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Abstract

For meeting the environmental challenges posed onto the community by its increasing demand for cheap energy, it is necessary that the electricity generation is shifted from nuclear and fossil fuel fired power plants to renewable energies. In photovoltaics, thin film solar cells in general and CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) solar cells in particular have a significant potential for cost reduction compared to classical Si-based solar cells due to less material usage, easier interconnection, and potentially faster production processes. The first part of the thesis focuses on the CIGS absorber layer and how changes to the layer processing can be used to increase the solar cell performance. It is also investigated how different evaporation profiles for the absorber layers could be used to make the production process cheaper by reducing layer thickness, resulting in less raw material demand and higher throughput in the deposition equipment. It was shown that by introducing an intentional band gap grading into the CIGS absorber layer, a 4% increase in the open circuit voltage can be obtained while limiting the loss in short circuit current to 1.5% or less, with the potential of reducing the loss even more by further optimization of the deposition process. This, among other optimizations, lead to a new internal record efficiency of 18.8% ($V_{oc} = 715$ mV, $J_{sc} = 34.7$ mAcm$^{-2}$, $FF = 75.9\%$). Additionally, significant changes to the distribution of the dopant Na were found when the three stage deposition process is altered, namely the duration of the Cu rich growth regime is changed. For absorber layers grown with a short time in Cu rich composition, a localization of Na at the absorber surface was found, while those layers where the Cu rich regime is maintained for a longer time show a shallower slope from the surface into the bulk and the Na more evenly distributed throughout the top region of the absorber layer. Furthermore, the potential of thickness reduction of CIGS was investigated with absorber deposition by a physical vapor deposition (PVD) three stage process. It was found that several changes in the deposition sequence and metal ramps need to be introduced to maintain $V_{oc}$ and fill factor. The best solar cell obtained showed a PV efficiency of $\eta = 11.7\%$, with $V_{oc} = 653$ mV, $J_{sc} = 25.1$ mAcm$^{-2}$, and $FF = 71.4\%$ at an absorber layer thickness of 500 nm.
When optical confinement measures are taken to avoid the current loss with respect to the thick layers, efficiencies of 15 to 16% should be possible at a thickness of 500 nm instead of the 1.6 to 2 µm usually used today.

The second part of the thesis deals with tandem cells to enhance the utilization of the energy of sunlight by reducing thermalization losses. Stacks of dye sensitized cells (DSC) as top cells and CIGS bottom cells were assembled by both mechanical stacking and monolithical integration. In both cases, the most sensitive point was the good interconnection of the cells without allowing for leakage currents. In the case of mechanical stacks, leaking of silver paste from the wiring to scribelines was most challengeing, while in the more elegant monolithic approach, the CIGS bottom cell was corroded by the electrolyte used in the DSC. The issue of the stability of the CIGS cell against the electrolyte could not be satisfyingly resolved in the work done for this thesis. While the performance of the tandem exceeded the CIGS cell by 5% and that of the DSC by 45% in the monolithically interconnected stack, the performance degraded to that of the DSC alone pretty fast by creating shuntways through the CIGS layer by electrolyte corrosion. Furthermore, some preliminary studies for CGS/CIS tandem cells were performed. A CIGS solar cell on an ZnO:Al back contact was manufactured yielding a conversion efficiency of 13.5%. The main challenge here is the manufacturing of a well-working wide-gap chalcopyrite cell, i.e., a CGS cell. Due to changes in the band alignment at the p-n heterointerface with CdS, changes in the recombination regime limit the available open circuit voltage of the top cell. This could be overcome by finding an alternative n-type buffer layer or a different material for the top cell (e.g., AgIn_{1-x}Ga_{x}Se_{2} or CuIn_{1-x}Ga_{x}(Se_{1-y}S_{y})_{2}, where the valence band is shifted downwards instead of a lift of the conduction band).
Zusammenfassung

Um die Herausforderungen an die Gesellschaft durch den wachsenden Durst an billiger Energie zu bewältigen muss in der nahen Zukunft eine Verschiebung der Stromproduktion weg von fossilen Energieträgern hin zu erneuerbaren Energien stattfinden. Dünnschichtsolarzellen im Allgemeinen und CuIn\textsubscript{1-x}Ga\textsubscript{x}Se\textsubscript{2}-(CIGS-)Solarzellen im Speziellen bieten hier ein Potential für signifikante Kosteneinsparungen verglichen mit klassischen Si-basierten Solarzellen durch geringeren Materialeinsatz, einfachere Verschaltungsmöglichkeiten der Zellen zu Modulen und potentiell kostengünstigere Produktionsprozesse. Der erste Teil dieser Arbeit konzentriert sich auf die CIGS-Absorberschicht und wie Veränderungen in den Prozessen genutzt werden können um die Leistung der Solarzellen zu verbessern. Darüberhinaus wird dargelegt wie unterschiedliche Dampfungsprofile für die Absorberschichten den Herstellungsprozess vergünstigen können, indem die Schichtdicke reduziert wird. Dies würde in geringerem Bedarf an Rohmaterial und höherem Durchsatz in den Depositionsanlagen resultieren. Die präsentierte Arbeit zeigt dass durch den bewussten Einbau eines Gradienten in das Bandlückenprofil der CIGS-Absorberschicht eine 4%-ige Erhöhung der $V_{oc}$ bei gleichzeitiger Limitierung der Verluste bei der Stromdichte auf 1.5% oder weniger erreicht werden kann. Dies führte – neben weiteren Optimierungen – zu einer neuen internen Rekordeffizienz von 18.8% ($V_{oc} = 715\ \text{mV}, J_{sc} = 34.7\ \text{mAcm}^{-2}, FF = 75.9\%$). Die Verluste können durch weitere Optimierung potentiell noch weiter gesenkt werden. Weiters wurden signifikante Änderungen in der Verteilung des Dotierstoffes Natrium in der Absorberschicht bei Änderungen im Depositionsprozess gefunden. Wenn die Zeitdauer, in der sich die Schicht während der Beschichtung in einer kupferreichen Zusammensetzung befindet, variiert wird, ändert sich auch die Verteilung des Na: für Absorber, die nur kurz überstöchiometrisch waren, findet sich das Natrium lokalisiert an der Oberfläche der CIGS-Schicht. Wenn diese Zeitdauer nun verlängert wird, findet man ein flacheres Na-Profil von der Oberfläche in die Schicht hinein und eine ausgeglichenerere Verteilung des Natriums in der oberen Schicht des Absorbers. Außerdem wurde das Potential der Schichtdickenreduktion von CIGS-Absorbern
untersucht. Während der Arbeit kristallisierte sich heraus, dass einige Änderungen im Verdampfungsprofil und das Einbringen von Metallflussrampen in den Beschichtungsprozess notwendig sind um \( V_{oc} \) und Füllfaktor auf Werten vergleichbar mit dicken Referenzproben zu halten. Die beste hergestellte Solarzelle zeigte eine Effizienz von \( \eta = 11.7\% \) mit \( V_{oc} = 653 \text{ mV} \), \( J_{sc} = 25.1 \text{ mAcm}^{-2} \) und \( FF = 71.4\% \) bei einer Absorberschichtdicke von 500 nm. Wenn optische Maßnahmen ergriffen werden um den Verlust in der Stromdichte im Vergleich zu dickeren Schichten zu minimieren, sollte eine Effizienz von 15 bis 16\% bei Schichtdicken von 500 nm möglich sein – statt den 1.6 bis 2 \( \mu \text{m} \), die heute üblicherweise verwendet werden.

Chapter 1

Introduction

The modern world is currently facing environmental challenges unprecedented in history. Global energy demand in 2009 is as high as 12000 million tonnes of oil equivalent (Mtoe), with a forecast annual growth of 1.5% until 2030 when global demand is expected to exceed 16800 Mtoe. More than three quarters of that energy is predicted to be generated from fossil fuels (figure 1.1) [1]. World electricity demand is expected to grow even faster, at an annual rate of 2.5%, thus being the primary driver for the use of fossil fuels [1]. On this path, CO$_2$ emissions will increase from 28.8 Gt/a in 2007 to more than 40 Gt/a in 2030 [1].

In recent history, the global average temperature has increased significantly. Figure 1.2 from Hansen et al. [2] shows the global mean temperature anomaly development from 1880 to 2009. The calculation methodology is also described in the cited paper. Simultaneously, as shown in figure 1.3, annual global CO$_2$ emissions increased from 3 million t in 1751 to 236 million t in 1880 and to 8365 million t in 2007 [3]. To limit the average global temperature increase to 2 °C, it will be necessary to achieve a global CO$_2$ emission of less than 10 Gt/a in 2050, with the peak of emission being earlier than 2020 [4]. With the scenario predicted by the International Energy Agency in the World Energy Outlook 2009, this goal is missed by a wide margin, suggesting a long-term global warming as high as 6 °C [1]. While the share of non-hydro renewable power is expected to increase from 2.5% in 2007 to 8.6%, the forecast sees a decrease in hydro power from 16 to 14% [1]. This corresponds to an increase of the share of renewables from 18.5 to 22.6%, or 4.1 percentage points, while the total energy consumption is expected to increase by 40%, resulting in an increase in fossil fuel consumption by 32%.

In contrast to the environmental benefits from the use of renewable energy sources, there are also drawbacks. Most renewable energy sources such as solar, wind, and – to a certain extent – hydro are limited by external, uncontrolled
Figure 1.1: Global primary energy demand by sources in the World Energy Outlook 2009 (redrawn with data from [1]).

Figure 1.2: Global temperature anomaly from 1880 to 2009 [2] (updated by NASA via http://data.giss.nasa.gov/gistemp/graphs/).
Figure 1.3: Annual global CO\textsubscript{2} emissions from burning of fossil fuels and cement production from 1751 to 2007 [3].

events such as weather conditions, time of the day, and season. Thus, in combination with the lack of efficient and cheap electricity storage technologies, each technology on its own cannot be used as a standalone basis for electricity generation guaranteeing power to the grid 24/7. However, the combination of technologies, decentralization of power production facilities, and promoting efficient electricity storage such as pump-stored hydro power, some of these drawbacks can be mitigated. The second notable drawback of most renewable energies is cost. To increase the share of renewables in the future energy mix, the power generation cost from those sources needs to be competitive with power generation from fossil fuels. In early 2010, the average price of solar energy ranged between 0.19 USD/kWh and 0.35 USD/kWh for industrial and residential applications, respectively [5]. As a comparison, in 2008 the average retail price of electricity in the United States was 0.068 USD/kWh for industrial customers and 0.113 USD/kWh for residential power supply [6]. The corresponding prices in the second half of 2009 in the European Union were 0.1023 EUR/kWh for industry and 0.1638 EUR/kWh for residences [7]. The power generation cost is even less, ranging between 0.03 and 0.06 USD/kWh for coal-fired plants, 0.03 and 0.07 USD/kWh for power plants fuelled by natural gas, and between 0.02 and 0.03 USD/kWh for nuclear power [8].

These numbers clarify the need for solar electricity to become cheaper if it should gain a significant market share in a sustainable energy mix for powering the world’s needs in the future. Conventional photovoltaic modules based on silicon wafers have several limitations when it comes to cost reductions. Due to
Chapter 1. Introduction

Figure 1.4: Scribing procedure for monolithic interconnection of modules. Step 1: patterning of the back contact to define the single cells. Step 2: deposit absorber and apply patterning to provide space for the front contact material to make a connection to the back contact. Step 3: deposit front contact and insulate the single cells by scribe 3.

the indirect band gap of silicon, a comparably thick absorber of approximately 200 $\mu$m thickness is needed and as the wafers are sawed from crystal ingots, there is always sawing waste. Furthermore, modules can only be manufactured by mechanically apply wiring to the front and back of the absorber wafers and the whole module then needs to be encapsulated. Thin film technologies can eliminate several of these drawbacks. CIGS and CdTe have direct band gaps with a high absorption coefficient, resulting in complete absorption of the sunlight in absorber layers of 2 $\mu$m thickness or less which can be grown directly on the carrier substrate. The single cells can be monolithically interconnected to a PV module by scribing the layer during different stages of the deposition as shown in figure 1.4, resulting in the front contact of one cell being electrically connected to the back contact of the next cell. Finally, one half of the encapsulation can be used as substrate where the solar cell stack is deposited onto, thus only one side needs to be encapsulated by means of mechanical glueing. These advantages promise significant potential for a reduction in manufacturing cost of thin film PV modules over conventional Si-based modules.

Thin film technologies like CuIn$_{1-x}$Ga$_x$Se$_2$ and CdTe are now in the early stages of large scale industrial production. Annual production of CdTe is already high, with First Solar planning for a capacity of 2.3 GW/a by the end of 2011 [9], and Abound Solar currently expanding from 65 MW/a to 840 MW/a [10]. On the CIGS side, Solar Frontier is currently expanding to 900 MW of annual module production capacity [11], and AVANCIS is planning for an increase from 20 to 220 MW/a when the factories currently under construction come online [12]. Of
course, in both fields several other companies are currently starting and upscal-
ing production (Würth Solar, Solibro, GlobalSolar,...). Despite CuIn$_{1-x}$Ga$_x$Se$_2$
being on the brink of industrialization, there are still scientific questions waiting
to be answered and possibilities to be found for enhancing the efficiency. The
work described in this thesis should point out possible ways in achieving cheap
solar power by increasing the efficiency of CuIn$_{1-x}$Ga$_x$Se$_2$ thin film solar cells and
combining the cost-effectiveness of thin film solar cells with advanced concepts
such as tandem solar cells to reduce loss of photon energy to heat and wavelength
converting dyes to improve the spectral response of CIGS solar cells in the short
wavelength spectral region.
Chapter 2

Theoretical Background

2.1 Basic Properties of Photovoltaic Devices

A solar cell is a device directly converting sunlight into electricity by photogeneration of charge carriers in a semiconducting absorber. Incident photons excite electrons from the valence band of the semiconductor into its conduction band, creating an electron hole pair which can be separated by a p-n junction. The charge carriers are then collected by electrical contacts and flow through an external circuit where they can be used to power an electric load.

The efficiency of a solar cell is determined by the output power divided by the irradiating power of sunlight. Figure 2.1 shows a typical diode curve of a solar cell illustrating the basic PV parameters. To calculate the efficiency of the device, the power along the $I - V$ characteristic needs to be maximized by

$$\frac{dP}{dV} = \frac{d(I \cdot V)}{dV} = 0.$$  \hspace{1cm} (2.1)

The point determined this way is called the maximum power point (MPP) of the solar cell. The efficiency is then given by

$$\eta = \frac{J_{\text{MPP}} \cdot V_{\text{MPP}}}{P_{\text{irrad}}}.$$  \hspace{1cm} (2.2)

For short circuit conditions, the voltage is zero and the corresponding photocurrent is called $J_{sc}$ or short circuit current density, for open circuit conditions the current is zero and the voltage called $V_{oc}$ or open circuit voltage. If one now defines the fill factor as

$$FF = \frac{J_{\text{MPP}} \cdot V_{\text{MPP}}}{J_{sc} \cdot V_{oc}},$$  \hspace{1cm} (2.3)
efficiency can be written as

\[ \eta = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{irrad}}. \]  

(2.4)

Figure 2.2 shows the circuit equivalent to a solar cell and more detailed explanations can be found in textbooks such as [13]. \( R_s \) denotes the serial resistance in the device, \( R_p \) the parallel resistance or shunt resistance over the solar cell, and \( J_{photo} \) the photocurrent. If the \( R_p \) and \( R_s \) values are infinity and zero, respectively, the diode is ideal and has an almost rectangular shape \( (FF \ll 1) \) with a \( J(V) \) characteristic of

\[ J(V) = J_{dark} + J_{photo} = J_0 \cdot \left( \exp\left( \frac{qV}{BkT} \right) - 1 \right) - J_{photo}, \]  

where \( B \) is the diode ideality factor – \( B = 1 \) for an ideal diode – and \( J_0 \) the reverse saturation current density of the diode. With zero current, the open circuit voltage can be expressed as

\[ V_{oc} = \frac{BkT}{q} \ln\left( \frac{J_{photo}}{J_0} + 1 \right). \]  

(2.6)

Obviously, when the voltage is zero,

\[ J = -J_{photo} = J_{sc}. \]  

(2.7)
2.2 Illuminated p-n Junctions in More Detail

When a p-n junction is illuminated with light of an energy exceeding the band gap of the semiconductor, electron-hole-pairs are generated. If this generation
occurs in the depletion region, or within the minority carrier diffusion length of the depletion region, the charge carriers are separated by the built-in electrostatic potential as shown in figure 2.4. This results in an excess of electrons on the n side and an excess of holes on the p side. While in the equilibrium situation, the quasi Fermi levels $\Phi_p$ and $\Phi_n$ can be assumed as flat, the excess charge carriers generated under illumination result in a splitting of $\Phi_p$ and $\Phi_n$ by $q \cdot V_{oc}$. For an ideal junction, the open circuit ($J = 0$) voltage can then be calculated by

$$V_{oc} = \frac{kT}{q} \cdot \ln \left( \frac{L_{d,p} + L_{d,n}}{(L_{d,p}/\tau_p)p_n + (L_{d,n}/\tau_n)n_p} \cdot g_{opt} + 1 \right), \quad (2.10)$$

where $L_{d,p}$ and $L_{d,n}$ are the minority carrier diffusion length, $\tau_p$ and $\tau_n$ the minority carrier lifetimes, $g_{opt}$ the optically induced electron hole generation, and $p_n$ and $n_p$ are the minority carrier densities. For more detailed calculations one can refer to Dervos et al. [14].

To calculate the current in a solar cell, the Gärtner model can be used as described in depth by Lewerenz and Jungblut [15]. Starting off with the continuity equation

$$\frac{1}{q} \frac{d j}{d x} + \frac{\partial p}{\partial t} = 0, \quad (2.11)$$
2.2. Illuminated p-n Junctions in More Detail

with the change of charge with time written as

\[
\frac{\partial p}{\partial t} = \frac{\partial p}{\partial t} - (g_{opt} - U),
\]

(2.12)

where \( p \) is the total hole concentration on the n side, i.e., the equilibrium concentration \( p_0 \) plus the photogenerated hole concentration \( \Delta p \), and \( U \) is the recombination rate. Thus, in the stationary case \( (\frac{\partial p}{\partial t} = 0) \), equation 2.11 changes to

\[
\frac{1}{q} \frac{d}{dx} j + g_{opt} - U = 0.
\]

(2.13)

The recombination rate \( U \) can be approximated by \( \Delta p/\tau_p \).

The Gärtner model differentiates between a drift photocurrent from charge carriers generated in the space charge region, and a diffusion current from carriers generated outside. Under the assumption that all minority carriers generated in the space charge region contribute to the photocurrent, the drift component is given by

\[
J_{dc} = qI_0 (1 - \exp(-\alpha w)),
\]

(2.14)

where \( I_0 \) is the photon irradiation at the surface of the device, \( \alpha \) the absorption coefficient of the semiconductor, and \( w \) the width of the space charge region. \( g_{opt} \) is given by \(-dI/dx\) with the photon flux density \( I = I_0 \cdot \exp(-\alpha x) \).

To calculate the diffusion part of the photocurrent in a stationary regime

\[
J_{diff} = -qD_p \frac{dp}{dx},
\]

(2.15)

one has to solve the differential equation for the hole concentration

\[
D_p \frac{d^2 p}{dx^2} + g_{opt} - U = 0,
\]

(2.16)

where \( D_p \) is the diffusion coefficient for holes. With the ansatz

\[
p = p_0 - (p_0 + A \cdot \exp(-\alpha w)) \cdot \exp\left(\frac{w - x}{L_p}\right) + A \exp(-\alpha x),
\]

(2.17)

\[
A = \frac{I_0}{D_p \alpha(1 - \alpha^2 L_p^2)} \frac{\alpha^2 L_p^2}{D_p \alpha(1 - \alpha^2 L_p^2)}
\]

and the boundary conditions

\[
p = 0 \quad \text{for} \quad x = 0,
\]

\[
p = p_0 \quad \text{for} \quad x = \infty,
\]
Chapter 2. Theoretical Background

**Figure 2.5**: Band structure of a CuIn$_{1-x}$Ga$_x$Se$_2$/CdS heterointerface with recombination paths: A - interface recombination, B - space charge region recombination, and C - bulk recombination.

The diffusion part can be written as

$$J_{diff} = q \left( I(w) \frac{L_{d,p}}{\alpha^{-1} + L_{d,p}} - p_0 \frac{D_p}{L_{d,p}} \right). \quad (2.18)$$

The total photocurrent is then of course given by

$$j_{\text{photo}}^{\text{tot}} = J_{dr} + J_{diff}$$

$$= -q \cdot I_0 \left( 1 - \exp(-\alpha w) \right) - \frac{q p_0 D_p}{L_{d,p}}. \quad (2.19)$$

### 2.3 Recombination Paths in CuIn$_{1-x}$Ga$_x$Se$_2$ Solar Cells

Figure 2.5 shows the band structure of a CIGS/CdS heterointerface and illustrates the recombination paths as presented by Rau and Schock [16], for further reading on recombination mechanisms one might refer to textbooks such as [13]. The open circuit voltage in such a non-ideal junction is determined by the dominant recombination path [16]. If recombination in the quasi-neutral region is dominant (path C), $V_{oc}$ is given by

$$V_{oc} = \frac{E_g}{q} - \frac{kT}{q} \cdot \ln \left( \frac{q D_n N_c N_i}{J_{sc} N_A L_d} \right), \quad (2.20)$$
where $D_n$ is the electron diffusion constant, $N_{c/v}$ the density of states in the conduction and valence bands, respectively, $N_A$ the acceptor density of the absorber, and $L_d$ the diffusion length of the electrons in the absorber layer. If $L_d$ is comparable to the thickness of the quasi-neutral region $d$, the back contact recombination velocity $S_b$ needs to be considered and $L_d$ needs to be replaced by

$$L_{eff} = L_d \frac{\cosh(l^{-1}) + s_b \sinh(l^{-1})}{s_b \cosh(l^{-1}) + \sinh(l^{-1})}, \quad s_b := \frac{S_b L_d}{D_n}, \quad l := \frac{L_d}{d}. \quad (2.21)$$

The reverse saturation current density is then given by

$$J_0 = \frac{n_i^2}{N_A} q \frac{L_{d,n}}{\tau_n}, \quad (2.22)$$

where $n_i$ is the intrinsic minority carrier concentration ($n_i^2 = N_V N_C \cdot \exp(E_g/kT)$).

With $L_d = \sqrt{D_n \tau_n}$, $\tau_n$ the electron lifetime, a similar expression can be found for $V_{oc}$ if B is the dominant recombination path:

$$V_{oc} = \frac{E_g}{q} - \frac{2kT}{q} \cdot \ln \left( \frac{kT D_n \pi \sqrt{N_c N_v}}{J_{sc} F_m L_d^2} \right), \quad (2.23)$$

where $F_m = \sqrt{2qN_A V_{bm}/\varepsilon_s}$ is the electrical field at the point of maximum recombination ($\varepsilon_s$ the dielectric constant of the absorber, $V_{bm}$ the band bending) and $J_0$ of

$$J_0 = q n_i \left[ \frac{1}{\sqrt{\tau_0 \tau_p}} \right] \left[ \frac{\pi kT}{4(V_B - V)} \right]^w. \quad (2.24)$$

One can conclude that in both regimes, recombination in the quasi-neutral region and recombination in the space charge region, the absorber band gap is the determining figure for the open circuit voltage. This however changes when the dominant recombination mechanism changes to interface recombination. The expression for the open circuit voltage is then given by

$$V_{oc} = \frac{\Phi_p}{q} - \frac{kT}{q} \cdot \ln \left( \frac{qS_p N_v}{J_{se}} \right), \quad (2.25)$$

where $S_p$ stands for the interface recombination velocity for holes and $\Phi_p$ is the barrier as indicated in figure 2.5. The dominant figure for $V_{oc}$ is then given by $\Phi_p$, which is smaller than the band gap and the saturation current density – if
the thermal velocity of the electrons is larger than the interface recombination velocity – can be expressed as

$$J_0 = q s_I N_v \exp\left(-\frac{q V_D}{kT}\right),$$

(2.26)

where $s_I$ stands for the interface recombination velocity. If the thermal velocity is smaller, this changes to

$$J_0 = B T^2 \exp\left(-\frac{q V_D}{kT}\right).$$

(2.27)

More detailed explanations about recombination mechanisms can be found in [13, 16, 17].

## 2.4 CuIn$_{1-x}$Ga$_x$Se$_2$ Solar Cells

### 2.4.1 Cell Structure

This thesis focuses on enhancements mainly of the band gap profile of the absorber layer of CuIn$_{1-x}$Ga$_x$Se$_2$ solar cells. For the standard devices investigated in this thesis, the structure as shown in the schematic in figure 2.6 has been used. Soda-lime glass (SLG) substrates were used both as carrier for the device and Na source for the solar cells. A small amount of Na is necessary for good working CIGS solar cells, as it increases the charge carrier density and enhances both $V_{oc}$ and fill factor. Furthermore, the p-type conductivity of the CIGS layer is increased [18–20]. The role of Na is investigated in more detail in section 4.2.1. Soda-lime glass contains, depending on the manufacturer, 12 to 16% of Na$_2$O. During the deposition, Na can diffuse out of the glass substrate through the Mo back contact layer into the device.

As a back contact, molybdenum is used. During the deposition of the absorber layer, a thin layer of molybdenum selenide forms which facilitates the formation of a quasi-ohmic contact to the p-type CIGS layer, which would otherwise be a Schottky barrier [21]. Furthermore, MoSe$_2$ hinders the formation of a highly resistive n-type Ga$_2$O$_3$ layer at the back contact interface [22, 23].

The useful light absorption takes place in the p-type CIGS absorber layer. The evaporated layer can be band gap engineered between 1.0 and 1.7 eV to taylor the absorption characteristics and will be explained in more detail in the subsequent subsections.
2.4. CuIn$_{1-x}$Ga$_x$Se$_2$ Solar Cells

Figure 2.6: Schematic structure of a CIGS solar cell.

To create the necessary p-n junction, an n-type CdS buffer layer is deposited on top of the absorber layer. Its direct optical band gap is approximately 2.42 eV [24]. This layer optimizes the band alignment in the junction and protects the CIGS absorber layers during the subsequent deposition steps against sputter ion damage.

Finally, a bilayer of intrinsic highly resistive n-type ZnO which prevents shunting of the absorber layer by the front contact layer and ZnO:Al as conductive transparent electrical contact is used to complete the cell structure. The sheet resistance of the front contact layer is approximately 20 to 30 $\Omega$. To enhance current collection and facilitate contacting, a Ni/Al metal grid is used on top of the TCO front contact.

2.4.2 Crystallography and Phase Composition of CIGS

Figure 2.7 a) shows the phase diagram along the Cu$_2$Se – In$_2$Se$_3$ pseudo-binary line of the Cu-In-Se system. The p-type semiconducting phase useful for photovoltaic power generation is the $\alpha$-CIS phase with a slightly Cu poor stoichiometry. This phase corresponds to a chalcopyrite crystal structure as illustrated in figure 2.7 b). The chalcopyrite structure is a lattice of ternary compounds, similar to the single-element diamond lattice and the binary zincblende (sphalerite) structure.

There are several ways of CIGS growth. For the CIGS layers used in this thesis, a multistage coevaporation process was chosen, the growth mechanism used in the experiments can be followed in the phase diagram. Starting with an (In$_{1-x}$Ga$_x$)$_2$Se$_3$ precursor layer deposited first, Cu is added into the film at a comparably high temperature of 550 to 600 °C. Via the $\gamma$-phase of CuIn$_3$Se$_8$ and the $\beta$-phase of an ordered defect compound, the film crosses through the $\alpha$-phase until it gets Cu-rich. When the layer is further enriched with Cu, Cu$_{2-x}$Se starts to
2.4.3 Composition and its Influence on the Band Structure

As it is of interest to control the band gap of an absorber layer in a photovoltaic device, alloying CuGaSe$_2$ into CuInSe$_2$ can be used for band gap engineering. The influence of the alloying on the band structure was investigated in detail by Wei et al. [26]. The band gap increases following the formula

$$E_g(x) = (1 - x) \cdot E_{g}^{\text{CIS}} + x \cdot E_{g}^{\text{CGS}} - bx(1 - x),$$

(2.28)

where $x$ stands for the $[\text{Ga}]/[\text{In+Ga}]$ ratio and $b$ denotes a bowing coefficient, which depends on the growth properties and is empirically usually measured between 0.15 and 0.24. The theoretical calculations show a bowing coefficient of 0.21, agreeing well with the measured values. The calculated band offsets show that under unstrained conditions, the valence band maximum of CGS is only 40 meV lower than that of CIS, while the conduction band minimum of CGS is 600 meV higher than that of CIS with respect to the vacuum level. This means that the valence band maximum is almost maintained and the change in band gap affects mostly the conduction band [26], which is an important information...
to understand the problems in manufacturing good wide-gap chalcopyrite solar cells as discussed later in sections 4.1 and 5.2.1.

2.5 Dye-sensitized Solar Cells

Figure 2.8 shows the basic structure of a dye-sensitized solar cell. In contrast to a classical solar cell, where an excitation of electrons from the valence band to the conduction band of a semiconducting absorber material occurs, the dye cell uses excitation of a molecule and a redox reaction to convert sunlight to electricity as explained in detail for example by Grätzel in [27]. A nanoporous TiO$_2$ layer is immersed into a photoactive dye, most often ruthenium complexes, which cover the TiO$_2$ grains. If light with a high enough energy is absorbed by the dye, the molecule is excited and can inject an electron into the conduction band of the semiconducting TiO$_2$. The sensitized nanoporous layer is surrounded by a redox electrolyte, usually an organic solvent containing the I$^-$/I$_3^-$ redox pair. The missing electron of the sensitizer molecule is stripped from a iodide ion, much faster than the recombination velocity of the injected electron with the excited dye. The generated iodine atoms form I$_2$ molecules and oxidize with another iodide ion to I$_3^-$. The redox cycle is completed at the counterelectrode, usually a Pt-coated TCO layer, where electrons coming from the load reduce the triiodide back to iodide again.
Chapter 3

Experimental Details

3.1 Substrate Preparation

As substrates for the samples described in this thesis, soda-lime glass (SLG) sheets of 5x5 cm$^2$ were used. After cleaning with various solvents, a back contact was deposited. For baseline samples, a molybdenum layer of 1 to 1.2 µm thickness was applied by DC magnetron sputtering, using a three layer structure of approximately 400 nm Mo deposited at high power (2 kW) and low Ar pressure ($3.7 \times 10^{-3}$ mbar) to ensure good adhesion of the Mo layer to the substrate, followed by 600 nm at low power (300 W) and low Ar pressure. To achieve a good adhesion of the following layers, the back contact was finalized with a 200 nm Mo layer deposited at low power and higher Ar pressure ($8.6 \times 10^{-3}$ mbar).

When fabricating semi-transparent cells, e.g., to be used as top cells in multijunction devices, a transparent back contact is needed. In this work, ZnO:Al was used as back contact TCO. This was deposited by rf-sputtering at FZ Jülich from a ceramic ZnO target doped with 1%-wt Al$_2$O$_3$. The sheet resistance of the back contact layer was between 4 and 6 Ω. As a direct ZnO:Al/CIGS contact shows strong rectifying behaviour [28], a thin (5 nm) layer of Mo was applied on top, which selenizes to a semitransparent molybdenum selenide layer during CIGS deposition, which forms a quasi ohmic contact to the CIGS absorber [21].

3.2 CuIn$_{1-x}$Ga$_x$Se$_2$ Deposition

After completion of the substrate and back contact, the CuIn$_{1-x}$Ga$_x$Se$_2$ absorber layer was deposited by coevaporation of the constituent elements using a three
stage evaporation process as designed by NREL and modifications thereof [29,30]. Figure 3.1 shows a schematic diagram of the metal fluxes during a baseline three stage process. In the first stage, a precursor layer of \((\text{In}_{1-x}\text{Ga}_x)_2\text{Se}_3\) is deposited at a rather low substrate temperature of 400 °C. Subsequently, at the beginning of the second stage, the substrate temperature is increased to 450 to 600 °C, depending on the substrate. As ZnO:Al loses conductivity when heated, this effect limits the temperature to 450 °C when using this back contact, while when using a Mo back contact the upper limit of the substrate temperature is given by the softening temperature of the soda-lime glass substrates. During the second stage, only copper is evaporated onto the precursor layer while maintaining a Se background pressure exceeding the necessary amount for layer formation several times. The Cu diffuses into the precursor layer and forms CIGS until the layer gets stoichiometric. After this point of stoichiometry, \(\text{Cu}_{2-y}\text{Se}\) phases start to segregate. This segregation occurs on the surface of the grains, meaning that a stoichiometric CIGS grain nucleus is enclosed by a quasi-liquid \(\text{Cu}_{2-y}\text{Se}\) layer [31,32]. As this material has a higher emissivity compared to understoichiometric CIGS, the point of stoichiometry can be determined by a method called end-point detection. The heater output power needed to maintain the substrate temperature is observed, and at the point of stoichiometry, the power demand increases abruptly due to the higher emissivity of the \(\text{Cu}_{2-y}\text{Se}\) [33]. After a well-defined amount of time, the Cu evaporation is ceased. This Cu rich phase is needed as a recrystallization of the layer occurs and the layer quality improves significantly. The maximum copper content during the evaporation sequence is reached now. If the maximum \([\text{Cu}] / [\text{In} + \text{Ga}]\) ratio is for instance 1.25, it is from hereon called a deposition process using 25% Cu excess.

Finally, in the third stage, In and Ga are once more evaporated onto the Cu rich layer to finalize the CIGS absorber with the desired slightly Cu poor composition, with a final \([\text{Cu}] / [\text{In} + \text{Ga}]\) ratio of around 0.90 in the layer.

### 3.3 Buffer Layer

Onto the finished absorber layer, a CdS layer of 50 nm is applied by chemical bath deposition. The solution of the baseline process uses a mixture of 185 ml H\(_2\)O, 15 ml of Cd(CH\(_3\)COO)\(_2\) in an aqueous solution of 6.742 g/l, and 35 ml of NH\(_4\)OH (28%) which are pre-mixed in a bath heated to 70 °C for one minute. After pre-mixing, 15 ml of thiourea (H\(_2\)NCSNH\(_2\)), an aqueous solution of 28.48 g/l, is added to the solution, the samples are placed in the heated bath and the deposition runs for 22 min.
3.4 Front Contact

The cells are then finished by the application of the front contact. A bilayer of i-ZnO and ZnO:Al is used as standard front TCO, which is deposited by rf-sputtering. A thickness of 50 nm i-ZnO is applied by sputtering for 4 min at 150 W, followed by 270 nm of ZnO:Al, deposited in 7 min at 200 W sputtering power. Both depositions are performed without heating the sample. To enhance current collection, a metal grid is subsequently deposited by e-beam evaporation. 50 nm of Ni form a good contact to the TCO, and 2 \( \mu \)m of Al are deposited on top to achieve a highly conducting grid.

3.5 Characterization Techniques

3.5.1 Electrical and Electronic Characterization

\( I - V \) parameters were recorded using a solar simulator with a spectrum close to AM1.5G, as shown in figure 3.2. The output power was calibrated using a silicon reference cell for which the current at the correct spectrum was known. A Keithley power source/meter was used to apply a voltage to the cell and measure the current, starting with a small reverse bias.

Quantum efficiency curves were recorded using a mercury vapor lamp as light...
source. After passing through a grating monochromator and a light chopper this generated a current with the frequency of the light chopper. Via a lock-in amplifier, the signal was processed by a home-programmed software. As reference, a silicon photodiode with known spectral response was used.

Temperature dependent $I-V$, $C-V$, and $C-f$ measurements were performed in a home-built cryostate with LN2 cooling of a copper plate in vacuum. $I-V$ parameters were recorded similarly to the room temperature case, while capacity measurements were performed using an HP semiconductor parameter analyzer.

### 3.5.2 Structural Characterization

Compositional measurements were performed using a home-built x-ray fluorescence spectrometry (XRF) system. Using an acceleration voltage of 45 kV, the Cu-K, In-L, Ga-K, and Se-K lines were detected and quantified using a commercially available software. Compositional depth profiles were recorded with time-of-flight secondary ion mass spectrometry (ToF-SIMS). Bi$^+$ ions were used in the primary ion beam (25 kV, 1 pA, 100 x 100 mm) while the sample was sputtered with Cs$^+$ ions (2 kV, 60 nA, 300 x 300 µm). MCs$^+$ secondary ions were recorded where M stands for the investigated element.

To determine surface phase compositions, a Raman microscope with an excitation laser wavelength of 633 nm was used. The spot size of the laser was approximately 0.25 mm$^2$ and the morphology was investigated using a Hitachi scanning electron microscope (SEM).
Chapter 4

\textbf{CuIn}_{1-x}\text{Ga}_x\text{Se}_2\text{ Solar Cells}

4.1 Variation of Ga Content

Changing the Ga content in a CIGS layer mainly affects the band gap of the absorber layer. Pure CIS has a band gap of 1.04 eV, which can be increased to close to 1.67 eV by adding Ga until a pure CGS layer is reached. Figure 4.1 shows the band structure of a CIGS solar cell with a rather wide-gap absorber. When a widening of the band gap occurs due to addition of Ga, this mainly affects the conduction band minimum which is shifted to higher energies [17]. $\Delta E_{cb}$ in figure 4.1 denotes the conduction band offset between the absorber layer and the buffer which can be both positive or negative, depending on the conduction band level of the absorber layer.

General theory of solar cells (see also section 2.2) usually shows that with increasing band gap of the absorber the open circuit voltage should increase. However, when looking at the $I - V$ parameters recorded for CIGS solar cells with different [Ga]/[In+Ga] ratios as presented in tables 4.1 and 4.2, reported in [34], grown both on Mo and ZnO:Al back contacts, it becomes obvious that the increase in $V_{oc}$ is limited when going beyond a certain $x$ value where $V_{oc}$ does not significantly increase any more but rater stays stable or even decreases.

While the decrease in short circuit current can be reasonably explained by the shift of the absorption edge of the CIGS layer due to increasing minimum band gap, further considerations need to be taken into account to explain the only slightly higher $V_{oc}$ for high Ga absorbers. In section 2.3 the different recombination paths in heterojunction solar cells were explained. In a short review, if recombination in the space charge region is the dominant path, the upper limit
Figure 4.1: Band structure of a wide gap CIGS solar cell (redrawn after [17]) \( \Delta E_{cb} \) is the conduction band offset between absorber and buffer layer, \( \Phi_{pb} \) the interface hole recombination barrier. \( A \) is the interface recombination path, \( B \) the recombination path for SCR recombination.

<table>
<thead>
<tr>
<th>( x )</th>
<th>( J_{sc} )</th>
<th>( V_{oc} )</th>
<th>( FF )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mA cm(^{-2})</td>
<td>mV</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>0.00</td>
<td>34.2</td>
<td>459</td>
<td>67.4</td>
<td>10.5</td>
</tr>
<tr>
<td>0.25</td>
<td>30.2</td>
<td>671</td>
<td>71.2</td>
<td>14.4</td>
</tr>
<tr>
<td>0.50</td>
<td>23.2</td>
<td>678</td>
<td>59.0</td>
<td>9.3</td>
</tr>
<tr>
<td>0.75</td>
<td>18.1</td>
<td>682</td>
<td>57.6</td>
<td>7.1</td>
</tr>
</tbody>
</table>

Table 4.1: \( I - V \) data of CIGS solar cells with different \([Ga]/[In+Ga]\) ratios on Mo back contact.
4.1. Variation of Ga Content

<table>
<thead>
<tr>
<th>$x$</th>
<th>$J_{sc}$</th>
<th>$V_{oc}$</th>
<th>$FF$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mAcm$^{-2}$</td>
<td>mV</td>
<td>%</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>0.24</td>
<td>29.1</td>
<td>644</td>
<td>71.5</td>
<td>13.5</td>
</tr>
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<td>24.9</td>
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<td>13.0</td>
<td>748</td>
<td>59.0</td>
<td>5.8</td>
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<td>0.76</td>
<td>&lt; 5.0</td>
<td>≈ 630</td>
<td>≈ 30</td>
<td>&lt; 1.0</td>
</tr>
</tbody>
</table>

Table 4.2: $I-V$ data of CIGS solar cells with different [Ga]/[In+Ga] ratios on ZnO:Al back contact.

for $V_{oc}$ is given by

$$V_{oc} = \frac{E_g}{q} - \frac{2kT}{q} \cdot \ln\left( \frac{kTD_n\pi \sqrt{N_cN_v}}{J_{sc}F_mL_D^2} \right)$$

(4.1)

where $D_n$ stands for the diffusion constant for electrons, $N_c$ and $N_v$ for the effective density of states in the conduction and valence band, $L_D$ the diffusion length of electrons and $F_m = \sqrt{2qN_A V_{bm}/\varepsilon}$ the electrical field at the position of maximum recombination [16]. If however buffer layer interface recombination is the most dominant mechanism, this limit changes to

$$V_{oc} = \frac{\Phi^p}{q} - \frac{kT}{q} \cdot \ln\left( \frac{qS_pN_v}{J_{sc}} \right)$$

(4.2)

where $S_p$ is the interface recombination velocity for holes and $\Phi^p$ the recombination barrier as indicated in figure 4.1. It is readily observable from figure 4.1 that in case of wide gap chalcopyrites where the conduction band offset between the absorber and the buffer layer is positive, i.e., the conduction band minimum of the absorber is higher than that of the buffer layer, $\Phi^p$ is always lower than the band gap of the absorber layer. As the measurements suggests that there seems to be a limit for the open circuit voltage in CIGS solar cells when increasing the band gap, this suggests a switch from space charge region recombination to buffer layer interface recombination when the average Ga concentration exceeds a certain value of $x \approx 0.4 - 0.5$ which was also reported by Gloeckler and Sites [35].
4.2 Optimization of the Growth Process

4.2.1 Duration of Cu Excess and its Influence on Layer Properties

Influence on Ga Grading and Morphology

The most efficient CIGS solar cells are grown by the three stage process as described in section 3.2. The key element of the process is the end of stage 2 when the layer reaches a Cu-rich composition and Cu evaporation is continued for a well-defined amount of time. The duration of this continued evaporation and thus the maximum [Cu]/[In+Ga] ratio (Cu excess) affects several properties of the CIGS absorber layers.

As the Cu rich segment of the growth regime is crucial for grain growth, recrystallization, and interdiffusion of elements, the most prominent property changed by variations in the Cu rich duration is morphology. Figure 4.2 shows SEM micrographs of CIGS absorber layers grown with different Cu excess. The easily visible increased grain size for layers grown with high Cu excess can be explained by an enhanced crystallization growth model. This model predicts the segregated growth of quasi-liquid Cu$_{2-y}$Se on the surface of stoichiometric CIGS grain nuclei, allowing In and Ga to diffuse inside, accumulate at the existing CIGS nucleus and enlarging it. With higher Cu excess, the duration of this growth regime is increased and thus allows more time for the enlargement of CIGS grains [36]. As a consequence, the number of grain boundaries decreases but their width is increased [37].

For a more detailed understanding of the changes in elemental composition gradients, SIMS depth profiles of CIGS absorber layers grown with different Cu
4.2. Optimization of the Growth Process

Figure 4.3: SIMS depth profiles of the [Ga]/[In+Ga] ratio in CIGS layers grown with different Cu excess.

excess shown in figure 4.3 are investigated. The maximum [Cu]/[In+Ga] ratio was varied between 5% and 50%. At a first glance, two major changes in the Ga grading can be observed: first, the minimum [Ga]/[In+Ga] position shifts further into the layer, and second, the minimum [Ga]/[In+Ga] ratio and thus the minimum band gap increases for layers grown with higher Cu excess.

When looking at the corresponding $I-V$ values shown in table 4.3, changes determined by these grading variations are also observable. A tendency of increasing $V_{oc}$ can be seen when increasing the Cu excess. Although rather small, this increase is highly reproducible and thus deemed as real effect rather than statistical variation. This can be explained by the shallower decrease of the [Ga]/[In+Ga] ratio from the buffer layer interface towards the bulk of the absorber layer, resulting in a higher band gap in the space charge region. As the open circuit voltage in CIGS solar cells with the comparably low average [Ga]/[In+Ga] ratio of 0.3 to 0.4 is usually limited by recombination in the space charge region, this band gap is the determining value for $V_{oc}$ [38]. On the other hand, the decrease of $J_{sc}$ is less obvious from the $I-V$ data than the band gap profile would suggest. Figure 4.4 however shows the quantum efficiency of the CIGS cells mentioned in table 4.3, with the absorption edge region shown in more detail in the inset. The shift in the absorption edge caused by the shallower grading profile is readily observable there, however, variations in the QE profile at lower wavelengths disturb the effect on the short circuit current recorded during $I-V$ measurements. This may be a consequence of slightly different TCO thicknesses or slightly different grid line widths.
Chapter 4. CuIn\textsubscript{1−x}Ga\textsubscript{x}Se\textsubscript{2} Solar Cells

<table>
<thead>
<tr>
<th>Cu excess</th>
<th>$J_{sc}$</th>
<th>$V_{oc}$</th>
<th>FF</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>mA cm$^{-2}$</td>
<td>mV</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>5</td>
<td>32.3</td>
<td>691</td>
<td>74.1</td>
<td>16.6</td>
</tr>
<tr>
<td>25</td>
<td>30.8</td>
<td>695</td>
<td>75.2</td>
<td>16.0</td>
</tr>
<tr>
<td>50</td>
<td>31.1</td>
<td>702</td>
<td>75.7</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table 4.3: Photovoltaic $I − V$ data of CIGS solar cells grown with different Cu excess.

Figure 4.4: Quantum efficiency curves of CIGS solar cells grown with different Cu excess. The absorption edge region is shown in the inset.
4.2. Optimization of the Growth Process

As a conclusion, it can be observed that from just changing the duration of the three stages and thus the amount of Cu excess, no significant gains in efficiency can be obtained as gains in the open circuit voltage are mitigated by losses in the short circuit current due to a higher minimum band gap caused by more pronounced interdiffusion of In and Ga in the center of the CIGS absorber layer.

**Influence on Na Distribution**

Another layer property influenced by the changes in the deposition regime is the distribution of Na in the CIGS absorber layer. Na has several important beneficial properties when incorporated into CIGS. Fill factor and open circuit voltage increase [19,20] and also the conductivity of the CIGS films increases [18]. In the standard process used throughout the work for this thesis, Na was provided by diffusion from the soda-lime glass substrate. The distribution of the sodium in the layer may therefore be affected by the different growth regimes as Na is present throughout the whole deposition process. Several indications point towards an accumulation of Na at the front surface of the absorber layer for CIGS deposited with low Cu excess while the Na seems to be more spread out through the layer for CIGS deposited with high Cu excess [37].

Figure 4.5 shows a SIMS depth profile of CIGS grown with 5 and 50% Cu excess. For low Cu excess, the sodium content stays flat at a low value from the bulk to about 350 nm from the surface, while the 50% CIGS Na signal already starts to increase 750 to 800 nm from the surface. This is highly reproducible for several samples. At a depth of approximately 70 nm the 5% Cu excess CIGS Na intensity even crosses the signal from the high excess CIGS. However, at the very surface of the layer SIMS has a relatively large margin of error and can thus not be used as single indication for Na accumulation at the surface.

Other evidence pointing towards higher Na accumulation at the front surface of low Cu excess layers comes from Raman spectroscopy. The presence of Na is known to hinder the formation of a group III rich phase, the so-called ordered vacancy compound (OVC) [39], which is known tending to form on the surface of CIGS layers [40]. Raman spectra as shown in figure 4.6 show that while the OVC peak is readily observable for samples grown with high Cu excess, the intensity of this peak compared to the chalcopyrite $A_1$ peak decreases for decreasing Cu excess, also very reproducible for several samples. One possible explanation for this is the presence of Na on the surface of the absorber layer.

The last indirect evidence for the Na accumulation at the front surface is shown in figure 4.7. For samples grown at low Cu excess, a very small-grained
Figure 4.5: SIMS depth profile of the Na content of CIGS grown with 5 and 50% Cu excess.

Figure 4.6: Raman spectra of CIGS absorber layers grown with different Cu excess.
4.2. Optimization of the Growth Process

Figure 4.7: **SEM top view image of the absorber layer surface of CIGS films grown with 5% (left) and 50% (right) Cu excess.**

<table>
<thead>
<tr>
<th>Cu exc</th>
<th>Cu</th>
<th>In</th>
<th>Ga</th>
<th>Se</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>at-%</td>
<td>at-%</td>
<td>at-%</td>
<td>at-%</td>
<td>at-%</td>
</tr>
<tr>
<td>5</td>
<td>18.83 ± 0.57</td>
<td>26.37 ± 1.91</td>
<td>6.02 ± 0.21</td>
<td>46.93 ± 0.85</td>
<td>0.22 ± 0.11</td>
</tr>
<tr>
<td>25</td>
<td>18.92 ± 0.48</td>
<td>22.07 ± 1.78</td>
<td>8.83 ± 0.80</td>
<td>50.04 ± 1.04</td>
<td>0.15 ± 0.06</td>
</tr>
<tr>
<td>50</td>
<td>19.07 ± 1.20</td>
<td>26.13 ± 1.40</td>
<td>6.00 ± 0.48</td>
<td>48.81 ± 1.07</td>
<td>0.08 ± 0.04</td>
</tr>
</tbody>
</table>

Table 4.4: **Elemental composition of the surface of CIGS absorbers grown with different Cu excess measured by WDX.**

layer on the surface can be observed, completely covering the surface. This is not, or in much smaller quantity and density, observed for layers grown with high Cu excess. This may be a Na containing compound segregating on the surface of the absorber layer for films grown with low Cu excess.

To determine a quantitative value of Na in the front part of the absorber layer, a very surface sensitive measurement technique is needed. The samples were thus analyzed by wavelength dispersive X-ray spectroscopy (WDX), using 5 keV electrons as primary irradiation, resulting in a probing depth of 50 to 100 nm. Several spots on each sample were investigated. For the analysis of the samples, the CIGS constituent elements Cu, In, Ga, Se as well as the impurity Na were detected. The results of the first series of measurements is shown in table 4.4. Looking at those values, the obtained sodium concentration for the absorber layer grown with 50% Cu excess corresponds very well to the bulk sodium value.
found in good working CIGS solar cells of approximately 0.1%-at [41]. However, when going to higher Cu excess values, a steady increase in the surface sodium concentration can be found, resulting in a Na concentration of 0.22, or more than double the value found in the 5% Cu excess absorber layers, when going to 50% Cu excess.

As the relative errors of the WDX results are rather large and the Na signals rather small, a more surface sensitive technique was desired to further corroborate the results found with WDX and strengthen the point of accumulation of Na on the surface of the absorber layers. Thus, absorber layer surfaces were investigated by X-ray photoelectron spectroscopy (XPS), with an information depth of only several nanometers. The results obtained from these measurements are shown in table 4.5. These samples were stored in vacuum until right before taking them to the XPS measurements, and handled equally during preparation, to minimize external influences on the measurement [42]. Again, a much higher amount of Na on the absorber surface can be found for the samples grown at low Cu excess compared to the absorber grown with 50% Cu excess. Thus, it can be concluded that an accumulation of sodium on the surface of the CIGS absorbers does occur when the three stage process is executed with a comparably small Cu excess.

A possible explanation for the changes in the surface Na concentration are changes in the diffusion behavior. As mentioned in section 3.2, Wada et al. as well as Niki et al. [31,32] found the Cu$_{2-y}$Se to cover stoichiometric CIGS grain nuclei. When the Cu excess is increased, the thickness of this covering Cu$_{2-y}$Se layer will increase. If one assumes that Na is mainly migrating at the grain boundaries, it seems clear that at the beginning of the Cu rich regime in the three stage process, some Na is located at the surface of the absorber, as this is of course a grain boundary region. As Cu$_{2-y}$Se is known to be in a quasi-liquid
4.2. Optimization of the Growth Process

Figure 4.8: Illustration of metal flux rates during the ramped three stage process.

phase at the temperatures involved in the third stage in these experiments (550 to 600 °C), Na can probably diffuse into and evenly distribute itself in the copper selenide layer rather easily. Thus, with high Cu excess a broader Na profile going from the grain boundary into the bulk of the grain and less Na accumulated directly on the absorber surface can be expected, consistent to what has been found in the above experiments.

4.2.2 Optimization the Ga Grading by Changing the Evaporation Profile

The results presented in section 4.2.1 show that no significant enhancements in efficiency could be obtained by simply changing the amount of Cu excess when maintaining a constant In and Ga flux during stages one and three. Thus, subsequent experiments have been performed to investigate the possibility of efficiency enhancements by changing the metal flux profiles during the first and the third stage. As a higher surface band gap was desired, combined with a deeper Ga dip, for the experiments the Ga flux was decreased during the first stage and increased back up during the third stage by changing the Ga source temperature. The evaporation profiles were chosen such that the ratio of fluxes $\Phi_{\text{In}}/\Phi_{\text{Ga}}$ at the end of stage one and the beginning of stage three was the same as in the baseline process. Figure 4.8 illustrates the flux rates during the ramped three stage process. The Ga source temperature was varied by 5, 10, and 20 °C
Chapter 4. CuIn$_{1-x}$Ga$_x$Se$_2$ Solar Cells

Figure 4.9: Ratio between the band gap in the space charge region and the minimum band gap for PV devices using CIGS absorbers grown with different Ga evaporation profiles.

and the Cu excess was fixed at 5%. Figure 4.9 shows the variations in the depth of the Ga dip by illustration of the band gap ratios $E_{g_{SCR}}^{min}/E_{g_{min}}$, where the band gap in the space charge region $E_{g_{SCR}}$ was determined by temperature dependent $I-V$ measurements and the minimum band gap $E_{g_{min}}$ by linear extrapolation of the tail of the quantum efficiency squared.

First observations of figure 4.9 easily show that with the changed evaporation rates, indeed a deepening of the Ga dip can be observed. Figure 4.10 shows the quantum efficiency of solar cells with the corresponding CIGS absorber layers. The absorption edge shift is significantly lower than when changing the Cu excess, and it is decoupled from the Ga ramp. Thus, one can conclude that a Ga ramp does not significantly impact the minimum band gap of the absorber layer and it is possible to introduce a band gap profiling by changing the Ga evaporation rate during stages one and three. With this knowledge, it was possible to tailor the grading properties of the absorber layers in a way such that the high $J_{sc}$ values are more or less conserved but the open circuit voltage is increased by the increased band gap in the space charge region. Figure 4.11 shows the changes in $V_{oc}$ and $J_{sc}$ relative to the baseline sample with no introduced Ga ramp. A minor decrease of up to 1.5% is observable in $J_{sc}$, especially for the 20 °C Ga ramp, which can be attributed to some limited interdiffusion of In and Ga, slightly increasing the minimum band gap for the highest Ga ramp. A significantly higher increase can be observed in $V_{oc}$, up to 4% in the cells using absorbers grown with the highest Ga ramp. With further improvement of the sequence and flux ratios in the center,
4.2. Optimization of the Growth Process

the process has the potential of yielding the 4% increase in $V_{oc}$ while maintaining the short circuit current.

The work performed during these experiments, combined with optimizations in other layers, resulted in a CIGS solar cell with a new internal record efficiency of 18.8% using a process with 5% Cu excess. The corresponding $I - V$ curve is shown in figure 4.12.

4.2.3 Reduction of Layer Thickness

To reduce cost of CIGS modules, one way would be to reduce the thickness of the absorber layer containing scarce materials such as indium, gallium, and selenium. To maintain a high efficiency in those thinner layers, several adaptions to the growth process are necessary. When reducing the layer thickness to values below 1 $\mu$m, the absorption of light starts to get incomplete as the absorption coefficient for low energy photons is too low for ensuring complete absorption. Thus, the short circuit current decreases. Aside from that, when using a standard three stage process for the deposition of down to 500 nm of CIGS, decreases in open circuit voltage and especially fill factor are observed as shown in table 4.6. Furthermore, the amount of non-working, i.e., shunted, cells on the samples drastically increases at values below 1 $\mu$m, which can be attributed to scribing problems.
Figure 4.11: Relative changes in open circuit voltage and short circuit current for CIGS solar cells using absorbers grown with different Ga ramps.

Figure 4.12: $I - V$ curve of the best CIGS solar cell obtained during the work, using a 5% Cu excess three stage process.
4.2. Optimization of the Growth Process

<table>
<thead>
<tr>
<th>thickness</th>
<th>$J_{sc}$</th>
<th>$V_{oc}$</th>
<th>$FF$</th>
<th>$\eta$</th>
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</table>

**Table 4.6:** *Photovoltaic I–V data of CIGS solar cells with different absorber layer thickness.*

The microstructure however changes little when thickness is reduced. Figure 4.13 shows cross section SEM micrographs of the CIGS layers used as absorbers in the solar cells mentioned in table 4.6. The reduction in the layer thickness can be easily observed. However, no significant changes in grain size or the microstructure are observed in thin CIGS layers. While in the thicker layers, there are grains on top of each other, for the thinner layers the growth is more columnar. This phenomenon has two origins: first, the final layer thickness is now in a range where also in the thick absorber the layer is still in its first level of grains. Secondly, due to operational requirements the second stage for the thin absorbers had to be slowed down. Thus, compared to the thick samples, the layer is for a longer part of the process kept at the higher temperature of 600 °C, resulting in more time for the interdiffusion and recrystallization. The same can be said about surface morphology. The SEM images shown in figure 4.14 show the top views of the same absorber layers, illustrating the unchanged morphology for the surface of CIGS absorber layers with thicknesses between 1600 and 500 nm.

To avoid the losses observed in $V_{oc}$ and fill factor, changes to the grading were investigated on their influence onto the photovoltaic performance of the solar cells. The thickness of the absorber layers was fixed at approximately 500 nm. In a first series of experiments, the Cu excess was changed from 5 to 50% to get the Ga dip out of the space charge region as reducing band gap in the space charge region increases the recombination probability [43]. Furthermore, as in such thin CIGS layers a high amount of light absorption occurs near the back contact, a back surface field (BSF) was introduced to obtain a repulsive force from the back contact to avoid recombination at the back contact and enhance collection. This BSF was incorporated by evaporating Ga only at the beginning.
Figure 4.13: SEM cross section images of CIGS absorber layers with thicknesses of a) 1.6 µm, b) 1.2 µm, c) 0.8 µm, and d) 0.5 µm.

Figure 4.14: SEM images of the surface of CIGS absorber layers with thicknesses of a) 1.6 µm, b) 1.2 µm, c) 0.8 µm, and d) 0.5 µm.
4.2. Optimization of the Growth Process

Figure 4.15: Working principle of a back surface field. A higher band gap near the back contact creates a repulsive potential forcing electrons in the conduction band towards the p-n junction.

of the first deposition stage to increase the conduction band minimum near the back contact. The working principle of such a BSF is illustrated in figure 4.15.

Table 4.7 shows the corresponding $I - V$ parameters of the best cell of each substrate for samples grown at different Cu excess and with/without BSF. While in the 5% Cu excess case, no beneficial influence of the BSF can be observed, the deposition with 50% Cu excess and BSF yields an increase in $V_{oc}$ of more than 100 mV compared to the case without BSF. When the absorption edge region of the quantum efficiency as shown in figure 4.16 is looked at more closely, it becomes obvious that some interdiffusion occurs. The absorption edge is shifted by approximately 0.05 eV in both the 5% and the 50% Cu excess grown sam-

<table>
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Table 4.7: $I - V$ data of CIGS solar cells using a 500 nm thick absorber layer grown with different deposition sequences.
This corresponds to a shift in the minimum $\frac{[Ga]}{[In+Ga]}$ ratio of approximately 4%-at. XRF measurements reveal a changing average composition from $\frac{[Ga]}{[In+Ga]} \approx 0.4$ to $\approx 0.5$ when introducing the back surface field. SIMS measurements were performed to investigate the influence of the localized Ga layer at the back surface onto the $\frac{[Ga]}{[In+Ga]}$ depth profile.

However, when comparing the efficiencies, $V_{oc}$, and fill factors obtained for cells with the thin absorber layers to those with standard thickness, it becomes obvious that with increased Cu excess and introduced BSF the cells with thin absorbers still lag behind the baseline ones. In order to achieve cost savings, $V_{oc}$ and fill factor should be similar for all but $J_{sc}$, the current could then be increased by back reflector layers such as TiN, Au, or Ag or by changes to the TCO optics such as texturing to achieve light trapping. Thus, it was necessary to further optimize the process for thin absorber layers by introducing Ga ramps to optimize the Ga grading, both towards the front and towards the back.

The first investigated option was the thickness of the back surface field Ga-only layer deposited during the first stage. Different thicknesses were obtained by changing the Ga-only evaporation time. Table 4.8 shows the relative changes in $V_{oc}$ and fill factor for different BSF thickness. Aside from the losses especially in fill factor for the device where 4 min of Ga only evaporation time was used, the observed changes in the overall cell efficiency are insignificant. For the subsequent experiments, the BSF layer was thus fixed at 30 s of Ga-only evaporation. To

**Figure 4.16**: Absorption edge region of the squared quantum efficiency of thin CIGS solar cells grown with different Cu excess and changed composition near the back contact.
4.2. Optimization of the Growth Process

<table>
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Table 4.8: Photovoltaic $I-V$ data of CIGS solar cells using a 500 nm thick absorber layer grown with different BSF thickness.

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<td>%</td>
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Table 4.9: Photovoltaic $I-V$ data of CIGS solar cells using a 500 nm thick absorber layer grown with different Ga ramps towards the surface of the absorber.

ensure high $V_{oc}$ and $FF$ intentional changes to the Ga depth profile were thus investigated. The metal flux profiles of the different deposition sequences are illustrated in figure 4.17, the profiles were introduced in a similar way as described in section 4.2.2. In a first step, the grading towards the front of the absorber layer was changed by introducing a Ga source temperature ramp in the third stage. Rampings to both higher and lower temperatures were investigated. Table 4.9 shows the photovoltaic parameters obtained in $I-V$ measurements of that series of samples. A trend towards better efficiency can be observed when going to a downramping of the Ga source temperature, i.e., the Ga grading towards the front of the absorber is reduced and the conduction band minimum is made flat.

To investigate the grading towards the back of the absorber, the front grading
Figure 4.17: Metal flux profiles of the different deposition sequences used for thin CIGS absorber layers.
4.2. Optimization of the Growth Process

<table>
<thead>
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<td>%</td>
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<td>642</td>
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Table 4.10: Photovoltaic I–V data of CIGS solar cells using a 500 nm thick absorber layer grown with different Ga ramps towards the back contact interface (without antireflective coating).

was fixed at -10 °C and a similar ramping process was introduced in the first stage, after deposition of the back surface field. As an increased amount of Ga was already deposited at the back contact interface by the BSF introduction, only reductions of the Ga temperature were investigated. In table 4.10, the I–V results are presented. Increases in $V_{oc}$ (through reduced recombination) and fill factor result in a PV conversion efficiency close to 12% when a layer with comparably flat grading, aside from the BSF, is deposited. Furthermore, a significant increase in short circuit current can be observed. When investigating the quantum efficiency plots in figure 4.18, it can be seen that this increase in $J_{sc}$ does not only have its origin in a lower minimum band gap by the introduction of In, but that also the charge carrier collection is enhanced over the whole spectral range.

Figure 4.19 shows compositional depth profiles of the $[\text{Ga}] / [\text{In+Ga}]$ ratio of thin absorbers grown with various deposition sequences as determined by SIMS. The first notable difference to absorbers grown at high temperatures is the grading of the baseline absorber. This is almost a single grading towards the front, i.e., the Ga dip is located at, or very close to, the back contact, when the layer is deposited with 50% Cu excess. This explains the huge gains when a BSF is introduced to these absorbers, as such a dip close to the back contact may act as a recombination center due to the energetically favourable conditions for electron – i.e., minority carrier – accumulation in the dip. The BSF evaporation, although located at the very back surface of the absorber layer, affects the rear half of the CIGS. Apart from the steep and high increase in the Ga profile at the back contact interface, the $[\text{Ga}] / [\text{In+Ga}]$ ratio is increased in the rear half, helping to smoothen out the Ga dip. When comparing the profiles of the samples with 60 s Ga evaporation with those of the sample with 30 s, it becomes obvious that more Ga in the BSF
Chapter 4. CuIn$_{1-x}$Ga$_x$Se$_2$ Solar Cells

Figure 4.18: Quantum efficiency graphs of CIGS solar cells with different Ga source temperature ramps towards the back contact.

Figure 4.19: SIMS depth profiles of the [Ga]/[In+Ga] ratio of CIGS layer with approximately 500 nm thickness grown with different evaporation profiles. Profiles were smoothed using an FFT algorithm for clarity.
4.2. Optimization of the Growth Process

Figure 4.20: Quantum efficiency curves of two thin CIGS solar cells with different Ga ramps towards the front of the absorber. The absorption edge region is shown in the inset.

evaporation phase does not significantly change the slope near the back contact but rather increases the average [Ga]/[In+Ga] ratio in the back of the absorber layer. Looking at the front region of the CIGS layer, the compositional profile behaves as expected. A Ga downramp from the beginning of stage 3 to the end of the deposition process results in a shallower slope in the Ga profile. The absolute changes in the minimum band gap between samples TH2145 and TH2146 can be explained in slightly varying flux rate ratios \( \Phi_{\text{Ga}}/\Phi_{\text{In}} \) in the different deposition runs. The change in the absorption edge is also clearly visible in the quantum efficiency curves presented in figure 4.20.

From subsequent C – V measurements, the charge carrier concentration as shown in figure 4.21 was calculated. The figure shows that there are no significant changes to the charge carrier concentration in CIGS solar cells when ramps or modifications of the absorber thickness are introduced to the three stage process.

From the results obtained in the course of the experiments in can be concluded that a flat band gap profile without the typical three stage process Ga dip is desired for very thin absorber layers, with a thin wide gap layer close to the back contact interface as a back surface field repelling the minority carriers from the interface to avoid recombination. By applying such an optimized grading, a solar cell using a 500 nm thin absorber layer yielding a conversion efficiency of 11.7% could be manufactured.
Current industrialized CIGS modules are deposited on glass and then laminated with another top glass sheet, which is stuck onto the CIGS cell with a polymer such as PMMA. Wavelength conversion dyes can be mixed into this polymer, forming a layer which could be used to improve the current of the CIGS cell by absorbing photons in a range absorbed in the ZnO or CdS layers, i.e., blue and UV photons, and reemitting them with an energy that can be used by the CIGS solar cell (luminescent downshifting – LDS) [44, 45]. The working principle is shown in figure 4.22. The dyed polymers for this work were supplied by Heriott Watt University, Edinburgh and the measurements were performed there.

Figure 4.23 shows the quantum efficiency of a CIGS cell in the blue spectral range, both with a clear polymer sheet and dyed ones in front. Both the violet and the yellow dye show a significant improvement in the spectral response in the region between 300 and 400 nm. The drawback is the incorrect matching of the dye absorption spectrum to the onset of the CIGS quantum efficiency, resulting in losses in the wavelength region up to 500 nm. The reason for these losses is the isotropic reemission of the converted photons by the dye. While many photons are emitted towards the cell, or reflected towards it internally at the polymer air interface, there is an escape cone of upwardly emitted photons which are lost again, thus reducing the quantum efficiency in said wavelength region.
4.3. Luminescent Downshifting for Current Improvement

**Figure 4.22:** Principle of luminescent downshifting. Fluorescent materials absorb short wavelength light and re-emit it at longer wavelengths in an isotropic way.

**Figure 4.23:** Quantum efficiency of a CIGS solar cell in the blue spectral range with differently dyed polymer sheets in front. The full spectral range is shown in the inset.
As the spectral response of the CIGS cell between 400 and 550 nm is dependent on the amount of photons transmitted through the CdS buffer layer, any gains in current will be more pronounced for thicker CdS layers. Table 4.11 shows the short circuit current density as calculated from the measured quantum efficiency curves, showing that most gains in the lower wavelengths are mitigated by the losses in the higher ones. However, when assuming a perfectly matched dye by calculating a hypothetical quantum efficiency by

\[
QE_{\text{hyp}}(\lambda) = \sup \{QE_{\text{combi}}(\lambda); QE_{\text{clear}}(\lambda)\},
\]

the gain increases from 0.7% to 1.7% which can potentially be further increased by increased dye concentration.

These preliminary results show that gains in current in CIGS solar cells are possible by the utilization of luminescent downshifting dyes. However, they are rather small with values in the single-digit percent range expected with further optimization. However, as rigid modules are laminated under a glass sheet with a polymer glue anyway, and the LDS dyes can be easily incorporated in that polymer, such dyes can be an easy and cheap way to boost the module efficiency.

Table 4.11: \(J_{sc}\) and relative changes in it of CIGS solar cells covered with differently dyed polymer sheets as calculated from QE curves.

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Chapter 5

Tandem Cells

To achieve grid parity with photovoltaic electricity generation, high light-to-electricity conversion efficiencies are crucial. In the Shockley-Queisser limit, the maximum achievable efficiency for a single junction solar cell is 31% with an optimum band gap of about 1.3 eV [46]. While photons with energies exceeding the band gap of the absorber create electron hole pairs parted by the photon energy, the electrons and holes will relax to the edge of the conduction and valence bands, respectively, almost instantly. The excess energy is lost to heat in the device [47]. To minimize these thermalization losses and optimize the utilization of the solar spectrum, it is possible to stack solar cells with different band gaps on top of each other, leading to high energy photons being absorbed in wide gap solar cells, while low energy photons are transmitted through the top cell and absorbed in a solar cell with a narrower band gap at the bottom as illustrated in figure 5.1. The optimum band gaps for the different cells in a double junction device under unconcentrated illumination are 0.98 eV for the bottom cell and 1.88 eV for the top cell. The efficiency limit is then 42.7%. For a stack of three cells, it is even higher: with band gaps of 0.83, 1.45, and 2.26 eV, under unconcentrated illumination an efficiency of 49.1% is possible [48].

As in serially connected circuits with multiple power sources the total current is limited by the component yielding the lowest current, technologies where the photocurrent can be easily tailored to the requested values are desirable for multijunction solar cells. Due to the potential of band gap adjustment between 1.0 and 1.7 eV by changing the ratio between indium and gallium [34], CIGS is a prime candidate for application in such tandem devices. In DSCs the generated photocurrent can be adjusted by changing the absorption range by replacing the dye, and by changing the thickness of the TiO$_2$ layer in which the dye is embedded, so this technology offers some flexibility in the design of multijunction solar cells.
5.1 Dye Sensitized/CuIn$_{1-x}$Ga$_x$Se$_2$ Tandem Cells

When combining the two technologies mentioned above, two different approaches for device manufacturing were explored. In the mechanical stack approach, both a CIGS and a DSC cell are manufactured separately, serially connected by wiring and stuck on top of each other, forming a two-terminal dual junction tandem cell. In contrast hereto, the monolithic integration approach uses a finished CIGS solar cell as substrate for the DSC manufacturing. The front contact TCO of the CIGS cell serves as a counterelectrode of the DSC in this approach. Figure 5.2 illustrates the two different approaches.

5.1.1 Mechanically Stacked Tandem Cells

Double Junction Devices

As mentioned above, the current generated in top and bottom cell, respectively, should be equal to each other. In section 4.1 it was shown how variations of the Ga content change microstructure and $I-V$ parameters of CIGS solar cells. These properties can now be used to taylor the absorption characteristics of both the CIGS cell and the DSC to achieve current matching. Figure 5.3 shows the incident photon-to-electron conversion efficiency (IPCE) of CIGS solar cells with different [Ga]/[In+Ga] ratios under the simulated AM1.5G spectrum and when the irradiating light is filtered through a DSC using the JK-2 dye. Table 5.1 shows the corresponding $I-V$ parameters.
5.1. Dye Sensitized/Culn$_{1-x}$Ga$_x$Se$_2$ Tandem Cells

Figure 5.2: Mechanical stack (left) and monolithic integration (right) approaches for dual junction DSC/CIGS tandem solar cells.

Figure 5.3: IPCE graphs of CIGS solar cells with different [Ga]/[In+Ga] ratios under full and DSC-filtered illumination. Noise was smoothened out by using a 5-point FFT algorithm.
Table 5.1: \( I-V \) data of CIGS solar cells with different \([Ga]/[In+Ga]\) ratios under full and DSC-filtered illumination.

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Table 5.2: \( I-V \) data of dye sensitized solar cells using two different dyes.

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</tbody>
</table>

As potential top cells, DSCs using different dyes were available with \( I-V \) parameters as mentioned in table 5.2. Considering the highest performing CIGS cell, using an \([Ga]/[In+Ga]\) ratio of 0.25, yields a current of only 11.8 mAcm\(^{-2}\) after filtering through a dye sensitized solar cell, while the top cells operate at currents of 14 to 15.5 mAcm\(^{-2}\) it becomes evident that the stacking needs to be modified to ensure current matching while using both CIGS solar cells and DSCs of maximum performance.

Basic means were used to calculate the potential current of CIGS solar cells with different \([Ga]/[In+Ga]\) ratios under AM1.5G illumination filtered by a dye sensitized solar cell. The standard AM1.5G spectrum was taken and multiplied by the transmittance data of the dye cells as well as the TCO front contact and the buffer layer of the CIGS cell and then used to estimate the photocurrent from the CIGS quantum efficiency. The calculated QE graphs are shown in figure 5.4 in comparison to the QE curves actually measured. The corresponding calculated current values are shown in table 5.3. It is evident from these values that a significant portion of the light not absorbed in the DSC is lost. Reflections between the two individual cells were identified as the most probable origin of these losses. When simply stacking the cells on top of each other, a small gap
5.1. Dye Sensitized/Culn$_{1-x}$Ga$_x$Se$_2$ Tandem Cells

Figure 5.4: Calculated (solid lines) and measured (dashed lines) quantum efficiency curves for CIGS solar cells with different [Ga]/[In+Ga] ratios after filtering the light by a DSC using the JK-2 dye.

of air remains between the two components such that the light travels trough a glass-air-TCO stack. Differences in refractive index between air, the TCO, and glass cause multiple reflections. To avoid these losses, when manufacturing a mechanically stacked tandem cell, an index matching liquid with a refractive index of $n \approx 1.7$ was applied such that the refractive index remains approximately the same between the DSC back TCO and the CIGS front TCO.

However, even when being able to harvest the full transmitted light in the CIGS cell, a gap of approximately 2 mAcn$^{-2}$ remains if one wants to use the high performance C-101 dye in the DSC. As a high transmittance is especially important in the red and near infrared region of the spectrum, the free carrier absorption in the TCO layers is most important to be overcome. Free carrier absorption is a resonance effect of the electron ensemble vibrating with the alternating electric field of the irradiating near infrared light. Drude’s theory yields for the free carrier absorption

$$\alpha = \frac{\lambda^2 q^3 N_{opt} d}{4\pi^2 e_0 c n m^* \mu_{opt}}$$

where $\lambda$ denotes the wavelength, $q$ the electron charge, $N_{opt}$ the optical electron density, $d$ the layer thickness, $m^*$ the effective mass of the electrons, and $\mu_{opt}$ the optical mobility. $N_{opt}$ and $\mu_{opt}$ correspond to the density and mobility of the electrons in the TCO grains [51]. As can be seen in equation 5.1, this can be reduced by either reducing the electron density or increasing mobility.
Table 5.3: Calculated photocurrent of CIGS solar cells with different [Ga]/[In+Ga] ratios after light filtering with different dyes.

<table>
<thead>
<tr>
<th>dye</th>
<th>x</th>
<th>( J_{sc,calc}^{filt} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>JK-2</td>
<td>0.00</td>
<td>17.37 mAc㎡⁻²</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>14.09 mAc㎡⁻²</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>9.96 mAc㎡⁻²</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>6.87 mAc㎡⁻²</td>
</tr>
<tr>
<td>C-101</td>
<td>0.00</td>
<td>16.70 mAc㎡⁻²</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>13.33 mAc㎡⁻²</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>9.27 mAc㎡⁻²</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>6.12 mAc㎡⁻²</td>
</tr>
</tbody>
</table>

As conductivity is given by

\[
\sigma = n \cdot \mu \cdot e
\]  

where \( n \) is the charge carrier density, \( \mu \) the charge carrier mobility, and \( e \) the electron charge, when increasing charge carrier mobility the carrier density can be reduced to achieve a similar conductivity as before, resulting in a double gain in transmittance. Most promising candidates for such high mobility TCOs are \( \text{In}_2\text{O}_3: \text{Mo (IMO)} \) and \( \text{In}_2\text{O}_3: \text{Ti (ITiO)} \). While the mobility of classical TCOs such as \( \text{In}_2\text{O}_3: \text{Sn (ITO)} \), \( \text{SnO}_2: \text{F (FTO)} \), and \( \text{ZnO}: \text{Al (AZO)} \) are ranging between 25 and 30 cm²V⁻¹s⁻¹, mobilities of around 100 cm²V⁻¹s⁻¹ can be achieved with ITiO or IMO [52]. Figure 5.5 shows how the transmittance of a DSC is increased when the counterelectrode is changed from FTO to ITiO. The effect on the potential current is significant. Similar to above, the potential photocurrent of the CIGS bottom cells was calculated. The corresponding values are shown in table 5.4. With those gains, finally currents in the vicinity of the values achieved by the top cell could be expected from the CIGS bottom cells [53]. With these values and optimized manufacturing of both DSC and CIGS cells, tandem cells were manufactured. The first published result of a mechanically stacked DSC/CIGS solar cell by Liska et al. [54] reported an efficiency of 15.1% with an open circuit voltage of 1.45 V, a short circuit current of 14.1 mAc㎡⁻² and a fill factor of 74%. Using the new dye and contacting procedure, a two-wire tandem cell was assembled and measured under simulated AM1.5G illumination with results as
5.1. Dye Sensitized/Culn_{1-x}Ga_xSe_2 Tandem Cells

![Graph showing transmittance curve of two DSCs using the C-101 dye, one using FTO, the other one ITiO as back contact TCO.](image)

**Figure 5.5:** Transmittance curve of two DSCs using the C-101 dye, one using FTO, the other one ITiO as back contact TCO.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(J_{\text{sc,calc}}^{\text{filt},\text{FTO}})</th>
<th>(J_{\text{sc,calc}}^{\text{filt},\text{ITiO}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>17.37 mAcm(^{-2})</td>
<td>18.69 mAcm(^{-2})</td>
</tr>
<tr>
<td>0.25</td>
<td>14.09 mAcm(^{-2})</td>
<td>14.64 mAcm(^{-2})</td>
</tr>
<tr>
<td>0.50</td>
<td>9.96 mAcm(^{-2})</td>
<td>10.04 mAcm(^{-2})</td>
</tr>
<tr>
<td>0.75</td>
<td>6.87 mAcm(^{-2})</td>
<td>6.37 mAcm(^{-2})</td>
</tr>
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**Table 5.4:** Calculated photocurrent of CIGS solar cells with different [Ga]/[In+Ga] ratios after light filtering with a DSC using the JK-2 dye and different back contacts.
Chapter 5. Tandem Cells

<table>
<thead>
<tr>
<th>cell</th>
<th>$J_{sc}$</th>
<th>$V_{oc}$</th>
<th>$FF$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>tandem</td>
<td>17.6</td>
<td>1.14</td>
<td>73.7</td>
<td>14.8</td>
</tr>
<tr>
<td>top</td>
<td>16.0</td>
<td>0.76</td>
<td>74.0</td>
<td>8.4</td>
</tr>
<tr>
<td>bottom</td>
<td>28.2</td>
<td>0.63</td>
<td>70.8</td>
<td>12.6</td>
</tr>
</tbody>
</table>

Table 5.5: $I - V$ parameters of a mechanically stacked DSC/CIGS tandem solar cell.

Figure 5.6: $I - V$ curve of a mechanically stacked DSC/CIGS tandem solar cell.

shown in table 5.5, figure 5.6 is the corresponding $I - V$ curve.

While the current is high as expected, the open circuit voltage is significantly lower than expected. Before assembly of the tandem cell, the top cell has had a $V_{oc}$ of 0.76 V, the bottom cell one of 0.63 V, thus, in a serial connection, an open circuit voltage between 1.35 and 1.4 V would have been expected. The $V_{oc}$ loss is attributed to leakage currents along the scribes on the CIGS caused by the silver paste used in assembling the device. With a $V_{oc}$ of 1.35 V and all other parameters similar, the tandem cell would have yielded an efficiency of more than 17%, significantly exceeding the values measured for the individual cells [53,55].
Preliminary Studies on Triple Junction Devices

The current calculation method mentioned before was also used to assess the potential of a DSC/CdTe/CIS triple junction cell. As top cell, a DSC with C-101 dye, FTO front and ITiO back contact was assumed. For the middle cell, a CdTe solar cell using an AZO front contact and an ITO back contact was used. Finally, as bottom cell, a standard CIS cell was assumed.

Transmittance data of the different cells is shown in figure 5.7. With the given transmittance, a short circuit current of only 5.1 mAcm\(^{-2}\) is estimated, way lower than the approximately 15 mAcm\(^{-2}\) of the top cells. If one looks at the transmittance data of the TCOs alone as illustrated in figure 5.8, the significant increase in potential becomes clear. At 1200 nm, replacing FTO with ITiO increases the available light by 65%, a substitution of ITO with ITiO still yields a gain of 15%. Considering there is one FTO layer and three ITO or AZO layers in front of the CIS cell, an increase by a factor of 2.5 could be achieved by replacing all TCO layers with ITiO, resulting in approximately 12 to 13 mAcm\(^{-2}\) generated in the bottom CIS cell, only slightly below the values seen in the C-101 DSC top cell [55]. However, deposition of these high mobility TCOs still requires higher temperatures than the completed CIS or CdTe cells can withstand, thus significant efforts to decrease this required temperature, or increase the temperature stability of CIS and CdTe, would be required to apply ITiO to said solar cell types.

**Figure 5.7:** Transmittance data of a DSC (C-101 dye, FTO front contact, ITiO back contact), a CdTe cell (AZO front, ITO back contact), and both cells combined.
5.1.2 Monolithically Integrated Tandem Cells

Another more elegant way to construct a double junction solar cell is the monolithic integration. In this approach, one cell is directly grown on top of the other one, omitting one layer of TCO and a sheet of glass. In case of the DSC/CIGS tandem cell, a completed CIGS device was used as a counterelectrode for the DSC. A working DSC/CIGS tandem device was manufactured in this way, with $I-V$ parameters as given in table 5.6. One of the major problems when doing this is the corrosivity of the iodide electrolyte used in DSC manufacturing significantly affecting the stability of the completed tandem device, leading to the reduced open circuit voltage in the tandem cell. Internal shuntways are suggested by non-ideal rectification behaviour at low light intensities [50]. Figure 5.9 shows SEM images of the surface of both a bare CIGS absorber and a completed CIGS device, i.e., the ZnO:Al surface after exposure to the electrolyte for 40 min in ambient air without any encapsulation. Highlighted with black rectangles are cracks in the respective layers, which are evenly distributed over the whole surface. These cracks were not observed on any sample before exposing it to the electrolyte. Within the same timeframe of electrolyte exposure, the effects also get observable in the electrical characteristics of the CIGS solar cell. While the original measurement of the exposed cell has shown a parallel resistance of $1868 \, \Omega \cdot \text{cm}$, this decreases to $1455 \, \Omega \cdot \text{cm}$ after the electrolyte treatment while the fill factor decreases from 67.5% to 59.1% [53]. The same electrolyte in the encapsulated environment of the monolithic tandem cell has an even more severe impact onto the performance. Within two hours of manufacturing, the (conducting) elec-
5.1. Dye Sensitized/Culn$_{1-x}$Ga$_x$Se$_2$ Tandem Cells

<table>
<thead>
<tr>
<th>cell</th>
<th>$J_{sc}$</th>
<th>$V_{oc}$</th>
<th>FF</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>tandem</td>
<td>13.9</td>
<td>1.22</td>
<td>72</td>
<td>12.2</td>
</tr>
<tr>
<td>top</td>
<td>15.3</td>
<td>0.74</td>
<td>74</td>
<td>8.4</td>
</tr>
<tr>
<td>bottom</td>
<td>27.3</td>
<td>0.62</td>
<td>68</td>
<td>11.6</td>
</tr>
</tbody>
</table>

Table 5.6: $I - V$ parameters of a monolithic DSC/CIGS tandem solar cell.

Figure 5.9: CIGS absorber and TCO of completed cell after exposure to DSC electrolyte.
trolyte has etched through the layers of the CIGS cell to the molybdenum back contact, effectively shunting the CIGS cell and leaving only the DSC for power generation. $I - V$ graphs of the monolithic tandem cell mentioned before (table 5.6) showing the degradation can be seen in figure 5.10 [50,53].

5.2 Preliminary Studies to All-chalcopyrite Tandem Cells

5.2.1 Growth of Wide Gap CuIn$_{1-x}$Ga$_x$Se$_2$

Another approach for double junction tandem cells is the combination of two chalcopyrite solar cells with different [Ga]/[In+Ga] ratios. As CuInSe$_2$ has a band gap of approximately 1 eV, and CuGaSe$_2$ one of approximately 1.7 eV, those two materials are pretty close to the theoretical optimum of double junction devices [48].

In addition to the recombination problems already reported in section 4.1, also the morphology is drastically affected when the Ga content is increased to values exceeding [Ga]/[In+Ga] = 0.5. Figure 5.11 shows SEM micrographs of the cross section of CIGS solar cells with different Ga content in the absorber layer. The grain size decreases with increasing Ga thickness, and the block-like
grain structure is completely lost in the CIGS absorber layer in the sample with \([\text{Ga}] / [\text{In}+\text{Ga}] = 0.79\) [34].

On transparent ZnO:Al back contacts as needed for wide-gap top cells in multijunction devices, two fundamental parameters differ from the case on SLG/Mo substrates discussed above: firstly, as the ZnO:Al back contact acts as a diffusion barrier, no sodium is present in the absorber layer during growth. Secondly, to maintain conductivity of the TCO back contact, the substrate temperature is limited to 450 °C in contrast to the 580 to 600 °C used with Mo back contacts.

The influences of those differences are manifold, but the most important point is their influence of interdiffusion of elements. The lower temperature results in less interdiffusion of Ga and In into the center of the absorber layer, whose formation is determined by the second stage. As the diffusivity of In is higher as the one of Ga, and this gets more pronounced for low deposition temperatures as used here on the TCO contact layer, the Ga dip as mentioned in section 4.2.1 gets deeper. Furthermore, due to less diffusion, the grain size is expected to be lower. However, the presence of Na during the layer growth also affects diffusivity. Especially Ga diffusion is hindered by sodium present during the layer deposition [56]. As Na is added using a post deposition treatment to the absorber layers grown on ZnO:Al back contacts rather than using a precursor or co-evaporation, the CIGS layer is formed under Na-free conditions.
Figure 5.12: Cross section of CIGS solar cells with different Ga content on ZnO:Al back contact. a) x=0.00 b) x=0.24 c) x=0.56 d) x=0.76.

Figure 5.12 shows cross section SEM micrographs of CIGS solar cells grown on ZnO:Al with different Ga content. The corresponding PV characteristics were already shown in table 4.2 on page 25. In the low Ga content samples, smaller grains compared to those found in the baseline high temperature process on SLG/Mo substrates are observed. However, when increasing the [Ga]/[In+Ga] ratio to higher values exceeding 0.5, grain size is notably larger on AZO [34]. Thus, we can conclude that there are two different regimes when changing the Ga concentration in samples grown at low temperature on a Na free substrate: for low Ga concentrations, up to approximately 0.5, the grain size is dominated by the substrate temperature decrease and smaller grains than on the high temperature Na-containing process are found. When the Ga content is increased to higher values, the absence of Na becomes the dominant effect over the lower substrate temperature and grain growth is enhanced compared to the baseline process and larger grains are found.

5.2.2 Back Contact Interface on TCO Back Contacts

As explained in section 2.4.1, a thin MoSe$_2$ layer is needed at the interface between the CIGS absorber and the back contact, in this case the ZnO:Al back layer. To achieve this, approximately 5 nm of Mo are sputtered on top of the TCO
5.2. Preliminary Studies to All-chalcopyrite Tandem Cells

Layer. This thin Mo layer selenizes during the CIGS deposition process resulting in a good contact between TCO back contact and CIGS [21]. However, this molybdenum selenide layer also has drawbacks. MoSe\textsubscript{2} has an indirect band gap of 1.05 to 1.12 eV, with the lowest direct band distance being 1.35 eV [57]. Thus, the layer is not entirely transparent in the photon energy region relevant for the bottom cell between 1.7 and 1.0 eV. Figure 5.13 shows the transmittance of a wide-gap CIGS cell compared to that of a DSC. Figure 5.14 shows the imaginary part of the complex index of refraction $k$ of a CIGS layer which relates to the absorption factor by

$$\alpha = \frac{8\pi k}{\lambda},$$

showing that the absorption at long wavelengths has to be attributed to an effect of the contacts as beyond the band gap the absorption in the CIGS itself is almost zero. As the transmittance of the CIGS cells is significantly lower than that measured in a DSC and given in figure 5.13 as a reference, which uses the generally less transparent FTO in its contacts, the light losses can be attributed to parasitic absorption in the MoSe\textsubscript{2} layer.

Furthermore, as mentioned above, one is limited to lower substrate temperatures when using a TCO back contact. To determine the maximum temperature useable for the CIGS deposition process, a series of three depositions was performed and the resistance across the diagonal of the 5 x 5 cm\textsuperscript{2} substrate was measured before and after the CIGS deposition using a multimeter, the test leads were held onto two opposite corners of the sample and the measurement was re-

![Figure 5.13: Transmittance of CIGS with different Ga content $x = [Ga]/[In+Ga]$ on ZnO:Al back contacts and a DSC with FTO contacts as comparison.](image-url)
repeated three times to ensure that the value is not deteriorated by a contact error. The substrate temperature was set to 450 °C, 490 °C, and 535 °C, respectively. With an initial resistance of 44 Ω across the samples, the 450 °C grown sample shows hardly any change in resistance. However, the resistance of the sample heated to 490 °C was measured at 60 Ω, and that of the sample heated to 535 °C even at 79 Ω. Thus, 450 °C seems to be the maximum substrate temperature useful for CIGS deposition on ZnO:Al back contacts. As a consequence, the series resistance of the finished solar cell devices changes for the CIGS cells where the absorber was deposited at higher temperatures: while $R_s$ in the sample grown at 450 °C maximally has values of 2.7 to 3.0 Ωcm, the maximum values of the serial resistance for the samples grown at higher temperature are around 3.9 to 4.1 Ωcm. Thus, the fill factor is limited to values of 62 to 63% in the highest $R_s$ cells on the sample, while in the low temperature grown samples, fill factors of 66 to 67% are observed for the cells with highest $R_s$.

Figure 5.14: Wavelength dependent $k$ value of a CIGS absorber determined by ellipsometry.
The work in this thesis shows that even though CuIn$_{1-x}$Ga$_x$Se$_2$ solar cells are on their way to industrialization, there are still possibilities to further enhance the efficiencies and reduce production cost. For achieving high efficiency CIGS solar cells, the understanding of the band gap grading in the absorber layer, achieved by changing the [Ga]/[In+Ga] ratio, with its influence on both electronic and optical properties as well as the band alignment in the junction are most crucial. The results presented in this thesis show possibilities how intentional variation of the energy band gap of CIGS across the layer can increase the efficiency. This is accomplished by increasing the band gap in the space charge region to boost the open circuit voltage, while the minimum band gap is kept at a low value to maximize the amount of absorbed photons which in consequence maximizes the current. During these experiments, a new laboratory internal efficiency record of 18.8% using a CIGS absorber grown with 5% Cu excess could be achieved. Subsequent work in this field should focus on finding the optimum band gap profile for high efficiency solar cells, not only in the shape of the band gap profile but also with regard to the absolute value of the band gap.

Furthermore, it was pointed out how the important parameters $V_{oc}$ and fill factor can be maintained when reducing the thickness of the absorber layer when depositing the CIGS by a three stage process. The importance of the band gap grading for the conversion efficiency was shown and it was found that for 500 nm thin absorbers, the profile with a Ga dip yielding the highest efficiency for baseline 2 $\mu$m thick samples should be replaced by a constant band gap throughout the absorber, only near the back contact interface a higher band gap should be used as a back surface field to repel minority carriers from the interface which acts as a recombination center. Regarding the thickness reduction, further work should focus on enhanced optical confinement to maintain the current next to the
other parameters. The 11.7% efficiency shown in this thesis could be increased to approximately 15% with optical confinement measures to increase \( J_{sc} \) from 25 mAcm\(^{-2}\) to values of approximately 30 to 31 mAcm\(^{-2}\). Texturing of the front contact TCO could be used for light scattering to increase the effective path of the light within the 500 nm thin absorber layers, or highly reflective back contact coatings could be used to keep the light transmitted through the whole solar cell within the absorber layer. Approximately 1 mAcm\(^{-2}\) could also be gained by applying a luminescent downshifting layer onto the thin absorber layer cells. A further 10% increase in current could be obtained by applying an anti-reflective coating to the devices. Further optimization of the band gap grading should focus on a grading where the maximum band gap is located at the back contact interface, continuously narrowing towards the front of the absorber layer where the minimum band gap should be located. Furthermore, the absolute band gap value to achieve the best \( J_{sc}/V_{oc} \) ratio should be determined.

Tandem cells combining a DSC with a CIGS bottom cell are an interesting prospect for highly efficient and cheap solar cells, and the feasibility of monolithically integrated DSC/CIGS tandems was shown in the thesis. However, huge efforts would need to be put into making the bottom cell corrosion resistant and the manufacturing would have to be really cheap to make any gains in the dollar-per-wattage figure as the efficiency gains over the CIGS efficiency are pretty low so far. Especially the open circuit voltage of the DSC is a bottleneck as with absorption edges corresponding to approximately 1.6 to 1.7 eV they show \( V_{oc} \) values between 700 and 800 mV only. To make the combination economically feasible, i.e., to achieve significant efficiency gains, these values should be 200 mV higher. With a combined \( V_{oc} \) of 1.6 V, a \( J_{sc} \) of 15 mAcm\(^{-2}\), and a fill factor of 75%, a conversion efficiency of 18% can be expected from a CIGS/DSC tandem cell. A further challenge which should be worked on is achieving highly transparent front cells to maximize the light provided to the back cell. Possible approaches here could be high mobility TCOs for low temperature deposition to reduce free carrier absorption in the red and near infrared part of the spectrum. Another interesting field are p type TCOs whose usage could eliminate the need of the MoSe\(_2\) layer at the chalcopyrite/back contact interface due to a more favorable band alignment, resulting in higher transmittance. Finally, research on less corrosive electrolytes for DSCs, or a more stable intermediate TCO layer, could result in a significantly increased stability of monolithically integrated DSC/CIGS solar cells.

The use of luminescent downshifting shows the potential for small gains in \( J_{sc} \) with prospects for relative increases in the single-digit percentage range. As the incorporation of such dyes into the manufacturing of modules by mixing them into the encapsulation polymer is almost a non-issue, even such small gains may be
worthwhile for getting more power per dollar. However, further research is needed to find an optimum dye or dye combination to match the CIGS absorption onset and the optimum concentration of said dyes.
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<td>5.2</td>
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<td>Calculated photocurrent of CIGS solar cells with different [Ga]/[In+Ga] ratios after light filtering with different dyes.</td>
<td>54</td>
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<td>5.4</td>
<td>Calculated photocurrent of CIGS solar cells with different [Ga]/[In+Ga] ratios after light filtering with a DSC using the JK-2 dye and different back contacts.</td>
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