Back contact, doping and stability of CdTe thin film solar cells in substrate configuration

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Publication Date:
2015

Permanent Link:
https://doi.org/10.3929/ethz-a-010538566

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Back contact, doping and stability of CdTe thin film solar cells in substrate configuration

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

presented by
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2015
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Abstract

The direct conversion of sunlight into electricity by photovoltaic (PV) devices represents a clean and sustainable way to meet the world’s rising demand for energy. CdTe solar cells grown in superstrate configuration are an advanced PV technology with high efficiencies up to 21.5% and contribute to sustainable energy production with over 10 GWp capacity installed worldwide. The ability to grow efficient CdTe solar cells also in the inverted substrate configuration would allow for the use of non-transparent and flexible substrates compatible with cost-effective roll-to-roll production. Substrate configuration furthermore enables a better control over junction formation and gives the opportunity for a deepened understanding of the chemical and electronic processes and properties of the solar cell. Yet, the problems of barrier formation at the back contact as well as the limited electronic properties of the CdTe layer and p-n junction caused efficiencies of substrate configuration solar cells to remain below 8%.

In this thesis, processes for the growth of CdTe/CdS solar cells in substrate configuration are developed which enable conversion efficiencies up to 13.6% with $V_{oc}$ (~850 mV) and fill factor (~75%) reaching the level of superstrate configuration. An important step was to decouple CdTe recrystallization from heterojunction formation with CdS by applying two separate CdCl$_2$ treatments to the CdTe and the CdS layers. This leads to a recrystallized CdTe layer, passivation of the CdTe grain boundaries and improved junction quality.

A novel concept for the controlled acceptor doping of CdTe with copper or silver in substrate configuration is presented. The doping is achieved by evaporation of sub-monolayer amounts of copper or silver onto the recrystallized CdTe layer and subsequent annealing. It results in hole densities of $\sim 10^{14}$ cm$^{-3}$, enhanced collection of photogenerated carriers as well as a reduction of the barrier height for majority carriers at the back contact from 0.7 eV to 0.5 eV. The electronic properties of the back contact are
further improved by the introduction of a back contact buffer layer between the metallic part of the back contact and the CdTe layer. Efficiencies of 11.4% and 12.6% could be reached using antimony and Sb$_2$Te$_3$ back contact buffers, respectively. Highest performance of up to 13.6% is achieved with a MoO$_x$ back contact buffer layer. This material is found to transform from the as deposited MoO$_3$ to the metal-like, high work function compound MoO$_2$ upon solar cell processing explaining its suitability as a contact material to CdTe.

Finally, the developed substrate configuration CdTe solar cells are used to study the degradation mechanisms in CdTe solar cells. Such cells exhibit a good performance stability with 90% of the initial power output after 1000 hours of accelerated stress testing at 80 °C and ~1 sun illumination. This is enabled by the use of the novel doping process which allows to prevent two commonly observed degradation mechanisms, namely copper loss at the back contact and copper accumulation in the CdS layer. The remaining performance degradation of substrate configuration solar cells by 10% is found to be caused by a decrease in net acceptor concentration. This mechanism is not limited to substrate configuration but can also explain possible degradation of superstrate configuration CdTe solar cells.

The ability to grow substrate configuration solar cells with high $V_{oc}$ and fill factor offers a new perspective to research on CdTe solar cells and represents a first step towards the industrialization of CdTe solar modules on flexible metal foil. However, further research is required to improve the efficiency of substrate configuration solar cells to the value reached by superstrate configuration. Possible routes are to increase $J_{sc}$ by the use of alternative n-type materials like oxygenated CdS, to further reduce the back contact barrier by changing the properties of the back contact buffer layer or to increase hole densities and minority carrier lifetime by replacing the dopant or changing the dopant properties by alloying CdTe with isovalent elements.
Zusammenfassung (In German)


Im Verlauf dieser Arbeit werden verschiedene Prozesse zur Herstellung von CdTe/CdS Solarzellen in Substrat-Konfiguration entwickelt, womit Effizienzen von bis zu 13.6% erreicht werden können. Dabei werden der Superstrat-Konfiguration ebenbürtige $V_{oc}$ (~850 mV) und Füllfaktor (~75%) Werte erzielt. Durch die Anwendung von zwei separaten CdCl$_2$ Behandlungen von CdTe und CdS kann die Rekristallisation der CdTe Schicht von der Bildung des p-n Übergangs entkoppelt werden. Dieses Vorgehen führt zu einer rekristallisierten CdTe Schicht, Passivierung der CdTe Korngrenzen und einer verbesserten Qualität des p-n Übergangs, jedoch zu keiner erkennbaren Durchmischung von CdTe und CdS.

Ein neuartiges Konzept für die kontrollierte Dotierung der CdTe Schicht mit Kupfer oder Silber in Solarzellen in Substrat-Konfiguration wird vorgestellt. Die Dotierung wird durch die Verdampfung von weniger als einer Monolage Kupfer oder Silber auf der Cd-
Te Schicht und darauffolgendem Tempern erreicht. Dies ermöglicht Lochdichten von \( \sim 10^{14} \, \text{cm}^{-3} \), eine verbesserte Sammlung von erzeugten Ladungsträgern und eine Reduktion der Rückkontaktbarriere von 0.7 auf 0.5 eV. Der Kupfergehalt am Rück kontakt kann durch diese Methode drastisch reduziert werden. Eine weitere Verbesserung der elektronischen Eigenschaften des Rückkontaktes wird durch die Einführung einer Pufferschicht zwischen dem metallischen Teil des Rückkontaktes und der CdTe Schicht erreicht. Mit Rückkontaktpuffern aus Sb und Sb\textsubscript{2}Te\textsubscript{3} konnten Effizienzen von 11.4\%, respective 12.6\% erreicht werden. Die beste Effizienz von 13.6\% wurde mit einer Pufferschicht aus MoO\textsubscript{3} erzielt. Diese wandelt sich während der Prozessierung der Solarzelle von unterstoichiometrischem MoO\textsubscript{3} zu MoO\textsubscript{2}, welches eine metallische Leitfähigkeit und eine hohe Austrittsarbeit aufweist, um.


1.1 Photovoltaics

Recent history including major oil spills, numerous blackouts and even a nuclear disaster has clearly shown our need for clean, renewable and sustainable energy sources. As fossil fuels will run out in the foreseeable future and our need for energy is still rising alternatives have to be found quickly. Besides wind and hydro power solar energy is one of the most important renewable energy sources. Energy from the sun can either be made available by collecting the energy in form of heat (solar thermal) or by directly converting the sunlight into electricity (photovoltaics). Photovoltaics (PV) is one of the fastest growing renewable energy sources and it still offers tremendous potential. In 2013 the world’s cumulative installed PV capacity reached 139 GW, an amount capable of producing at least 160 TWh of electricity every year [1].

Today’s PV market is dominated by silicon based solar modules which account for about 90% of the annual PV production [2]. Although this technology is well established its potential for cost reduction is limited and the energy payback time rather long. In these aspects thin film PV is superior to silicon. High absorption coefficients of the absorber materials allow for thicknesses of the complete solar cell of only a few μm. This reduces the material and energy usage during production and therefore also production costs and energy payback time. Another important advantage of thin film solar cells is their suitability to be grown on flexible substrates such as polymers or steel foil. Apart from the numerous new application possibilities this fact enables the production to be carried out in a roll-to-roll process further reducing the production cost.
Various materials are already used in thin film solar cells. There are inorganic materials like Cu(In,Ga)Se$_2$ (CIGS), CdTe, Cu$_2$ZnSn(S,Se)$_4$ (CZTS) and amorphous silicon, the hybrid organic-inorganic CH$_3$NH$_3$PbI$_3$ (Perovskites) as well as dye-sensitized and organic materials. Each technology has its own advantages like high efficiency, abundant raw materials or low production costs. The up to date highest efficiencies achieved with various materials are given in Table 1.1.

<table>
<thead>
<tr>
<th>Technology</th>
<th>η (%)</th>
<th>Laboratory/Company</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>28.8</td>
<td>Alta Devices</td>
<td>[3]</td>
</tr>
<tr>
<td>crystalline Si</td>
<td>25.6</td>
<td>Panasonic</td>
<td>[3]</td>
</tr>
<tr>
<td>CIGS</td>
<td>21.7</td>
<td>ZSW</td>
<td>[4]</td>
</tr>
<tr>
<td>CdTe</td>
<td>21.5</td>
<td>First Solar</td>
<td>[5]</td>
</tr>
<tr>
<td>thin Si</td>
<td>21.2</td>
<td>Solexel</td>
<td>[3]</td>
</tr>
<tr>
<td>CZTSS</td>
<td>12.6</td>
<td>IBM</td>
<td>[3]</td>
</tr>
<tr>
<td>amorphous Si</td>
<td>10.2</td>
<td>AIST</td>
<td>[3]</td>
</tr>
<tr>
<td>Perovskite</td>
<td>20.1</td>
<td>KRICT</td>
<td>[6]</td>
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<tr>
<td>Dye-sensitized</td>
<td>11.9</td>
<td>Sharp</td>
<td>[3]</td>
</tr>
<tr>
<td>Organic</td>
<td>11.0</td>
<td>Toshiba</td>
<td>[3]</td>
</tr>
</tbody>
</table>

Table 1.1: Highest reported efficiencies for different kinds of solar cells.

### 1.2 CdTe thin film solar cells

Thin film solar cells usually consist of a p-n junction sandwiched between two electric contacts one of which has to be transparent to allow light to enter the solar cell. The electric field between the p and the n-type semiconductor allows to separate the electron hole pairs which are formed when a photon is absorbed in the solar cell and the current can be collected through the electric contacts. In this manner, light is directly transformed into electricity. Because electrons feature larger mobilities in semiconductors than holes the absorber is commonly used as the p-type side of the junction. Carriers generated in the n-type material are barely collected and therefore the n-type material should absorb as little photons as possible.
In CdTe solar cells the p-n junction is formed between a p-type CdTe absorber layer and an n-type CdS layer. As light has to enter from the n-type side of the junction to allow collection of the carriers where they are produced the electric contact to CdS has to be transparent and is called front contact (FC). The contact to the p-type CdTe can be opaque and is called back contact (BC). Figure 1.1 shows the energy band diagram of a CdTe thin film solar cell.

**Figure 1.1:** *Energy band diagram of a CdTe/CdS thin film solar cell. Incidence of light as well as separation and collection of electron hole pairs are indicated with arrows.*

CdTe solar cells hold the highest market share among all thin film technologies as they account for about 5% of the total annual PV production [2]. This is first of all due to the company First Solar Inc. the first thin film PV module manufacturer in the world to achieve 10 GW of installed capacity [7]. First Solar was also the first company to lower the module production costs below 1 $/Wp and in the mean time they have reached production costs as low as 0.63 $/Wp [8]. This company furthermore holds both the records for cell and module efficiency of CdTe PV with 21.5 and 17.5%, respectively [3, 5, 9].

In addition, CdTe solar cells offer the shortest energy pay-back time of all PV technologies which is around 3 times shorter than the one of conventional mono-crystalline silicon [2].
1.2.1 Device structure

The conventional device structure of CdTe solar cells is the so-called superstrate configuration first introduced by Adirovich et al. in 1969 [10]. In this architecture light enters the solar cell through the substrate which has to be transparent as shown in Figure 1.2a. This structure is well compatible with rigid glass substrates. However, the choice of flexible substrates is very limited due to restrictions on the transparency of the substrate. Highest efficiencies achieved on flexible substrates are 16.2% on flexible Corning Willow glass [11] and 13.8% on transparent polyimide foil [12, 13].

Figure 1.2: Schematic and scanning electron micrograph of CdTe solar cells grown in superstrate (a) and substrate (b) configuration. The yellow arrows indicate the direction of incident sun light.

The limitation of a transparent substrate can be overcome by reversing the deposition order of the solar cell layers such that light enters the cell from the side opposite to the substrate. This architecture is called substrate configuration and is depicted in Figure 1.2b. Growing solar cells in substrate configuration enables the use of opaque substrates such as flexible metal foils. Significant price reduction when growing on flexible substrates can be expected by implementation of high throughput roll-to-roll processing. The reversed deposition order furthermore allows better control over the p-n junction properties as the recrystallization of CdTe and the CdTe/CdS junction formation can be decoupled.

However, the reversal of the deposition order is not trivial and has resulted in low ef-
ficiencies in the past. The electrical back contact - the last layer to be deposited in superstrate configuration - becomes the layer which has to withstand all processing steps in substrate configuration. This raises the requirements on thermal and chemical stability of the material as a high contact quality has to be ensured in the finished device. Back contacts conventionally used for superstrate configuration cells do not fulfill these criteria. Additionally, the diffusion of impurities is changed upon reversal of the growth order, doping and layer interdiffusion therefore have to be reconsidered.

1.2.2 Layer properties and processing

1.2.2.1 Back contact

The formation of a good electrical contact to CdTe is challenging due to Schottky barrier formation at the metal-CdTe interface. As in thermal equilibrium the Fermi levels \( E_F \) of the metal and the semiconductor align the semiconductor bands have to bow at the interface forming a Schottky barrier to conserve the electron affinity of the semiconductor \( \chi_s \) and the metal work function \( q\Phi_m \). Figure 1.3a shows the energy band structure of a metal and a semiconductor before coming into contact. If the electron affinity of the semiconductor is large (as in case of CdTe) the bands bend downwards when a contact with a metal is established as shown in Figure 1.3b. In theory, the height of the Schottky barrier \( q\Phi_B \) which is measured between the top of the semiconductor valence band and the Fermi level at the metal-semiconductor interface is given by [14]:

\[
q\Phi_B = q\Phi_m - (\chi_s + E_G).
\]  

(1.1)

In case of CdTe this gives:

\[
q\Phi_B = q\Phi_m - (4.3\,\text{eV} + 1.5\,\text{eV}) = q\Phi_m - 5.8\,\text{eV}
\]  

(1.2)

implying that the barrier can only be reduced to zero if a metal with a work function of at least 5.8 eV is applied.

However, due to its covalent nature CdTe does not follow Schottky theory rigorously. To balance surface charges the bands of CdTe bend downwards towards its surface giving rise to a space charge region. At the point when surface charge and space charge
Figure 1.3: Energy band diagrams of a metal and semiconductor before (a) and after (b) being contacted illustrating the process of Schottky barrier formation. Two approaches, the use of a high work function material (c) or the inclusion of a strongly p-type doped layer (d, green) are used to enable a good contact.

are equal the bands are fixed. This effect is called Fermi level pinning. The Fermi level pinning in CdTe further hinders the formation of a (quasi-)ohmic contact.

There are two approaches how to enable a good contact to CdTe. Both rely on the introduction of a buffer layer between the metallic part of the back contact and the CdTe. In the first approach, depicted in Figure 1.3c, a high work function material is used as buffer layer thus reducing the barrier height and allowing holes with less energy to overcome the barrier. For the second approach a strongly p-type doped layer is included at the metal-CdTe interface (cf. Figure 1.3d). Due to the high acceptor density the space charge region and therefore also the barrier become narrower. This enables holes to tunnel through the barrier [15].
1.2. CdTe thin film solar cells

In superstrate configuration the most common buffer layer is the heavily p-type Cu$_x$Te. It is mostly formed by preferential Cd etching of the CdTe surface followed by the addition of copper to the surface [16–18]. As metallic part of the back contact often gold is used and the contact is finalized with an annealing step. Other buffer layers used include ZnTe:Cu [19], Sb$_2$Te$_3$ [20], Sb [20], As$_2$Te$_3$ [21] and MoO$_3$ [22]. Generally, efficiencies are increased with the addition of copper to the back contact.

Back contact buffer layers usually cannot easily be transferred from superstrate to substrate configuration. Due to the reversed deposition order etching of the CdTe surface is not possible. Also thermally unstable contact materials like copper or gold should be avoided because of the enhanced diffusion during processing.

1.2.2.2 CdTe layer

CdTe is an excellent material as absorber for thin film solar cells with its direct band gap of 1.49 eV at 300 K and its high absorption coefficient (> $10^4 \text{ cm}^{-1}$) for photons with energies above the band gap [23]. The theoretical limit to the efficiency of CdTe based solar cells is about 30% under AM1.5 irradiation calculated from the Schockley-Queisser detailed balance limit [24]. The simple phase diagram of CdTe and its congruent evaporation characteristics enable high-rate deposition by various deposition techniques [23]. Common methods are close space sublimation (CSS) [25], vapor transport deposition [26], sputtering [27], metal organic chemical vapor deposition (MOCVD) [28], electrodeposition [29] and high vacuum evaporation (HVE) [18].

CdTe grows in zincblende structure and allows both n- and p-type doping. In CdTe solar cells p-type CdTe is used and the acceptor doping is mainly caused by in-diffusion of copper [30]. In superstrate configuration copper is supplied from the back contact. Also the CdCl$_2$ treatment which occurs in the presence of oxygen influences the acceptor concentration of CdTe [31–33].

The polycrystalline nature of the CdTe absorber influences the performance of CdTe solar cells. Grain boundaries (GBs) can induce trap states which can serve as recombination centers for photogenerated carriers and should therefore be passivated [34]. The better performance achieved with polycrystalline compared to crystalline CdTe solar cells is explained by a hole depletion of the GBs which assists the separation of generated charge carriers [35].
1.2.2.3 CdS layer

As n-type part of the p-n junction usually CdS is used. The main function of this layer is the proper band alignment of valence and conduction band to the CdTe absorber. CdS can be grown by various means as HVE [36], CBD [37], sputtering [27], CSS [25] and MOCVD [28]. CdS grows intrinsically n-type, has a band gap of ~2.4 eV and produces no conduction band offset at the CdTe/CdS interface [38,39]. Charge carriers produced in this layer are barely collected therefore the absorption losses in CdS are desired to be minimized. This is achieved by reducing the thickness of the CdS layer. A very thin CdS layer, however, is prone to have holes leading to shunting between the CdTe layer and the front contact. This shunting can be prevented by introducing a highly resistive layer between the CdS and the conductive front contact.

1.2.2.4 CdCl₂ treatment

For the production of highly efficient CdTe solar cells a heat treatment in a chlorine and oxygen containing ambient is necessary [40–42]. Chlorine can be introduced in different ways of which the most common is the deposition of CdCl₂. The temperature needed for the treatment is in the range of 400 - 500 °C. In superstrate configuration the CdCl₂ treatment is done after the deposition of CdTe, meaning it affects the CdTe absorber layer as well as the n-type CdS layer. In substrate configuration the treatment can be applied after the deposition of CdTe, after the deposition of CdS or after each.

The CdCl₂ treatment has a strong influence on the structure of the CdTe and CdS layers and their interface. The treatment induces recrystallization and grain growth of the CdTe layer where chlorine acts as sintering flux enhancing the growth and the coalescence of the grains [43]. Also the stacking faults in CdTe are reduced and the texture changes [36, 44].

The lattice constants of CdTe and CdS differ by about 10% possibly leading to interface defects [43, 45]. This effect can be moderated by intermixing of CdTe and CdS caused by the CdCl₂ treatment where CdS₁₋ₓTeₓ forms at the interface. The intermixing partially consumes the CdS layer. This is beneficial as it enhances the spectral response in the short wavelength region as long as there remains a covering CdS layer. When the intermixing gets excessive and at some spots all the CdS is converted to CdS₁₋ₓTeₓ weak junctions form thus decreasing the device performance [44].
1.3. Aim of the thesis

The aim of this thesis is to develop a process for CdTe solar cells grown in substrate configuration. In order to achieve this a back contact has to be identified which enables a low resistive contact to CdTe after the subsequent processing steps. In addition, a novel approach has to be found how to introduce sufficiently large acceptor concentrations in substrate configuration solar cells and decouple the doping from the back contact formation. Last but not least the performance stability of substrate configuration solar cells should be studied and if possible improved. Understanding present degradation mechanisms can help to reveal stability limitations and to develop strategies of avoiding them.

1.2.2.5 Front contact

Light enters the solar cell through the front contact therefore the front contact material has to be transparent in the wavelength region between 300 and 850 nm. Obviously, it also has to offer a high electrical conductivity as it links the solar cell to an external circuit. There is always a tradeoff between conductivity and transparency because the free charge carriers needed to transport current cause free carrier absorption (i.e. the excitation of an electron by a photon with energy below $E_F$). These requirements are met by a material class called transparent conductive oxides (TCOs). Commonly used TCOs for PV applications are fluorine doped SnO$_2$ (FTO) [46], tin doped In$_2$O$_3$ (ITO) [47], aluminum doped ZnO (AZO) [18] and Cd$_2$SnO$_4$ [25] which can be applied by different deposition techniques including sputtering [18, 25], chemical vapor deposition [48] and spray deposition [49].

In highly efficient CdTe solar cells a highly resistive and transparent (HRT) layer is introduced between the TCO and the CdS to limit electrical losses at local shunts and grain boundaries. Materials commonly used for this purpose are SnO$_2$ [40], In$_2$O$_3$ [50], ZnO [18] and Zn$_2$SnO$_4$ [25].
Chapter 2

Solar cell processing and characterization

2.1 Sample preparation

2.1.1 CdTe solar cells in substrate configuration

In this section, the typical treatment and doping procedure used for samples presented in Chapters 4-6 is described. A description of the parameters used during optimization of the treatment procedure can be found in Section 3.2.

2.1.1.1 Substrate and back contact

The solar cells were grown on Corning 7059 borosilicate glass (BSG) substrates. The substrates were hand washed with water and soap and subsequently put into a series of ultrasonic baths; one containing a mixture of soap and water and two filled with deionized water (18 MΩ). Finally, the substrates were blow dried with a nitrogen gun.

As metallic back contact molybdenum was DC-sputtered at a base pressure of about $1 \times 10^{-7}$ mbar. The contact consists of three consecutively sputtered molybdenum layers. First an adhesion layer is sputtered at high energy (4 W/cm²), $3 \times 10^{-3}$ mbar argon partial pressure) for 90 seconds. This is followed by a layer sputtered at medium energy (4 W/cm²), $7 \times 10^{-3}$ mbar argon partial pressure) enabling high conductivity and small compressive stress. The last layer is deposited at low energy (1.7 W/cm²), $8 \times 10^{-3}$ mbar argon partial pressure) enabling high conductivity and small compressive stress.
mbar argon partial pressure) what leads to a higher surface roughness beneficial for the adhesion of the back contact buffer or the CdTe. The resulting trilayer system has a total thickness of about 600 nm and a sheet resistance of 0.2 $\Omega/\square$.

To lower or narrow the Schottky barrier between molybdenum and CdTe a back contact buffer layer is introduced. Different materials were tested for this purpose (for details on the motivation for the selected materials refer to Section 3.3). Whenever more than one material was used as back contact buffer the materials are given in the order of growth starting from the material in contact with the metallic back contact layer. The following materials were evaporated from molybdenum boats in a high vacuum evaporation (HVE) system at a typical base pressure of $1 \times 10^{-6}$ mbar onto unheated substrates: Cu, Sb, Te as well as MoO$_x$ and Sb$_2$Te$_3$ (both from the compound). Sb$_2$Te$_3$ was furthermore also deposited by coevaporation of Sb and Te in the same system at various substrate temperatures. For the formation of CuO$_x$, evaporated Cu layers on molybdenum were annealed in air at 400 °C.

MoO$_x$ layers were also prepared by reactive radio frequency (RF) and direct current (DC) sputtering in mixed oxygen-argon atmosphere either from a metallic molybdenum target (RF and DC) or from a ceramic MoO$_3$ target (RF). RF sputtering was performed in an AJA Orion-5-UHV system with a base pressure of $2 \times 10^{-8}$ mbar and a sputter power of 7.4 W/cm$^2$. During sputtering the total gas pressure was $3 \times 10^{-3}$ mbar and the O$_2$ content in the O$_2$+Ar mixture was changed from 20% to 50%. The substrate was placed onto a rotating holder which could be heated up to 400 °C. Pulsed DC sputtering of MoO$_x$ was performed at room temperature in the same system as molybdenum sputtering without breaking the vacuum. A sputter power of 4 W/cm$^2$, a frequency of 200 Hz, a reverse time of 1.5 µs, a total sputtering pressure of $4 \times 10^{-3}$ mbar and an oxygen content of 55% were used.

The typically used back contact buffer is a 100 - 150 nm thick, evaporated MoO$_x$ layer.

### 2.1.1.2 CdTe deposition, treatment and doping

4-7 µm of CdTe were deposited from the compound by HVE (base pressure $\sim 5 \times 10^{-7}$ mbar) at 350 °C substrate temperature and a rate of 10-15 Å/s. A CdCl$_2$ treatment of the CdTe layer (called CdTe treatment) was carried out by deposition of 400 nm of CdCl$_2$ by HVE and annealing in a tube furnace for 25 minutes at 435 °C in an am-
2.1. Sample preparation

bient consisting of 40% oxygen and 60% argon. Subsequently, doping was carried out by evaporation of small amounts (0.08 to $8.0 \times 10^{15}$ atoms per cm$^2$) of copper or silver followed by annealing at 400 °C in oxygen/argon mixture (40%/60%) to promote diffusion into CdTe. In case of undoped samples this step was omitted. Best efficiencies are achieved by using $1.0 \times 10^{15}$ atoms cm$^{-2}$ of copper or $0.8 \times 10^{15}$ atoms cm$^{-2}$ of silver corresponding to an equivalent layer thicknesses of 1.2 Å and 1.0 Å, respectively.

Arsenic doping was performed by placing as-deposited CdTe thin films on standard Mo/MoO$_x$ back contacts together with pieces of arsenic (4-1000 mg) in a glass ampoule. The ampoules were then evacuated and sealed and subsequently annealed at 500 °C for 18 hours to allow evaporation and incorporation of arsenic into the CdTe layer. If an additional CdCl$_2$ treatment and copper doping were performed, standard treatments as described in Section 2.1.1.2 were performed after arsenic doping.

2.1.1.3 CdS deposition and treatment

CdS was deposited by chemical bath deposition (CBD) at 70 °C from a precursor solution of cadmium acetate (0.0016 mol/l), ammonium hydroxide (1.48 mol/l) and thiourea (0.022 mol/l) in deionized water. The solution was preheated and stirred for 1 minute before the samples were immersed. Samples were left inside the bath for typically 19-20 minutes, in this time around 60 nm of CdS were deposited. Subsequently, a CdCl$_2$ treatment of the CdS layer (called CdS treatment) was performed by deposition of 100 nm of CdCl$_2$ by HVE and annealing for 25 minutes at a temperature between 360 and 400 °C in an ambient consisting of 50% oxygen and 50% argon. After the CdS treatment a second CdS layer was deposited with the same parameters as the first one. The final CdS thickness therefore sums up to around 120 nm.

2.1.1.4 Front contact

The front contact consists of an i-ZnO/ZnO:Al bilayer deposited by reactive RF magnetron sputtering. i-ZnO was sputtered at 1.9 W/cm$^2$ and $4 \times 10^{-3}$ mbar (3% oxygen) for typically 12 minutes. ZnO:Al was sputtered from a ZnO target containing 2 wt% Al$_2$O$_3$ at 2.5 W/cm$^2$ and $1 \times 10^{-3}$ mbar (3% oxygen) for typically 10 minutes. This lead to layer thicknesses of 250 and 350 nm for i-ZnO and ZnO:Al, respectively. No intentional heating was applied in both steps. In most cases, a metallic Ni/Al grid (50/2000 nm) was
applied by electron beam evaporation (base pressure $\sim 1 \times 10^{-6}$ mbar, rates 5/20 Å/s) to increase the conductivity. In some cases, an anti-reflective (AR) coating consisting of $\sim 85$ nm MgF$_2$ was deposited by electron beam evaporation (rate 1-5 Å/s). The cell area was defined by mechanical scribing and the typical cell area was 0.3 or 0.6 cm$^2$.

2.1.1.5 Post-processing annealing

Finished solar cells were annealed at a temperature between 190 and 250 °C (but mostly 210 °C) for 10 minutes in air followed by a fast cool down to room temperature on a copper plate. The effect of this post-processing annealing is discussed in Section 4.4.2.

2.1.2 CdTe thin films on glass

To assess the CdTe layer properties by Hall and transmission line method (TLM) measurements $\sim 5$ μm thick CdTe layers were directly grown on washed BSG. The CdTe layers were treated and doped in the same manner as the solar cells described in Section 2.1.1.2. Two different contacting methods were used:

**Top contact**  For Hall measurements, to assess the specific resistivity of (doped) CdTe and for contact resistance measurements in superstrate configuration the layers were contacted by evaporation of Au through a mask. The mask has openings in van der Pauw and in TLM geometry (cf. Section 2.2.5.1).

**Bottom contact**  To measure the contact resistance in substrate configuration, Mo/MoO$_x$ contacts as used for substrate configuration solar cells were deposited on BSG. Contacts in TLM geometry were then defined by partially removing the Mo/MoO$_x$ layers with a laser. Only then the CdTe layer was deposited. Hence, the contacts also underwent the CdTe deposition, treatment and doping in the very same manner as the back contact in substrate configuration solar cells does.

Finished layer stacks were heated to 210 °C followed by a fast cool down to room temperature.

Arsenic doped CdTe thin films on glass were prepared alongside the arsenic doped solar cells as described in Section 2.1.1.2.
2.2 Characterization

2.2.1 Structural characterization

2.2.1.1 Electron microscopy and X-ray spectroscopy

Structural properties of layers and solar cells were analyzed by scanning electron microscopy (SEM) using a FEI Nova NanoSEM 230. To avoid electrostatic charging samples were coated with a thin layer of carbon in some cases. The typical accelerating voltage used was 5 kV. In order to get images of layer cross-sections samples were broken over an edge (with the layer facing upwards). Elemental composition analysis was conducted using energy dispersive X-ray spectroscopy (EDX) at a relatively low accelerating voltage of 5 kV to minimize the excitation volume.

2.2.1.2 X-ray diffraction

Ex-situ x-ray diffraction measurements were performed with a Siemens Diffractometer 5000 using Cu-Kα radiation (\( \lambda = 1.54184 \) Å) in \( \theta-2\theta \) geometry. The lift-off sample presented in Section 3.3.2 was measured in grazing incidence x-ray diffraction (GIXRD) configuration with an incident angle of 1.0°. The patterns were scanned either from 10° to 50° or from 20° to 80°. The step size and acquisition time were 0.05° and 0.5 sec per step, respectively.

In-situ GIXRD patterns were obtained using a PANalytical X’Pert PRO MPD system with Cu-Kα radiation (\( \lambda = 1.541 \) Å) at 45 kV and 40 mA. The incident angle was 1.0°. The diffraction patterns were scanned from 20° to 80° (2θ) with an angular step interval of 0.05° and 0.5 sec per step. The samples were heated up to 400 °C in air or nitrogen atmosphere with a heating rate of 10 °C/min.

The preferred orientation of certain crystal planes (hkl) was determined by calculating the texture coefficients (TC) with the formula [51]:

\[
TC(hkl) = \frac{I(hkl)/I_0(hkl)}{(1/N) \sum N I(hkl)/I_0(hkl)} \tag{2.1}
\]

where \( I \) is the measured intensity, \( I_0 \) is the standard intensity of the corresponding powder and \( N \) is the reflection number.
2.2.2 Layer thickness measurements

Layer thickness of CdTe, ZnO and Mo was determined by a surface profiler (Ambios Technology XP-1) while the thickness and evaporation rate of evaporated Cu, Au, MoO$_x$, Sb, Sb$_2$Te$_3$, CdTe, CdCl$_2$, Ni, Al and MgF$_2$ was measured by a quartz crystal microbalance (Inficon XTM/2) during the growth process. The thickness of the CdS layers was extracted from Transmission Electron Micrographs.

2.2.3 Elemental distribution and concentration

2.2.3.1 Rutherford back scattering

To determine the O/Mo ratio in Section 3.3.2, Rutherford back scattering (RBS) measurements of MoO$_x$ layers deposited on Si wafers were performed. In the used setup He atoms with 2 MeV kinetic energy (6 MV Van de Graaff EN tandem type accelerator) hit the sample and back-scattered particles were detected by a silicon detector.

2.2.3.2 Secondary ion mass spectroscopy

Depth dependent elemental distribution was investigated by secondary ion mass spectroscopy (SIMS) with a TOF-SIMS$^5$ from ION-TOF using dual beam depth profiling. For the depth profiles with high mass resolution and low lateral resolution Bi$^+$ ions with energy of 25 keV and a current of 1 pA were used as primary ions and an area of (100 µm)$^2$ was analyzed. For the investigation of electropositive ions, sputtering was done using O$_2^+$ (2 kV, 400 nA) and positive secondary ions were detected. For the investigation of electronegative ions, sputtering was done using Cs$^+$ (2 kV, 120 nA) and negative secondary ions were detected. In both cases, an area of (300 µm)$^2$ was sputtered for 2 s after each (most cases) or after 10 (Figure 6.2) analysis steps.

Quantification of SIMS copper counts in CdTe was done by comparing the normalized copper SIMS signal (${}^{63}$Cu$^+$/${}^{114}$Cd$^+$) in the absorber with the normalized copper SIMS signal of a CdTe thin film on glass/molybdenum with a known copper concentration. The copper concentration in the CdTe thin film was determined using inductively coupled plasma mass spectrometry (ICPMS).
2.2.3.3 Inductively coupled plasma mass spectroscopy

For quantification of copper traces in copper doped, CdCl₂ treated CdTe thin films on glass/Mo, an Agilent 7500ce inductively coupled plasma mass spectroscopy (ICPMS) apparatus was used, performing external calibration from certified single elemental standards (1 mg/ml). Only high purity PE-LD or Teflon vessels were employed during sample preparation and measurement. For the analysis, approximately 25 mg of the absorber were scratched with the tip of a glass pasteur pipette from the molybdenum layer and dissolved in 10 ml 65% nitric acid. Afterwards, the acidic solution was adjusted to a final volume of 50 ml with deionized water. For quality assurance, a reference material (NIST SRM 1643e) and spiking of known copper concentrations to the measurement solution was conducted, resulting in recoveries not lower than 90%.

2.2.4 Optical characterization

Transmission and reflection spectra between 200 and 1500 nm were recorded with a Shimadzu UV 3600 spectrometer in 2 nm steps and a slit width of 32 nm. The energy gap (E_G) of the layers was determined by calculating the absorption coefficient

\[ T = (1 - R)e^{-\alpha x} \]  

(2.2)

and linearly extrapolating the Tauc plots, assuming an indirect band transition \((\alpha h\nu^{1/2}\) vs. \(h\nu)\).

2.2.5 Electrical characterization

2.2.5.1 Resistance measurements

Sheet resistance of molybdenum and ZnO:Al doped films was measured by a four-point probe technique using a SD-600 from Nagy Instruments.

Transmission line method (TLM) measurements, as introduced by Shockley [52, 53], were used to determine specific resistivities of (doped) CdTe as well as the contact resistances. For this measurement contact stripes with well-defined distances x to each other (e.g. 0.2 mm, 0.5 mm, 1 mm and 2 mm) were deposited. The current-voltage
(I-V) characteristics for all contact distances were measured by four-point probe in the dark at room temperature with a Keithley 2400 source meter (cf. Figure 2.1a). The resistance for each contact distance is given by Ohm’s law and was obtained by linear interpolation of the current-voltage plot. The resistance values are plotted against the contact distance as shown in Figure 2.1b. From the slope of the linear fit of the data points $\frac{\Delta R}{\Delta x}$ the specific resistivity $\rho$ can be calculated by:

$$\rho = \frac{\Delta R}{\Delta x} \cdot l \cdot d \quad (2.3)$$

where $l$ is the contact length and $d$ is the CdTe thickness.

The contact resistance equals half the y-intercept of the linear fit, since the current always travels through two contacts.

$$\Delta R_{C} = \frac{1}{2} \Delta R$$

**Figure 2.1:** For TLM measurements I-V characteristics between contacts with different distances are recorded (a). The contact geometry is shown in the inset drawing. Linear interpolation of the I-V data gives the resistance values $R$ for the different contact distances $x$ (b). From the slope of the linear fit the specific resistivity and from the intercept with the y-axis the contact resistance can be calculated.

### 2.2.5.2 Hall effect measurements

Hole densities and partly also in-plane resistivities of doped CdTe films were measured with an HMS 3000 Hall effect measurement system at room temperature in the dark.
2.2. Characterization

Measurements were performed several hours after the final annealing to ensure a stable acceptor concentration during measurement. Each measurement was carried out ten times and the mean value was taken.

2.2.5.3 Current-Voltage characteristics and spectral response

Current-Voltage (J-V) measurements were performed in a steady-state sun simulator under simulated standard testing conditions (STC) (AM1.5G, 1000 W/m², cell temperature 25 °C).

The spectral response of the solar cells was measured with the external quantum efficiency (EQE) technique. EQE measurements were performed with a 900 W white light helium lamp, a chopping frequency of 360 Hz, a dual grating shape monochromator and a calibrated c-Si reference solar cell. Measurements were taken at 25 °C with white light bias of around 0.5 suns. The short circuit current density under AM1.5G was calculated from spectral response measurements using the reference spectrum from IEC 60904-3 Ed.2. Absorber band gaps were calculated from the EQE measurements by extrapolating the linear part of the \((hνEQE)^2\) vs. \(hν\) plot.

2.2.5.4 Capacitance measurements

Capacitance-voltage (C-V) measurements of solar cells were performed in dark with an Agilent E4980A precision LCR meter at a frequency of 300 kHz, an oscillating voltage of 50 mV, and bias voltages between -1.5 and +1.0 V. Assuming the solar cell to be a plate capacitor with an abrupt one-sided n⁺-p junction the apparent acceptor concentration \(N_a\) of the p-doped side can be written as [14, 54]:

\[
N_a(x) = \frac{-2}{q\epsilon_0\epsilon_r A^2} \left( \frac{d(1/C^2)}{dV} \right)^{-1}
\]

(2.4)

with the apparent profiling depth \(x = \epsilon_0\epsilon_r A/C\), the elemental charge \(q\), the vacuum permittivity \(\epsilon_0\), the relative permittivity \(\epsilon_r = 10\) and the area of the solar cell \(A\). The apparent acceptor concentration can be read from the minimum of the \(1/C^2\) vs. \(V\) plot, whereas the width of the space charge region (SCR) at 0 V can be calculated from the formula for the capacitance of a plate capacitor:
\[ C = \epsilon_0 \epsilon_r A/d_{SCR}. \] (2.5)

### 2.2.5.5 Temperature dependent J-V measurements

To measure the majority carrier barrier height at the back contact the method proposed by Koishiyev [55] was used. For this purpose, we recorded temperature dependent dark \( J-V \) using a Keithley 2400 Source Meter in a four-wire connection configuration. Temperature was controlled in the range of 183 K to 303 K using a liquid-nitrogen-cooled cryostat. From the dark \( J-V \) characteristics we extracted the turning current \( J_T \); the current at which the rollover sets in [9]. The turning current equals the reverse saturation current of the back contact diode visible in the rollover in the \( J-V \) characteristics caused by the back contact barrier and is related to temperature by [14, 56]:

\[ J_T = A * T^2 * e^{-q\Phi_B/kT} \] (2.6)

where \( A \) is the Richardson constant. By drawing an Arrhenius plot of \( \ln(J_T/T^2) \) vs. \( 1/T \), \( q\Phi_B \) can be calculated directly from the slope of the linear fit.

### 2.2.5.6 Time-resolved photoluminescence

Time-resolved photoluminescence (TRPL) was used to measure the minority carrier lifetime (MCLT) in the CdTe layer of the solar cells.

TRPL measurements presented in Chapter 4 was measured with a near infrared compact fluorescence lifetime spectrometer C12132 by Hamamatsu using a YAG excitation laser with a wavelength of 532 nm, a spot size of 3 mm and an excitation power of 42.4 mW and a repetition rate of 15 kHz. The system had a time resolution of approximately 0.2 ns. The detection wavelength was set to the photoluminescence (PL) maximum at 825 nm and light was detected using a photomultiplier tube. MCLT was evaluated using deconvolution and fitting of the initial section of the PL decay with a single exponential function [57]. High laser powers were used in the presented experiments to be in the region of constant MCLT and to characterize the recombination properties in the CdTe layer in the presence of a p-n junction [58].
2.2. Characterization

For TRPL measurements presented in Chapter 6 a FluoTime 300 from PicoQuant GmbH was used. A 639 nm diode laser with pulse duration of 92 ps was used as excitation source. The number of photons per area and pulse was approximately $5 \times 10^{12}$ cm$^{-2}$ and the luminescence decay was measured again at 825 nm.

2.2.5.7 Electron beam-induced current

Electron beam-induced current (EBIC) measurements were performed to identify the position of efficient charge carrier collection in the solar cell. EBIC measurements were performed in a FEI Strata 235 Dual Beam focused ion beam and secondary electron microscopy at accelerating voltage of 25 kV and spot size 3 without applied bias at the cell. The current was measured with a SR570 Preamplifier from SRS at a gain of $10^7$. Samples were prepared by mechanical cleaving and electrical contacts to the FC and BC were made with silver paste and indium wires.

2.2.6 SCAPS simulations

The 1-D solar cell simulation software SCAPS (version 3.1.02) [59] was used for simulations of $J-V$ and EQE measurements. The SCAPS definition file CdTe-base.def (22.5.2009) was used for simulation of the optimally doped sample with the following modifications: CdTe and CdS layer thicknesses were set to 5 µm and 100 nm, ZnO electron affinity was set to 4.4 eV instead of using the value of SnO$_x$, and hole capture cross-section of the donor-type mid-gap defect in CdTe was set to $1 \times 10^{-13}$ cm$^2$. The majority carrier barrier height at the back contact was raised to 0.46 eV and reflection was reduced to 6%. To simulate the relatively deep acceptor-type defect states of copper in CdTe, the shallow acceptor concentration in CdTe was set to zero and an acceptor-type defect with energy of 220 meV above the valence band (Cu$_{Cd}$ [60]) was introduced. Acceptor-type defect concentration was set to $6.5 \times 10^{14}$ cm$^{-3}$ and hole and electron cross-sections of $1 \times 10^{-15}$ cm$^2$ were used. The concentration was chosen to result in a hole density of $3.8 \times 10^{14}$ cm$^{-3}$ in the CdTe layer outside the SCR consistent with the mean value determined by Hall effect measurements.

In Section 4.3.6, the cell without copper doping was simulated by using the aforementioned values with the concentration of the acceptor-type defect set to zero. In addition, the majority carrier barrier height at back contact was set to 0.7 eV. For simulation of the
sample with excessive copper doping, the values of the optimally doped sample were used but the concentration of the acceptor-type defect was increased to $1 \times 10^{15}$ cm$^{-3}$. Furthermore, a compensating donor-type defect was introduced with concentration of $9 \times 10^{14}$ cm$^{-3}$, energy of 380 meV below the conduction band [Cu$_i$ [60]], and electron and hole capture cross-sections of $1 \times 10^{-11}$ cm$^2$ and $2 \times 10^{-14}$ cm$^2$, respectively.

For the calculation of the acceptor ionization degree in Section 4.4.2 the CdTe thickness was set to 10 µm in order to eliminate the junction influence. A single acceptor was introduced and concentration and depth were varied as shown in Figure 4.10. The ionization degree was defined as minimum acceptor defect occupation (around the center of the CdTe).

For the simulation of the stressed device in Chapter 6 the acceptor concentration was lowered to $3.3 \times 10^{14}$ cm$^{-3}$ compared to the optimally doped device with all other parameters remaining unaltered. To simulate what happens when only the back contact barrier increases its value was raised from 0.46 to 0.52 eV while keeping the acceptor concentration at $6.5 \times 10^{14}$ cm$^{-3}$.

### 2.2.7 Accelerated stress testing

A setup for accelerated stress testing (AST) was built and improved during this thesis. The tests were conducted in a Memmert VO 500 vacuum oven which was evacuated and refilled with dry synthetic air or nitrogen repeatedly to minimize moisture during stress. Light was supplied by white LEDs and intensity was adjusted to generate a comparable $J_{sc}$ in mounted cells as for 1 sun AM1.5G illumination. Samples were placed on a heating plate and contacted in four point probe geometry. ASTs presented in this thesis were all conducted at 80 °C. During stressing cells were operated at MPP which was tracked using a perturb-and-observe algorithm. $J$-$V$ characteristics of cells under stress were measured in-situ (at 80 °C) with an Agilent source meter at 30 minutes intervals. An exception are the AST investigations shown in Section 3.4, where the cells were placed in a box facing a halogen lamp resulting in a stressing temperature of ~50 °C and an illumination intensity of ~0.5 suns.
Chapter 3

Processes for substrate configuration
CdTe solar cells

This chapter is in part based on the following publications:
Parts of the results of this chapter were obtained during the Semester thesis of Curdin Bächler [61] and the Master thesis of Luisa Kneer [62].

3.1 Introduction

The growth of CdTe solar cells in superstrate configuration was intensively investigated in the past, and is now well established and industrialized. Its substrate configuration counterpart, on the other hand, was examined significantly less and the record efficiency at the beginning of this thesis was 7.8% [63] - less than half the record value of superstrate configuration at that time [37]. However, the growth in substrate configuration offers several advantages that justify the efforts to overcome the challenge of reversing the deposition order (cf. Section 1.2.1).
The main challenges for achieving high efficiencies in substrate configuration are the formation of a quasi-ohmic electrical back contact which withstands all the subsequent deposition and annealing steps for activation, as well as the formation of the p-n heterojunction with minimized recombination losses. The high electron affinity and relatively large band gap of CdTe cause a severe Schottky barrier formation at the metal-CdTe interface with most of the metals [64]. Additionally, CdTe shows strong Fermi level pinning due to its covalent nature. The common approach to circumvent these problems is the introduction of a buffer layer between the absorber and the metallic part of the back contact. This buffer layer can either lower the Schottky barrier height when a high work function material is used or the barrier can be narrowed by the inclusion of a p-type layer with high acceptor density allowing the holes to tunnel through the barrier [15].

### 3.2 Absorber properties and junction formation

In superstrate configuration the formation or activation of the p-n junction between CdTe and CdS is promoted by the CdCl$_2$ annealing treatment of the CdS/CdTe stack. This causes grain growth, recrystallization and enhancement of the p-type conductivity of CdTe as well as intermixing at the CdS/CdTe interface relaxing the lattice mismatch and thereby reducing the number of interface defects [23]. These beneficial effects of the CdCl$_2$-treatment would also be desirable for substrate configuration, however, the treatment procedure has to be adapted due to the reversed deposition order. Strong intermixing and a total consumption of the CdS layer were found when the as deposited CdS on CdTe stack was treated together for 25 minutes at 420 °C in the presence of CdCl$_2$ in substrate configuration. This intermixing can be observed in the XRD measurements (cf. Fig. 3.1) by a broadening of the CdTe peaks towards larger angles implying the emergence of Te rich CdS$_x$Te$_{1-x}$. The broadness of the peaks indicates the presence of a range of alloys with a S content of up to x=0.04 calculated from Vegard’s law [65]. As the solar cells processed with this procedure showed very low efficiencies even when an additional CdS layer was deposited after the treatment, we decided to treat the layers separately. The CdCl$_2$ annealing treatment of the CdTe layer will be referred to as CdTe treatment and the treatment of the CdS on top of the treated CdTe stack as CdS treatment.
3.2. Absorber properties and junction formation

The CdTe treatment at 420 °C for 25 minutes resulted in a CdTe grain growth from less than one µm to a few µm similar to that observed in superstrate configuration (Figure 3.2). Also the texture change from a strong preferential orientation in cubic (111) direction with a texture coefficient of TC(111)=3.8 to a more random structure with TC(111)=1.3 as observed in XRD measurements (Fig. 3.3) proves the similarity of the recrystallization behavior of the absorber layer in both configurations. A comparison of the texture coefficients for both configurations is given in Table 3.1. However, as the CdS is not yet deposited, higher treatment temperatures can be applied in substrate configuration leading to even further grain growth and therefore a reduction of grain boundary to bulk ratio. Increasing temperature of the CdTe treatment leads to better $V_{oc}$ and fill factors (see Figure 3.4). However, at a temperature of 460 °C crack formation and delamination of the CdTe layer occurs. The possibility of treating the CdTe layer at higher temperatures before the CdS deposition permits a better control over the heterojunction formation and interface properties. This is an advantage of using substrate configuration as the temperature of the CdCl$_2$-treatment in superstrate configuration is limited at the point where the intermixing gets excessive and the CdS layer gets totally consumed in the CdTe.

![Figure 3.1: X-ray diffractograms of the CdTe 311 peak showing CdS-CdTe intermixing before (blue) and after (red) the treatment in case of CdTe and CdS treated together (a) and the absence of intermixing when CdTe and CdS are treated separately (b).](image-url)
Chapter 3. Processes for substrate configuration CdTe solar cells

3.2.2 The CdS treatment

CdS from CBD consists of small crystals (20-50 nm) that smoothly cover the CdTe grains. After the CdS treatment at 400 °C the CdS has recrystallized to an approximately μm sized plate like structure, randomly distributed on the surface (Fig. 3.5).

Figure 3.6 shows the XRD patterns of CdS on treated CdTe before and after the CdS treatment. The as deposited CdS is mainly oriented in the cubic (111) direction. Upon the CdS treatment the CdS undergoes a phase transformation from the cubic zincblende to the hexagonal wurtzite structure with a random orientation. This can be explained
by the fact that the wurtzite structure is more stable in CdS films at high temperatures than the zincblende [66]. The presence of CdCl$_2$ during annealing in air has been shown to promote recrystallization of CBD deposited CdS and to prevent its oxidation [67].

The change of microstructure and phase of the CdS might impact the device. The band gap of hexagonal CdS is reported to be 2.5 eV exceeding the value for cubic CdS by 0.1 eV hence allowing for enhanced response in the short wavelength range [68].
Figure 3.5: SEM pictures of the CdS layer deposited by CBD on CdCl₂-treated CdTe before (left) and after (right) the CdS treatment at 400 °C.

Figure 3.6: Comparison of the XRD patterns of chemical bath deposited CdS before and after the 2nd treatment. Black labels correspond to CdTe and orange labels to CdS peaks.

The XRD measurements give no evidence that the CdTe and CdS layers intermix during the CdS treatment (cf. Figure 3.1 b) although this might be difficult to deduce from XRD measurements considering small changes in lattice spacing depending on the amount of intermixing. However, another indication for this can be found in the absorber band gaps measured by quantum efficiency measurements.

In Figure 3.7 the EQE curves of typical substrate and superstrate configuration cells are shown. The shift of the right edge towards longer wavelengths for the superstrate cell reveals the occurrence of intermixing. The corresponding absorber band gaps can be
3.2. Absorber properties and junction formation

Figure 3.7: Comparison of EQE measurements of a typical substrate and superstrate cell respectively. The inset shows the determination of the absorber band gaps by the linear fitting of the \((h\nu EQE)^2\) vs. \(h\nu\) plot.

Read from the intercept with the x-axis of the linear fit of the \((h\nu EQE)^2\) vs. \(h\nu\) plot displayed in the inset graph in Figure 3.7. Superstrate cells with well intermixed CdS\(_x\) Te\(_{1-x}\) absorbers exhibit band gaps of around 1.46 eV, while substrate configuration cells have a higher band gap of 1.48 eV independent of performing a CdS treatment. This value corresponds also to the sulfur free superstrate reference devices grown in our lab. This trend is confirmed in numerous samples and statistics are displayed in Figure 3.8.

Figure 3.8: Comparison of CdTe absorber band gaps of cells grown in substrate and superstrate configuration extracted from EQE measurements. The larger average band gap of substrate cells indicates less intermixing at the p-n junction.
Chapter 3. Processes for substrate configuration CdTe solar cells

Hall measurements of CdS layers revealed an increase in carrier concentration from $8 \times 10^{15}$ cm$^{-3}$ to $3 \times 10^{17}$ cm$^{-3}$ upon CdS treatment. Furthermore, we found that during the CdS treatment sulfur and chlorine diffuse along the CdTe GBs and segregate there as described in more detail in [69]. This passivates defects at the GBs leading to reduced recombination and thus longer MCLT in CdTe.

3.2.3 Correlation of treatment procedure and copper addition

The increase in cell efficiency upon the CdS treatment strongly intercorrelates with the copper content of the cell. In Figure 3.9 the efficiency of single and double treated cells is plotted against the copper layer thickness of a cell with a Cu/Sb back contact buffer layer. The efficiency of the single treated cells increases with higher copper amount whereas copper addition is detrimental to the double treated cells. This is true for all investigated back contact materials. These observations imply the harmfulness of annealing the cells containing copper amounts of 0.5 nm and more to high temperatures when CdS is already deposited. Annealing at high temperatures enhances the diffusion of copper from the back contact to the CdTe-CdS junction and to the front contact. This diffusion and its detrimental effect at the junction or in the CdS have already been reported by several other groups [70,71].

![Figure 3.9](image)

**Figure 3.9:** Comparison of the efficiencies of single and double treated cells plotted against the copper layer thickness at the Sb back contact. The error bars give the standard deviation of the measured cells.

Additionally, it is well known that in superstrate solar cells addition of a small, optimized amount of copper to the back contact significantly increases the cell efficiency [72].
3.2.4 Conclusion on absorber properties and junction formation

Treating the CdTe/CdS layer stack as whole in analogy to superstrate configuration leads to excessive intermixing and a total consumption of the CdS layer. Therefore, the treatment was split into separate CdTe and CdS treatments. The CdTe treatment leads to grain growth and texture change very similar to what is observed in superstrate configuration, however, as the CdS is not yet present, higher temperatures of up to 440 °C can be applied. This enables a reduction of the grain boundary area and as a consequence possibly larger $V_{oc}$ and fill factors. Temperatures exceeding 440 °C, however, lead to crack formation and delamination of the CdTe layer. The CdS treatment causes a phase transformation of the CdS but no observable CdTe/CdS intermixing. Further, it leads to increased carrier concentration in CdS and via sulfur diffusion to a prolonged MCLT in CdTe. The addition of copper influences the optimal treatment procedure. When copper (0.5 nm and more) is added at the back contact the CdS treatment decreases the cell performance substantially, presumably due to excessive copper diffusion to the junction.

3.3 Evaluation of different electrical back contacts

The formation of a quasi-ohmic back contact to CdTe which additionally has to withstand the subsequent processing steps is a difficult task to be solved for the development of highly efficient substrate configuration solar cells. Using the low temperature CdTe deposition procedure developed in our lab we were able to reduce the back contact requirements regarding temperature stability such that the highest temperature to be endured during the CdTe/CdS growth or the CdCl$_2$ treatment(s) is in the range of 400 - 450 °C.

As metallic part of the back contact molybdenum has been chosen since this material matches the thermal expansion coefficient of CdTe and is compatible with a variety of substrates. Yet, the work function difference between molybdenum and CdTe will result in a severe Schottky barrier for the holes traveling from the absorber to the back contact.

There are two approaches to the formation of a quasi ohmic back contact to CdTe, both of which add a buffer layer between CdTe and the metallic part of the back contact. One possibility is to introduce a buffer layer with a very high work function in order to
reduce the Schottky barrier height such that the holes can overcome it at the operating temperature. Another approach is to use a strong p-type buffer layer with high acceptor density, thereby narrowing the barrier width and enabling the tunneling of holes through the barrier. This second approach is usually used for back contact formation in superstrate configuration where buffer layers of Cu$_x$Te or Sb$_2$Te$_3$ are often applied [72,73].

Table 3.2 lists the investigated buffer layers with the corresponding solar cell parameters measured under simulated standard AM1.5G test conditions. Whenever more than one material was used as back contact buffer the materials are given in the order of growth starting from the material in contact with the metallic back contact layer. Sb$_2$Te$_3$, Sb and CuO$_x$ are all of strong p-type conductivity [74, 75] while MoO$_3$ features a very high work function of up to 6.8 eV [76] with a band gap of 2.7 eV to 3.4 eV depending on the crystal structure [77] and has already proven to be a suitable candidate for back contact applications [22].

<table>
<thead>
<tr>
<th>Buffer layer</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO$_x$/Te</td>
<td>10.0</td>
<td>733</td>
<td>62.3</td>
<td>22.0</td>
</tr>
<tr>
<td>Sb$_2$Te$_3$</td>
<td>8.6</td>
<td>658</td>
<td>61.2</td>
<td>21.4</td>
</tr>
<tr>
<td>MoO$_x$</td>
<td>5.9</td>
<td>597</td>
<td>48.4</td>
<td>20.3</td>
</tr>
<tr>
<td>Sb</td>
<td>4.6</td>
<td>446</td>
<td>49.6</td>
<td>21.1</td>
</tr>
<tr>
<td>Cu/Te/MoO$_x$</td>
<td>11.3</td>
<td>768</td>
<td>68.6</td>
<td>21.4</td>
</tr>
<tr>
<td>Cu</td>
<td>8.9</td>
<td>751</td>
<td>61.2</td>
<td>20.0</td>
</tr>
<tr>
<td>Cu/Sb$_2$Te$_3$</td>
<td>7.7</td>
<td>622</td>
<td>58.2</td>
<td>21.2</td>
</tr>
<tr>
<td>CuO$_x$</td>
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<td>49.2</td>
<td>22.0</td>
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<tr>
<td>Cu/Sb</td>
<td>6.1</td>
<td>658</td>
<td>51.3</td>
<td>18.3</td>
</tr>
</tbody>
</table>

**Table 3.2:** Explored buffer layers in substrate configuration and the measured photovoltaic parameters. $J_{sc}$ is assessed by EQE measurements.

Not intentionally adding copper to the back contact does not necessarily imply that the resulting device is copper-free. Indeed, the 10% efficient device with the MoO$_x$/Te back contact buffer was found to be copper contaminated with an amount of copper corresponding to a copper layer thickness of 0.03 nm (the other devices presented here were not checked). This issue is further discussed in Chapter 4.4.

As mentioned in Section 3.2.3 the addition of copper to the back contact increases cell performance if the cell is processed with only one CdCl$_2$-treatment, therefore, all
cells with copper at the back contact were only single treated whereas the cells without copper addition were treated twice.

In the following, more details on the preparation and characteristics of the best two back contact buffer materials Sb$_2$Te$_3$ and MoO$_x$ will be given.

### 3.3.1 Sb$_2$Te$_3$ back contact buffer

The work presented in this section was performed in collaboration with Julian Perrenoud and is partly also published in his PhD thesis [13].

The first approach was to grow Sb$_2$Te$_3$ by thermal evaporation from the compound material to an unheated substrate. However, the resulting layers exhibited large stoichiometry variations. Figure 3.10 shows the Te/Sb ratio for 7 subsequent depositions from the same source measured by EDX. The layers are Te rich in the beginning and become Sb rich later on indicating a preferential evaporation of Te enriching the source material with Sb. This trend was also reported by Piacente et al. [78] who suggest the reaction $Sb_2Te_3(s) \rightarrow Sb_2Te_{3-x}(s) + \frac{1}{2}xTe_2(g)$ to explain the Te loss. It was concluded that the large stoichiometry variations make compound evaporation an unsuitable process for solar cell fabrication.

![Figure 3.10: Te/Sb ratio measured by EDX in 7 subsequently grown layers evaporated from the Sb$_2$Te$_3$ compound. While the layers are Te rich for the first depositions they become Sb rich for later depositions.](image-url)
Figure 3.11: Stoichiometry of SbTe$_3$ in dependence on the Te/Sb flux ratio (a) and the substrate temperature (b) during growth. For the experiment shown in a the substrate temperature was held constant at 200 °C while for the one shown in b the Te/Sb flux ratio was set to 2. Even though precise temperature controlled sources are used stoichiometric Sb$_2$Te$_3$ is hard to achieve.

To gain more control over the stoichiometry co-evaporation of Sb and Te from two separate, temperature controlled sources was implemented. The flux of each source was monitored individually by a quartz crystal monitor. Figure 3.11a displays the dependence of the layer stoichiometry on the Te/Sb flux ratio from the two sources at a constant substrate temperature of 200 °C. A Te/Sb flux ratio of about 2.5 is needed to obtain stoichiometric Sb$_2$Te$_3$. The layer composition is also strongly dependent on the substrate temperature as shown in Figure 3.11b. At a Te/Sb flux ratio of 2 a substrate temperature of about 200 °C gives the layer closest to Sb$_2$Te$_3$.

Figure 3.12a shows a top view SEM picture of a co-evaporated Sb$_2$Te$_3$ layer grown at 200 °C substrate temperature. The layer is compact with a homogeneous grain size of about 100 nm. A cross section SEM image of a finished solar cell with Sb$_2$Te$_3$ back contact buffer is shown in Figure 3.12b. Even though 100 nm Sb$_2$Te$_3$ were initially deposited the Sb$_2$Te$_3$ layer is not visible. This indicates a reduced thickness caused by re-evaporation or chemical interaction. Arguing against the latter are the calculations and experiments by Schmidt et al. [79] demonstrating the chemical stability of Sb$_2$Te$_3$ at the CdTe back contact interface.
3.3. Evaluation of different electrical back contacts

Figure 3.12: a) Top view SEM of an Sb$_2$Te$_3$ layer grown by co-evaporation at 200 °C substrate temperature. b) SEM cross section through a solar cell with an Sb$_2$Te$_3$ back contact buffer. Although 100 nm Sb$_2$Te$_3$ were deposited the layer cannot be observed in the finished device.

The highest efficiencies obtained with an Sb$_2$Te$_3$ back contact buffer are 7.7% and 8.6%, with and without copper addition, respectively. The corresponding $J$-$V$ and QE measurements are displayed in Figure 3.13 while the PV parameters can be read from Table 3.2. Contrary to most other back contact buffer layers Sb$_2$Te$_3$ seems to work better without the addition of copper. However, as the reproducibility of the layer stoichiometry is very hard to handle one has to be careful to draw definitive conclusions.

Figure 3.13: $J$-$V$ characteristics and quantum efficiency measurements of solar cells employing an Sb$_2$Te$_3$ back contact buffer with (Cu/Sb$_2$Te$_3$) and without (Sb$_2$Te$_3$) the use of copper. PV parameters are given in Table 3.2.
Conclusion on the $\text{Sb}_2\text{Te}_3$ back contact buffer  Compound evaporation of $\text{Sb}_2\text{Te}_3$ was found to be not suitable for reproducible $\text{Sb}_2\text{Te}_3$ layer growth. The stoichiometry of such layers varies over consecutive depositions due to preferential Te evaporation causing the source material to get enriched with Sb. Coevaporation of Sb and Te from separate sources allows control over the Te/Sb flux ratio. However, stoichiometry also depends on substrate temperature which makes process control difficult and reproducibility limited. Efficiencies of up to 8.6% (without copper, double treated) and 7.7% (with copper, single treated) could be achieved using this back contact buffer layer.

3.3.2 $\text{MoO}_x$ back contact buffer

Thermally evaporated $\text{MoO}_x$ layers (cf. Section 2.1.1.1) were characterized using different methods. Since the XRD of as-deposited layers revealed their amorphous nature RBS was used for determination of chemical composition (Figure 3.14). The average O/Mo ratio in the thin film was found to be $2.94 \pm 0.04$, and no significant variation was detected throughout the successive $\text{MoO}_x$ deposition runs until the boat was emptied. The morphology (inset Figure 3.14) is compact and no pinholes were observed making this layer suitable for solar cell growth.

![RBS measurement of an evaporated MoO_x thin film on a Si wafer substrate. The measured O/Mo ratio is 2.94 ± 0.04. The inset graph shows an SEM picture of the surface of evaporated MoO_x on a molybdenum coated glass substrate.](image-url)
Using such evaporated MoO\textsubscript{x} buffer layers with 100 nm thickness solar cells with efficiencies of up to 11.3\% (Cu/Te/MoO\textsubscript{x} buffer layer) could be produced. Without addition of copper an efficiency of 10.0\% (MoO\textsubscript{x}/Te) could be achieved. \textit{J-V} characteristics, quantum efficiencies and PV parameters of these cells are displayed in Figure 3.15 and Table 3.2.

![Graph of J-V characteristics and quantum efficiency measurements of the best MoO\textsubscript{x} based solar cells achieved with (Cu/Te/MoO\textsubscript{3}) and without (MoO\textsubscript{3}/Te) the use of copper. PV parameters are given in Table 3.2.](image)

The following investigation was conducted with the cell giving the highest performance without copper addition. However, the measurements were also performed on other cells (also with copper addition) and always showed the same results.

Figure 3.16a shows the GIXRD pattern of the MoO\textsubscript{x} buffer layer from the 10.0\% solar cell, which was accessed by a lift-off process to detach the CdTe back surface from MoO\textsubscript{x}/Mo/BSG. All peaks which do not correspond to any residual CdTe (ICDD-No. 15-0770) and ZnO (ICDD-No. 80-0075) and the underlying molybdenum (ICDD-No. 04-0809) can be assigned to the MoO\textsubscript{2} phase. The strong oxygen deficiency in MoO\textsubscript{x} compared to the as-deposited layer may be caused by oxygen diffusion to adjacent layers in the solar cell. Such a reduction from evaporated MoO\textsubscript{3} to MoO\textsubscript{2} was also observed by Wu et al. [80] who proved a migration of oxygen from MoO\textsubscript{3} to N,N'-diphenyl-N, N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB) in their organic light emitting devices. A similar effect can be envisaged in case of our CdTe solar cells.
Figure 3.16: a) GIXRD measurement of the MoO$_x$ back contact buffer layer of a finished CdTe solar cell assessed by a lift-off process. Figures b) and c) show GIXRD measurements of evaporated MoO$_x$ layers annealed at 400 °C in air (b) and nitrogen (c) ambient. While the MoO$_x$ buffer layer exhibits only the MoO$_2$ phase, the peaks in the annealed layer can be assigned to MoO$_3$ and substoichiometric phases.

The electrical conductivity of the wide band gap semiconductor MoO$_3$ is substantially different from MoO$_2$, which shows metallic conductivity [22]. A strong increase in conductivity of MoO$_x$ when $x$ is lowered from 3 to 2 is reported [81, 82], and the changes are ascribed to defect states or defect bands in the band gap originating from the increasing number of oxygen vacancies and the emergence of the molybdenum 4d band [82–86].

Up to now, the usefulness of MoO$_x$ as the hole transport layer was mostly explained either by the high work function of MoO$_3$ (5.3 - 6.8 eV [87]), raising the work function of the electrode and thereby lowering the Schottky barrier to the semiconductor [22, 88] or pinning the Fermi level of the top electrode [89], or the presence of defect states in the band gap of substoichiometric MoO$_{3-x}$. These gap states may align with the semiconductor valence band and are thought to serve as hole transport pathway [90–92]. It is also proposed that the high electron affinity of MoO$_3$ causes an interfacial dipole due to charge transfer interaction between semiconductor and MoO$_3$, which leads to an upward bending of the semiconductor bands facilitating hole transport [90–93].

However, in our case of CdTe solar cells, the exclusive presence of MoO$_2$ suggests
3.3. Evaluation of different electrical back contacts

the plausibility of another explanation for the improved electrical contact behavior as for example p-type doping of CdTe by oxygen transfer from MoO$_3$ to CdTe in combination with the also high work function (5.9 eV) of MoO$_2$ [80]. For a better understanding further work is required in this direction.

In order to investigate the annealing induced transformation of chemical phases, evaporated MoO$_x$ layers were annealed in different ambient and in-situ GIIXRD measurements were performed. The GIIXRD patterns of layers annealed at 400 °C in N$_2$ atmosphere and air are displayed in Figure 3.16 b and c. In contrast to the lift-off sample no MoO$_2$ (ICDD-No. 32-0671) peaks are present in the diffractograms of the annealed layers. Peaks of the N$_2$-annealed layer can be assigned to MoO$_3$ (ICDD-No. 05-0508) and the substoichiometric phases Mo$_4$O$_{11}$ (ICDD-No. 86-1269) and Mo$_9$O$_{26}$ (ICDD-No. 84-1466). Annealing in air resulted in more pronounced MoO$_3$ diffraction peaks. However, the substoichiometric phases were still present. Clearly, the as-deposited MoO$_x$ transforms differently during processing a CdTe solar cell in substrate configuration than during annealing even in a non-oxidizing atmosphere.

To understand the chemical phase formation and transformation, studies on the properties of RF-sputtered MoO$_x$ layers were performed since the plasma based deposition method allows more variability of deposition conditions compared to simple thermal evaporation.

The formed phases as well as the microstructure of reactively sputtered MoO$_x$ layers strongly depend on the substrate temperature and the O$_2$ content during sputtering. Figure 3.17 shows XRD patterns of thin films sputtered reactively from a metallic molybdenum target. Layers sputtered without substrate heating show a very broad peak for both 20% and 50% relative O$_2$ contents, in agreement with other reports of MoO$_x$ sputtered at low temperatures [94, 95]. In order to determine layer composition, layers were sputtered under identical conditions onto Si wafers and analyzed by RBS. The measured O/Mo ratio was $2.85 \pm 0.10$ and $3.00 \pm 0.10$ for 20% and 50% O$_2$, respectively. Using an O$_2$ content of 20%, the formation of MoO$_2$ prevails at 200 °C substrate temperature while the stoichiometry is displaced towards Mo$_9$O$_{26}$ at 400 °C. At a higher O$_2$ content of 50% MoO$_3$ was found in the layers deposited at 200 °C or 400 °C. In addition to MoO$_3$, a strong (020) peak of Mo$_9$O$_{26}$ is observed for the 200 °C layer. At 400 °C the deposition was extremely inhomogeneous and the layer was very thin, resulting in weak XRD peaks. The visible peaks correspond to MoO$_3$ and MoO$_2$. 
Figure 3.17: XRD patterns of MoO$_x$ thin films reactively sputtered from a metallic molybdenum target at different temperatures with 20% (a) and 50% (b) relative O$_2$ content during sputtering in $\Theta$-2$\Theta$ geometry.

X-ray diffractograms of reactively sputtered MoO$_x$ layers from a ceramic MoO$_3$ target are displayed in Figure 3.18. Sputtering at room temperature with 20% O$_2$ content led, as in the case of a metallic target, to a broad and flat peak. Conditions of substrate temperature 200 °C and 20% O$_2$ enhance the formation of MoO$_3$. Also a peak, which can be assigned to the Mo$_9$O$_{26}$ phase, is present. Increasing the O$_2$ content to 50%
3.3. Evaluation of different electrical back contacts

An overview on the microstructural evolution and phase formation of the layers sputtered from the molybdenum target is given in Figure 3.19. The formation of nano-rods can be observed for the growth conditions of 200 °C with 50% O₂ and 400 °C with 20%. To explain the growth mechanism of MoO₃ nano-rods, Navas et al. [96] proposed a competing effect of sputtering and re-sputtering during deposition, which leads to a nuclei growth along their preferential growth direction 0k0 resulting in the formation of nano-rods. This is in good accordance with the result of our XRD measurements, which clearly show that both layers exhibit nano-rod growth of Mo₉O₂₆ with the preferential [020] orientation.

The films sputtered from the MoO₃ target exhibit mainly small grains even if the substrate is heated to 200 °C. Transmission and reflection spectra of thin films sputtered directly on glass were measured. The energy gap (E₆₇) of the layers was determined by calculating the absorption coefficient and linearly extrapolating the Tauc plots, assuming an indirect band transition (αhν¹/² vs. hν). The results are shown in Figure 3.20, where a clear trend of decrease in E₆₇ with decreasing O₂ content from 50% to 20% can be observed. This behavior has been reported for MoOₓ deposited by various me-

**Figure 3.18:** XRD patterns of MoOₓ thin films sputtered from a ceramic MoO₃ target at different O₂ contents and substrate temperatures in Θ-2Θ geometry.
Figure 3.19: Microstructure shown by SEM pictures and dominant crystalline phases of MoO$_x$ thin films grown under different sputtering conditions from a metallic molybdenum target. The phase of MoO$_x$ thin films grown at room temperature could not be assessed by XRD therefore composition measured by RBS is indicated.

Methods [81, 97, 98] and it can be attributed to the fact that reduced molybdenum oxidation states induce acceptor-like defects near the valence band edge and therefore decrease the optical bang gap [97]. Band gap values in the range from 2.9 eV to 3.7 eV were determined in good agreement with literature [97–100].

Since with reactive sputtering it is possible to control the oxygen content of the MoO$_x$ back contact buffer its impact on the solar cell parameters could now be studied. Figure 3.21 shows the dependence of efficiency, $V_{oc}$ and fill factor on the oxygen content of the sputtering gas when sputtering from the ceramic MoO$_3$ target. Results for cells without copper addition as well as with addition of 10 nm copper to the back contact are shown. A trend towards higher values of all parameters is visible especially for the cells without copper addition. This indicates that the additional oxygen which presumably diffuses into the CdTe layer upon device processing helps to lower the back contact barrier by inducing acceptors in the CdTe adjacent to the back contact. However, when
3.3. Evaluation of different electrical back contacts

Figure 3.20: The optical energy gaps as a function of oxygen content and substrate temperature for thin films reactively sputtered from the metallic molybdenum and the ceramic MoO$_3$ target.

Figure 3.21: Dependency of Efficiency, $V_{oc}$ and fill factor on the oxygen content of the sputtering gas when sputtering from the MoO$_3$ target.

copper is present in the cell this effect is much less pronounced. This might be due to the doping of CdTe with copper which makes the additional oxygen doping dispensable.

Conclusion on the MoO$_x$ back contact buffer  Molybdenum oxide is a promising candidate for a back contact buffer layer because of its high work function possibly reducing the back contact barrier and its widespread success as hole transport layer in many devices. Various forms of molybdenum oxides from MoO$_2$ to MoO$_3$ can be deposited by
Chapter 3. Processes for substrate configuration CdTe solar cells

thermal evaporation or by reactive sputtering either from a metallic molybdenum or a ceramic MoO$_3$ target. Highest conversion efficiency of 11.3% could be achieved using a thermally evaporated MoO$_x$ layer. Analyses of the CdTe-back electrical interface of such devices revealed the exclusive presence of MoO$_2$ at the MoO$_x$/CdTe interface. The metal-like compound MoO$_2$ exhibits totally different electrical and optical properties as compared to the extensively discussed hole transport layer MoO$_3$. Therefore, further work is required to explain the high efficiency of CdTe solar cells in substrate configuration employing MoO$_2$ buffer layers. In situ GIXRD experiments of differently annealed MoO$_x$ layers suggest that phase transformation of evaporated MoO$_x$ depends on whether the layer is bare or incorporated into the solar cell device. The properties RF-sputtered MoO$_x$ thin films depend on the oxygen partial pressure and substrate temperature. By choosing the appropriate sputter conditions MoO$_2$ phase can be obtained but along with some residues of a sub-stoichiometric phase of MoO$_3$. Increasing oxygen content in RF-sputtered MoO$_x$ layers used as back contact buffer led to increasing $V_{oc}$ and fill factor in cells with no copper addition. The effect is much less pronounced in copper containing cells suggesting that oxygen induced doping of CdTe is more beneficial when no copper is present in the cell.

3.4 Stability

First tests on the stability of solar cells under continuous illumination and heat showed the very poor stability of all devices with copper loaded back contact. The detrimental impact of copper on the cell stability is a well-known effect [101] and although there are promising results on stabilizing copper containing devices [102] this problem has not yet been completely solved. In contrast the preliminary results for devices without copper addition are very promising. Most of the cells stabilize at a high efficiency after an initial improvement. Figure 3.22 shows the efficiency development of solar cells with three different back contact buffers at around 50 $^\circ$C and 0.5 sun illumination. As pointed out before, copper addition leads to degradation of the solar cell (Cu/MoO$_x$) while cells without copper addition are relatively stable (Sb$_2$Te$_3$) or even improve over time (MoO$_x$). This stability test allows only a short glance at the degradation behavior since its conditions were neither well controlled nor near the solar cell’s real operating conditions. Further, more elaborate stability studies are presented in Chapter 6.
3.5. Conclusion

A process for CdTe/CdS solar cells in substrate configuration has been established. The CdCl$_2$-treatment procedure has been adapted for the use in substrate configuration. Two separate annealing treatments were applied in order to have control over the properties of the CdTe layer (CdTe treatment) and the heterojunction formation with CdS (CdS treatment). The CdTe treatment resulted in a recrystallization of the CdTe very similar to superstrate configuration, however, as the junction is not yet formed higher treatment temperatures can be applied, leading to further grain growth and thus possibly higher $V_{oc}$ and FF. The CdS treatment was found to be beneficial for junction quality and cell performance but as excessive copper diffusion to the junction and into the CdS has detrimental effects cells with copper added to the back contact buffer were only treated once while cells without copper addition could be double treated.

Various materials have been tested as back contact buffer layers. The best efficiency of 11.3% was achieved using a Cu/Te/MoO$_x$ buffer. Since copper is a prominent cause for degradation, buffer layers without copper addition were also investigated. MoO$_x$/Te buffer structure yielded the best result of 10.0% conversion efficiency. MoO$_x$ which is deposited as slightly sub-stoichiometric MoO$_{3.5}$ on the molybdenum back contact of the solar cell was found to transform to MoO$_2$ upon further processing of the solar cell.
This transformation can explain the good functionality of the MoO$_x$ containing back contacts as MoO$_2$ is a metal-like compound with a high work function allowing for a small Schottky barrier to CdTe.

### 3.6 Outlook

The work presented in this chapter reveals three main problems to be solved in order to achieve reproducible, highly efficient and stable CdTe solar cells in substrate configuration.

The necessity to skip the CdS treatment, which was found to benefit junction quality, when copper is present in the cell shows that the optimal processing has not yet been identified. It is desirable to profit from the positive effects of copper on the doping and contact quality while omitting its detrimental effects on the junction. Therefore, in Chapter 4, copper addition will be carefully controlled and its impacts on the electronic properties of the solar cell will be investigated in detail.

The presented studies on the back contact buffer materials identified MoO$_x$ and Sb$_2$Te$_3$ as suitable contact materials. However, their entanglement with the addition of copper to increase contact and/or absorber quality makes it difficult to characterize them independently. At this stage it is also not possible to determine to what extent the back contact quality limits the device performance or to compare it to back contacts used in superstrate configuration. That is why as soon as copper can be added to the cell in a well controlled manner independent from back contact formation the investigations on the back contact buffers should be resumed and deepened. This is done in Chapter 5 where the back contact properties are characterized in detail and compared to superstrate configuration in order to identify possible limitations.

With the initial stability studies it was shown that copper addition as well as the employed back contact buffer material influence performance stability. After having decoupled and optimized copper doping and back contact formation in the previous chapters, Chapter 6 investigates their respective impact on device stability by performing well controlled accelerated stress tests.
Chapter 4

Doping of CdTe solar cells

This chapter is in part based on the following publications:


Parts of the results of this chapter were obtained during the Master thesis of Michael Wyss and the Master project of Elias Rehmann [103, 104].

4.1 Introduction

One of the major challenges of CdTe solar cell research is the achievement of a high hole density in the CdTe layer by means of controlled acceptor doping [105, 106]. It is impeded by the spontaneous formation of compensating donors, a phenomenon commonly observed in the field of II-VI semiconductors [107]. For example, first principle calculations suggest that copper dopants in CdTe can occupy the Cd atomic site acting
as an acceptor as well as interstitial positions acting as a donor [60]. Copper is the most common dopant added to CdTe solar cells. Originally, it has been added to the BC of CdTe solar cells in superstrate configuration with the purpose to improve the contact properties to CdTe by forming a degenerate semiconductor layer, e.g. in the form of Cu$_x$Te, ZnTe:Cu, HgTe:CuTe doped graphite paste or As$_2$Te$_3$:Cu [16, 21, 25, 108, 109]. During back contact processing, part of the copper has also been found to diffuse into CdTe, where it increases acceptor concentration and affects carrier lifetime [30, 110].

As described in Chapter 3, in substrate configuration copper is commonly added using the same approach as developed for devices in superstrate configuration, i.e. the use of a copper containing layer with an equivalent copper thickness of several nanometers in the electrical BC structure [111–113]. However, we found that this approach prohibits the use of the CdS treatment and hence its beneficial effects on the solar cell because of excessive copper diffusion to the junction and into the CdS and is therefore not optimal. Attempts have also been made to apply copper at different processing steps by dipping the cell into warm CuCl solution, however, efficiencies remained around 7% [114].

Copper doping is the historic path of achieving well-working solar cells. However, the expected copper on cadmium site point defect (Cu$_{Cd}$) is a rather deep acceptor, predicted to be positioned between 220 and 310 meV above the valence band by first principle calculations [60, 115]. The alternative intrinsic and extrinsic acceptor type defects in CdTe are listed in Table 4.1 along with their hole binding energy as calculated by Wei et al. [60].

For substitutional doping on cadmium sites sodium and silver could be considered. Although Na$_{Cd}$ probably is a shallow acceptor, it does not seem an appropriate choi-

<table>
<thead>
<tr>
<th>Intrinsic</th>
<th>On Cd site</th>
<th>On Te site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defect</td>
<td>$E_B$ (meV)</td>
<td>Defect</td>
</tr>
<tr>
<td>$V_{Cd}$ (0/-)</td>
<td>130</td>
<td>Na$_{Cd}$</td>
</tr>
<tr>
<td>$V_{Cd}$ (-/2-)</td>
<td>210</td>
<td>Ag$_{Cd}$</td>
</tr>
<tr>
<td>Te$_i$</td>
<td>570</td>
<td>Au$_{Cd}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu$_{Cd}$</td>
</tr>
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<td></td>
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</tbody>
</table>

Table 4.1: Intrinsic, Cd and Te substitutional acceptor type defects and their hole binding energies $E_B$ as calculated by Wei et al [60].
ce because the Na donor-type defect has very low formation energy and therefore this element is expected to display even stronger self-compensation than copper [60]. In addition, sodium has significant effects on the structural properties of CdTe solar cells [116]. The Ag\textsubscript{Cd} acceptor is reported to have a hole binding energy of around 50 meV lower than Cu\textsubscript{Cd} as derived from both first principle studies [60] as well as optical measurements [117] while the formation energy is comparably low [60]. Therefore, silver doping appears to be a promising alternative to the traditional copper doping and the doping mechanisms of these two elements will be studied in parallel in this chapter.

In order to introduce acceptor type defects on tellurium sites there are several possibilities. The N\textsubscript{Te} defect is very shallow but also exhibits a very high formation energy and is accordingly hard to introduce into the CdTe layer. The P\textsubscript{Te} acceptor would be the next to consider, however, phosphorous is rather difficult to handle and therefore not the first choice as dopant. Arsenic induces an acceptor on Te sites with a much lower hole binding energy than Cu\textsubscript{Cd} while the formation energy is only slightly larger [60]. Furthermore, it has already been successfully employed for p-type doping of CdTe solar cells [118]. The effect of arsenic doping on CdTe layers and solar cells is studied and the results are presented in Section 4.5.

Previously presented approaches for copper doping did not prove suitable to achieve desired bulk doping of the CdTe layer in substrate configuration and hence the cell efficiencies remained low. In this chapter, a novel process is introduced for the controlled doping of the CdTe layer by means of vapor deposition of copper or silver after the recrystallization treatment of the CdTe layer and subsequent annealing. A small amount of dopant with the equivalent thickness of less than a monolayer is deposited on top of the recrystallized CdTe layer and diffusion into CdTe is promoted by annealing at 400 °C. The process used for the doping of CdTe thin films on glass and solar cells is depicted in Figure 4.1.

For arsenic doping untreated CdTe layers are placed in closed glass ampoule together with pieces of arsenic and then annealed at 500 °C. The CdTe treatment is performed after removing the sample from the ampoule.

As the CdS treatment was found to be beneficial for junction quality (cf. Chapter 3) all the solar cells produced in this chapter received this treatment. When the doping is optimized on double treated cells the positive effects of the doping and the CdS treatment can potentially be united. For better coverage of the CdTe an additional CdS
layer is deposited after the CdS treatment. As back contact buffer layer evaporated MoO$_x$ (as described in Section 3.3.2) was used for all the solar cells presented in this chapter.

4.2 Copper and silver doping of CdTe thin films

The effect of copper and silver doping on the resistivity and hole density of CdCl$_2$-treated CdTe layers on glass was investigated. Figure 4.2a shows the evolution of resistivity as assessed by Hall effect measurements in dependence of the deposited amount of the dopant atoms. For both elements an abrupt initial drop of resistivity is observed. By adding 1.2×10$^{15}$ silver atoms per cm$^2$ (sub-monolayer with equivalent thickness of 1.5 Å) the CdTe:Ag film reaches a minimal resistivity of 5.9×10$^3$ Ωm while the resistivity of CdTe:Cu drops to 5.8×10$^3$ Ωm when adding 1.0×10$^{15}$ copper atoms per cm$^2$ (equivalent thickness of 1.2 Å). The resistivity drop is caused by an increase in hole density from below 1×10$^{12}$ cm$^{-3}$ to 1.4×10$^{14}$ cm$^{-3}$ in case of silver doping and to 3.8×10$^{14}$ cm$^{-3}$ for copper doping (Figure 4.2b). This shows that copper doping is slightly more efficient when doping CdTe with the selected parameters.

Upon exceeding the optimum dopant concentration the CdTe resistivity stagnates and even increases again slightly. Simultaneously, the hole density decreases what can be attributed to the formation of compensating donor-type defects. The compensation seems to be stronger in case of CdTe:Ag as the hole density is more significantly reduced. This demonstrates that the hole density in polycrystalline CdTe can be ma-
4.2. Copper and silver doping of CdTe thin films

ximized by carefully controlling the concentration of the dopant. The similarity of the measurements for copper and silver doping furthermore indicate an equivalent doping mechanism for these two elements, as expected because of their atomic character as members of the group IB and their similar diffusion dynamics [119].

Figure 4.2: Influence of copper doping on (a) resistivity and (b) hole density of CdCl\textsubscript{2}-treated CdTe thin films on glass as well as on (c) efficiency and (d) MCLT of CdTe solar cells in substrate configuration as determined by J-V and TRPL measurements, respectively. The regions of doping and compensation are indicated with color gradients.
4.3 Copper and silver doping of substrate configuration solar cells

4.3.1 Solar cell performance

CdTe solar cells in substrate configuration were processed and the doping was carried out after the CdCl₂-treatment of the CdTe layer (cf. Section 2.1.1.2). The effect of varying dopant concentration on the cell efficiency is depicted in Figure 4.2c. Copper as well as silver doped solar cells exhibit highest efficiencies around the dopant concentration providing the lowest film resistivity and highest hole concentration. Excessive copper and silver doping both lead to a decrease in efficiency.

Figure 4.3 shows the $J-V$ and QE characteristics of undoped as well as the best performing copper and silver doped solar cells in substrate configuration. The corresponding PV parameters are summarized in Table 4.2. The controlled doping of CdTe with copper ($1.0 \times 10^{15} \text{ cm}^{-2}$) has enabled unprecedented efficiencies of up to 13.6% with high $V_{oc}$ and fill factor of 852 mV and 75.3%, respectively. By doping the CdTe absorber material with silver ($0.8 \times 10^{15} \text{ cm}^{-2}$) conversion efficiency of 11.6% has been achieved with also a remarkably high $V_{oc}$ of 841 mV. The fill factor of the CdTe:Ag cell, however, remained somewhat lower at 68.2% compared to the case of CdTe:Cu.

![Graph showing J-V characteristics](image1)

![Graph showing Quantum Efficiency](image2)

**Figure 4.3:** $J-V$ (a) and EQE (b) characteristics of the highest efficiency solar cells achieved with copper and silver doping. For comparison, an undoped cell is plotted.
4.3.2 Dopant distribution

The dopant distributions in the optimally doped CdTe:Cu and CdTe:Ag solar cells were investigated by measuring an elemental depth distribution with TOF-SIMS (Figure 4.4). Highest signal for copper and silver is observed in the CdS as well as at the back contact interface. Inside the CdTe layer a small homogeneously distributed concentration can be observed for both copper and silver.

The copper concentration in the polycrystalline CdTe was quantified by SIMS and ICPMS measurements to \((5 \pm 3) \times 10^{17} \text{ cm}^{-3}\), in agreement with measurements of devices in superstrate configuration [70, 120]. The insets of Figure 4.4a show that copper is present in the CdTe layer and the mass of \(^{63}\text{Cu}^+\) is clearly distinguishable from \(^{126}\text{Te}^{2+}\) and that also the \(^{107}\text{Ag}^+\) peak is not overlapping with another element.

**Figure 4.4:** TOF-SIMS measurements of the depth dependent dopant distribution of optimally copper and silver doped CdTe solar cells in substrate configuration. Insets show the mass spectra in the CdTe layer, \(^{63}\text{Cu}^+\) is well distinguishable from \(^{126}\text{Te}^{2+}\) and also \(^{107}\text{Ag}^+\) shows no overlap with other elements.
4.3.3 Back contact barrier

Copper precipitation at the CdTe/back contact interface has been reported to lower the surface ionization potential and therefore enable the formation of a (quasi-) ohmic contact [121]. As shown before, SIMS measurements show the highest dopant signal at the back contact for both copper and silver doping indicating an accumulation of dopant at the back contact in both cases. In order to investigate if both copper and silver enable a (quasi-) ohmic contact formation the back contact barrier height was evaluated. For this purpose temperature dependent dark $J-V$ measurements were recorded to extract the turning currents $J_T$ of which then Arrhenius plots were made as displayed in Figure 4.5 (cf. Section 2.2.5.5). The calculated back contact barrier heights are in the range of 0.4 eV for both dopants. This demonstrates that CdTe:Cu and CdTe:Ag allow a similar contact quality.

\[ q\Phi_B(Cu) = 0.43 \text{ eV} \]
\[ q\Phi_B(Ag) = 0.39 \text{ eV} \]

![Arrhenius plots of turning currents $J_T$ for copper and silver doped solar cells. Back contact barrier heights $q\Phi_B$ as calculated from the slope of the linear fits are displayed.](image)

4.3.4 Net acceptor concentration

Using $C-V$ measurements (cf. Figure 4.6 and Table 4.2), a strong increase in net acceptor concentration from below $1 \times 10^{13}$ to $1.7 \times 10^{14}$ and $1.5 \times 10^{14}$ can be observed for
copper and silver doping, respectively. This is accompanied by a shrinkage of the SCR from 5 µm to 1.5 µm for copper and 1.7 µm for silver doping. While the extracted acceptor concentrations and SCR widths are on par, the shapes of the $C-V$ profiles differ. The observed maximum on the right hand side of the silver doped cell might stem from a deep defect state present in the CdTe:Ag [122]. Although slightly higher hole densities as measured by Hall effect measurements are reached with CdTe:Cu than with CdTe:Ag the resulting acceptor concentrations in the solar cell absorbers measured with $C-V$ profiling are at the same level for both dopants explaining the consistency of the $V_{oc}$ values.

![Figure 4.6: Room temperature $C-V$ measurements of copper and silver doped CdTe solar cells in substrate configuration. Vertical lines indicate the SCR width measured at 0 V. Horizontal dotted lines mark the measured acceptor concentration.](image)

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>$N_{CV} \times 10^{14}$ cm$^{-3}$</th>
<th>SCR (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>0.5</td>
<td>345</td>
<td>50.7</td>
<td>2.7</td>
<td>&lt;0.1</td>
<td>5.0</td>
</tr>
<tr>
<td>Cu</td>
<td>13.6</td>
<td>852</td>
<td>75.3</td>
<td>21.2</td>
<td>1.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Ag</td>
<td>11.6</td>
<td>841</td>
<td>68.2</td>
<td>20.2</td>
<td>1.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

**Table 4.2:** PV parameters and electronic properties of CdTe solar cells undoped and doped with copper and silver.
4.3.5 Carrier collection

To study the depth-dependent collection efficiency EBIC measurements of an undoped and an optimally copper doped cell were performed (Figure 4.7a,b). In the undoped solar cell, the only carriers that are efficiently collected are those generated close to the electrical BC. Upon optimum copper doping, the effective carrier collection is observed in a region close to the CdS. Effective carrier collection is desirable in a region where carriers are generated by the incoming sunlight. Over 90% of the usable sunlight is absorbed in the first micrometer of the CdTe layer near the interface to the n-type CdS layer. As such, copper doping shifts the region of effective carrier collection to the region of carrier generation, resulting in a dramatic increase in efficiency from less than 1% to over 13% (Figure 4.3a). All PV parameters are improved and EQE increases from ~10% to ~90% (Figure 4.3b). The EQE of the copper free cell exhibits highest values for photons with wavelength of 800-850 nm, which have a higher probability to penetrate deeper into the CdTe layer towards the region of effective carrier collection.

4.3.6 Simulations

The 1-D simulation software SCAPS [59] was used to investigate the influence of doping on $J-V$ and EQE characteristics. This was done for the case of copper in proxy for the investigated group IB elements. Figure 4.8a and b display measurements of an undoped, an optimally copper doped and an excessively copper doped solar cell while c and d depict the corresponding simulations. EQE simulation of a solar cell without acceptor doping of the absorber confirms the experimentally obtained curve for the cell without copper addition. For the simulation of the optimally copper doped device, acceptor-type defects with a concentration of $6.5 \times 10^{14}$ cm$^{-3}$ were introduced into CdTe in order to obtain a hole density of $3.8 \times 10^{14}$ cm$^{-3}$ consistent with the value obtained by Hall effect measurements of CdTe layers. This results in a change in the EQE as observed upon copper addition. To reproduce the observed behavior of the $V_{oc}$ completely, the valence band energy barrier at the BC/CdTe interface has to be increased from 0.46 eV to 0.7 eV in the simulation of the sample without acceptor doping. This is motivated by the reported observation that copper reduces this barrier [108, 121] and by the SIMS measurement shown in Figure 4.4, which indicates that copper accumulates at the BC/CdTe interface.
4.3. Copper and silver doping of substrate configuration solar cells

Figure 4.7: a,b) EBIC measurements of CdTe solar cells processed without dopant (a) and with $1 \times 10^{15}$ cm$^{-2}$ copper atoms deposited on the CdTe layer with subsequent annealing at 400 °C (b). EBIC signal is normalized to 100%. For better visualization, EBIC signal below 30% is not shown. Grain contrast arises from topography due to cleaving of the sample. The profiles on the left show the horizontally averaged EBIC signal (black, collection). Furthermore, a schematic of the depth dependent carrier generation under normal operation in sunlight is shown (red, generation). c,d) Proposed energy band diagrams for CdTe solar cells without (c) and with optimum copper doping (d). Conduction band energy $E_C$, valence band energy $E_V$ and built-in voltage $V_{bi}$ are indicated.

4.3.7 Excessive doping

Excessive doping with copper or silver leads to a decrease of all PV parameters and a reduced EQE in the long wavelength region (Figure 4.8a,b). The net hole density is reduced (inset of Figure 4.2a) and the MCLT decreases as confirmed for the case of copper with TRPL measurements (Figure 4.2d). In simulations, an increase of the acceptor-type defect concentration to $1 \times 10^{15}$ cm$^{-3}$ together with the introduction of compensating donor-type defects with a concentration of $9 \times 10^{14}$ cm$^{-3}$ reproduce $J$-$V$ and EQE characteristics of the sample with excess copper (Figure 4.8c,d). The results
Chapter 4. Doping of CdTe solar cells

Figure 4.8: a,b) J-V (a) and EQE (b) measurements of CdTe solar cells processed without copper, with optimum copper ($8 \times 10^{14}$ cm$^{-2}$ copper atoms) and with excessive copper ($2.4 \times 10^{15}$ cm$^{-2}$ copper atoms). Efficiencies $\eta$ of the corresponding cells are given in the inset. c,d) Simulations of J-V (c) and EQE (d) characteristics of CdTe solar cells with undoped (no acceptors), doped ($6.5 \times 10^{14}$ cm$^{-3}$ acceptors) and compensated ($1 \times 10^{15}$ cm$^{-3}$ acceptors and $0.9 \times 10^{15}$ cm$^{-3}$ donors) absorber. The undoped sample is simulated both with standard (0.46 eV, dashed line) and with increased (0.7 eV, solid line) valence band energy barrier at the BC/CdTe interface.

support an explanation of the reduced device performance with excessive doping by the formation of deep donors, which act as recombination centers and reduce the net acceptor concentration.
4.4 Discussion of copper and silver doping

4.4.1 Amphoteric doping

The results show that the electronic properties of CdTe and the efficiency of the solar cells are enhanced by carefully controlling the doping of the CdTe and that this can be achieved by both copper and silver doping. These observations can be explained by the amphoteric doping behavior of copper and silver in CdTe. Dopant addition up to an optimum amount increases acceptor concentration, e.g. due to the formation of Cu$_{Cd}$ or Ag$_{Cd}$. Further increase in dopant concentration decreases hole density and MCLT owing to the formation of compensating donor-type defects, e.g. Cu$_i$ or Ag$_i$ [60]. This assumption is supported by recent first principle calculations by Krasikov and his coworkers [115].

They calculated the defect formation energy in dependency on the position of the Fermi level within the band gap of CdTe at 200 °C and the results are shown in Figure 4.9. In undoped CdTe the Fermi level is located in the middle of the band gap around 0.75 eV above the valence band maximum (VBM) and the formation energy is lowest for the Cu$_{Cd}$ acceptor. This acceptor will form and thereby lower the Fermi energy until its formation energy equals the one of the donor type Cu$_i$ defect. In Krasikov’s calculations this happens when the Fermi level approached the VBM up to 0.3 eV. From then on, both Cu$_{Cd}$ and Cu$_i$ will form leading to compensation of the acceptors. Copper doping of CdTe will therefore result in a pinning of the Fermi level to a value around 0.3 eV above the VBM what is part of the explanation for the limited $V_{oc}$ in copper doped CdTe solar cells.

4.4.2 Ionization, solubility and GB segregation

The measured copper concentration in the doped polycrystalline CdTe of $(5 \pm 3) \times 10^{17}$ cm$^{-3}$ is three orders of magnitude higher than the measured hole density of $3.8 \times 10^{14}$ cm$^{-3}$. A part of this difference can be attributed to the large activation energy of the Cu$_{Cd}$ acceptor. However, according to numerical simulations only $6.5 \times 10^{14}$ cm$^{-3}$ copper atoms are required to obtain the measured hole density assuming the energetic depth of the copper related acceptor level to be 220 meV. A detailed investigation of the degree of acceptor ionization and its dependence on the acceptor ionization energy...
and concentration was performed using SCAPS simulations and the results are shown in Figure 4.10a. The degree of ionization of the acceptor varies depending on its activation energy and concentration; however, it remains above 20% in the region where CdTe:Cu layers are suspected. This also explains why no higher acceptor concentration could be achieved by silver doping even though $\text{Ag}_{\text{Cd}}$ is reported to be a shallower acceptor than $\text{Cu}_{\text{Cd}}$. Assuming acceptor positions above the valence band of 220 meV for $\text{Cu}_{\text{Cd}}$ and 150 meV for $\text{Ag}_{\text{Cd}}$ (as calculated by Wei et al. [60]) and inserting the measured acceptor concentrations the resulting ionization degrees are 92.7% and 99.5% for $\text{Cu}_{\text{Cd}}$ and $\text{Ag}_{\text{Cd}}$, respectively. Both acceptors are nearly fully ionized in spite of their different positions within the band gap. Figure 4.10b depicts the dependency of $V_{\text{oc}}$ on the acceptor position and concentration as found by a large series of SCAPS simulations. At the measured acceptor concentrations in the low $10^{14}$ range the $V_{\text{oc}}$ is nearly independent of the acceptor position in agreement with our measured PV parameters.

The main part of the difference between the measured copper concentration and hole density thus cannot be explained by partial ionization arising from the energetic depth of the acceptor. The difference is mainly attributed to the preferential accumulation of copper at GBs, which is reported to be energetically favored [123]. An additional indicator for this is the bulk solubility of copper in CdTe. The solubility of copper in CdTe single crystals was measured by Woodbury et al. [124], Grytsiv et al. [125] and Jones et al. [126] in the temperature range of 400-1000 K. As shown in Figure 4.11b, an extrapolation of their data suggests a copper solubility between $3 \times 10^{13}$ and $3 \times 10^{14}$ copper.
4.4. Discussion of copper and silver doping

Atoms cm$^{-3}$ in single crystals at room temperature. However, the solubility is not an absolute limitation for copper concentration at a given temperature. The concentration can exceed the room temperature solubility by fast cooling the CdTe from a higher temperature (quenching). The diffusion constant of Cu$_{Cd}$ acceptors is reported to be around $1 \times 10^{-10}$ cm$^2$s$^{-1}$ at 200 °C [115, 126]. Hence Cu$_{Cd}$ can diffuse µm distances within minutes inside the CdTe bulk. At room temperature diffusion is slower and takes hours for µm distances. Therefore, CdTe can be supersaturated with copper by annealing it at around 200 °C for some minutes and subsequent quenching. The last step of our solar cell and CdTe layer processing comprises such an annealing at 210 °C followed by a quenching. Figure 4.11a displays the hole densities of CdTe layers doped with copper and silver directly after quenching and after a relaxation time of two months. Directly after the quenching the hole density is high what can be explained by the supersaturation of CdTe with copper/silver. This effect, however, decays with time probably due to diffusion of copper/silver towards the grain boundaries. The relaxed value of hole concentration fits well into the range of extrapolated single crystal solubility.

4.4.3 Carrier collection

Copper doping changes the position of effective carrier collection as measured with EBIC. This is explained with the energy band diagrams in Figure 4.7c,d. A copper free cell has a SCR that extends over the whole ~5 µm absorber as confirmed with C-V

Figure 4.10: Ionization degree of acceptors (a) as well as solar cell $V_{oc}$ (b) in dependence on acceptor position $E_a$ and concentration $N_a$ as calculated using SCAPS simulations.
measurements. The low acceptor concentration leads to a small band bending and small electric field close to the CdS layer - the result being that carriers are collected less efficiently even in the SCR. Only close to the electrical BC, Fermi level pinning at the BC/CdTe interface can cause sufficient band bending to allow efficient collection of carriers. Doping CdTe with $1 \times 10^{15}$ cm$^{-2}$ copper atoms results in a SCR of about 1.5 µm (from $C-V$ measurements) and causes sufficient band bending close to the CdS to generate a strong electric field, leading to effective carrier collection and therefore a strongly increased $J_{sc}$. Since the silver doped solar cells show nearly the same decrease in SCR from 5 to 1.7 µm and increase in acceptor concentration it is reasonable to assume that the same shift of the region of carrier collection is responsible for the increase in $J_{sc}$ in silver doped CdTe solar cells.

### 4.4.4 Unintentional doping

It was found that it is crucial to carefully control the copper or silver amount added to the solar cell in order to achieve well doped CdTe solar cells with good performance. The necessity for this precise control of the dopant amount is explained by the amphoteric behavior of copper and silver in CdTe. Cells without dopant addition were stated to have
4.4. Discussion of copper and silver doping

A bad collection and thus low $J_{sc}$ as well as a low $V_{oc}$ resulting in an efficiency of less than 1% (cf. Section 4.3.1). However, also cells with no intentional copper addition and efficiency exceeding 10% were produced during this thesis (cf. Section 3.3) and are also reported in literature [127]. This apparent contradiction is discussed in the following.

Figure 4.12 shows the added dopant amounts, copper concentrations measured in CdTe and $J$-$V$ characteristics of four different devices. Although to both devices number 1 and 2 no copper was added they show a tremendous difference in performance. The reason can be found in the copper concentration in the CdTe layer measured with SIMS and ICPMS (cf. Section 2.2.3.2). While in device number 1 the copper concentration in CdTe is below $0.5 \times 10^{17} \text{ cm}^{-3}$ (value is at the measuring limit) device number 2 exhibits a copper concentration in CdTe of $0.8 \times 10^{17} \text{ cm}^{-3}$. The difference in copper concentration is enough to dope the CdTe sufficiently to get a device with good collection and high $V_{oc}$. Upon addition of the optimum copper amount (device 4) the copper concentration in CdTe is increased to $5 \times 10^{17} \text{ cm}^{-3}$ resulting in an even higher $V_{oc}$ and fill factor.

<table>
<thead>
<tr>
<th>Device</th>
<th>Cu added</th>
<th>Ag added</th>
<th>Cu in CdTe measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no</td>
<td>no</td>
<td>$&lt;0.5 \pm 0.4$</td>
</tr>
<tr>
<td>2</td>
<td>no</td>
<td>no</td>
<td>$0.8 \pm 0.1$</td>
</tr>
<tr>
<td>3</td>
<td>no</td>
<td>20</td>
<td>$0.8 \pm 0.2$</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>no</td>
<td>$5.0 \pm 0.5$</td>
</tr>
</tbody>
</table>

**Figure 4.12:** Top: Intentionally added amounts of copper and silver and copper concentrations in CdTe measured by SIMS and ICPMS for four differently doped devices. Bottom: Corresponding $J$-$V$ characteristics.
This can also be achieved by the addition of the optimum silver amount to the solar cell (device 3).

Even though not intentionally adding any copper to a device it can still exhibit a substantial copper concentration in CdTe. The copper contamination is strongly dependent on the purity of the source materials used during processing. What is important is therefore not the added amount of copper but rather the resulting copper concentration in CdTe in the finished device. The term “copper-free” should hence be avoided or only used with great care.

4.5 Towards further increased hole density by arsenic doping

The work presented in this section was performed in collaboration with Lukas Kranz and is partly also published in his PhD thesis [128].

4.5.1 Arsenic doping of CdTe thin films

Arsenic has already been successfully employed for p-type doping of CdTe solar cells [118]. As mentioned in the introduction of this chapter arsenic impurities are reported to induce relatively shallow acceptor states in CdTe, around 100 meV above the valence band, when substituting Te atoms [60, 129]. For the experiments described in the following, arsenic doping of CdTe was performed by annealing the sample together with arsenic pieces in a closed glass ampoule. The effect of arsenic doping on the hole density in the CdTe layer (measured by Hall effect) is studied together with the effects of the CdCl₂ treatment and copper doping. Table 4.3 shows the highest achieved hole densities and the corresponding processes. The highest hole density of $5.7 \times 10^{16} \text{ cm}^{-3}$ could be achieved by doping the CdTe layer with arsenic without addition of copper and no CdCl₂ treatment. The corresponding samples, which are identically processed but additionally doped with copper exhibit hole densities, which are almost an order of magnitude lower than in the reference without copper doping. This can be explained by the amphoteric behavior of copper in CdTe. Figure 4.9 shows that in highly doped CdTe - i.e. when the Fermi level is close to the VBM - the formation energy of the donor
4.5. Towards further increased hole density by arsenic doping

Type Cu\textsubscript{i} defect is lower than the one of the Cu\textsubscript{Cd} acceptor. Therefore, already present acceptor states will be compensated by additional copper doping. From Table 4.3 it can be read that the same supersaturation of CdTe than with copper and silver (cf. Section 4.4.2) can be achieved with arsenic leading to high hole densities in the quenched and lower ones in the relaxed state.

<table>
<thead>
<tr>
<th>Process</th>
<th>( N_{\text{Quenched}} ) (cm(^{-3}))</th>
<th>( N_{\text{Relaxed}} ) (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As (mg)</td>
<td>CdCl(_2) treatment</td>
<td>w/o Cu</td>
</tr>
<tr>
<td>4</td>
<td>no</td>
<td>( 5.7 \times 10^{16} )</td>
</tr>
<tr>
<td>1000</td>
<td>yes</td>
<td>( 4.4 \times 10^{16} )</td>
</tr>
<tr>
<td>20</td>
<td>yes</td>
<td>( 2.1 \times 10^{16} )</td>
</tr>
<tr>
<td>20</td>
<td>no</td>
<td>( 1.6 \times 10^{16} )</td>
</tr>
</tbody>
</table>

Table 4.3: Achieved hole densities in CdTe thin films on glass as measured with Hall effect measurements and the corresponding process. Hole density is given for the quenched state (within few hours after post-processing annealing) and in the relaxed state (after at least 2 weeks of storage). Samples which were processed identically but with additional copper doping are shown for comparison.

Temperature dependent resistivity measurements were performed to obtain the activation energies for lateral charge transport in undoped, copper and arsenic doped CdTe thin films. The activation energies were extracted from a linear fit of the Arrhenius plot of the lateral conductivity (Figure 4.13) and are 60 meV, 350 meV and 780 meV for arsenic, copper and no doping, respectively. For the undoped cell, the activation energy corresponds approximately to half the band gap value of CdTe what is expected for an intrinsic material. Both the values obtained for copper and arsenic doping are in the range of the acceptor positions reported in literature and are in agreement with the shallower nature of the As\textsubscript{Te} compared to the Cu\textsubscript{Cd} acceptor [60,129–131].

Arsenic incorporation into the CdTe layer is investigated by SIMS measurements (not shown). Arsenic was found to accumulate at the surface of the CdTe layer and arsenic counts within the main part of the CdTe layer are below the detection limit of the system. Considering relative sensitivity factors of Cu\textsuperscript{+}- and As\textsuperscript{-}-detection with SIMS [132] and the results on quantitative SIMS presented above, an upper limit of the arsenic concentration of \( 4 \times 10^{17} \) cm\(^{-3}\) is estimated. This value is about an order of magnitude above the measured hole density. Even though presence of arsenic in the main part of
Figure 4.13: Arhenius plot of the lateral conductivity measured in undoped, copper and arsenic doped CdTe thin films on glass. Activation energies calculated from the slope of the linear fits are given next to the curves.

the CdTe film could not be proven, arsenic concentration in the CdTe layer can be large enough to explain the measured hole density.

4.5.2 Arsenic doping of substrate configuration solar cells

Figure 4.14a displays the $J-V$ characteristics of solar cells doped in the same manner as the CdTe layers described above with hole densities above $1 \times 10^{16}$ cm$^{-3}$. The efficiency of the purely arsenic doped cell is very low at 5.3% with a $V_{oc}$ of 532 mV and a fill factor of 47.4%. Additional copper doping increases the $V_{oc}$ to 669 mV, the fill factor to 54.3% and the efficiency to 7.6%. Although it enables high hole densities, arsenic doping does not lead to improved performance. The fact that copper doping is still needed for good performance suggests that its role comprises more than only doping of the CdTe layer. As already mentioned in Section 4.3.6 copper can also influence the back contact properties what will be further discussed in Chapter 5.

The net acceptor concentration in the arsenic doped solar cells was calculated from $C-V$ measurements (Figure 4.14b). The measured net acceptor concentrations are with $\sim 10^{14}$ cm$^{-3}$ 2 - 3 orders of magnitude lower than the hole densities measured for the same doping process. Proskuryakov et al. observed very similar net acceptor
concentrations in their MOCVD grown arsenic doped devices in superstrate configuration despite a high arsenic concentration in CdTe (up to \( \sim 10^{19} \, \text{cm}^{-3} \)) [118]. They suggest compensation by Cd\( ^{2+} \) donor-type deep defects as the origin of the low net acceptor concentration.

The measured net acceptor concentration is lower for the purely arsenic doped cell compared to the additionally copper doped cell. This accords with the measured \( V_{oc} \) values, but contradicts the trend of the measured hole densities that will be further discussed below. Purely arsenic doped solar cells exhibit comparably high \( J_{sc} \) values as copper doped cells confirming that increased acceptor concentration in CdTe compared to undoped cells allowing collection near the junction (cf. Section 4.4.3).

Also in case of solar cells, segregation of arsenic at the CdTe surface was found with SIMS (not shown). Such a segregation can deteriorate the p-n junction properties. Furthermore, the hole densities obtained from in-plane Hall effect measurements, are probably dominated by a highly doped surface layer. In contrast, \( C-V \) measurements are of through-plane nature yielding the bulk CdTe net acceptor density explaining the different results obtained from this two methods. For future experiments the segregation of arsenic at the CdTe surface should be circumvented. For this purpose processes should be employed which enable homogeneous distribution in the CdTe layer, as for example by using co-evaporation of CdTe and arsenic or MOCVD [118].

![Figure 4.14](image.png)

**Figure 4.14:** a) \( J-V \) characteristics of arsenic doped solar cells with and without the addition of Cu. b) Corresponding \( C-V \) measurements of the same cells.
4.6 Conclusion and outlook

In this chapter, a process was introduced which enables the controlled doping of substrate configuration CdTe solar cells. The precisely controlled copper and silver doping of CdTe allows for reduced compensation of acceptors, maximized hole density, improved MCLT and enhanced collection of photo-generated charge carriers in the CdTe close to the p-n junction. Conversion efficiencies of up to 13.6% and 11.6% could be achieved with copper and silver doped substrate configuration CdTe solar cells, respectively. Copper and silver were shown to dope CdTe in the same manner and their amphoteric behavior is suggested as the cause why the dopant concentration has to be controlled with high precision.

In an attempt to further increase the hole density CdTe thin films and solar cells were doped with arsenic. Hole densities beyond $1 \times 10^{16} \text{ cm}^{-3}$ could be reached in arsenic doped CdTe thin films, however, they were always diminished by additional copper doping. Again, the amphoteric behavior of copper serves as an explanation for this effect. In spite of the large hole densities in the quenched CdTe layers $V_{oc}$ could not be increased. In order to achieve this also other aspects of the process need to be adapted and possible routes are discussed.

The presented process for controlled copper doping minimizes the needed copper amount such that the CdS treatment can be applied without detrimental effects on the junction. Furthermore, the doping can now be performed independently from the back contact formation, although there still appears to be some interplay between doping and back contact properties as shown in the simulations in Section 4.3.6. This allows to study the back contact properties in more detail and to identify possible related limitations what will be presented in Chapter 5. The minimization of the needed copper amount is very promising to reduce or even eliminate copper related performance degradation which will be studied in Chapter 6.
Chapter 5

Electrical back contact

This chapter is in part based on the following publications:


5.1 Introduction

In Chapter 4 a method enabling the well controlled doping of substrate configuration CdTe solar cells was presented. With the help of this process the understanding of how CdTe solar cells are doped could be improved. Efficiencies of substrate configuration cells could be increased up to 13.6% where it has to be noted that the $V_{oc}$ as well as the fill factor reached the level of superstrate configuration solar cells and only $J_{sc}$ is still lagging behind. Since the doping approach relies on the selective addition of sub-monolayer amounts of copper directly to the recrystallized CdTe layer copper addition to the back contact can be avoided. Hence CdTe as well as CdTe/CdS junction properties stay comparable and independent of the used back contact. This makes it possible to compare different back contact materials minimizing undesired influences biasing the results.
The formation of an ohmic contact has always been stated as one of the main challenges when producing CdTe solar cells. Due to its high electron affinity combined with its relatively large band gap p-type CdTe suffers from Schottky barrier formation when brought into contact with a metal [64]. Additionally, as a covalent semiconductor, CdTe exhibits Fermi level pinning reducing the influence of the metal work function on the barrier height [133].

Attempts to reduce the barrier mostly incorporate the introduction of a back contact buffer layer between the CdTe and the metal. This buffer can either consist of a high work function material lowering the Schottky barrier height or have a strong p-type character with high acceptor density allowing the holes to tunnel through the narrowed barrier [15]. In superstrate configuration the formation of a heavily p-type Cu$_x$Te layer on CdTe, often using an etching process to form a tellurium rich layer, followed by a metal contact including copper addition and finalized by an annealing has proven to be successful [16–18]. However, adaptations have to be made when processing substrate configuration solar cells. Because of the reversed deposition order etching of the CdTe surface is not possible and thermally unstable contact materials are unfavorable because of enhanced diffusion during processing.

Such back contact buffer layers have been investigated and described in Section 3.3. The most successfully applied back contact buffer for substrate configuration is thermally evaporated MoO$_x$. This material was shown to transform from the as deposited semiconductor MoO$_3$ to the high work function metal-like compound MoO$_2$ upon solar cell processing. Also Sb and Sb$_2$Te$_3$ proved to be suitable as back contact buffers.

In this Chapter, the novel doping process is applied to allow direct comparison of substrate configuration CdTe solar cells with different back contact buffers. Furthermore, substrate and superstrate configuration solar cells are examined to identify and explain remaining differences in their series resistances. Finally, the influence of copper doping on the back contact properties is examined.

### 5.2 Comparison of back contact buffers

In Section 3.3 MoO$_x$ and Sb$_2$Te$_3$ were identified as promising back contact buffers. Also with an Sb back contact buffer working solar cells could be processed. Figure 5.1 shows
the influence of varying the thickness of these three back contact buffer layers on $V_{oc}$ and fill factor of optimally copper doped substrate configuration solar cells. The first data points for all back contact buffers are at 0 nm implying a pure molybdenum back contact. Although the $V_{oc}$ is rather low, around 600 mV, reasonable fill factors of up to 70% can be achieved with a molybdenum back contact. However, when comparing the three cells it becomes clear that the use of a molybdenum back contact does not yield reproducible results.

Figure 5.1: Influence of varying back contact buffer layer thickness on $V_{oc}$ and fill factor for Sb (a), $\text{Sb}_2\text{Te}_3$ (b) and $\text{MoO}_x$ (c) back contact buffers.
The optimum thickness of the Sb back contact buffer is 4 nm. Adding more Sb causes a distinct drop of both $V_{oc}$ and fill factor. In case of Sb$_2$Te$_3$ the optimum is slightly shifted to a larger value of 16 nm. Again, when depositing thicker Sb$_2$Te$_3$, $V_{oc}$ and fill factor decrease. Too thick Sb or Sb$_2$Te$_3$ layers could be detrimental due to excessive Sb diffusion into the CdTe layer possibly altering the electronic properties of CdTe. Another possible explanation for the decreasing performance is that a chemical reaction at the CdTe/BC buffer interface happens which increases the contact resistance.

In case of the MoO$_x$ back contact buffer the optimum thickness was found to be around 125 nm. Both $V_{oc}$ and fill factor increase up to this amount of MoO$_x$. But while $V_{oc}$ remains constant at larger amounts the fill factor decreases again. MoO$_x$ thicknesses exceeding 150 nm furthermore lead to adhesion problems between the back contact and the CdTe most probably due to the water solubility of MoO$_x$.

Figure 5.2: Comparison of $J$-$V$ (a) and QE (b) characteristics of CdTe solar cells in substrate configuration with Sb, Sb$_2$Te$_3$ and evaporated MoO$_x$ back contact buffers.

<table>
<thead>
<tr>
<th>Buffer layer</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>11.4</td>
<td>726</td>
<td>71.7</td>
<td>21.9</td>
</tr>
<tr>
<td>Sb$_2$Te$_3$</td>
<td>12.6</td>
<td>796</td>
<td>71.7</td>
<td>22.1</td>
</tr>
<tr>
<td>MoO$_x$</td>
<td>13.4</td>
<td>824</td>
<td>74.3</td>
<td>21.9</td>
</tr>
</tbody>
</table>

Table 5.1: PV parameters for substrate configuration solar cells with Sb and Sb$_2$Te$_3$ back contact buffer layers. A simultaneously processed cell with a baseline evaporated MoO$_x$ back contact buffer serves as a reference.
5.2. Comparison of back contact buffers

The $J$-$V$ and QE characteristics of the best solar cells produced with these three buffer layers and processed in the same batch (cells differ only by their back contact buffer layer) are displayed in Figure 5.2. The corresponding PV parameters can be read from Table 5.1. While the cell with the Sb back contact buffer exhibits a substantially lower $V_{oc}$ compared to the MoO$_x$ baseline cell, the Sb$_2$Te$_3$ buffer layer yields a $V_{oc}$ close to 800 mV. Although both Sb and Sb$_2$Te$_3$ enable fill factors above 70% they are still inferior to MoO$_x$ yielding a fill factor of more than 74%.

In order to investigate whether the deposition method of MoO$_x$ influences the functionality of the back contact, cells with DC sputtered MoO$_3$ were processed. Analogous to evaporated MoO$_3$ the sputtered counterpart was found to transform to MoO$_2$ upon solar cell processing as verified by GIXRD measurements (not shown here). Figure 5.3 compares the $J$-$V$ and QE characteristics of two cells processed alongside each other with an evaporated and a sputtered MoO$_x$ back contact buffer, respectively. Both cells yield the same high $V_{oc}$ values while the fill factor is slightly lower for the cell with the sputtered MoO$_x$ (Table 5.2). Apparently, this is correlated with the stronger roll-over present in the first quadrant of the $J$-$V$ characteristics. A more pronounced roll-over indicates a higher barrier at the back contact, however, the solar cell parameters are only marginally lower showing that also sputtered MoO$_x$ makes an appropriate back contact buffer for substrate configuration CdTe solar cells.

![Graphs showing J-V and QE characteristics](image)

**Figure 5.3:** Comparison of $J$-$V$ (a) and QE (b) characteristics of CdTe solar cells in substrate configuration with evaporated and sputtered MoO$_x$ back contact buffers.
Table 5.2: PV parameters of substrate configuration solar cells with evaporated and sputtered MoO\textsubscript{x} back contact buffer layers.

<table>
<thead>
<tr>
<th>Buffer layer</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA·cm\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO\textsubscript{x} evaporated</td>
<td>13.2</td>
<td>838</td>
<td>73.7</td>
<td>21.3</td>
</tr>
<tr>
<td>sputtered</td>
<td>12.8</td>
<td>837</td>
<td>72.4</td>
<td>21.1</td>
</tr>
</tbody>
</table>

5.3 Finding limitations: Comparison with superstrate configuration

When comparing superstrate and substrate configuration devices with similar high $V_{oc}$ values a distinct difference is the more pronounced roll-over and higher series resistance for the latter (Figure 5.4a). This might be explained by the assumption that the MoO\textsubscript{x} contact used for substrate configuration exhibits a higher contact resistance caused by a larger back contact barrier height compared to the gold contact of superstrate configuration. In order to assess these quantities two types of measurements were carried out.

![Image](image.png)

**Figure 5.4:** Measured (a) and simulated (b) $J$-$V$ characteristics of a superstrate and a substrate configuration solar cell. All parameters are set to the same values apart from $q\Phi_B$, the majority carrier barrier height at the back contact.
5.3. Finding limitations: Comparison with superstrate configuration

Figure 5.5: Contact resistance values to CdTe for gold, molybdenum and different MoO$_x$ thicknesses normalized to the gold to CdTe contact resistance.

The contact resistances between CdTe and gold, molybdenum and different thicknesses of MoO$_x$ were measured by means of the transmission line method (cf. Section 2.2.5.1). To ensure that the contacts are working in the same way as in the finished solar cells the gold contacts were deposited on top of treated and doped CdTe while the molybdenum and Mo/MoO$_x$ contacts were formed before CdTe, which was treated and doped subsequently. The extracted contact resistances normalized to the gold contact are displayed in Figure 5.5.

Contact resistance decreases for thicker MoO$_x$ proving its beneficial effect on the back contact. For a MoO$_x$ thickness of 100 nm, which is similar to the typical thickness used in substrate configuration solar cells, a contact resistance about 20% higher than for a gold contact in superstrate configuration is measured supporting the assumption that the higher series resistance originates from the back contact resistance.

To calculate the back contact barrier height temperature dependent dark $J$-$V$ measurements were recorded and Arrhenius plots of the turning currents $J_T$ where plotted and linearly fitted according to the method presented in Section 2.2.5.5. Figure 5.6 shows the temperature dependent dark $J$-$V$ measurements and the corresponding Arrhenius plots for both configurations with the calculated back contact barriers in the inset. The calculated barrier height values are 0.42 eV for the superstrate and 0.48 eV for the substrate cell again demonstrating the slightly better electrical contact quality in superstrate configuration.

To verify that this difference in back contact barrier height can explain the differences
in the $J$-$V$ characteristics the observed behavior was modeled using the 1D simulation software SCAPS [59]. As confirmed by SIMS measurements (quantified using ICPMS) the copper concentration and consequently also the acceptor concentration in CdTe is equal for the superstrate and substrate case [134, 135]. Therefore, it is reasonable to set the acceptor position and concentration to equal values for both configurations in the simulation. By merely setting the barrier height for majority carriers at the back contact to the rounded measured values of 0.4 eV for superstrate and 0.5 eV for substrate configuration the observed $J$-$V$ characteristics can be modeled (Figure 5.4b). The good agreement of measurement and simulation demonstrates that the main difference between superstrate and substrate configuration, responsible for the stronger

**Figure 5.6:** Temperature dependent dark $J$-$V$ measurements for substrate (a) and superstrate (c) configuration solar cells, respectively. Arrhenius plots of the turning current dependency on the Temperature for substrate (b) and superstrate (b) configuration. Back contact barrier heights $q\Phi_B$ read from the slope of the linear fit are displayed.
5.4 Influence of copper doping on the back contact properties

As already mentioned in Sections 4.3.3 and 4.3.6 the copper doping of the CdTe layer also influences the back contact properties. In our SIMS measurements (cf. Figure 4.4) we found that copper signal is high at the BC/CdTe interface. Copper precipitation at this interface has been reported to lower the surface ionization potential and therefore reduce the back contact barrier [108, 121].

Due to their low performance it is difficult to directly measure the back contact barrier height in undoped CdTe solar cells. Therefore, we performed TLM measurements on variously doped CdTe layers with the same Mo/MoO₃ contacts they have in a substrate configuration solar cell and extracted the contact resistances. Contact resistance values normalized to the value of the optimally doped sample $0.8 \times 10^{15}$ cm$^{-2}$ are shown in Figure 5.7. The contact resistance drastically decreases upon the addition of the optimum copper amount. However, further increasing the added copper amount only leads to a slight decrease in contact resistance.

Current transport over a Schottky barrier at a metal-semiconductor interface is described by thermionic emission theory. The total current flow over a barrier of height $q \Phi_B$ at a temperature $T$ when a voltage $V$ is applied is given by [14]:

$$J = A^* \cdot T^2 \cdot \left( e^{\frac{qV}{kT}} - 1 \right) \cdot e^{\frac{q \Phi_B}{kT}} \quad (5.1)$$

where $k$ is the Boltzmann constant and $A^*$ the effective Richardson constant for thermionic emission. Applying Ohm’s law the resistance of the barrier can be calculated:

$$R = \frac{V}{J} = \frac{V}{A^* \cdot T^2 \cdot \left( e^{\frac{qV}{kT}} - 1 \right)^{-1} \cdot e^{\frac{q \Phi_B}{kT}}} \quad (5.2)$$

As the barrier height in an optimally doped sample ($q \Phi_{B,\text{opt}}$) is already known from temperature dependent $J$-$V$ measurements the barrier heights for other amounts of copper addition can now be calculated from the normalized contact resistance $R/R_{\text{opt}}$: roll-over, higher series resistance and lower fill factor for the latter, is the higher barrier for majority carriers at the back contact.
Figure 5.7: Influence of copper addition on the normalized contact resistance between CdTe and the Mo/MoO<sub>x</sub> back contact (left scale) and the back contact barrier height (right scale). Contact resistance values are normalized to the value of the optimally doped sample.

\[ q\Phi_B = k \cdot T \cdot \ln\left(\frac{R}{R_{opt}}\right) + q\Phi_{B,\text{opt}}. \]  

Table 5.3 gives the majority carrier barrier height values calculated from Equation 5.3 for the measured copper amounts. Because of the logarithmic relationship between \( q\Phi_B \) and \( R/R_{opt} \) a linear scale for the barrier height can be added to Figure 5.7 if the correct scaling is chosen. In case of undoped CdTe the barrier height is 0.68 eV explaining the low \( V_{oc} \) of undoped cells. This value is in very good agreement with the barrier height value of 0.7 eV introduced in the simulation of an undoped CdTe solar cell to reproduce the measured \( J-V \) characteristics (cf. Section 4.3.6). Already the addition of \( 0.08 \times 10^{15} \text{ cm}^{-2} \) copper reduces the barrier height significantly. The barrier is lowered by 0.2 eV when adding \( 0.8 \times 10^{15} \text{ cm}^{-2} \) copper to an undoped device. This shows that copper addition not only leads to acceptor doping of CdTe but also improves the back contact quality. It is remarkable that upon addition of such a small amount of copper to the CdTe layer enough copper accumulates at the back contact to allow for a reduced majority carrier barrier height. Adding ten times more copper to the CdTe layer only causes a slight decrease of the barrier height by 0.01 eV. This result suggests that the presence of larger copper amounts at the back contact is at least one reason why superstrate configuration solar cells exhibit a smaller back contact barrier height and series resistance than substrate configuration solar cells.
5.4. Influence of copper doping on the back contact properties

<table>
<thead>
<tr>
<th>Cu amount (10^{15} \text{ cm}^{-2})</th>
<th>R/R_{\text{opt}}</th>
<th>q\Phi_B (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2233</td>
<td>0.68</td>
</tr>
<tr>
<td>0.08</td>
<td>112.5</td>
<td>0.60</td>
</tr>
<tr>
<td>0.8</td>
<td>1</td>
<td>0.48*</td>
</tr>
<tr>
<td>8.0</td>
<td>0.798</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Table 5.3: Normalized contact resistance $R/R_{\text{opt}}$ and majority carrier barrier height values $q\Phi_B$ calculated from Equation 5.3 for all measured copper amounts. The value for the majority carrier barrier height of the optimum doped cell $q\Phi_{B,\text{opt}}$ (*) was taken from the temperature dependent $J$-$V$ measurement shown in Figure 5.6a and b.

The dual role of copper on the doping of CdTe and the back contact properties can be further illuminated by comparing the influence of copper addition to superstrate and substrate configuration solar cells. Figure 5.8a and b display the $J$-$V$ characteristics of undoped, insufficiently doped and optimally doped solar cells in superstrate and substrate configuration, respectively. It is evident that while in superstrate configuration the $V_{oc}$ increases first upon doping in substrate configuration $J_{sc}$ is the first parameter to increase. When adding the optimum copper amount cells of both configurations perform similarly.

The behavior of the $J$-$V$ curves in superstrate and substrate configuration was modeled with SCAPS and the results are depicted in Figure 5.8c and d, respectively. The differing shapes of the insufficiently doped solar cells can be explained considering the different positions of copper addition in the two configurations. In superstrate configuration copper is added directly to the back contact where it first of all decreases the back contact barrier thus increasing the $V_{oc}$ (Figure 5.8c, blue). Only when enough copper is added the CdTe becomes sufficiently doped and the $J_{sc}$ increases as proper p-n junction is established (Figure 5.8c, green).

In contrast, in substrate configuration copper is added to the opposite side of CdTe, far away from the back contact. Copper primarily introduces acceptors into the CdTe layer hence increasing the built-in field and shifting the collection towards the junction resulting in an increased $J_{sc}$ (Figure 5.8d, blue). When more copper is added it can also diffuse to the back contact and improve its properties.
As previously shown the back contact barrier is still slightly higher in substrate configuration even upon optimum doping leading to the same acceptor concentration as in superstrate configuration.

**Figure 5.8:** a,b) $J$-$V$ measurements of solar cells in superstrate (a) and substrate (b) configuration solar cells processed using 0/2/32 Å and 0/0.1/1.0 Å equivalent of copper, respectively. c,d) SCAPS simulations using different back contact barriers $q\Phi_B$ and acceptor concentrations $N_a$ to reproduce the measurements of (a) and (b). Barrier height values are given in eV and acceptor concentrations in cm$^{-3}$. 
5.5 Conclusion and outlook

The application of the well-controlled acceptor doping process presented in Chapter 4 allows direct comparison of different back contacts with minimized undesired influences on the CdTe electrical properties or the CdTe/CdS junction. In this way, characteristics of solar cells with different back contact buffer layers could be compared. Efficiencies of 11.4% and 12.6% could be achieved using Sb and Sb$_2$Te$_3$ back contact buffers, respectively. So far, MoO$_x$ still allows highest efficiency of 13.6%, mainly due to higher $V_{oc}$ and fill factor. DC sputtered MoO$_x$ enables similarly high PV parameters as evaporated MoO$_x$ although it increases the roll-over hence slightly reducing the fill factor.

$J-V$ characteristics of substrate configuration solar cells commonly exhibit a stronger roll-over and series resistance then their superstrate configuration counterparts indicating a higher contact resistance caused by a larger back contact barrier of the former. This observation is supported by transmission line measurements demonstrating a 20% higher contact resistance for a substrate configuration MoO$_x$ than for a superstrate gold contact. Furthermore, extracting the back contact barrier height from temperature dependent dark $J-V$ measurements by linearly fitting Arrhenius plots of the turning current gives a higher value for a substrate (0.48 eV) than for a superstrate configuration cell (0.42 eV). Implementing these measured values to SCAPS simulations, the observed $J-V$ characteristics with the differing roll-overs can be modeled.

Copper doping of the CdTe was found to decrease the majority carrier barrier height at the back contact in addition to raising the acceptor concentration of CdTe. It does so not only in superstrate configuration where the copper is directly added to the back contact but also in substrate configuration. Yet, even though the same acceptor concentrations as in superstrate configuration are reached the back contact barrier remains slightly larger in substrate configuration.

The presented observations suggest that the fill factor of substrate configuration CdTe solar cells is still limited by the higher back contact barrier compared to superstrate devices. Therefore, higher fill factors well above 75% might be possible for substrate configuration by further improvement of the back contact properties.
Chapter 6

Performance stability of CdTe solar cells

This chapter is in part based on the following publication:


6.1 Introduction

In the previous chapters the development of a novel process for the production of CdTe solar cells in substrate configuration with efficiencies up to 13.6% was presented. However, efficiency is not the only important factor for the success of a PV technology. A further important step towards the industrialization of this process is to prove the long-term performance stability of the solar cells. In this chapter the impact of copper doping, back contact material and stress atmosphere on the performance stability are investigated in detail and present degradation mechanisms are discussed.

Performance stability of solar cells is an important economic and ecologic factor which has to be ensured for periods exceeding 20 years. Since it is not feasible to conduct such long lasting studies, accelerated stress tests (AST) are performed in order to gain information on the performance degradation. Each laboratory uses different sets of stress parameters. Commonly used stresses include: thermal stress (up to 200 °C),
light soaking (up to several 100 mW/cm² intensity), bias (from a few volts reverse to a few volts forward bias), various chemical atmospheres and humidity (up to 100%). For this study, conditions of 80 °C and illumination of about 100 mW/cm² intensity were chosen while the solar cells were constantly operated at their maximum power point (MPP) in an oxygen containing but humidity free environment. Measurements were conducted in-situ such that the stress parameters were unaltered during the test.

There is a broad consensus that copper plays a major role in performance degradation of CdTe solar cells [101, 136, 137]. However, opinions diverge on how exactly copper affects the device stability. Finding the responsible mechanism is complicated due to the high mobility of copper in CdTe, especially along the grain boundaries, causing copper to be found in every layer of the solar cell even in an unstressed device [138–140]. The models on the impact of copper on performance stability of superstrate configuration solar cells discussed in literature can be broadly divided into the following three groups, distinguished by the layer in which copper deteriorates the electronic properties.

### 6.1.1 Copper in CdS

Numerous studies report an increased concentration of copper in the CdS and/or at the CdTe/CdS interface in solar cells stressed under various conditions [70, 101, 141, 142]. Since copper can act as a p-type dopant in CdS a proposed degradation mechanism is the compensation of CdS n-type doping and the consequential reduction of the built-in field [101, 143, 144]. This p-type doping is also well known to increase the photoconductivity of CdS leading to increased light-dark crossover in the current-voltage characteristics of the device. While there are papers stating this as detrimental for the cell [137, 145], there are also others [141] confirming this effect but claiming that the photoconductivity is harmless for the performance of an illuminated device.

### 6.1.2 Copper at the back contact

The influence of AST on the back contact properties is strongly dependent on the back contact formation process. Therefore, it is difficult to identify a comprehensive cause for degradation. Most researchers report either a loss of copper [101, 146] or decomposit-
6.2. Performance stability of substrate configuration solar cells

on of a favorable copper-compound (like CuTe$_x$) [145] at the back contact. Furthermore, there are also papers ascribing the observed back contact degradation to oxidation or other non-copper related mechanisms [111, 141].

The features most often associated with degradation of the back contact are increased roll-over and series resistance after stress [141, 147]. They are believed to be reflective of an increased Schottky barrier between CdTe and back contact.

6.1.3 Copper in CdTe

In literature, it is reported that the copper concentration in CdTe is mostly unchanged during AST [141, 148–150] and therefore the CdTe layer is often not associated with degradation and the role of copper in this layer is neglected. However, even if the concentration in the CdTe layer is unchanged, the migration of copper atoms from Cd sites (acceptor states) to interstitial sites (donor states) or the grain to grain boundary diffusion of copper can influence the performance stability. Various papers report on a decreased net acceptor concentration in CdTe after stress [136, 146, 151, 152]. One proposed mechanism for this effect is the diffusion of excessive copper from the back contact into the CdTe grains leading to the formation of compensating defects [151]. The decreased net doping concentration of CdTe was also used to explain the formation of a blocking back contact [152]. Further, the formation of shunt pathways through the CdTe upon excessive copper in-diffusion is reported [153].

As all of these potential degradation mechanisms can occur simultaneously, it is desirable to develop solar cell architectures and fabrication methods, where at least some of these mechanisms can be avoided. This would allow better insights into the copper related degradation mechanism and could further lead to devices with improved stability.

6.2 Performance stability of substrate configuration solar cells

The process used for solar cells in substrate configuration minimizes the required amount of Cu by adding a small but well-controlled Cu amount to theCdTe layer after its recry-
Chapter 6. Performance stability of CdTe solar cells

The copper amount yielding highest efficiency is $0.8 \times 10^{15} \text{ cm}^{-2}$ (corresponding to an equivalent layer thickness of 1 Å) and is referred to as optimum doping. Such an optimally doped solar cell overall contains about 25 times less copper than a standard superstrate configuration solar cell fabricated in our lab. Despite the large difference in added copper amount solar cells in both configurations exhibit a very similar copper concentration inside the polycrystalline CdTe layer which is why they yield comparable $V_{oc}$ and fill factors [135]. Different ways are used to regulate the copper concentration in CdTe in substrate and in superstrate configuration. In the substrate configuration process the copper concentration in CdTe is controlled by the introduced amount of copper (which is distributed over the whole layer stack due to annealing at 400 °C) while in superstrate configuration it is controlled by adjusting the temperature (around 200 °C) and duration of the final annealing step. In the latter approach most copper stays at the back contact. For further details on the doping of CdTe please refer to Kranz et al. [134], Perrenoud et al. [135] and references therein. With the above described approach for solar cells in substrate configuration the doping of the CdTe layer can be well controlled without the need for copper diffusing from the back contact. This allows us to use a non-copper-based back contact. For all results shown in this chapter, except for those in Section 6.7, a molybdenum back contact with a MoO$_x$ back contact buffer on top was used.

The performance stability of optimally doped solar cells was investigated in a 1000 hours AST at 80 °C and 100 mW/cm$^2$ illumination where cells were constantly operated at their MPP. In Figure 6.1, the $J$-$V$ characteristics measured under STC before and after the AST are displayed in solid lines. Table 6.1 specifies the corresponding PV parameters. The cell showed good performance stability with 90% of initial power output after AST. The performance loss is mainly caused by a decrease in $V_{oc}$ and fill factor, while the $J_{sc}$ remained constant. This is accompanied by a stronger roll-over and thereby also a larger series resistance.

6.3 Copper redistribution

To identify the role of copper on the degradation mechanism, the redistribution of copper in the cell during AST was examined with SIMS. Figure 6.2 shows the copper signal of the optimally doped sample measured by SIMS before and after stress. The inset table
### 6.3. Copper redistribution

![Graph showing J-V characteristics of an optimally copper doped solar cell before and after a 1000 hour AST displayed in solid lines. Dashed lines show J-V curves simulated with SCAPS with the only parameter varied being the net acceptor concentration \( N_{A,\text{net}} \) which was lowered by 70% from “high” to “low”. The dotted line displays the simulation of a cell with increased back contact barrier height \( q\Phi_B \).](image)

**Figure 6.1:** *J-V* characteristics of an optimally copper doped solar cell before and after a 1000 hour AST displayed in solid lines. Dashed lines show *J-V* curves simulated with SCAPS with the only parameter varied being the net acceptor concentration \( N_{A,\text{net}} \) which was lowered by 70% from “high” to “low”. The dotted line displays the simulation of a cell with increased back contact barrier height \( q\Phi_B \).

<table>
<thead>
<tr>
<th></th>
<th>( \eta ) (%)</th>
<th>( V_{oc} ) (mV)</th>
<th>FF (%)</th>
<th>( J_{sc} ) (mA·cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement before AST</td>
<td>12.4</td>
<td>835</td>
<td>74.5</td>
<td>20.0</td>
</tr>
<tr>
<td>Simulation ( N_{A,\text{net}} ) high, ( q\Phi_B = 0.46 ) eV</td>
<td>12.3</td>
<td>837</td>
<td>73.6</td>
<td>20.0*</td>
</tr>
<tr>
<td>Measurement after AST</td>
<td>11.1</td>
<td>815</td>
<td>68.1</td>
<td>20.0</td>
</tr>
<tr>
<td>Simulation ( N_{A,\text{net}} ) low, ( q\Phi_B = 0.46 ) eV</td>
<td>11.1</td>
<td>809</td>
<td>68.8</td>
<td>20.0*</td>
</tr>
<tr>
<td>Simulation ( N_{A,\text{net}} ) high, ( q\Phi_B = 0.52 ) eV</td>
<td>11.4</td>
<td>832</td>
<td>68.7</td>
<td>20.0*</td>
</tr>
</tbody>
</table>

**Table 6.1:** PV parameters of the curves displayed in Figure 6.1. \( J_{sc} \) values of the simulated *J-V* curves (*) were normalized to fit the measurements.

shows the relative change of copper signal in certain layers or at interfaces. The back contact interface is broadened in the SIMS measurement due to the surface roughness of the sample an effect already described by Asher et al. [70].

Contrary to what most groups report for superstrate configuration cells, a slight decrease in copper signal in the CdS of substrate configuration cells upon AST was found,
indicating that the theories of degradation due to increased photoconductivity or reduced n-type doping of the CdS do not apply in our case. In the CdTe layer a small Cu loss is observed, however, because there are only very few counts in this layer the relative change is similar to the measurement error. The copper signal at the back contact, however, increases more than twofold indicating that there was little copper at the back contact in the unstressed device and that this amount was enlarged by copper diffusing from the CdS and CdTe layers. Therefore, also the degradation due to copper loss at the back contact can be excluded for our solar cells. Oxidation of the back contact is also an improbable explanation for degradation since an oxide is used as back contact material and the back contact is buried beneath the CdTe and window layers.

These measurements show that, when using this process, copper travels from the junction towards the back contact in the investigated devices, which is the opposite direction than described by other papers on AST of CdTe [101, 145, 154]. This can be clearly ascribed to the differences in copper concentration gradients. In a standard superstrate configuration solar cell the back contact acts as a copper reservoir providing copper for diffusion towards the junction and impeding diffusion towards the back contact.

By the use of SIMS measurements it was shown that two of the degradation mechanisms reported in literature, namely accumulation of copper in the CdS and loss of copper at the back contact, are not occurring in our substrate configuration solar cells. The
possibility of copper deficiency related degradation of the CdTe layer will be discussed in the following.

The copper concentration in the CdTe layer was found to decrease by 13%. Also many groups working on superstrate configuration observed only small changes in copper concentration in the CdTe layer by SIMS [70, 141, 148–150]. The copper concentration inside the CdTe layer was quantified with the help of ICPMS to $3 \pm 2 \times 10^{17}$ cm$^{-3}$. This agrees with values found by various other groups for superstrate configuration devices [155, 156].

### 6.4 Net acceptor concentration

To characterize the change in electronic properties of the CdTe layer $C$-$V$ measurements were performed. Figure 6.3 shows the depth dependent apparent acceptor concentration before and after AST. Upon stress the space charge region is extended from 3.3 to 6.1 µm and the apparent acceptor concentration $N_{CV}$ decreases by 70% from $3.1 \times 10^{13}$ cm$^{-3}$ to $0.9 \times 10^{13}$ cm$^{-3}$. This loss is substantially larger than the decrease in copper concentration measured by SIMS. The discrepancy between copper concentration and net acceptor concentration decrease might originate from a redistribution of copper between grains and grain boundaries or between donor and acceptor states. A similar depletion of the absorber and/or decrease in acceptor concentration after AST measured by $C$-$V$ is shown by several other researchers for superstrate configuration devices [136, 146, 151, 152].

To investigate if the observed net acceptor loss can explain the performance decrease SCAPS simulations are performed [59]. The dashed lines in Figure 6.1 present the results of the simulation and Table 6.1 lists the corresponding PV parameters. By lowering the net acceptor concentration of the CdTe layer in the simulation by 70% the measured $J$-$V$ characteristics after AST can perfectly be reproduced. The reduction is in agreement with the lowering of the net acceptor concentration found in $C$-$V$ measurements.

It is clearly visible that with the simulations not only the $V_{oc}$ and fill factor values but also the shape of the $V_{oc}$ curves could be matched accurately. It is noteworthy, that although the Schottky back contact barrier height remained unchanged in the simulation increasing series resistance and roll-over can be reproduced. The results show, that
Figure 6.3: Depth dependent apparent acceptor concentration $N_{CV}$ extracted from room temperature $C-V$ measurements for optimally doped cells before and after 650 hours of AST.

A stronger roll-over does not necessarily imply a degradation of the back contact. To compare the observed degradation with one caused by an increased back contact barrier an additional simulation was performed where the acceptor concentration remained unchanged at $6.5 \times 10^{14} \text{ cm}^{-3}$ but the back contact barrier was increased from 0.46 to 0.52 eV. Although the resulting $J-V$ curve exhibits a similar fill factor as the degraded cell the $V_{oc}$ did not drop to the same level and the roll-over and series resistance are much more pronounced, resulting in a different shape of the $J-V$ curve. The results show, that the reduced performance and increased rollover can be explained by a reduced net acceptor concentration leading to increased resistivity of the CdTe rather than an increased back contact barrier.

### 6.5 Correlation of copper concentration and performance stability

In order to investigate the correlation between copper concentration and performance stability, solar cells doped with copper amounts ranging from no intentionally added copper to up to 25 Å ($2 \times 10^{16}$ copper atoms per cm$^2$) were prepared. It is important to note that not intentionally adding any copper does not necessarily imply that the cell is completely copper free. The final copper content of the cell strongly depends on the purity of the source materials used.
6.5. Correlation of copper concentration and performance stability

The solar cells with varying amounts of copper were subjected to 650 hours of AST with the same conditions as described before in order to investigate the impact of introduced copper amount on cell stability. $J-V$ characteristics were recorded in-situ every half an hour. Please note that the measurement at elevated temperature leads to lower $V_{oc}$ values than under STC.

Figure 6.4a shows the development of $V_{oc}$ and fill factor of the differently doped cells during the period of the AST. The cell with optimum doping (green line) remains the best performing cell after the stressing. What stands out further is that the developments of both $V_{oc}$ (at 80 °C) and fill factor are strongly copper-dependent, during the first few hundred hours (underlaid with yellow color), while they are nearly identical for all copper amounts later on (underlaid with blue color). It seems that the more copper is introduced to a cell the longer the phase of copper-dependent development lasts (~50 hours for the smallest and 150 hours for the largest copper amount). This appears reasonable as for a larger amount of copper it takes longer to redistribute in reaction to the changed temperature and electric field in the AST.

![In situ measurements of $V_{oc}$ and FF recorded at 80 °C during a 650 hours AST for six cells doped with different amounts of copper. b) shows the first 200 hours of this measurement normalized to the first data point for each copper amount.](image)

**Figure 6.4:** a) In situ measurements of $V_{oc}$ and FF recorded at 80 °C during a 650 hours AST for six cells doped with different amounts of copper. b) shows the first 200 hours of this measurement normalized to the first data point for each copper amount.
For better comparability, Figure 6.4b displays the normalized \( V_{oc} \) and fill factor values for the first 200 hours of the AST. The extent of \( V_{oc} \) degradation is directly linked to the copper content of the cell; while the cell with no added copper (black) even shows an initial increase and the cell with \( 0.4 \times 10^{15} \) copper atoms per cm\(^2\) (blue) stays at the same level, cells with optimum copper or more show an initial decrease of \( V_{oc} \). This loss is comparable for cells processed using \( 0.8 \) to \( 8.0 \times 10^{15} \) copper atoms per cm\(^2\) added but substantially larger for the cell doped with \( 2 \times 10^{16} \) copper atoms per cm\(^2\) (red). Strikingly, after the large initial drop in \( V_{oc} \) by more than 15\% relative this cell even starts to recover. The fill factor of all cells with copper amounts of up to \( 0.8 \times 10^{15} \) \( \text{cm}^{-2} \) exhibits an initial improvement. Cells with more copper degrade from the beginning.

The phase of copper-dependent degradation fits well to the observed net acceptor loss. Lower than optimum copper doping amounts lead to lower net acceptor concentrations and therefore also to a smaller decrease of net acceptor concentration upon AST reflected in less degradation. It is also reasonable to assume that for the redistribution of smaller copper amounts, less time is needed.

The cause for the observed net acceptor loss upon stress might be found in the distorted thermal equilibrium at 80 °C stressing temperature. At elevated temperature the solubilities for copper and defect formation energies in the solar cell layers change triggering a redistribution of copper and related defects. When the new equilibrium is reached the second copper-independent phase of degradation becomes visible.

The second degradation mode becomes only clearly visible after the first few hundred hours of AST when the copper-dependent degradation ended. This degradation mode is independent of copper concentration and shows a constant degradation rate. As the degradation observed with STC measurements before and after AST could be exhaustively modeled with the decrease of acceptor concentration it seems that this part of the degradation recovered after the end of the AST. This degradation is therefore ascribed to a deterioration of the contact between the solar cell and the contacting needles in the AST setup. While for the ex-situ STC measurements before and after the AST fresh conductive silver paste was applied to the back contact, the needles were directly contacting the molybdenum back contact layer in the AST setup. As the AST is carried out in an oxygen containing ambient the part of the molybdenum layer which was exposed to allow contacting might have oxidized and thus the contact resistance increased. For future measurements the molybdenum layer in the contacting region of the AST should be coated with an oxidation resistant contact metal.
6.6 Origin of net acceptor loss

Since a decrease of net acceptor concentration is observed, both a direct loss of acceptors or compensation by an increasing amount of donors are possible explanations. To distinguish between these two effects TRPL measurements of a nominally undoped (0 cm\textsuperscript{-2}), an optimally copper doped (0.8 \times 10\textsuperscript{15} cm\textsuperscript{-2}) and an excessively copper doped (8.0 \times 10\textsuperscript{15} cm\textsuperscript{-2}) cell were performed before and after AST (Figure 6.5). The PL decay does not significantly change upon AST for the investigated doping amounts indicating a constant minority carrier lifetime (MCLT). Thus, the MCLT is not influenced by the decrease of the net acceptor concentration by 70%.

![TRPL measurements](image)

**Figure 6.5:** TRPL measurements of an undoped (0.0), an optimally copper doped (0.8) and a heavily overdoped (8.0) cell before and after AST. The MCLT is not significantly altered upon stress. Overdoping, however, shortens the MCLT due to the formation of compensating donor-type defects.

Perrenoud et al. measured a decrease in hole density by 70% from 1.0 \times 10\textsuperscript{14} cm\textsuperscript{-3} to 0.3 \times 10\textsuperscript{14} cm\textsuperscript{-3} when doping a CdTe layer with ten times the optimum amount of copper [135]. This is ascribed to the formation of compensating donor-type defects (e.g. Cu\textsubscript{i}). Overdoping a solar cell in the same manner results in a shortened MCLT as compared to optimum doping as displayed in Figure 6.5. The compensating defects act as recombination centers decreasing the lifetime of the minority carriers [134]. Hence, compensation leading to decrease in hole density by 70% causes a major decrease in MCLT.
The unchanged MCLT of the optimally doped cell upon stress is a strong evidence that the net acceptor loss upon AST is not caused by formation of compensating donors but rather by a decay of acceptor type defects.

The decay of copper related acceptor states over time has been observed by photoluminescence measurements in single-crystal as well as polycrystalline CdTe [157, 158]. It is assigned to the dissociation of Cu$_{Cd}$ and/or Cu$_i$ $^\text{+}-V^-_{Cd}$ states. It is suggested that copper atoms that are released from the defects upon aging leave the bulk towards the crystal surface or grain boundaries. These observations are in good agreement with the measured loss of acceptor states in our substrate configuration solar cells upon AST.

6.7 Influence of back contact buffer on performance stability

In Section 3.4 it was already shown in a preliminary stress test that the employed BC buffer material can have a large impact on the performance stability of the solar cell. Therefore, cells with Sb, Sb$_2$Te$_3$ and MoO$_x$ BC buffers - all doped with the optimum amount of copper - were subjected to a 1000 hours AST. The in situ (at 80 °C) measured values of $V_{oc}$ and fill factor are displayed in Figure 6.6a. For better comparability Figure 6.6b shows the relative changes in $V_{oc}$ and fill factor normalized to the first data point of the measurements for each BC buffer.

The MoO$_x$ BC buffer not only enables the highest initial efficiency but also offers the best performance stability after 1000 hours of stress. For all BC buffers an initial drop in $V_{oc}$ can be observed. While, however, the drop is rather small in case of the MoO$_x$ BC buffer, it is significantly larger for the Sb$_2$Te$_3$ and Sb BC buffers. Also the evolution of the fill factor differs strongly between the cell with the MoO$_x$ BC buffer and the cells with Sb and Sb$_2$Te$_3$ BC buffers. For the former the fill factor shows a slight but steady decrease after a short initial improvement. For the latter an initial drop similar to the drop in $V_{oc}$ is observed followed by a slower, roughly constant degradation.

Figure 6.7 displays the $J$-$V$ characteristics measured before and after AST of the cells with Sb and Sb$_2$Te$_3$ BC buffers. The corresponding PV parameters can be read from Table 6.2. The $J$-$V$ characteristics and PV parameters of the cell with MoO$_x$ BC buffer can be found in Figure 6.1 and Table 6.1, respectively. As already mentioned above
6.7. Influence of back contact buffer on performance stability

Figure 6.6: a) In situ measurements of $V_{oc}$ and FF recorded at 80 °C during a 1000 hours AST for cells with Sb, $Sb_2Te_3$ and $MoO_x$ back contact buffer layers. For better comparability b) shows the values normalized to the first data point of each measurement. Due to some technical issues for a period of ~100 hours data points were not logged, but the cells were still under stress.

The cell with the $MoO_x$ BC buffer still delivers 90% of its initial power output after AST. In contrast, the performance of the cells with Sb and $Sb_2Te_3$ BC buffer degraded to less than 70% of the initial power output. This performance degradation is caused by a pronounced decrease in $V_{oc}$ and fill factor for both antimony based BC buffers.

As discussed in Section 6.4 the performance degradation of the cell with the $MoO_x$ BC buffer can be fully explained by a decrease in net acceptor concentration of the CdTe. The more pronounced decrease in $V_{oc}$ and fill factor of the cells with antimony based back contacts indicates a stronger decrease in net acceptor concentration in the CdTe and/or an additional increase of the barrier height for majority carriers at the back contact. Both effects could be envisaged as antimony can act as acceptor in CdTe possibly influencing the net acceptor concentration.

Although the Sb and $Sb_2Te_3$ BC buffers enable substrate configuration CdTe solar cells with high performance, they are a source of performance degradation. Therefore, these BC buffers appear to be less favorable for the industrial use in substrate configuration...
Figure 6.7: $J$-$V$ characteristics measured under STC of cells with Sb (a) and $Sb_2Te_3$ (b) back contact buffers before and after the 1000 hour AST.

<table>
<thead>
<tr>
<th>BC buffer</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>before stress</td>
<td>10.6</td>
<td>690</td>
<td>70.4</td>
</tr>
<tr>
<td></td>
<td>after stress</td>
<td>7.0</td>
<td>586</td>
<td>55.4</td>
</tr>
<tr>
<td>Sb$_2$Te$_3$</td>
<td>before stress</td>
<td>12.4</td>
<td>778</td>
<td>71.9</td>
</tr>
<tr>
<td></td>
<td>after stress</td>
<td>8.6</td>
<td>679</td>
<td>59.6</td>
</tr>
</tbody>
</table>

Table 6.2: PV parameters of the curves displayed in Figure 6.7.

CdTe solar cells. The MoO$_x$ BC buffer, however, does not seem to be the origin of any degradation mechanism and enables solar cells with good performance stability.

6.8 Influence of stressing ambient on performance stability

In order to investigate whether the ambient in which the AST is performed has an influence on the performance stability of the tested solar cells two 650 hours ASTs one in nitrogen ($N_2$ stress) and one in dry synthetic air ambient ($O_2$ stress) were performed. In Figure 6.8 the evolution of $V_{oc}$ and fill factor upon stress of $N_2$ and $O_2$ stressed cells are contrasted. It is clearly visible that the influence of stressing ambient on performance stability is only minor. However, a slight trend towards increased performance stability when stressing in oxygen containing ambient can be observed.
6.8. Influence of stressing ambient on performance stability

Figure 6.8: Evolution of $V_{oc}$ (top) and fill factor (bottom) measured under STC of solar cells stressed in nitrogen (a, blue) and oxygen containing (b, red) ambient. The values of several solar cells from the same ASTs are displayed to get some statistics.

Figure 6.9 displays the $J$-$V$ characteristics of the two most stable cells from the N$_2$ and O$_2$ AST before and after stress. The corresponding PV parameters are listed in Table 6.3. A smaller loss in $V_{oc}$ than for the cell stressed in nitrogen and even an increase in fill factor can be observed for the cell stressed in oxygen containing ambient. The overall performance after 650 hours of constant operation at MPP at 80 °C was still 97% of the initial performance. This represents the most stable cell measured during this Thesis.

Oxygen is known as an important factor when processing CdTe solar cells and it is often present during the growth [159] and/or the activation of CdTe [160]. Oxygen has been reported to enhance the p-type doping of CdTe solar cells [161] and CdTe thin films [162]. Furthermore, Metzger et al. reported on the increase of the MCLT in CdTe upon addition of oxygen during the CdTe growth [57]. Kranz et al. proposed a mechanism how oxygen increases the MCLT in substrate configuration CdTe solar cells [69];
Figure 6.9: *J*-V characteristics measured under STC of the most stable cells stressed in nitrogen (blue) and oxygen containing (red) ambient before (full lines) and after (dashed lines) the respective AST.

<table>
<thead>
<tr>
<th>Ambient</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$ stress before stress</td>
<td>11.9</td>
<td>824</td>
<td>71.5</td>
<td>20.3</td>
</tr>
<tr>
<td>N$_2$ stress after stress</td>
<td>10.3</td>
<td>755</td>
<td>68.7</td>
<td>20.0</td>
</tr>
<tr>
<td>O$_2$ stress before stress</td>
<td>11.6</td>
<td>809</td>
<td>71.0</td>
<td>20.2</td>
</tr>
<tr>
<td>O$_2$ stress after stress</td>
<td>11.2</td>
<td>784</td>
<td>71.5</td>
<td>19.9</td>
</tr>
</tbody>
</table>

Table 6.3: PV parameters of the $J$-$V$ curves displayed in Figure 6.9.

Oxygen located at the CdTe grain boundaries serves as exchange partner for sulfur diffusing in during the CdS treatment. The sulfur passivates the grain boundaries reducing recombination and therefore prolonging the MCLT.

Nakano observed a degradation of his CdTe solar modules when no oxygen was present in the module encapsulation [163]. The degradation could be suppressed by leaving some air filled space inside the encapsulation or incorporating an oxygen releasing agent.

Although only a minor improvement in performance stability is observed when the stressing ambient contains oxygen it can be envisaged that it is important to prevent oxygen loss in the solar cell during stress. Oxygen loss might have a direct negative impact.
on the performance for example via a decreased acceptor concentration or an indirect effect on other impurities degrading the performance. The presence of oxygen in the stressing ambient could prevent an oxygen loss in the solar cell due to the higher oxygen partial pressure outside the cell.

6.9 Conclusion and outlook

The performance stability of CdTe solar cells was investigated with the help of CdTe solar cells grown in substrate configuration with an optimized copper doping process which reduces copper content at the back contact. After 1000 hours of accelerated stress test such devices still deliver 90% of their initial power output. SIMS measurements showed that neither Cu loss in the back contact nor Cu accumulation in the CdS layer, which are often associated with degradation of CdTe solar cells, occurred in such cells. As the dominant origin of degradation, a loss in net acceptor concentration by 70% was identified using C-V measurements. SCAPS simulations confirmed that the loss in net acceptor concentration can fully explain the observed change in device performance. TRPL measurements suggest that not the formation of compensating defects but a decay of acceptor states is responsible for the observed decrease in net acceptor concentration.

The influence of various back contact buffers on performance stability was investigated. While antimony based back contact buffers were found to cause degradation of the solar cells during stress the MoO\textsubscript{x} back contact buffer proved to be not only suitable for high efficiency but also for good performance stability.

Stressing in oxygen containing ambient was found to lead to a slight trend towards increased performance stability compared to stressing in an oxygen free ambient. This could be explained by the prevention of oxygen out-diffusion from the solar cell when stressing in oxygen containing ambient. As oxygen directly and indirectly influences for example the acceptor concentration and the MCLT in CdTe its loss might lead to a decrease in performance and should therefore preferably be avoided. In this investigation the most stable solar cell of this thesis was measured. It exhibited 97% of the initial performance after 650 hours of MPP operation at 80 °C and 100 mW/cm\textsuperscript{2} irradiation intensity.
The identified degradation mechanism of net acceptor loss in the CdTe seems to be a fundamental phenomenon which can also explain degradation of superstrate configuration CdTe solar cells. In agreement with our findings, several groups observed similar small changes in Cu concentration by SIMS and measured a decrease of net acceptor concentration with C-V in superstrate configuration solar cells. While the degradation of back contact and CdS layer could be avoided by the use of a MoO$_x$ back contact buffer layer and an optimized Cu doping process the stabilization of the net acceptor concentration is expected to be a serious challenge for future research.

One strategy to overcome this problem is to alter the Cu solubility and acceptor formation energy via alloying CdTe with isovalent elements [164]. Another approach is to introduce alternative, possibly less diffusive dopants like arsenic or phosphorous. Work around solutions would be to reduce the doping density requirements via thickness reduction in combination with back contact passivation concepts and/or increasing minority carrier lifetime and mobility by reducing defects. Whether the observed acceptor decay is distinct to the case of Cu doping cannot be judged from our data. It is also possible that the observed acceptor loss stems from a low energy lattice instability of the CdTe itself [165]. In the latter case exchanging the doping element might not help and alloying CdTe might be the only way to overcome the challenge of net acceptor concentration decay.
Chapter 7

Conclusions and outlook

In this thesis, a novel process for the growth of CdTe solar cells in substrate configuration is developed. A CdCl$_2$ treatment procedure comprising of two separate treatments allows enhanced control over the properties of the CdTe layer (CdTe treatment) and the heterojunction formation with CdS (CdS treatment). The CdS treatment improves junction quality by passivation of interface and grain boundary defects but is not compatible with the presence of large amounts of copper in the cell.

Therefore, a method for the controlled doping of substrate configuration CdTe solar cells is introduced. Sub-monolayer amounts of copper or silver are evaporated on top of the recrystallized CdTe layer and diffusion of the dopant into the CdTe is promoted by annealing at 400 °C. With the precisely controlled copper and silver doping of CdTe hole densities of the order of $\sim 10^{14}\,\text{cm}^{-3}$ are achieved. It furthermore leads to improved MCLT and enhanced collection of photo-generated charge carriers in substrate configuration CdTe solar cells. Conversion efficiencies of up to 13.6% and 11.6% are achieved by copper and silver doping, respectively. The necessity for the precise control of the dopant amount is explained by the amphoteric behavior of copper and silver in CdTe.

Arsenic doping of CdTe was used in order to achieve higher hole densities and values beyond $1 \times 10^{16}\,\text{cm}^{-3}$ could be reached. Nevertheless, the $V_{oc}$ in substrate configuration solar cells could not be increased beyond the values reached by copper doping.

By means of the new method for controlled doping of CdTe, the doping process could be decoupled from back contact formation. Thus the back contact properties could be studied with minimized undesired influences on the CdTe electrical properties or the CdTe/CdS junction. Different back contact buffer layers were used to reduce the Schott-
ky barrier between CdTe and the metallic molybdenum back contact. Efficiencies of 11.4% and 12.6% could be reached using antimony and Sb$_2$Te$_3$ back contact buffers, respectively. These highly p-type semiconducting materials are applied to narrow the back contact barrier thus allowing holes to tunnel through. Highest efficiency of 13.6% could be achieved by using a MoO$_x$ back contact buffer. This layer is deposited as slightly sub-stoichiometric MoO$_3$ but it transforms to MoO$_2$ during solar cell processing. MoO$_2$ is a metal-like compound with a high work function allowing for reduced back contact barrier to CdTe. Yet, this contact was found to still show a higher contact resistance to CdTe than a standard superstrate configuration contact demonstrating that the back contact properties are still reducing the performance of substrate configuration solar cells. In addition to increasing the acceptor concentration copper doping of substrate configuration CdTe solar cells was found to substantially decrease the majority carrier barrier height at the back contact.

Copper doped substrate configuration CdTe solar cells were used to investigate the degradation mechanisms in CdTe solar cells. After 1000 hours of accelerated stress test such devices still delivered 90% of their initial power output representing a good performance stability. This result was enabled by the use of the optimized copper doping process which allowed to prevent copper loss in the back contact and copper accumulation in the CdS layer - both common degradation mechanisms in CdTe solar cells. The remaining performance degradation of 10% was found to be caused by a decrease in net acceptor concentration. Since the MCLT is found to be unaffected by this decrease a decay of acceptor states in the CdTe is suggested as the cause of the net acceptor loss. This degradation mechanism is not expected to be limited to substrate configuration but can also explain degradation of superstrate configuration CdTe solar cells.

The process for the growth of substrate configuration CdTe solar cells with $V_{oc}$ and fill factor at the level of superstrate configuration offers new opportunities to overcome technological challenges and find answers to long standing scientific questions of CdTe PV. Not only the recrystallization and p-type doping of CdTe can be controlled better in substrate configuration as they are decoupled from the p-n junction formation but also the p-n junction itself is better accessible thus facilitating adjustments of the junction and investigations of its properties. Furthermore, scientific insights on the role of processing steps, impurities and chemical reactions can be gained by comparing CdTe solar cells with similar performances in both configurations.
There are still various opportunities to improve performance of CdTe solar cells in substrate configuration. The parameter that needs improvement most to reach the values of superstrate configuration is the short circuit current. To increase $J_{sc}$ either the CdS thickness has to be reduced which has proven to be a very difficult task [128] or an alternative n-type layer has to be found. A very promising candidate is oxygenated CdS (CdS:O) as it has a tunable band gap (2.5 - 3.1 eV) allowing for better transmission while offering the same favorable band alignment to CdTe as CdS [166]. It has already been successfully implemented in superstrate CdTe solar cells [166–168]. This material allows to increase $J_{sc}$ even without reducing the n-type layer thickness.

It was found that the back contact still limits the fill factor of substrate configuration cells. Further efforts should be made to find a back contact enabling an even lower contact resistance to CdTe thereby raising the fill factor towards 80%.

Despite the rather large band gap of 1.5 eV of CdTe the $V_{oc}$ of polycrystalline CdTe solar cells has never reached values higher than ~850 mV until recently $V_{oc}$ values exceeding 900 mV were presented [169]. On the one hand this demonstrates that the $V_{oc}$ is not fundamentally limited but on the other hand it shows that it is not trivial to raise the it beyond 850 mV. To increase the $V_{oc}$ the acceptor concentration or the MCLT of CdTe have to be increased. By means of copper doping of CdTe hole densities not higher than $\sim 10^{14}$ cm$^{-3}$ are achieved. This value could be increased by either changing the dopant, for example to arsenic or phosphorous, or by increasing the solubility and/or decreasing the acceptor formation energy of copper by alloying CdTe with isovalent elements like selenium [164]. Alloying CdTe with selenium would furthermore allow to increase $J_{sc}$ due to the smaller band gap of CdSe$_x$Te$_{1-x}$ down to 1.4 eV [170]. Such changes in the doping and thus defects in CdTe could also (positively) influence the MCLT. In addition, concepts for passivation could be applied to prolong the MCLT and thereby increase the $V_{oc}$.

Since the dominant degradation mechanism was identified to be a decay of acceptor type (probably Cu$_{Cd}$) defects also the stability of CdTe solar cells might be improved by a changed acceptor position, formation energy or solubility in CdTe.
First of all, I would like to thank Prof. Ayodhya N. Tiwari and Stephan Bücheler for their support, advice and supervision during my PhD thesis. Further, I thank Prof. Stuart Irvine and Prof. David Norris for agreeing to be co-examiners of this thesis, dedicating their time and expertise.

Special thanks goes to Julian Perrenoud and Lukas Kranz for excellent teamwork, many fruitful discussions and cheerful time in the CdTe lab.

The female group members Melanie, Chantal, Caro, Debora and Karla I would like to thank for all the enjoyable girl talk and their compassion. To the ones already mentioned and to all the other current and former members of the Laboratory for Thin Films and Photovoltaics, namely Alex, Beni, Davood, Enrico, Fabian, Fan, Georgi, Harald, Jachen, Jérome, Johannes, Michael, Patrick B., Patrick R., Peter, Romain, Ruben, Saji, Shiro, Sigi, Stefan, Thomas, Till, Timo and Yaroslav goes my gratitude for the great time I could spend in the group. I enjoyed the interesting and inspiring discussions with all of you and also our fun activities outside the lab.

Thank you also to all the Master, Bachelor and Semester students who contributed to this thesis: Curdin Bächler, Elias Rehmann, Erik Cheah, Fabian Jähnig, Hannah Eggimann, Luisa Kneer, Micheal Dietrich, Michael Wyss and Rafael Schmitt.

Furthermore, I would like to thank Songhak Yoon for his help with the GIXRD measurements, Andreas Brun for the laser scribing of my samples as well as Guillaume Stechmann and Stephan Zäfferer for the interesting collaboration on 3D EBSD of CdTe solar cells.

Financial support from the Competence Center Energy and Mobility in ETH-Domain (CCEM) in the DURSOL project is gratefully acknowledged.
I would like to express my gratitude to my family for their continuous and generous support. My father for supporting me on my way, for proofreading and for answering all my questions until late in the evening, my mother for her understanding and care and my brother Alexander for his interest in my work and for always cheering me up.

Finally, I would like to thank my partner Nico who always believed in me, helped me take my mind off work and supported me in any way possible. Without you this would not have been possible.
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-D</td>
<td>One dimensional</td>
</tr>
<tr>
<td>AM1.5G</td>
<td>Reference global spectrum at air mass 1.5</td>
</tr>
<tr>
<td>AR</td>
<td>Anti-reflection</td>
</tr>
<tr>
<td>AST</td>
<td>Accelerated stress test(ing)</td>
</tr>
<tr>
<td>AZO</td>
<td>Aluminum doped ZnO</td>
</tr>
<tr>
<td>BC</td>
<td>Back contact</td>
</tr>
<tr>
<td>BSG</td>
<td>Borosilicate glass</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>CIGS</td>
<td>Cu(In,Ga)Se$_2$</td>
</tr>
<tr>
<td>C-V</td>
<td>Capacitance-voltage</td>
</tr>
<tr>
<td>CSS</td>
<td>Close space sublimation</td>
</tr>
<tr>
<td>CZTS</td>
<td>Cu$_2$ZnSn(S,Se)$_4$</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>EBIC</td>
<td>Electron beam induced current</td>
</tr>
<tr>
<td>$E_C$</td>
<td>Conduction band energy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi energy</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Efficiency</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>$E_V$</td>
<td>Valence band energy</td>
</tr>
<tr>
<td>FC</td>
<td>Front contact</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>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>GB</td>
<td>Grain boundary</td>
</tr>
<tr>
<td>GIXRD</td>
<td>Grazing incidence X-ray diffraction</td>
</tr>
<tr>
<td>HRT</td>
<td>Highly resistive and transparent</td>
</tr>
<tr>
<td>HVE</td>
<td>High vacuum evaporation</td>
</tr>
<tr>
<td>ICPMS</td>
<td>Inductively coupled plasma mass spectroscopy</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>J_T</td>
<td>Turning current density</td>
</tr>
<tr>
<td>MCLT</td>
<td>Minority carrier lifetime</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal organic chemical vapor deposition</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
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<tr>
<td>RBS</td>
<td>Rutherford backscattering spectroscopy</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
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<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 spectroscopy</td>
</tr>
<tr>
<td>SLG</td>
<td>Soda-lime glass (float glass)</td>
</tr>
<tr>
<td>STC</td>
<td>Standard test conditions</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TC</td>
<td>Texture coefficient</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conductive oxide</td>
</tr>
<tr>
<td>TLM</td>
<td>Transmission line method</td>
</tr>
<tr>
<td>TRPL</td>
<td>Time resolved photoluminescence</td>
</tr>
<tr>
<td>V_{bi}</td>
<td>Built-in voltage</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence band maximum</td>
</tr>
<tr>
<td>V_{oc}</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>W_p</td>
<td>Watt-peak</td>
</tr>
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<td>XRD</td>
<td>X-ray diffraction</td>
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Bibliography


Curriculum Vitae

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**Conference proceedings**


**Patent application**