,Se)$_2$ secondary phase [112]. b) Range between 12.5° – 17.5° from the respective XRD pattern of “high” alkali content samples.

The set of XRD patterns in Figure 5.26 a) displays the “high” Na content for different nominal Sn concentrations. Bragg reflexes originating from the kesterite phase are marked with red circles and additional Bragg reflexes at 31.6° and 56.5° indicate Mo(S,Se)$_2$ [178]. The Sn(S,Se)$_2$ secondary phase can be identified from the XRD patterns of samples with 33.3% nominal Sn content and more. Other secondary phases cannot be distinguished,
however Zn(S,Se) and Cu$_2$Sn(S,Se)$_3$ cannot be excluded since their Bragg reflexes coincide with those of CZTSSe [152]. The XRD patterns of the other alkali elements and different concentrations look qualitatively similar with the exception of the appearance of Sn(S,Se)$_2$ secondary phase. Therefore the range from 12.5° to 17.5° was magnified in Figure 5.26 b) for all alkalines to present the appearance of Sn(S,Se)$_2$ by the intensity of its 001 Bragg reflex, which is located at 14.42° for the pure selenide compound [112]. Samples treated with heavier alkali elements exhibit Sn(S,Se)$_2$ formation already at lower Sn contents, indicated by the appearance of the Sn(S,Se)$_2$ 001 Bragg reflex. Additionally, the XRD pattern of the layer with K exhibits a double Bragg reflex that may stem from Sn(S,Se)$_2$ phases with different S/Se ratios. In the case of Cs a small but invariant Bragg reflex appears for all Sn concentrations, but here the Bragg reflex overlaps with a possible secondary phase of Cs$_2$Se$_3$. Therefore the Sn(S,Se)$_2$ secondary phase for the high Cs content sample cannot be unambiguously identified.

Cu$_x$Se secondary phase could not be seen in the XRD patterns of any sample, although the device PV parameters for low Sn content and a Cu/Sn ratio of more than 2.0 are shunted and exhibit large, roundish grains, which are typically associated with a Cu-rich material and the formation of Cu$_x$Se [179].

The comparison of the nominal Sn content with the Sn content inside the absorber layer

Figure 5.27: a) Sn/(Cu+Zn+Sn) ratio of the absorber and the nominal ratio in the precursor solution. b) Measurements of Sn/(Cu+Zn+Sn) ratio of various alkali treatments for an identical nominal Sn content. No significant change or trend in dependence of alkali element or concentration can be observed.
after selenization measured by XRF in Figure 5.27 shows a significant Sn loss compared to the nominal Sn concentration that typically occurs during the high temperature annealing [43]. Additionally, XRF results seem to indicate a reduced Sn loss for samples including heavier alkali elements. This however is a measurement artefact and disproved by ICP-MS measurements. In Figure 5.27 b) the Sn content for 8 samples with various alkali elements and concentrations show that the alkali treatment has no impact on the final absorber composition. From the Sn content in the absorber layer measured by XRF and ICP-MS we conclude that the Sn loss is proportional to the overall nominal Sn content and that it is invariant under the addition of various alkali elements as well as their concentrations.

5.4.2 Opto-electronic properties

The EQE measurements with none and “high” alkali content are shown in Figure 5.28. The EQE spectra of cells with none and the light alkali elements exhibit qualitatively similar features from “low” to “high” nominal Sn content, which are a strong initial increase of the EQE followed by an increase in squareness and finally an overall decrease. The low EQE values at low Sn concentrations are due to shunting of the devices possibly caused by Cu$_x$Se secondary phase. The increase in squareness at intermediate Sn concentrations could be either an improvement in diffusion length of minority carriers or an increase in the space charge region width. Additionally, the bandgap is increasing steadily with increasing Sn concentrations. In comparison the EQE spectra of Rb and Cs exhibit only a slight Sn dependency.

The bandgap trends of the kesterite layers are presented in Figure 5.29 as derived from the inflection point in the long-wavelength region of the EQE signal. An increase in nominal Sn content correlates with a concurrent increase in bandgap. The increase in bandgap can be attributed to the change of metal ratios resulting in an increase in ordering of the Cu/Zn sublattice [61]. Because of the abundance of Zn in the absorber layer composition, an increase in Sn concentration results in the formation of kesterite phase material with a lower Cu content. The change of the kesterite phase composition can explain the bandgap change for Na and K addition but Li, Rb and Cs exhibit a different
Figure 5.28: a)-d) The EQE spectra of none and “high” Li, Na, K exhibit similar qualitative features indicated by the arrows in a). e)-f) Variations in nominal Sn content show only a minor influence on the EQE spectra of “high” Rb and Cs.
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Figure 5.29: Bandgap $E_g$ for the samples with “high” alkali content. The bandgap is determined from the inflection point of the EQE signal in the long-wavelength region.

behavior. Li-containing samples exhibit a sudden increase of the bandgap for Sn nominal concentrations above 31.5%, meaning that the bandgap change is taking place once the kesterite composition is considerably Cu poor and is associated with an incorporation of Li onto Cu sites inside the kesterite structure [97].

Alloying of Li was reported to increase the bandgap and it seems that in the case of thin film synthesis a notable amount of Li can only be incorporated into the lattice if the chemical potential of Cu is lower than a certain threshold. The substitution energy for Li$_{Cu}$ was reported to be 0.27 eV in contrast to Na and K with 0.55 eV and 1.55 eV, respectively [95]. Therefore alloying of Li with the kesterite phase is more likely than for Na, K or heavier alkali elements, which is in line with the presented findings and the results of the Li alloying experiments in Section 5.3. Furthermore, the tetragonal distortion of the “high” LiCl samples (Figure 5.30) is decreasing with an increasing Sn content and exhibits an overall lower value for the “high” LiCl samples compared to the untreated samples. The offset between “high” LiCl samples and untreated samples is caused by Li alloying with the kesterite phase, which increases the $a$ parameter as shown in Section 5.3 [97]. The observed decrease of the tetragonal distortion with increasing Sn content for both “high” LiCl samples and the untreated samples is due to a change in the order/disorder of the Cu/Zn sublattice, caused by a change in the metal ratios to a more copper poor kesterite
composition.

Figure 5.30: a) 400/008 Bragg reflexes for “high” Li containing samples. From the peak positions the tetragonal distortion $\eta = \frac{c}{2a}$ is calculated. b) Tetragonal distortion of none and “high” Li containing Samples. The shift to lower values for the Li containing samples indicates Li alloying with the kesterite phase. The decrease of the tetragonal distortion with increasing Sn content is attributed to an increase in ordering of the Cu/Zn sublattice.

Based on the bandgaps, the following explanation for the appearance of secondary phases at different nominal Sn concentrations is suggested. The XRD results indicate that the alkali elements influence the composition specifically of the kesterite phase (not absorber layer). The kesterite composition correlates with the measured bandgap and Cu poor kesterite exhibits a higher bandgap than Cu rich kesterite [167,180]. Further investigations are needed to understand the effect of alkali treatments on the kesterite phase composition. The presented results indicate that the kesterite composition is less Cu poor for Na containing samples compared to K containing samples for the same nominal Sn content, based on the bandgap measurements from Figure 5.29. Conclusively, the remnant Sn not incorporated into the kesterite phase leads to the formation of Sn(S,Se)$_2$ secondary phase. For Rb and Cs the bandgap barely changes suggesting a constant kesterite composition.

In comparison to Li, Na and K the EQE spectra of Rb and Cs show only a slight Sn dependency. In order to further scrutinize the dependency of the optoelectronic properties on the Sn concentration, the apparent carrier concentration of all devices was determined by room temperature C-V measurements. In Figure 5.31 a)–f) the apparent carrier
5.4. Comparison of alkali metals

Figure 5.31: The apparent carrier concentration and space charge region width for representative sample sets with none alkali and “high” alkali content samples, calculated from room temperature C-V measurements.
concentration and space charge region width for representative sample sets with none and “high” alkali content are shown. The sample sets for the lighter alkali elements exhibit a distinct correlation of the apparent carrier concentration with the Sn content. From approximately 25% to 36% Sn concentration the apparent carrier concentration decreases by three orders of magnitudes from the range of $1 \times 10^{18} \text{cm}^{-3}$ down to $1 \times 10^{15} \text{cm}^{-3}$.

This change is directly correlated with the simultaneous increase in space charge region width from 20–40 nm to up to 500 nm. By assuming that the apparent carrier concentration is proportional to the doping concentration the evolution of EQE in Figure 5.28 can be correlated to the $C-V$ results and explain the increase in squareness of the EQE by the widening of the space charge region [181]. At the same time, the low carrier concentrations result in a weaker electric field in the SCR that eventually leads to the reduction of the overall EQE for the whole wavelength region, which could be either caused by a barrier or a relatively low carrier lifetime in the SCR [149]. The lower doping concentration induces a drop in $V_{OC}$, but is obscured by the increase in bandgap that is obvious from the long-wavelength EQE behaviour in Figure 5.28.

The sample sets for Rb and Cs exhibit a comparably stable carrier concentration of approximately $1 \times 10^{16} \text{cm}^{-3}$ and $2 \times 10^{17} \text{cm}^{-3}$, respectively. The steady carrier concentrations consequently result in similar EQE spectra for Rb and Cs. The constant doping concentrations of Rb and Cs are in agreement with the constant bandgap and PV parameters that are independent of the nominal Sn content.

Further device analysis by TR-PL did not reveal any correlation of device parameters, alkali elements and alkali concentration with the PL decay times in Figure 5.32. The issue of deducing the minority carrier lifetime from TR-PL measurement in kesterite solar cells has been described by Hages et al. [154]. Minority carrier trapping, surface effects and energetic relaxation of carriers have been identified to severely affect the PL transient times, thus the measured PL decay times do not represent the real minority carrier lifetime in kesterite absorber layers.
5.4. Comparison of alkali metals

5.4.3 PV properties

The main findings of this chapter are aggregated in Figure 5.33, which shows the device efficiency as a function of the nominal Sn content (y-axis) and the alkali elements from Li to Cs with the “high” alkali content (x-axis). The color code resembles the average efficiency of 9 cells (designated illumination area measurement) and the stars indicate the Sn content yielding the highest efficiency for a given alkali element. The highest device efficiency (average of 9 cells) for each alkali element increases from 6.5% for Cs to more than 10.5% for Li. The optimal Sn content that results in the best efficiency increases concurrently from 26.5% for Cs up to 33.3% for Li.

The range of Sn content that yields comparable high efficiency is dependent on the alkali element and narrows down from Li to Na to K. The average efficiencies in the case of Rb and Cs are only weakly dependent on the Sn content and therefore exhibit a comparably homogeneous efficiency distribution, however resulting in overall lower device efficiency values. The reduction of efficiency at high and low Sn contents that is most prominent for
Li, Na and K can be attributed to the formation of secondary phases which deteriorate \( FF \), \( V_{OC} \) and \( J_{SC} \). The dependency of the Sn content on the highest device performance of different alkali elements has neither been reported before nor taken into account in earlier publications that compared effects of alkali elements on kesterite solar cells [100–103].

The influence of the Sn content on \( V_{OC} \), \( J_{SC} \) and \( FF \) is shown in Figure 5.34 a)–c) for the “high” alkali content samples. As a result of the qualitatively distinct behaviour of Li, Na and K (light alkali elements) on the one hand and Rb, Cs (heavy alkali elements) on the other it is helpful to separate them into two groups. The maximum \( V_{OC} \) for a given alkali element increases from K to Na to Li while simultaneously the maximum \( J_{SC} \) decreases, which will be addressed later. Rb exhibits intermediate values for both \( V_{OC} \) and \( J_{SC} \), while Cs exhibits comparably low values. The \( FF \) shows highest values of up to 65%
for Li while the other alkali elements can reach values up to 60%. The optimal Sn content for highest $FF$ coincides with the highest efficiency and the degradation of $FF$ at high Sn contents is associated with the appearance of Sn(S,Se)$_2$ secondary phase, that segregates on top of the samples, similar to Figure 5.18, and appears at Cu/Sn ratios < 1.65 in the absorber layer [182]. At low Sn concentrations the devices show a degradation of $V_{OC}$, $J_{SC}$ and $FF$ simultaneously, which is caused by the shunting Cu$_x$Se phases that occur at Cu/Sn ratios > 2.0 [55].

![Figure 5.34](image)

Figure 5.34: $V_{OC}$, FF and $J_{SC}$ are shown in a) – c) for the “high” alkali content samples. d) $V_{OC}$-deficit for “high” alkali content samples.

Figure 5.35 a) shows the efficiency for the “low” alkali content as well as without intentional alkali addition. The overall efficiencies for the samples containing light alkali elements is lower compared to the “high” alkali content case, while for the heavy alkali elements better efficiencies are observed. Furthermore, no obvious trend in the optimal Sn content for the different alkali elements is visible in contrast to the “high” alkali concentration results in Figure 5.33.
Figure 5.35: a) The average efficiency of 9 cells for none and “low” alkali content samples. b) Evolution of efficiency from 0 to “low” to “high” alkali content for a specific Sn content. The required alkali concentration for maximum device performance is lower for heavier alkali elements.

Figure 5.35 b) illustrates the device efficiency for each alkali element for specific Sn concentrations yielding highest efficiency. It can be seen that the lighter alkali elements require higher concentrations in order to yield best device performance. For heavier alkali elements a considerable improvement in the efficiency is already present at the low alkali content. At the “high” alkali content Li, Na and K exhibit further increase in device performance in contrast to Rb and Cs which decrease in efficiency.

5.4.4 PV parameters of the 11.5% - efficient champion device

Finally in Figure 5.36 the PV parameters, J-V and EQE of the champion solar cell with a “high” Li content and 33.3% nominal Sn concentration are presented. The efficiency of 11.5% was determined by designated illumination area measurement including the front contact metal grid on an area of 0.29 cm² (active area efficiency: 12.3%). The sample with 8 cells showed an average efficiency of 11.0% ± 0.5%.
Figure 5.36: *PV parameters of the champion device with a “high” Li content and 33.3% nominal Sn content. The cell exhibits a high bandgap of $E_g = 1.11 \text{ eV}$ because of Li alloying with the kesterite phase.*
5.4.5 Conclusion

This study reveals the complex dependency of metal ratios, alkali elements and alkali concentrations on device performance in highly efficient kesterite solar cells. From Li to Cs the nominal Sn concentration ($\frac{Sn}{Cu+Zn+Sn}$) required for best device properties should be reduced from 33.3% to 26.5%, i.e. more than 20% (relative). Additionally, the alkali concentration resulting in the best devices for Li (11.1%), Na (10.0%) and K (10.0%) was 100 mM while for Rb (8.8%) and Cs (9.1%) only 10 mM were required. The PV parameters correlate with the changes in morphology with best devices exhibiting large grains throughout the whole absorber layer with a low density of grain boundaries. The formation of Sn(S,Se)$_2$ secondary phase is increased for the heaver alkali elements and for high concentrations. As revealed by EQE and C-V measurements the carrier concentration varies by three orders of magnitude depending on the Sn content, except for high Rb and Cs content where a constant kesterite composition and therefore constant doping concentration is observed. A ranking of best device performances employing alkali treatment resulted in the order of Li > Na > K > Rb > Cs based on the statistics of more than 700 individual cells. Finally, a champion device with 11.5% efficiency (12.3% active area) is presented using “high” Li concentration with an optimized Sn content.
In this thesis CZTSSe absorbers were prepared from a solution approach based on dimethyl sulfoxide (DMSO) as the solvent via a two-step process comprised of precursor synthesis and subsequent selenization. The DMSO approach is a safe and low-toxic fabrication route that requires only readily available metal salts.

Commonly reported challenges of all solution processed kesterite absorber layers are their high porosity, non-uniformity, and numerous grain boundaries that can lead to undesirable recombination. Studying the effects of open, semi-open and closed reactors for high-temperature annealing in selenium atmosphere on the absorber morphology and optoelectronic properties resulted in an improved understanding of the impact of the reactor design. Best kesterite absorber properties are obtained for the semi-open reactor, realized by a closable graphite box, which combines the advantages of high selenium partial pressure with a sufficient possibility for organic residuals to escape the absorber layer during sintering. Furthermore, the 3-stage temperature profile is leading to further improvements in the recrystallization while keeping decomposition reactions of the kesterite phase to a minimum. An 11.2%-efficient (designated illumination area measurement) CZTSSe solar cell is fabricated featuring a $V_{OC}$-deficit of only 0.57 V, which is amongst the lowest for solution processed kesterite solar cells. The reduced $V_{OC}$-deficit is attributed to a low diode saturation current and ideality factor, which are signatures of the semiconductor material with a low concentration of recombination centres.

Based on the improved precursor synthesis and absorber selenization the effects of alkali treatments are investigated. Potassium-flouride post deposition treatment of solution processed solar cells with various KF thicknesses exhibits a decrease in short circuit cur-
rent, fill factor and efficiency with increasing KF thickness that originates from a severe blocking of the photocurrent. However, the open circuit voltage is improved suggesting a decrease of interface recombination. The CdS buffer layer growth was not affected but the buffer layer exhibits a significant photoconductivity effect in external quantum efficiency measurements. In conclusion, KF-PDT improves the $V_{OC}$ but the different surface chemistry does not yield a beneficial interface layer, in contrast to the CIGS case.

Potassium bulk treatment of kesterite solar cells leads to a significantly enhanced grain growth and improved PV parameters resulting in devices close to 10\% conversion efficiency. Compared to Na, a ten-fold lower K amount is sufficient to achieve similar grain size and device performance. The reduction of series resistance of solar cells previously reported is confirmed by this study. Potassium doping increases the carrier concentration as derived from $C$- $V$ measurements. Higher nominal Potassium concentrations require an adjustment of the Sn content in the absorber layer in order to avoid formation of Sn(S,Se)$_2$ secondary phase and thus deterioration of the device performance. Synergetic effects between K and Na are not observed and both alkali elements exhibit similar beneficial effects on the kesterite solar cell performance.

In contrast to Na and K, Li bulk treatment results in the successful incorporation of Li into the kesterite crystal structure. Li alloying is a highly promising route to further improve the device performance of kesterite solar cells, leading to the best devices for solution processed, non-hydrazine solar cells. Li treatment improves the grain growth and leads to a dense and large-grained morphology. The alloying into Cu$_{1-x}$ Li$_x$ ZnSn(S,Se)$_4$ is verified by the increase in tetragonal distortion of the kesterite lattice and the linear increase in bandgap.

Finally, a comparison of bulk treatments with Li, Na, K, Rb and Cs reports for the first time the complex dependency of metal ratios, alkali elements and alkali concentration on the device performance in high-efficiency kesterite solar cells. From Li to Cs, the nominal Sn concentration ($\frac{Sn}{Cu+Zn+Sn}$) required for best device properties is reduced from 33.3\% to 26.5\%. Additionally, alkali concentrations resulting in highest device efficiencies are lower by an order of magnitude for the heavy alkali elements (Rb, Cs) compared to the lighter
ones (Li, Na, K). The PV parameters correlate with changes in morphology with the best devices exhibiting large grains and a low density of grain boundaries. As revealed by EQE and C-V measurements the doping concentration varies by three orders of magnitude depending on the Sn content, except for high Rb and Cs content, for which a constant kesterite composition and therefore constant doping concentration is observed. A ranking of best device performances employing alkali treatment results in the order of Li > Na > K > Rb > Cs based on the statistics of more than 700 individual cells. A champion device with 11.5\% efficiency (12.3\% active area) is presented using a “high” Li concentration with an optimized Sn content.

The results of this thesis trigger several questions that could be tackled in future. One of the major issues for kesterite research is the irreproducibility that is predominantly ascribed to the annealing process. A novel reactor concept that allows for precise control of sample temperature and chalcogen partial pressure could significantly improve the reproducibility, allowing for more detailed analysis and accelerated research advancement. Also, several pathways sketched out by the mature CIGS technology have still to be implemented for kesterite solar cells, e.g. bandgap grading and alkali post deposition treatment of the CZTSSe/CdS interface. Due to the different surface chemistry in CIGS, KF-PDT on CIGS resulted in significant improvements of the junction quality and CdS coverage due to the formation of a KInSe$_2$ phase. However, similar effects could not be observed for KF-PDT on Kesterite. Other alkali metals like Li could yield beneficial interface properties and thus further investigations on alkali PDT are promising. In order to get a better insight to the chemical nature of the modified interface, further experiments utilizing XPS measurements could be conducted. Concerning alkali bulk treatment, future research needs to focus on the fine-tuning of alkali concentrations especially for the heavy alkali elements Rb and Cs. Cu based issues like the Cu/Zn disorder, Cu$_x$(S,Se) secondary phases and possibly detrimental defects at interfaces associated with the presence of Cu could be solved by (partial) replacement of Cu with Li.

In a broader perspective, kesterite exhibited a steady improvement in device performance. The fundamental understanding of the material properties and possible constraints were identified in recent years. Kesterite could not yet fulfil the high expectations of re-
placing the successful chalcogen-based thin film solar cell technologies CIGS and CdTe with an earth abundant and non-toxic alternative. The answers to the question “why are kesterite solar cell not 20% efficient” have not yet been satisfactorily given, but the steady improvements with many research groups being able to produce kesterite solar cells with more than 10% efficiency suggests that this will not be the end of the story.
Bibliography


Bibliography


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List of publications

Publications in peer-reviewed journals


**Submitted manuscripts / Manuscripts under preparation**

manuscript under preparation (2017).


Alejandro N. Filippin, Michael Rawlence, Tanja Zünd, Kostiantyn Kravchyk, Sami Bolat, **Stefan G. Haass**, Aneliia Wäckerlin, Maksym V. Kovalenko, Yaroslav E. Romanyuk, Stephan Buecheler, *Ni-Al-Cr superalloy as high temperature cathode current collector for advanced thin film Li-ion batteries*, manuscript under preparation (2017).
