Intermediate Band Solar Cells Based on Cr:ZnS

Device Characterization and Simulation

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Preface

This thesis marks the end of a Master of Science degree in Physics at the Norwegian University of Science and Technology (NTNU), in Trondheim, Norway.

I would like to express my gratefulness to some people who have helped me and contributed directly or indirectly to this thesis. First of all I would like to thank my supervisor Turid Worren Reenaas for including me in her research group, reading my thesis several times, and giving valuable comments and questions on my work to discuss. Furthermore I would like to thank Xiaodong (Donny) Yang and Mohamadreza Nematollahi for their help in my work and for all interesting and informative discussions we had. I am also indebted to my fellow master’s students, especially Carl Philip Heimdal, for countless unforgettable moments during the process of writing this thesis. Special thanks also go to Marion Han for proofreading the manuscript and motivating and encouraging me all the time. Last but not least, I’m very thankful to my parents for all their support throughout the years, which has enabled me to be now where I am!
Abstract

Intermediate band solar cells (IBSCs) are emerging, potentially high efficiency, solar cells. In this work, IBSCs based on zinc-sulfide with a high chromium doping density (Cr:ZnS), are fabricated, characterized and gradually improved. The first devices showed an efficiency of (0.008 ± 0.001) %. Improvements in the cell design led to a record efficiency of (2.05 ± 0.12) %.

Thin undoped and Cr-doped ZnS films, on a silicon substrate, were processed into complete devices and characterized with current-voltage and open circuit voltage versus light intensity measurements. Solar cell simulations were made with a numerical simulation program (SCAPS), to get a better understanding of our solar cells. Different solar cell parameters, absorption coefficients, and ZnS film thicknesses were varied and investigated in the simulations. Addition of the chromium doping in the zinc-sulfide films resulted in large improvements in the cell efficiencies, compared to the undoped cells, due to below band gap absorption and a higher conductivity in this layer. This was seen in both the experimental and simulated cells. Aging effects were observed for some of the solar cells, when the zinc-sulfide layer is exposed to air. However, when a thin top layer of aluminum doped zinc-oxide was used, the aging effect was strongly reduced or removed.

This work is a contribution to the realization of high performance IBSCs, based on abundant, non-toxic, and inexpensive materials. The total efficiencies achieved are still low, in comparison to established solar cell technologies, but the trend is going the right direction. Hopefully, these solar cells will approach their theoretical limits in near future and contribute to a revolution in the worldwide electricity production.
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1 Introduction

The worldwide electricity production has almost doubled in the last two decades. In 2012, on a global basis 22.6 PWh\(^1\) electrical energy was produced, compared to 11.9 PWh in 1990 [1]. Until 2040 another increase of 93 % is expected [2]. This enormous increase in such a short time gives rise to concerns about the security of energy supplies, since more than 80 % of the global total energy is still produced from fossil fuels [3]. Non-renewable energy sources are limited, have local environmental consequences and they release greenhouse gases like CO\(_2\) when consumed, leading to global climate changes. It is, therefore, of worldwide interest to find and implement more sustainable energy alternatives.

One renewable energy source with a very large potential is solar energy. The total solar irradiance at sea level in one year is about 1.1 \(10^6\) PWh and more energy is provided by the sun each hour than the worldwide energy consumption every year [4]. Solar cells convert solar energy directly into electricity and are an obvious way to utilize this great amount of renewable energy.

The first discovery of electrical current arising from a light-induced chemical reaction was made by Becquerel in 1839 [5]. However, it took more than a century of many discoveries of material and light properties and the formulation of the quantum theory until the first working silicon solar cell was announced by Chapin et al. in 1954 [6]. This solar cell had an efficiency of 6 %. Only four years later the first solar cells were used as an energy source on a satellite. Since that time, photovoltaic technology developed steadily. Events like the oil crisis in the early 1970s and the rising awareness about climate changes have led to a lot of interest in solar cells. With increased research, new technical methods, and large-scale industrial production, the efficiencies of solar cells have increased, while the production costs have decreased.

Generally, one refers to three generations of solar cells. First generation solar cells are crystalline solar cells with record power conversion efficiencies at 25 % [7]. Second generation solar cells are thin film devices with the aim to reduce the costs significantly, using low cost fabrication methods and a lower amount of material. These cells have lower efficiencies, due to poorer material quality, with current record efficiencies at 19.8 % [7]. Third generation solar cells are based on new approaches that exceed the efficiencies of the previous generations, with a currently record efficiency at 44.4 % [7].

\(^1\) 1 PWh (Petawatt hour) = \(10^{15}\) Wh = \(3.6 \times 10^{19}\) J (Joule)
One of the approaches to such a high efficiency solar cell is the so-called ‘intermediate band solar cell’ (IBSC), which is the topic of this thesis. The main question covered in this thesis is the development of IBSCs with chromium doped zinc-sulfide as intermediate band material. To answer this question, work was done on the processing of thin film samples to complete solar cell devices and the characterization of their performance. Different factors, like the cell contact, the cell structure, and the film thickness, were improved stepwise. The solar cell performances were characterized with current-voltage measurements at a standard “1 sun” illumination and for concentrated light, where the open circuit voltage was measured as a function of light intensity, so called Suns-Voc measurements. Some solar cells were also monitored over a longer time to see aging effects on the performances. To get a better understanding of the developed cells, simulations of the IBSCs were carried out and compared to some experimental results. The aim of this work was not only to get record efficiencies, but also to establish the fundamentals for the production of high performance IBSCs based on abundant, non-toxic, and inexpensive materials. The deposition of thin film samples used for the solar cells and material characterizations are not part of the scope of this thesis.

A general background over the basic working principles of solar cells is given in the first part of chapter 2. The second part is a presentation of the three solar cell generations, with a focus on the third generation approaches, where also the concept of the IBSCs is introduced.

Chapter 3 contains a review of the state of the art within IBSC research, and a presentation of our contribution. Further, the materials used for our solar cells (especially chromium doped zinc-sulfide) are discussed, together with a presentation of the structural design of our cells.

The methodology and the experimental setups are presented in chapter 4. The first part deals with the production of the samples and the solar cell devices, while the second part is about the characterization techniques, which were used. This chapter is followed by chapter 5, in which the simulation methodology is presented, together with some simulated results for our cells.

The main results, of the work done for this thesis, are presented and discussed in chapter 6. It opens with a description of an initial setup test, followed by the results of the different development steps for our solar cells and the presentation of a long time study on aging effects for our cells. The last part of this chapter is about the ideal thickness of the IB-layer in the best cell structure used.

A final conclusion of this thesis and suggestions for further work on our solar cells to achieve highly efficient IBSCs are given in chapter 7 and chapter 8.
2 Solar Cell Theory and Solar Cell Generations

Solar cells convert solar energy in the form of electromagnetic radiation into electrical energy. The first section in this chapter presents the basic working principles of solar cells, such as the absorption of light in the solar cell and various loss mechanisms. Then the structure of a solar cell is described, how a p-n junction works and what other forms of junctions can be used in a solar cell. The last part of this section explains the characterization parameters of an illuminated solar cell.

The second part of this chapter is about the different solar cell generations and the third generation photovoltaic in particular. This generation of solar cells is multifaceted and a lot of research is going on within this area. Some of the most promising concepts and theories will be presented, as well as a concluding overview of the best research solar cells up to date.

2.1 Basic Working Principles of Solar Cells

This chapter about the basic working principles of solar cells is mainly based on Refs. [8-10].

2.1.1 Light Conversion into Electrical Energy

Solar cells are devices that absorb sunlight and convert parts of the photon energy directly into electrical energy. Fig. 2.1 schematically shows the structure of a basic solar cell. It consists of a semiconductor material that has two regions with opposite majority carrier types (n-type and p-type). A metal contact covers the whole back side surface, while on the front side a metallic grid forms the electrical contact. The grid design minimizes the shadowing of the semiconductor. In addition, an antireflective layer on top of the semiconductor reduces the amount of light reflected from it.

When the solar cell structure is illuminated by electromagnetic radiation, a voltage and/or an electric current is created in the material due to the photovoltaic effect. Photons with energies larger than the band gap of the semiconductor can be absorbed and excite electrons within the material to a higher energy level, above the band gap, creating electron-hole pairs. These excited electrons, now in the so called ‘conduction band’, are freer to move within the semiconductor until they return back to the ‘valence band’ by recombination with a hole. Light induced electron-hole pairs at the p-n junction will be separated due to the electric field built up at the junction, electrons being collected to the n
2.1 Basic Working Principles of Solar Cells

region and holes to the p region. In addition, a voltage across an illuminated junction is generated, which can drive the charge carriers into an external circuit. If a load is connected in the external circuit, power can be extracted from the solar cell since both, a photo-generated current and voltage are produced in the cell. See chapter 2 in Ref. [8].

Absorption, charge carrier generation and recombination

The basis of the photovoltaic production of energy is the generation of free charge carriers via incoming light. Therefore, the largest possible fraction of the light shining onto the device should be absorbed within the material. Yet a complete absorption of light is not possible due to several reasons. On the one hand, some light is reflected at the surface of the device. Different antirefection coatings and texturing methods can lower the loss to a minimum. On the other hand, some light is not absorbed in the material but directly transmitted through it. Whether the incoming photon is absorbed or transmitted is mainly determined by its energy

\[ E_{ph}(\lambda) = \frac{h \cdot c}{\lambda} \]  

(1)

where \( h \) is the Planck constant, \( c \) is the speed of light, and \( \lambda \) is the wavelength of light. If the energy of a photon is lower than the band gap energy \( (E_g) \) of the semiconductor material, it does not have enough energy to create an electron-hole pair (see Fig. 2.2). Since the interaction is very weak, the material is transparent for this wavelength and the solar cell will not produce any power. Photons with energies higher than the band gap may be absorbed and excite an electron to the conduction band and leave behind a hole in the valence band. If the energy of the photon exceeds that of the band gap, it will excite the
electron high up into the conduction band, where it will quickly relax back to the band edge and lose the excess energy as heat. Therefore, any photons with energies higher than the band gap energy will contribute the same amount as photons with energies exactly the same as that of the band gap, but additionally heat up the device.

The reverse process to generation is recombination, where electrons from the conduction band return back to the valence band and thereby recombine with holes. The three recombination processes in solar cells are illustrated in Fig. 2.3.
A recombination process, which is preliminarily dominant in direct band gap materials, is the so-called ‘radiative recombination’. It is the reverse process of absorption of a photon. By returning back to the valence band, the electrons will emit photons with energies equal to the energy difference between the initial and final state, typically close to the band gap energy. Semiconductor lasers and light emitting diodes operate according to this process. Indirect semiconductors, however, require an additional phonon and therefore the radiative recombination lifetimes are much longer in comparison. Therefore, other recombination processes will be more dominant for such materials.

Another recombination process is the so-called ‘Shockley-Read-Hall (SRH) recombination’ or the ‘recombination through defects or impurities’. Defects and impurities affect the material in such a way as that they create localized energy levels inside of the band gap. Electron-hole pairs can recombine via these levels in a two-step process: In the first step, an electron is trapped in the localized level, and in the second step a hole is trapped in the same level and the electron and hole recombine.

The SRH recombination rate is strongly dependent on the position of the localized energy level. A level near the middle of the band gap will notably increase the recombination. In comparison, a level close to one of the band edges will not be able to trap both an electron and a hole and will not increase the SRH recombination significantly. Excessive SRH recombination occurs on the surface of any (untreated) semiconductor material, because the surface inherently contains defects and therefore has a high number of energy levels within the band gap.

A third major recombination process is ‘Auger recombination’. This process involves three carriers. The electron recombining with a hole does not release a photon, but instead the released energy is transferred to kinetic energy of another electron within the conduction band or a hole in the valence band. This third carrier rapidly thermalizes and energy is released as phonons.

All of these three recombination processes can occur simultaneously, whereby the total recombination rate is the sum of the rates of all processes.

**Loss mechanisms**

In a solar cell, several loss mechanisms appear. The solar cell conversion efficiency is the ratio between the incoming solar power and the delivered electric power. Therefore, a maximized product of the voltage and the current delivered by the cell is wanted. The current is limited by the amount of electrons extracted from the solar cell, while the voltage is limited by the band gap. Hence a smaller band gap will increase current generation, but give rise to a lower voltage. In contrast, a large band gap will result in a lower current, but a higher voltage. In Fig. 2.4 the main current and voltage losses in a solar cell are shown.
As mentioned earlier, the photo-generated current is limited by the size of the band gap and incomplete light absorption (not shown in Fig. 2.4), and the current delivered is further limited by recombination losses, shown as process number 4 in the figure.

The voltage losses are mainly due to process number 1, 2 and 3 in Fig. 2.4. The loss in process 1 is the thermalization loss of the excited electron-hole pairs. Process 2 and 3 are voltage losses in the junction and the contact respectively, and are unavoidable. The choice of the material used for the contact will affect the size of the voltage loss, but it will also affect the contact properties and resistance (this will be discussed later). A main challenge in solar cell development is to keep all of these losses as small as possible.

### 2.1.2 A p-n Junction in Dark Conditions

A p-n junction, i.e. a diode, is the basis of conventional solar cells. It is an interface between two different ‘doped’ regions in a semiconductor. In n-type material excess electrons dominate and in a p-type material excess holes dominate. When a p-n junction is formed, the concentration difference between electrons and holes on both sides will give rise to electrons diffusing from the n-type material into the p-type material and holes diffusing conversely. As a result, positive and negative ions will be created near the junction boundary and an electric field is set up. The electric field gives rise to an electrostatic potential difference that is called ‘built-in voltage’. The region between these two different doped materials is referred to as ‘space-charge region’ or ‘depletion region’. In thermal equilibrium, the Fermi level of the two quasi-neutral regions, this means outside the depletion region, must be aligned.
The current-voltage characteristics of an ideal diode is described by the Shockley equation

\[ I_D = I_0 \left( e^{qV/kT} - 1 \right) \]  

where \( I_0 \) is the reverse saturation current, \( V \) the voltage over the junction, \( k \) the Boltzmann constant, \( q \) the electron charge and \( T \) the absolute temperature. \( I_0 \) equals

\[ I_0 = qA \left( \frac{D_{p/n}}{L_{p/n}} p_n + \frac{D_{n/p}}{L_{n/p}} n_p \right) \]

where \( A \) is the cross-sectional area of the junction, \( D_{p/n} \) is the diffusion coefficient for holes/electrons, \( L_{p/n} \) is the diffusion length for holes/electrons, and \( p_n \) and \( n_p \) are the minority carrier concentrations on the n- and p-side, respectively.

In the ideal diode equation it is assumed that no recombination or thermal generation of carriers occur in the space charge region (\( W \)). If the width of the space charge region is not very small, compared with the carrier diffusion lengths, significant recombination can take place within \( W \). This deviation from the ideal behavior can be included in the diode equation with an ‘ideality factor’ \( n \) in the exponent:

\[ I_D = I_0' \left( e^{qV/nkT} - 1 \right) \]

The ideality factor \( n \) varies normally between 1 and 2, depending on the material and temperature, describing the departure from the ideal diode characteristic, hence also the name. See chapter 5.6.2 in Ref. [13].

**Alternative junction structures**

In the following, two modifications of the p-n junction are briefly presented: ‘p-i-n junctions’ and ‘heterojunctions’.

A p-i-n junction is a p-n junction with an additional undoped (intrinsic, \( i \)) layer sandwiched between the two usually very thin and doped regions. The built-in voltage is the same as in the p-n junction, but the electric field in the junction extends over the intrinsic region. This is advantageous for materials where the minority carrier diffusion length is short in the doped regions, because the lifetimes of the carriers in the intrinsic layer usually are higher and they will survive for a longer distance. A drawback is the usually poor conductivity in the intrinsic layer, giving rise to series resistance, and charged impurities that may cause the electric field to vanish within the intrinsic region. See chapter 5.5.2 in Ref. [8].

A heterojunction is a junction made out of two different materials with typically different band gaps. At the junction, a discontinuity will appear at the conduction and/or valence band edges due to the difference in band gaps. This discontinuity causes different effective fields for electrons and holes. For the most part it will increase the electrostatic field for one carrier type, while counteracting it for the other carrier type. The exact band alignment
depends on the electron affinity and work function of the two materials at the junction. See chapter 5.5.3 in Ref [8].

**Schottky barrier and ohmic contact**

When a junction is made between a metal and a semiconductor material, two possible cases can occur, dependent on the work functions of the materials. In the first case, the work function of the metal is larger than the one of the semiconductor, and a barrier for the electrons will arise. The barrier is called a ‘Schottky barrier’ and has, from the semiconductor side, a height equal to \( q(\Phi_m - \Phi_s) \), where \( q \) is the electron charge, \( \Phi_m \) the metal work function, and \( \Phi_s \) the semiconductor work function. From the metal side, the barrier has a height equal to \( q(\Phi_m - \chi) \), where \( \chi \) is the electron affinity of the semiconductor, as illustrated Fig. 2.5(a).

The second case of a semiconductor-metal junction is the so called ‘ohmic contact’. In this case, the work function of the metal is smaller than the one of the n-type semiconductor. The band bending at the junction will happen in such a way so that the transport of the majority carriers will be unhindered. Therefore, current can flow easily as it is a low resistance contact for majority carriers. This band alignment is shown in Fig. 2.5(b).

![Schottky barrier and ohmic contact](image)

*Fig. 2.5 Schottky barrier (a) and ohmic contact (b) between metal and n-type semiconductor. Fermi level (\( E_F \)) of both materials align, resulting in a band bending in the semiconductor material (strength dependent on the doping concentration). Figure adapted from Ref. [13].*
In the two cases, the requirement for the work function is the opposite, if the n-type semiconductor material is changed to a p-type material. In basic solar cells, as the one shown in Fig. 2.1, ohmic contacts are desired to easily extract the photocurrent. See chapter 5.4 in Ref [8].

A practical method to form ohmic contacts is one in which the metal (that might not have the desired work function) is deposited onto a highly doped semiconductor. The barrier height might be significant, but the width of the depletion region (W in Fig. 2.5) is so small that charge carriers can tunnel through the barrier. A doping concentration of \( N_{D/A} > 10^{19} \text{ cm}^{-3} \) (donors/acceptors) will typically result in a barrier thin enough so tunneling will be possible [14].

### 2.1.3 Performance Parameters of a Solar Cell

**Current-voltage curves**

When a p-n junction is illuminated, a current proportional to the light intensity, \( I_L \), will be produced in addition to the dark current \( I_D \), given by Eq. 2. \( I_L \) and \( I_D \) flow in opposite directions. The sum of these two current contributions is the characteristic IV curve for an ideal solar cell and is shown in Fig. 2.6. This figure also shows an equivalent electrical circuit for this ideal device. The normal sign convention for solar cell devices is that \( I_L \) is positive. The resulting formula for the current, as a function of the voltage over the solar cell, is therefore

\[
I(V) = I_L - I_D = I_L - I_0 \left( e^{qV/kT} - 1 \right) 
\]

where \( I_L \) is the photo-generated current and \( I_D \) the dark current.

![Figure 2.6](image)

*Fig. 2.6 a) Current-voltage characteristic of an ideal solar cell. The dark current (dashed red line) shows the behavior of the p-n junction, whereas the blue curve is the current when the cell is illuminated. Additionally the cell power (dotted green line) and the fill factor (grey box) are shown. b) Equivalent circuit for an ideal solar cell with photo-generated current \( I_L \).*
Chapter 2 - Solar Cell Theory and Solar Cell Generations

An IV curve of a solar cell contains some basic performance parameters of the device. When the voltage over the cell is zero (that means the solar cell is short-circuited) the current through the cell is called ‘short-circuit current’ \(I_{SC}\). This is the maximum current that can be drawn from a solar cell and, in the ideal case, is the amount of photo-generated current. When the extracted current is zero (i.e. when nothing is connected and we have an open circuit), the voltage over the cell is maximum. This voltage is called the ‘open circuit voltage’ \(V_{oc}\). Zero extracted current corresponds to the situation when the dark current exactly cancels out the photo-generated current.

Whenever a load is attached to the cell, power \(P\) can be extracted. The maximum power output \(P_m\), will be at the maximal product of \(I \times V\) (see dotted line in Fig. 2.6). The current and voltage at this maximum power point are referred to as \(I_m\) and \(V_m\). The fill factor \(FF\) is a value that shows how rectangular the shape of the IV curve is and is defined as

\[
FF = \frac{I_m V_m}{I_{SC} V_{oc}}.
\]

For solar cells with so-called parasitic resistances (non-ideal values of series and parallel resistances, see below), the fill factor will be reduced.

The efficiency \(\eta\) is the key performance parameter of a solar cell. It is defined as the ratio of the maximum power produced \(P_{out}\) to the incident radiation power \(P_{in}\), and can be expressed as

\[
\eta = \frac{P_{out}}{P_{in}} = \frac{I_m V_m}{I_{SC} V_{oc} FF}.
\]

As the cell performance depends strongly on the conditions (actual solar spectrum and cell temperature), the cells should be tested by using a standard reference solar spectrum and it should be kept at a cell temperature of 25 °C. The solar spectrum generally used is the so-called ‘AM1.5’ spectrum (Air mass 1.5). This spectrum describes the solar radiation after travelling through the atmosphere to sea level in an inclined angle. The irradiance power is 100 mW/cm\(^2\) referred to as ‘one sun’.

Resistances in non-ideal solar cells

In real solar cells, two resistances often have to be added to the ideal case. One resistance is added in parallel to the cell and takes account for shunting effects (shunt resistance, \(R_{sh}\)), and the other in series (series resistance, \(R_s\)). In the ideal case \(R_s = 0\ \Omega\) and \(R_{sh} = \infty\ \Omega\). Fig. 2.7 a) shows the equivalent circuit of a solar cell with both shunt and series resistances included. In addition, Fig. 2.7 b) and c) also shows schematically how these resistances will affect the IV-curve of a non-ideal solar cell.
2.2 Solar Cell Generations

Solar cells are commonly divided into three different categories, referred to as ‘solar cell generations’. The three generations are characterized by the efficiency of the cells compared to the cost of the cells. In general, the first generation solar cells are crystalline, wafer-based solar cells, and the second generation are so-called ‘thin film solar cells’ [15]. Thin film cells have been cheaper to fabricate, resulting in lower costs per watt generated under standard conditions. However, with the recent dramatic cost reduction of wafer-based solar cells, first generation cells are currently as cheap as second generation cells. Module prices vary for Si modules between 0.90 and 0.53 USD/Watt, and for thin film modules between 0.70 and 0.50 USD/Watt in April 2014 [16].
Both first and second generation cells have the same efficiency limit (41 %, for an ideal cell under ideal conditions), since they both operate based on the same principles as described in the preceding sections. The third generation cells, however, are based on significantly different operational principles, leading to a significantly higher efficiency limit (up 87 %). In the following, the three generations will be described in more detail.

### 2.2.1 First Generation

The first generation of solar cells is based on wafers and is the dominant device on the market. In 2008, almost 90 % of the worldwide solar cell production was based on mono- or multi-crystalline silicon wafers and ribbons [9](p.27). It is also the most mature solar cell technology, since it has been developed the longest and had from the beginning access to knowledge from the microelectronics industry about chemical and electrical properties of Si, how to grow pure crystalline structures, and about processing steps. Another reason for its success is the availability of silicon as an abundant, nontoxic and stable material with a suitable band gap for solar cell applications. State of the art silicon solar cell modules have an efficiency of typically 16-17 % for mono-crystalline silicon wafers and 13-15 % for multi-crystalline cells [9]. The record efficiencies for terrestrial modules were 22.9 % and 18.5 %, respectively for mono- and multi-crystalline cells in 2013, and the record laboratory cells had an efficiency of 25 % and 20.4 % [7]. The theoretical limit of a silicon cell with a band gap of 1.1 eV is about 30 % for unconcentrated light, as first calculated by Shockley and Queisser [17]. It is obvious that the record efficiencies are approaching the theoretical limit. Therefore research in new areas has been enforced although silicon wafers are so well established.

### 2.2.2 Second Generation

The second generation of solar cells is based on thin film technologies in order to use less semiconductor material and thus achieve lower production costs and the possibility to manufacture in larger scales. In comparison to the silicon wafers, only a very thin layer of a semiconductor material is needed, due to the high absorption of light of the materials used. The very thin films can be deposited on low cost substrates such as glass, plastic or metal. This brings some major advantages over the first generation cells, but there are also some reasons why the thin film solar cells do not dominate the market. The efficiencies of these cells are generally lower than those of silicon wafer devices. Also, research for thin film solar cells is not as established as the wafer based solar cell research and manufacturing. Some of the materials used for thin film solar cells are amorphous silicon (a-Si), CIGS (Cu(InGa)Se₂/CdS) and CdTe (CdTe/CdS), with current record cell efficiencies of 10.1 %, 19.8 %, and 19.6 %, respectively [7, 9].

Other thin film technologies are dye-sensitized and polymer-based organic solar cells, using quite different principles, almost more like photosynthesis than photovoltaics, as they are
solid-liquid junction devices. Currently, they have low efficiencies (record efficiencies of 11.9 % and 10.7 %, respectively [7]), but are promising for a good cost/performance ratio.

2.2.3 Third Generation

Several approaches have been proposed to achieve high-efficiency devices, so-called ‘third generation solar cells’. The goal is to overcome the Shockley-Queisser limit for single band gap devices [15].

The two main losses in solar cells are firstly, the loss of sub band gap photons and secondly, thermalization losses for photons with energies higher than the band gap. By using new approaches these losses can be minimized. Three different approaches have been suggested [8]: (i) Increasing the number of electron-hole pairs created per incoming photon, (ii) capturing highly excited carriers before thermalization and (iii) utilizing different photon energies more efficiently by increasing the number of band gaps.

Until now the only successfully used method to realize higher efficiencies than the limitation for single band gap solar cells is the use of multiple band gaps [15]. In the following, some approaches to third generation solar cells will be presented.

**Multiple electron-hole pair generation**

The third approach (i) mentioned above aims at using one high energy photon to produce several electron-hole pairs instead of losing the excess energy as heat. High energy photons with energy at least twice the band gap generate highly excited carriers, which can cause impact ionization events, producing additional electron-hole pairs. The impact ionization event has a very small probability to occur in bulk materials, but has a much larger likeliness of occurrence in quantum dots (QD) [15]. The phenomenon has been observed but not implemented in devices, showing any significant cell improvements.

**Spectrum modulation: up or down conversion**

To achieve multiple electron-hole pairs of one incoming photon (approach (i)), another method proposed is the up- or down-conversion of the incoming spectrum. Down-conversion means that a photon with at least twice the energy of the band gap of the cell is absorbed and then two photons with energies close to the band gap energy of the solar cell are emitted. Up-conversion is the opposite, where two (or more) low energy photons are absorbed and one photon with energy equal to the band gap is emitted. The light conversion takes place in layers that are electrically separate from the cell, but optically coupled to it. Although in theory this approach is promising, the implementation has not shown large increases in efficiencies yet. Fisher et al. [18], for example, have shown a relative efficiency increase of 0.19 % for an up-converting silicon solar cell due to utilization of sub band gap photons.
Hot carrier cells

The second approach (ii) is where carrier collection is more rapid than carrier thermalization. Such ‘hot carrier cells’ have promising high theoretical efficiencies (65% for unconcentrated illumination [15]), but also several problematic aspects still to be solved. The basic challenge is to slow down the rate of carrier thermalization, so that they can be collected at higher energies and give rise to a higher voltage. In addition to this thermalization delay effect, a contact material is needed at a narrow energy range, the so-called ‘selective energy contacts’. Both these aspects give rise to challenges when implementing the theory in actual devices.

Multiple junction cells

Up to now, the only approach on third generation solar cells that has been successful is where different band gap materials are used to utilize as many different photon energies as possible (approach (iii)). The concept of using several materials with different band gaps can be realized in different ways. The limiting efficiencies are often congruent for the structures when the same numbers of band gaps are used and the contact configurations are the same. The ‘tandem’ or ‘multiple band gap approach’ is basically a stack of two or more p-n junctions in different semiconductor materials with a decreasing band gap. Each cell in such a stack can either have two separate contact terminals or be contacted in series, so that just two terminals exist for one overall cell. The second design is the currently mostly used structure, due to the much greater ease of fabrication [15]. The top cell with the highest band gap will absorb the highest energy photons, whereas the lower energy photons will be absorbed in one of the following cells, as shown in Fig. 2.8. The efficiency limit of these devices depends on the number of band gaps. For 1,2,3, and ∞ subcells, the efficiency $\eta$ is 31.0 %, 42.5 %, 48.6 %, and 68.2 % for unconcentrated light, and 40.8 %, 55.5 %, 63.2 %, and 86.8 % for maximally concentrated light [15].

The highest achieved efficiencies with multi-junction devices are until now 37.9 % for unconcentrated light and 44.4 % for concentrated light, with a InGaP/GaAs/InGaAs three junction device structure [19].
2.2 Solar Cell Generations

Intermediate band solar cells (IBSC)

Another proposed realization of the multiple band gap concepts is the ‘intermediate band’ (IB) approach. In this structure, an additional intermediate energy band (IB) is introduced within the band gap of a single material. The benefit of this intermediate energy band is that no additional junction is needed to implement three band gaps in one device, as it is for the multiple junction devices. The purpose of the IB is to absorb photons that would have too low energies to excite electrons over the whole band gap, but have high enough energies to excite electrons from or to the IB, as shown in Fig. 2.9. The Fermi level must lie within the IB, so that it is partially filled with electrons. In that case, it can both accept excited electrons from the valence band and provide electrons to be excited from the IB to the valence band. The difference to the three-junction device is that the whole structure is placed within one junction and no tunneling junctions or multiple contacts to each layer are required.

In theory, an additional photocurrent is achieved without degradation of the output voltage of the solar cell. The efficiency limit is the same as for a three subcell multi-junction device, with 48.6 % for unconcentrated light and 63.2 % for concentrated light.
One way to create an IB within the band gap is to introduce quantum dots (QD). The IB arises from the confined states of the electrons in the QDs. Thereby, a narrow size distribution of high density QDs and high material quality are needed to form the intermediate level. Another way is to add a very high density of atoms forming a deep level to the host material, resulting in a so-called ‘bulk IBSCs’ of ‘deep level impurity IBSCs’. This will introduce a de-localized energy band due to the overlapping wave functions of the deep levels within the band gap. Deep levels will normally increase the amount of SRH recombination, but when the states are de-localized the most probable recombination process is the radiative recombination, which cannot be avoided in a solar cell.

Some of these attempts have been carried out, for example InAs/GaAs quantum dots and ZnTe:O, where the below band gap absorption has been demonstrated [21]. In 2006, Tablero proposed ZnS and ZnTe as a suitable material for bulk IBSCs if sufficiently doped with Cr as a transition metal [22]. A more detailed discussion of these approaches is given in the next chapter.
2.2 Solar Cell Generations
3 State of the Art and our Contribution to Intermediate Band Solar Cell Research

This chapter gives a review of the state of the art within the intermediate band solar cell (IBSC) research and a literature background on the materials used for the solar cells in this thesis. The first section presents a summary of the three different approaches made on the realization and demonstration of IBSCs: quantum dots, highly mismatched alloys, and bulk materials with deep-level impurities. The second section presents our design and a literature overview of the materials used in our solar cells.

3.1 Current Research on IBSCs

In the last two decades a great effort has been made on the IBSC research. One important starting point was the following statement given by Luque and Martí in 1997 [23]:

“In summary, we can state that a cell with an intermediate band gap has an efficiency limit higher than the SQ [Shockley and Queisser] model, if the intermediate band gap is radiatively connected with the two bands: of valence and of conduction. [...] this ideal structure shows better performances than any other ideal structure of similar complexity known today.”

The theoretical demonstration of a possible way to achieve simple, high-efficiency solar cells, made by Luque and Martí, has motivated the research on the realization of the concept. Recently, a review of experimental results related to the operation of IBSCs, which is written by Ramiro and Martí [24], was published. In this review, they give a short overview of the fundamental IBSC operation principles, characterization techniques for IBSCs, and the latest experimental results. The different characterization techniques, used to investigate whether the two basic IBSC principles are observed for real devices, are also part of the review. The two basic principles are: 1) the production of photocurrent when absorbing two photons with energies below the band gap, and 2) the preservation of the cell voltage limited by the main band gap.

As mentioned in the previous chapter, mainly three different technological approaches to implement IBSCs have been investigated. The first and most studied approach is the use of nanostructures, such as ‘quantum dots’. The second approach utilizes ‘highly mismatched semiconductor alloys’, while the third, and so far least investigated approach, uses semiconductor bulk materials containing a high density of ‘deep-level impurities’.
3.1 Current Research on IBSCs

Quantum Dot IBSCs

Quantum dot (QD) IBSCs were first proposed in 2000 by Martí [25], and have been the first and most studied IBSC realizations. The mainly used material for the prototypes of these cells have been In(Ga)As/GaAs QD systems [24]. This material is not optimal for an IBSC, because of the band gap distribution, but it is a reasonably well-known material and hence it was the best material to demonstrate the operating principles of IBSCs. Several other materials have subsequently been used for QD-IBSCs, like Ge/Si, GaSb/GaAs, InAs/AlGaAs, and GaAs/AlGaAs, demonstrating sub-band gap transitions and extra photocurrent (where X/Y means that X is the QD material and Y is the material of the matrix).

Highly Mismatched Alloys

Highly mismatched alloys (HMA) are semiconductors with a strong modification of its properties, due to the insertion of a small amount of elements of highly different ‘electronegativity’ [21]. One of the modifications is within the band gap structure, where the conduction band splits into two bands, not crossing each other, which can lead to the formation of an IB, known as the ‘band anticrossing effect’ [26]. In the review by Ramiro and Martí [24], ZnTe:O and Ga(P,Sb)As:N (where X:Y means that X is the host material and Y the introduced element) are listed as successfully implemented IBSCs with the HMA approach.

Bulk Materials with Deep-Level Impurities

Bulk materials with deep-level impurities (DLI) are so far the least investigated IBSCs. One of the challenges with these materials is the degradation of the electronic properties and the quality of the host material, often seen when introducing a very high density of impurities [24]. In 2006, Tablero [22] made a survey on DLI-IB materials and was the first to predict Cr-doped ZnS, as a candidate material. Other materials showing DLI-IBSC behavior at device level are Cr,Mn:GaN, Ti:GaAs, Sn,Fe:CuGaS$_2$, and Sn:CuInS$_2$, as reported in [24] (where X,Y:Z means X or Y as DLI in the host material Z). In the following a short overview of the IBSCs made of these materials is shown.

In Mn:GaN [27], the two sub-band gaps, in addition to the main band gap, have been measured with both transmission measurements and spectral response measurements, showing significant below band gap spectral response. In Cr:GaN [28], the sub-band gap absorption edges have been measured. The IV curves of the Cr:GaN cells are shown in Fig. 3.1. Two different structures of the cell were used, whereby the first structure (type A) is a device with a metal contact directly onto the Cr:GaN layer (thickness: 500 nm). The second structure (type B) is a device with an additional n-GaN layer (thickness: 50 nm) between the Cr-doped layer and the metal contacts. The type B device shows the highest current density, at the same open circuit voltage as for the type A device with an aluminum contact, as shown in Fig. 3.1.
Chapter 3 - State of the Art and our Contribution to Intermediate Band Solar Cell Research

Fig. 3.1 (a) and (b) show schematic the structure of type A and type B Cr:GaN DLI-IBSC devices. (c) IV curves of the devices under one sun irradiation. Results shown for the two different structure types, with two different contact metals for type A. Additionally, a reference curve is shown for a p-n junction in GaN (marked pn). Figure adapted from Ref. [28].

Another material showing DLI-IBSC behavior at device level is Ti:GaAs [29]. The cells in Ref. [29] showed below band gap photon absorption. It was however also detected in the reference (undoped) cell, as a likely contribution from arsenic (As) antisites and gallium (Ga) vacancies. By photo reflectance measurements, transition from the VB to deep-level states was shown, and voltage preservation was shown with the use of concentrated light illumination and lowered temperatures.

The last two materials showing DLI-IBSC behavior at device level are the chalcopyrite host materials CuGaS$_2$ and CuInS$_2$ with iron and tin as doping materials [30, 31]. Both materials have shown sub-band gap transition in absorption characterizations. The Fe:CuGaS$_2$ IBSC prototype also shows an increase in the sub-band gap quantum efficiency, while the solar cell parameters still decrease with the Fe concentration [30]. For the Sn:CuInS$_2$ an increase in the short circuit current is shown due to the IB. The $J_{sc}$ increased from 2.83 mA/cm$^2$ to 3.52 mA/cm$^2$ when introducing a Sn-doping of 4 % [31].

In summary, a wide range of solar cell prototypes show experimentally the operating principles of an intermediate band solar cell. The research within the last decade and future research is leading towards new high efficiency solar cells utilizing the IB theory.

3.2 Approach on IBSC used for this Thesis

This section will present a literature background on the materials used for the realization of IBSCs for this thesis. First, the base material of our solar cells, the Cr-doped ZnS thin film is reviewed. A section about the general design of our complete solar cells follows this.
3.2.1 Cr:ZnS as an IBSC Material

Zinc sulfide (ZnS) has been identified for several reasons as a good candidate material for an n-type front layer of a heterojunction solar cell. The rather easily n-type doped zinc-blend ZnS has a large band gap of 3.68 eV [32], and possesses good antireflection properties. ZnS has excellent surface passivation to some photovoltaic absorber materials (e.g. Si, GaAs, CdTe) and possesses a good lattice match with, for example, p-type Si. Furthermore, ZnS thin films can be grown on substrates by various established deposition techniques [33].

These benefits of the material as a front layer of solar cells support the choice of Cr-doped ZnS as a material for IBSCs. However, the most important feature is the availability of an intermediate band within the band gap. In 2006, Tablero [22] showed that Cr-doped ZnS can have isolated, partially filled intermediate bands in the band gap and is, therefore, a potential candidate material for the realization of IBSCs. An energy-level scheme for Cr:ZnS amongst other materials has been proposed in [34]. It was concluded that due to the Cr doping an acceptor level is introduced 1.1 eV below the conduction band (CB) and a donor level 2.8 - 2.9 eV below the CB. In [35], this interpretation was challenged and new energy levels proposed at 3.53 eV below the CB, hence very close to the VB, due to Zn$^{2+}$ ions substituted by Cr$^{2+}$ ions, and about 2.7 eV and 2.0 eV below the CB due to Cr$^+$ ions substituting Zn$^{2+}$ ions. These different energy levels arising from different ions and being located at different energies, make it difficult to predict exactly where the Cr related IB is located within the ZnS band gap.

Another reason supporting Cr:ZnS as an IBSC material is its environmental sustainability. Most of the other materials used for IBSCs, as presented in the previous chapter, contain toxic or scarce elements. Cr:ZnS is a compound of abundant, inexpensive, and non-toxic elements and therefore a good alternative. A major drawback with ZnS is its large band gap and hence mismatch with the solar spectra. Most of the solar spectral irradiance is at energies below the band gap and therefore just a small amount of electrons will be excited directly from the valence band to the conduction band. However, this might be a benefit for the demonstration of below band gap absorption due to an intermediate band. Another potential benefit of the large band gap in Cr:ZnS is the possibility to use it in tandem cells. Lee and Honsberg showed in [36], how the efficiency limit of an IBSC can be increased by a tandem configuration of multiple IB devices. Thereby, two connected IBSCs will correspond to a six junction series connected solar cell and have a theoretical efficiency of 73.2 % under full concentrated solar light for ideal band gaps. In these calculations, the ideal band gap of the larger band gap IBSC is 3.56 eV, which is close to the 3.68 eV band gap of Cr:ZnS.

Another benefit with Cr:ZnS as a material for IBSCs, is that this material has been investigated for laser purposes and therefore is already known to a great extent. For instance in Ref. [37], Sorokina, a professor at the physics department at NTNU, gives an overview of Broadband Mid-Infrared Lasers, where one of the materials is Cr:ZnS. However,
a solar cell needs other materials’ characteristics than a laser application, such as a much higher absorption coefficient below the band gap, i.e. a much higher Cr concentration.

**Aging of ZnS in air**

A ZnS thin film will be affected over time when it is exposed to air. It can be observed that oxygen is influential, because it is chemisorbed at the surface of the ZnS film. This adsorption results in a reduced concentration of free electrons at the surface, leading to an increase in resistance \[38\]. The interaction of oxygen with the surface is even stronger, when a ZnS film is annealed under ambient air. It was shown that annealing will convert an amorphous low quality ZnS film into a cubic ZnO film \[39\]. Furthermore, moisture in the air can affect the ZnS film properties. Such an aging effect was found for Mn-doped ZnS \[40\]. It was thereby seen that the Mn atoms, which are reacting with moisture diffusing into the structure, cause deep electron traps. These traps behave like non-radiative recombination centers, decreasing the performance of the device strongly.

### 3.2.2 The design of our Cr:ZnS IBSCs

The main component in the design of our solar cells is the Cr-doped ZnS thin film, due to its potential for an IBSC, as described in the previous section. The ideal design for a complete device would be a homojunction where the Cr:ZnS, with the IB is sandwiched between a p- and n-type ZnS film \(p\text{-ZnS}/IB\text{ Cr:ZnS}/n\text{-ZnS}\), as shown in Fig. 3.2.

![Fig. 3.2 Ideal homojunction structure for an IBSC.](image)

P-type ZnS, however, is not commercially accessible at a reasonable price and not easily produced, so we had to choose another material as p-emitter. Two possible p-type materials, Si and GaP were investigated. GaP would have a more similar band gap than ZnS, but Si is the most available p-type substrate material, with a good lattice match to ZnS, which is the reason for the usage for our cells at this stage. Yet, for the n-emitter highly n-type doped ZnS would be favored. It turned out that the deposition of highly n-type doped ZnS was not possible with our equipment, and so Al-doped ZnO is used as an n-emitter. Instead of the optimal homojunction out of one material with three regions, the structure of
our cells is at the present time a ‘double heterojunction’ (DH) cell, consisting of three different materials.

Fig. 3.3 shows the three different structures of solar cells used for this thesis as they had been developed over time. The first two cells show a ‘single heterojunction’ (SH) cell, with a contact improvement from 1 to 2, while the third cell is a full DH structure. The difference in the cell and contact structures will be described in more detail in the following chapters.

Previous work in our group was done until the first solar cell structure in Fig. 3.3, before I started my work for this thesis. It was found that ZnS (undoped and Cr-doped) is slightly n-type “as-deposited”, since a p-n junction could be made. However, the ZnS had a very low conductivity, which indicated a very low carrier concentration. For the Cr:ZnS film it was concluded that the carrier density is below $10^{15} \text{ cm}^{-3}$. Since the first SH structure showed solar cell behavior, the first step in the present work was to improve the contacts on the solar cell. In a second step, an n-emitter was added to get the full structure described above. The following two sections will give a brief review on the contact materials and the Al:ZnO as an n-emitter.

### 3.2.3 Achievement of Ohmic Contacts

Ohmic contacts are necessary for solar cell devices. These contacts should have a minimal resistance and no tendency to rectify signals so that the cell works properly. There are some general methods to identify materials that will provide ohmic contacts to II-VI compounds [41]:

First of all, the metal of choice for the contact material for n-type materials should have a smaller work function than the electron affinity of the semiconductor. Moreover, the material should provide majority carriers when it is diffused into the semiconductor. Finally, it should be possible to heat the metal on the semiconductor so that metal can diffuse into
the semiconductor material. In addition, the mechanical compatibility of the two materials should be considered.

Quite a few materials are proposed, and some tested, for making ohmic contacts to n-type ZnS. Al and Ag are regarded as good contact materials, as well as In and alloys of In. Excellent ohmic contacts are reported for In, Al and Ag on sufficiently high doped ZnS films, but for low doping, ohmic contacts were only achieved after annealing the contacts under vacuum at >300 °C [32].

In Ref. [42], a study has been made on the effect of high temperature treatment on ohmic contacts to high-resistivity (>10¹⁰ Ωcm) ZnS crystals and the effect on the optical properties of the crystal. According to this work, the optimized annealing temperature for In ohmic contacts to ZnS is 600 °C. At this temperature the diffusion of contact metal atoms into the crystal, will lead to a low-resistivity layer at the interface, resulting in an ohmic contact. Above this temperature level a large number of zinc vacancies in the crystal will allow contact metal atoms to diffuse further into the crystal. This will create a high-resistivity region at the metal-semiconductor interface, resulting again in a Schottky barrier. Below this temperature level the contact metal diffusion is too insignificant, also resulting in a Schottky barrier.

### 3.2.4 Al:ZnO as an n-emitter

Aluminum doped zinc oxide (Al:ZnO) and indium tin oxide (ITO) thin films have been widely used as transparent conductive oxides (TCO) in many thin film devices [43]. ITO thin films have the disadvantage of In scarcity and high price, and therefore Al:ZnO have recently arisen more interest. TCOs are, as the name already says, transparent and highly conductive films used in solar cell devices as window layers. The Al-doping in the ZnO film substantially improves the electrical conductivity, the charge carrier density, and the mobility [44]. The use of Al:ZnO as a top layer in a solar cell will therefore increase the contact and the carrier collecting properties.

In the next chapter it will be presented how these materials are used for the production of our solar cells, which methods of depositions are used and how the finished devices are characterized.
3.2 Approach on IBSC used for this Thesis
Chapter 4 - Methodology and Experimental Setups

4 Methodology and Experimental Setups

One of the main topics that this master’s thesis includes is the production of various simple solar cell devices based on ZnS thin films deposited on Si wafers. The film’s physical properties vary depending on the growth conditions and it will be important to investigate how the film properties affect the performance of the final solar cell. Several production and characterization steps are necessary to produce and test the devices, and reproducibility is essential. Some of these are covered in this thesis. The dependence on growth parameters on the cell performance is not treated in this work.

This chapter presents the methodology and the experimental setups for the different steps and procedures used. The first part is about the production of the solar cells. This includes the deposition of one or two thin films onto a substrate and the formation of metal contacts onto the cells. The second part is about the electrical characterization methods of the solar cells. It also includes an examination of current-voltage (IV) measurements and measurements of the open circuit voltage dependent on the light intensity (Suns-Voc measurements) procedures.

4.1 Production of Thin Films

All film depositions for the solar cells studied for this thesis were made by Xiaodong Yang, Postdoc in the solar cell research group at the Department of Physics at the NTNU. A brief description of the deposition process is given below for completeness.

The thin films are made by pulsed laser deposition (PLD). PLD is a deposition technique where a pulsed high power laser is used as an external energy source to vaporize material from a target and thereby deposit a thin film on a substrate. A schematic drawing of a PLD system is shown in Fig. 4.1.
A short laser pulse, with a pulse length of 20 ns in our case, is focused on a target material in a vacuum chamber. The laser pulse removes material from the target as a plasma plume. This plume moves away from the target towards the substrate at a high velocity. Reaching the substrate, the vaporized material recondenses and forms a film. The film quality depends on the laser parameters (wavelength, pulse length, energy density (fluence), repetition rate), the substrate’s temperature and material, the target-substrate distance, the chamber pressure and background gas (inert or reactive) [46].

In the course of this thesis we used p-type doped (boron doped) silicon (Si) wafers as substrate for the solar cells. The Si wafers are single crystal with a <100> orientation, a thickness of (525 ± 25) μm, and a resistivity of 1 - 30 Ωcm, provided by Si-Mat Germany. The principal components of our solar cells are the ZnS thin films (undoped or Cr-doped) deposited on the Si substrate. The as-received Si substrates are etched to remove the native oxide, and undergo a heat treatment in the vacuum chamber prior to film deposition. The targets for the undoped and Cr-doped ZnS films are ceramic targets with a polycrystalline structure. For the Cr-doped target the Cr concentration is nominally 3 wt%. The targets were provided by Kurt J. Lesker Company®. For the double heterojunction solar cells, with a Si/(Cr:)ZnS/Al:ZnO structure, the top layer is also deposited in the PLD chamber. The target is again ceramic with a polycrystalline structure and an Al concentration of nominally 5 wt%.

### 4.2 Metal Contact Deposition

A contact between the semiconductor material and an external circuit has to be made in order to extract current from the solar cell. During this work, two different approaches for
contacting were used. The first technique of making contacts was a “quick-and-dirty method” to get initial IV curves, if any, for some of the first samples. Liquid indium-gallium (In-Ga) was used to cover the backside, while small indium (In) balls were pressed onto the front side. One major problem of this method is to get reproducible contacts. For a comparison of different samples it is also necessary to know the exact size of the front contact.

The second technique of making contacts chosen was therefore a reproducible process, having a finger grid on the front side and a uniform metal layer covering the whole back side. For the metallization we used a Sputter and Evaporator, Model Custom ATC-2200V from AJA International Inc., located in the NanoLab at the NTNU. ‘Sputtering’ is a vaporization method for deposition of thin films, where a background gas, most frequently Argon, is ionized and bombarded onto a target in a vacuum chamber. This leads to ejection of atoms from the target surface which will hit the substrate and coat the surface with a thin film of this target material [47].

‘E-beam evaporation’ is another method for thin film deposition of metals. In this technique, an electron beam is directed onto a target, transforming the target material into a gaseous phase. In the high vacuum inside of the chamber, the atoms can evaporate freely and condense to form a film at the surface of the substrate [47]. In both techniques the deposition rate is some ångström per second. In the AJA Sputter and Evaporator both deposition methods are available in the same chamber and thus can be used consecutively without moving the sample, nor exposing it to atmosphere.

Since the deposition area in the AJA Sputter and Evaporator is relatively large compared to our samples, those regions of the sample that are not supposed to be metalized need to be covered. Since the area of the metal contact on the front side is a balance between shading losses and resistivity and recombination losses in the emitter, we used a finger pattern for the front electrode. The finger pattern is formed by covering the sample with a mask of a finer pattern, see Fig. 4.2. The mask is shaped in such a way that the contact on the film has a 1.0 mm thick busbar on one side, with four (up to six) 0.5 mm thick fingers reaching out orthogonally from the busbar. The spacing between the fingers is 1.0 mm.
4.3 Current-Voltage Measurements

The finger contacts on the SH cells were made out of (100 ± 5) nm aluminum (Al) covered with (30 ± 2) nm gold (Au) on the as-deposited (doped or undoped) ZnS films. The backside contacts were made of (100 ± 5) nm Al, covered with a (20 ± 1) nm titanium (Ti) layer and a (50 ± 3) nm Au coating. The Si backside was sputter etched right before the Al was deposited, where approximately 3 nm of Si were removed to clean the surface from SiO₂.

After some time we found that the thin Au layer, which is supposed to protect the Al from oxidation, easily got scratched at IV measurements and so increased the Au thickness to (100 ± 5) nm both on the back and front side. The Ti layer was used in the beginning as an adhesive for Au onto Al. However, since no problems occurred without the use of a Ti layer, we discarded this additional step in the deposition. All DH samples have a (100 ± 5) nm Al/ (100 ± 5) nm Au contact on both sides.

Both In and Al are known from literature as good materials for ohmic contacts to ZnS (see chapter 3.2.3). Al is also a commonly used metal for ohmic contacts on p-type silicon [48]. Due to this and the availability of Al for deposition, we chose Al during this thesis’ work. Although annealing is recommended in literature to obtain good ohmic contacts to ZnS, annealing is not part of the work for this thesis. The reason is that several other film properties can change due to heat treatment, leading to more unknowns for our cells, which is not wanted at this stage of the research. The focus is not on optimizing the devices, but comparing films made at various growth conditions, or with varying physical properties (Cr contents and ZnS film thickness).

4.3 Current-Voltage Measurements

Current-Voltage (IV) measurements are important to characterize the performance of solar cells, as described in chapter 2.1.3. Typically, an IV measurement system consists of a solar simulator light source, a temperature controlled sample stage, and a data acquisition system to measure the current and voltage as the voltage across the device or current through the device is varied with an external load or power supply. The simulated light gives a standardized irradiance with certain intensity and spectrum, simulating natural sunlight.
for reproducible measurements in laboratory conditions. The standard reference condition for solar cells is an irradiance of 1000 W/m² with a global (AM1.5) spectrum and a cell temperature of 25 °C. [49]

The setup used in the laboratory at the Department of Physics at the NTNU is shown in Fig. 4.3. A Sun 2000 Solar Simulator from Abet Technologies is used for the light generation. The sample stage is temperature regulated via a Supercool Regulator Board, which is controlled through a separate program. A Keithley 2440 SourceMeter is used for simultaneously measuring and sourcing currents and voltages. A LabVIEW virtual interface is used to control the SourceMeter and to provide a graphical interface for the user. Together with the step-size and dwelling time for each measured point, the scanning range of either the voltage or the current can be selected in the LabVIEW interface. There is also the possibility to make a quick measurement to determine the $V_{oc}$ and $I_{sc}$, as well as following the measurement in real time plots of the IV curve and the output power of the cell.

![Fig. 4.3 Setup for IV curve measurements at the Department of Physics at the NTNU. 1) Solar simulator, 2) temperature controlled sample stage, 3) sourcemeter and 4) PC with LabVIEW interface.](image)

When measuring an IV curve, several factors will influence the accuracy and the repeatability of the result [50]. One of these factors is the probe contact. For our IV measurements, the solar cell is laid on a copper plate with its backside downwards. Thus the connection between back contact and instrument is established. The front side is contacted with two sharp tips called ‘probes’, which touch the finger contact on top of the cell. This
procedure minimizes shading and also makes it possible to contact smaller structures on the cell surface.

Other factors influencing the results are the intensity of the light source and the temperature of the cell. The light intensity can be varied on the solar simulator and we use a calibrated solar cell to adjust the intensity before measurements, and checking it after each measurement series. The temperature of the sample stage is controlled by a separate program, which also displays the actual temperature during the measurement process. Since the cell is in full contact with the sample stage, its temperature is assumed to be the same as the regulated temperature of the stage. It takes some time (15 to 30 minutes) for the regulator to obtain a stable temperature, but after stabilizing it will stay fairly constant for the rest of the measurements.

Finally, another important factor to consider is the definition of the area of the cell measured. The size of our samples varies slightly, and in order to get a correct efficiency it is important to know the area, which is illuminated. For this, an aperture is placed on the sample when measuring the current. The current density is found by dividing the measured current by the illuminated cell area (not the area of the aperture).

4.4 Suns-Voc Measurements

The Suns-Voc technique measures the open circuit voltage of a solar cell, as a function of the simultaneously measured incident light intensity. It is a simple measurement, where a flash lamp is used as a monotonically varying illumination. The rate of the light intensity change is low enough so that a steady-state analysis of the data is permitted. A reference cell, which is integrated into the stage, is measuring the light intensity. Since only the open circuit voltage of the cell is determined, no current is drawn from the cell and therefore the series resistance in the cell has no influence on the result [51].

The laboratory at the NTNU uses a setup made by Sinton Consulting Inc., consisting of a Suns-Voc-150 stage together with a digital flash, Qflash X4d from Quantum Instruments, and software for data acquisition and analysis. The setup is shown in Fig. 4.4.
The investigated solar cell is placed on the brass chuck (c in Fig. 4.4) and as closely as possible to the reference cell on the top of the stage. The brass chuck is conductive and is used as the back contact for data acquisition, whereby a probe contacts the sample on the front side to measure the voltage over the cell. The sample stage is also temperature controlled close to 25°C. Since the program does not automatically capture the temperature, the temperature is measured with an external thermocouple and entered manually into the program. The reference cell provides information about the light intensity for the data acquisition. The light intensity can be varied through the positioning of the flash lamp or through varying the filters in front of the flash. The intensity will increase if the flash lamp is lowered to the sample. Normally the intensity range is from about 6 suns down to 0.03 suns.
4.4 Suns-Voc Measurements

Fig. 4.5 Output data of a Suns-Voc measurement with in- and output parameters in the top rows and four different plots showing the measurement results. 1) Light intensity and cell voltage versus time. 2) Light intensity versus cell voltage. 3) Current and power density versus voltage. 4) Effective lifetime versus carrier density.

Four different plots are generated for each measurement in the software, which is an excel spreadsheet (as shown in Fig. 4.5). For this work, only plot number 3 is used, which is an alternative form of plot 1 and 2, but for completeness, all of them are described shortly in the following.

The first plot shows the light intensity as a function of time measured by the reference cell in comparison to the voltage over the sample measured at the same time. It is clearly seen that the $V_{oc}$ responds to the light intensity without any significant delays and it only takes some milliseconds for a measurement. The second plot compares those two measurements with each other and is typically called the ‘Suns-Voc plot’. The third plot provides an alternative presentation of the Suns-Voc data. This plot shows the data as a “normal” IV curve at 1 sun, but without any series resistance influence. For an exact IV curve, the $I_{sc}$ must be determined by another measurement and entered into the software. By comparing this Suns-Voc-IV curve with an IV curve measured with a solar simulator of a sample, it is possible to see the effect of series resistance in a solar cell, and also to determine the series resistance.
Chapter 4 - Methodology and Experimental Setups

The fourth plot, which not used for this thesis, shows the effective lifetime as a function of the carrier density. The effective lifetime can be written as a function of the measured voltage, but to do this, the intrinsic carrier density and the dopant density of the semiconductor have to be known and the temperature has to be controlled carefully [51].

Further output parameters in the software are the $V_{oc}$ at one sun, the $V_{mp}$ (maximum power point voltage), $J_{mp}$ (maximum power point current), $PFF$ (pseudo fill factor), and pseudo efficiency. It is called 'pseudo', since it is not the actual value for a solar cell in normal use, but for the cell without the effect of series resistance.

All in all, the Suns-$V_{oc}$ measurement is a very quick and easy measurement, which, in theory, makes it possible to identify and separate recombination, shunting, and series resistance effects. However, while working with the Suns-$V_{oc}$ setup, it turned out not always to be as easy as expected. Sinton and Cuevas state in [51] that only a crude contact is required to the cell and that a comparison of the Suns-Voc curve with the actual measured IV curve of the finished solar cell will give a precise determination of the series resistance. It emerged that a good contact could sometimes be a real challenge for some of our samples, even for finished devices.
Chapter 5 - Simulation of our Solar Cells

5 Simulation of our Solar Cells

This chapter covers the use of simulations to evaluate our solar cells. The simulations are compared with the measured characteristics, leading to a better insight into the physical operation of our solar cells. The first section is about the simulation program used, followed by a section on simulations of our solar cells. The band structures of our cells are simulated, electrical properties like doping density and parasitic resistances investigated, the influence of below bang gap absorption determined, and the optimal thickness of the Cr:ZnS film simulated and compared to our solar cells.

5.1 SCAPS – Program Properties and Simulation Methods

An effective approach for getting a better insight into the internal physical operation of a solar cell is to simulate it with a computer program. This simulation can be compared to the actual measured characteristics to gain more information about the cell. In this work, the program used for simulations is SCAPS (Solar Cell Capacitance Simulator), developed at the Department of Electronics and Information Systems (ELIS) at the University of Gent, Belgium [52].

This program was chosen because of its well-suited capabilities for our solar cells. It is a one dimensional, numerical solar cell simulation program, developed for polycrystalline thin film solar cells. The latest version (SCAPS 3.2.00) of the program was released on 26th of April 2012, and is freely available to the PV research community. SCAPS has the option to model up to 7 semiconductor layers in one cell, with contacts on both sides and interfaces between the layers. At these interfaces, discontinuities in the energy bands and interface recombination can be set as defects. In the bulk material, three different recombination mechanisms can be varied (band-to-band (direct), Auger, SRH-type) and defects with different energetic distributions can be included. There is also a function for gradually varying almost all material parameters in one layer and specify tunneling within the cell. In calculations, the working point can be set for voltage, frequency (for alternating-current simulations), and temperature. For cell characteristics under illumination, a variety of standard spectra are included. The program is able to calculate energy bands, JV characteristics, concentrations and currents at a given working point, alternating-current characteristics (i.e. capacitance and conductance) and spectral response. There is also the possibility for batch calculations to compare different sets of parameters.
The two basic equations used in the software are the Poisson equation, relating the charge to the electrostatic potential, and the continuity equations for electrons and holes, together with the appropriate boundary conditions [52]. SCAPS calculates solutions in one dimension and in steady state conditions. The total cell (one dimensional) is divided into N intervals. The program is then solving the 3N non-linear equations for the potential and the electron and hole concentrations, three in each interval, numerically. The basic equations are non-linear due to the recombination term in the continuity equations.

The first step of a simulation is to construct the cell in the “Solar Cell Definition Panel”. Thereby each layer, contact and interface can be treated separately. Fig. 5.1 shows the parameters of a layer defining a p-type Si wafer, as used in our samples as a substrate.

![Fig. 5.1 Layer properties panel for a solar cell simulation in SCAPS. As an example, a p-type Si wafer is shown with a standard absorption file used, provided with the software.]

As shown in Fig. 5.1, a layer of the solar cell is defined by several parameters like thickness, band gap, electron affinity, dielectric permittivity, density of states, thermal velocities, and
charge carriers mobility. The doping of the layer is defined with the donor or acceptor density. The absorption coefficient can be selected in to be constant or taken from a file. It is therefore possible to use actual measured absorption coefficients. In this panel also the recombination model can be defined, but this is not shown in Fig. 5.1.

When all layers and interfaces are defined, and the contacts either are defined by their work function or chosen as flat band contacts, the next step is to define the calculation settings. In the main panel of SCAPS, the working point can be set, the light source selected, and the series and shunt resistance set. In this panel it is also selected what the program is supposed to calculate (IV characteristics, capacitance measurements C-V and C-f, and spectral response). The results of the simulation will be shown in a new panel and all results can also be saved as ASCII files for further editing and use in other programs.

Although the comparison between measured and simulated characteristics can lead to a better insight into the internal physical operation of a solar cell, the results should not be used as a real “proof” that the assumed parameters for the simulation are exactly the same as in reality. The large amount of input parameters allows that a different set of parameters could result in the same simulation outcome. It is therefore recommended by the developers of SCAPS to us several different conditions for measurements and simulations, in addition to select input parameters guided by independent, non-electrical measurements on complete and partial cell structures [52].

5.2 Simulation of our Solar Cells

This chapter will give an overview of the simulations of our solar cells. The first part will present the band diagrams of the ‘single heterojunction’ (SH) and the ‘double heterojunction’ (DH) structures of our cells. The second part will discuss the electrical properties chosen for the materials and the absorption data, and how these parameters influence the cell performance simulated.

5.2.1 Band Diagram

As described in the previous chapters, the main component in our solar cells was the Cr-doped ZnS layer. This layer was deposited onto a p-type Si wafer, resulting in SH cells. For the cells with the highest efficiencies an additionally Al-doped ZnO layer was deposited on top of the ZnS layer, resulting in DH cells. In the band diagrams in Fig. 5.2 and Fig. 5.3, the SH and DH structure of the cells are shown. The energy levels are shown with respect to the Fermi level, which is set to 0 eV in the band diagrams. For the plotting of the band diagrams, the thickness of the Si layer was reduced to 1/1000 of the real thickness. For all calculations, however, the real Si thickness of 525 μm was used.
Fig. 5.2 Band diagram of SH solar cell in equilibrium, calculated by the SCAPS software. The cell consists of a 525 nm Si substrate (in devices and for calculations a 1000 times thicker) with a 300 nm ZnS thin film and Al contacts on both back (left) and front (right) side.

Fig. 5.2 presents the band diagram of an SH cell with its parameters summarized in Table 5.1. The intermediate band(s) in the ZnS layer, due to the Cr doping, is not added into the band diagram, since its position is not verified, as described in chapter 3.2.1. Also, SCAPS is not capable of simulating and plotting an IBSC, but it is, nevertheless, well suited for our purpose. Since an ideal IBSC does not change the electrical properties of an equivalent normal solar cell, but just adds below band gap absorption, SCAPS can be used for IBSCs when the absorption for such cells is known. One drawback with the simulation of an IB with the below band gap absorption is that the unavoidable radiative recombination losses via the IB are not included. The exact effect on the performance is not determined, but the omitted radiative loss is most likely low in comparison to the total cell performance.

In the band diagram, the heterojunction between the Si and the ZnS is clearly seen. The band gap of ZnS is more than 3 times larger than a Si band gap. Due to the relatively low carrier concentration in the ZnS, an abrupt junction is formed, with the depletion region almost exclusively in n-ZnS layer and not in the p-Si. In the conduction band at the junction, a barrier of 0.15 eV occurs for electrons drifting from the p-side to the n-side, reducing the collected current. However, holes in the valence band do not have any barrier to overcome when drifting from the n-side to the p-side, but they will lose a lot of their potential energy due to the large band offset, and this leads to a large decrease in $V_{oc}$ compared to if a p-ZnS material had been used.
The barrier heights of metal-semiconductor systems are, in general, determined by both the metal work function and the interface states. In Ref. [53] it is shown that the contact to Si is strongly affected by the interface states, resulting in a barrier height of approximately 0.7 eV. The barrier height of a contact to ZnS is mainly determined by the work function of the metal, in our case Al, which is 4.28 eV [54]. The Al contact on the p-type Si produces hence a Schottky barrier with a quite large barrier height. This is significantly influencing our cell performance. On the ZnS side, the Al contact does not induce a barrier, but the potential drop is quite high. Both the small band gap of Si and the contact properties are the reason for the relatively lowly calculated open circuit voltage of about 0.3 V in our cells. As it will be later seen in some results, this calculated value agrees well to the experimentally obtained results for our cells.

In the double heterojunction cell, shown in Fig. 5.3, an additional highly n-typed Al:ZnO layer was introduced. This layer has a band gap close to the ZnS band gap, but a slightly different electron affinity. The potential step seen at the ZnS/ZnO junction is not hindering the flow of the photo-generated current. At the ZnO/Al junction a Schottky barrier occurs, which, however, is not high and very narrow, thus allowing electrons to tunnel through it.

These two solar cell structures were meant to represent the cells made in the course of this thesis. However, some material parameters were not known, but only parameters for

![Fig. 5.3 Band diagram of DH solar cell in equilibrium in dark conditions. In comparison to the SH cell, an additional 50 nm layer of Al:ZnO is introduced between the ZnS film and the Al front contact. Simulation is made with SCAPS.](image-url)
similar materials, which were found in literature, have been adapted as well as possible to our cells. Such parameters are, for instance, the densities of states, the velocities, and the mobilities. We know about the low conductivities of our films, but we have no experimental values on the above parameters. Therefore, reasonable values from literature are used. Table 5.1 is a summary of all parameters used for the modulation of the above band structures and the following IV characteristics shown.

Table 5.1 Parameters used for solar cell simulations in SCAPS. Material properties are taken from the following references: for Si (available in SCAPS) [55], Cr:ZnS [56-58], Al:ZnO [59, 60]; in SCAPS available absorption files [61]; Barrier height [53, 54].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Si</th>
<th>Cr:ZnS</th>
<th>Al:ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (µm)</td>
<td>525</td>
<td>0.300</td>
<td>0.050</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>1.12</td>
<td>3.70</td>
<td>3.67</td>
</tr>
<tr>
<td>Electron affinity (eV)</td>
<td>4.05</td>
<td>3.90</td>
<td>4.10</td>
</tr>
<tr>
<td>Dielectric permittivity (relative)</td>
<td>11.9</td>
<td>8.9</td>
<td>8.0</td>
</tr>
<tr>
<td>CB effective density of states (1/cm³)</td>
<td>2.80 x 10¹⁹</td>
<td>5.00 x 10¹⁸</td>
<td>1.00 x 10¹⁹</td>
</tr>
<tr>
<td>VB effective density of states (1/cm³)</td>
<td>2.65 x 10¹⁹</td>
<td>5.00 x 10¹⁸</td>
<td>1.00 x 10¹⁹</td>
</tr>
<tr>
<td>Electron thermal velocity (cm/s)</td>
<td>5.20 x 10⁶</td>
<td>3.00 x 10⁶</td>
<td>1.00 x 10⁷</td>
</tr>
<tr>
<td>Hole thermal velocity (cm/s)</td>
<td>5.20 x 10⁶</td>
<td>1.00 x 10⁶</td>
<td>1.00 x 10⁷</td>
</tr>
<tr>
<td>Electron mobility (cm²/Vs)</td>
<td>1450</td>
<td>140</td>
<td>400</td>
</tr>
<tr>
<td>Hole mobility (cm²/Vs)</td>
<td>500</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>Shallow uniform donor density ND (1/cm³)</td>
<td>0</td>
<td>1.00 x 10¹⁵</td>
<td>1.00 x 10¹⁹</td>
</tr>
<tr>
<td>Shallow uniform acceptor density NA (1/cm³)</td>
<td>1.00 x 10¹⁷</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Radiative recombination coefficient (cm³/s)</td>
<td>1.80 x 10¹⁵</td>
<td>1.00 x 10¹⁲</td>
<td>1.00 x 10¹²</td>
</tr>
<tr>
<td>Auger electron capture coefficient (cm⁶/s)</td>
<td>3.00 x 10⁻³¹</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Auger hole capture coefficient (cm⁶/s)</td>
<td>3.00 x 10⁻³¹</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Absorption (Calculated) barrier height to Al contact (eV)</td>
<td>0.7</td>
<td>0.38</td>
<td>0.18</td>
</tr>
</tbody>
</table>

5.2.2 Electrical Properties and Absorption of (Cr:)ZnS

In this part, the focus will be on the simulation parameters of the single heterojunction cell and there especially on the Cr-doped ZnS layer. The ZnO layer was not included in order to reduce the complexity of the simulation as much as possible and to gain information of one parameter at the time. The settings for the Si layer were from a file included in SCAPS, where most parameters are taken from Ref. [55]. These Si parameters were not changed during the simulations, since it was the ZnS film which was of interest.

The parameters used for the simulation of the Cr:ZnS layer were mainly from Refs. [56-58]. The effect of the Cr doping on some parameters is not known. Those parameters were varied within reasonable limits, compared to literature values for the undoped material. They might not be the same as the real values in our cells, but they are close enough to use for the following comparisons. Before these parameters were investigated, the contribution
of the Si layer, on the total cell performance, was investigated. Thereafter, the first parameter discussed is the influence of the donor density on the solar cell performance. The second simulation batch considers the influence of the below band gap absorption on the IV curves, due to the Cr doping. The third batch presented below shows the influence of the $R_s$ and $R_{sh}$ on the cell performance.

**Contribution to the cell performance of the absorption in Si or Cr:ZnS layer**

The purpose with this simulation was to test the influence of the Si-wafer, used as substrate for our cells, on the solar cell performance. A SH device, with the properties in Table 5.1, was simulated and is shown as black line in Fig. 5.4. In the next two steps, the absorption coefficient was set to zero, one time for the Si layer and one time for the Cr:ZnS layer. In Fig. 5.4 and Table 5.2, it is seen that the performance of the cell is only slightly reduced, if there was no absorption in the Cr:ZnS layer. If, however, the absorption of light in the Si-layer was set to zero, the performance strongly decreased.

![Graph showing IV curves for different conditions](image)

**Fig. 5.4** The black curve (Cr:ZnS + Si) shows the simulated JV curve for a SH cell with the parameters from Table 5.1. The orange curve is calculated for the case, when no light is absorbed in the Cr:ZnS layer, while the blue line is calculated for zero absorption in the Si substrate.
5.2 Simulation of our Solar Cells

<table>
<thead>
<tr>
<th>Absorbing layer</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$FF$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr:ZnS + Si</td>
<td>5.39</td>
<td>0.33</td>
<td>31.40</td>
<td>0.51</td>
</tr>
<tr>
<td>Si substrate</td>
<td>4.92</td>
<td>0.33</td>
<td>30.25</td>
<td>0.49</td>
</tr>
<tr>
<td>Cr:ZnS film</td>
<td>1.12</td>
<td>0.36</td>
<td>4.47</td>
<td>0.70</td>
</tr>
</tbody>
</table>

The conclusion of this simulation was that the highest contribution of the cell performance in our solar cell structure is due to the underlying Si substrate. The thickness of the Cr:ZnS layer was set to 300 nm. Most of the light will be absorbed in the Si substrate. However, changes in the undoped or Cr-doped ZnS will still affect the total cell performance significantly. In the following are some parameters of the Cr:ZnS layer investigated, and simulated how they will affect the solar cell performance.

**Simulation of the donor density in the Cr:ZnS layer**

In this simulation, the donor density was varied from $10^{10}$ cm$^{-3}$ to $10^{20}$ cm$^{-3}$. At room temperature the carrier density is equal to the dopant density, since all dopant electrons or holes are thermally excited into the conduction or valence band. The efficiency of the solar cell increased accordingly from 4.5 % to 13.0 % with increasing donor density. The solar cell parameters and the JV curves for the different donor densities are shown in Table 5.3 and Fig. 5.5. The JV curves, for donor densities below $10^{13}$ cm$^{-3}$ and above $10^{18}$ cm$^{-3}$, are not shown, since the deviation from the $10^{13}$ cm$^{-3}$ and $10^{18}$ cm$^{-3}$ curves was too small to be distinguished. An increase in the donor density, and hence to total electron density in the Cr:ZnS layer, will to a great extend effect the conductivity in the cell. The resistivity in the Cr:ZnS layer is reduced, and thus the $FF$ and the current extracted from the cell increased. The $V_{oc}$ decreased slightly for higher donor densities, which is in agreement with the theory. A high density dopant level close to the conduction band will decrease the effective band gap, due to a broadening of the impurity band and the formation of band tails on the edges of the conduction and valence band [62]. This will reduce the open circuit potential slightly, as it is seen in Fig. 5.5.

From previous work, a donor density of $10^{15}$ cm$^{-3}$ or lower is expected for the Cr:ZnS layer in our cells. As it was seen in the simulation, this resulted in a performance close to the lowest JV curves, and therefore an increase of the donor density in our cells would increase the cell performance significantly.
Simulation of below band gap absorption

In this section, the effect of sub band gap absorption on the IV curves was investigated. Since the band gap of ZnS is large, it does not correlate well with the solar spectrum. Most of the photons coming from the sun have below band gap energies and therefore a very small fraction of the light is absorbed in the ZnS layer. Cr-doping of the ZnS layer gives rise to absorption below the band gap and should hence influence the cell performance significantly. Simulations of this below band gap absorption in the ZnS layer were used, to estimate how much the cell performance will change due to this added absorption. Fig. 5.6 shows the absorption data used for the simulations. The two curves ‘Undoped’ and ‘Cr-
5.2 Simulation of our Solar Cells

doped’ were absorption curves obtained from ellipsometry data for two samples made and measured by Mohammadreza Nematollahi, PhD student in our research group. The curves ‘Level 1’ to ‘Level 5’ had the same absorption as the undoped curves above the band gap, which is below about 340 nm in terms of wavelength. However, they had arbitrarily chosen constant absorption coefficients from about 340 nm up to 1700 nm, which is below the band gap. These levels simulated absorption below the band gap, as in case of IBs. However, they did not simulate real absorption coefficients for IBSCs, since they, in general, will be more complex and not just constant below the band gap. Nevertheless, the arbitrary set levels showed what the performance of a solar cell could be for a relatively high below band gap absorption.

![Absorption Coefficient](image)

**Fig. 5.6** Absorption coefficient used in the simulation with the below band gap absorption. ‘Undoped’ and ‘Cr-doped’ were measured absorption coefficients, while ‘Level 1’ to ‘Level 5’ had arbitrary chosen below band gap absorption coefficients. The band gap of ZnS is at about 340 nm.

Fig. 5.7 and Table 5.4 present the results of the simulation with the different absorption coefficients for the ZnS layer. The undoped cell had an efficiency of 4.85 %, while the Cr-doped cell had an, about 1.11 times higher, efficiency of 5.39 %. For the cells with arbitrary set absorption coefficients, the performance improved with increasing below band gap absorption, as expected. For this SH solar cell structure it was seen that for a quite high below band gap absorption within the ZnS layer, the total solar cell efficiency did increases about 1.5 times. The simulation also showed that the change in the absorption had the
highest impact on the $J_{sc}$, while the $V_{oc}$ and the $FF$ both just slightly increase for higher below band gap absorptions.

![Simulation of our Solar Cells](image)

**Fig. 5.7** Simulated JV curves for increasing below band gap absorption in the ZnS layer, see Fig. 5.6.

**Table 5.4** Performance parameters for the JV curves shown in Fig. 5.7.

<table>
<thead>
<tr>
<th>Absorption coefficient</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$FF$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Exp.) Undoped ZnS</td>
<td>4.85</td>
<td>0.33</td>
<td>29.83</td>
<td>0.49</td>
</tr>
<tr>
<td>(Exp.) Cr-doped ZnS</td>
<td>5.39</td>
<td>0.33</td>
<td>31.40</td>
<td>0.51</td>
</tr>
<tr>
<td>Undoped + Level 1</td>
<td>5.65</td>
<td>0.33</td>
<td>32.82</td>
<td>0.51</td>
</tr>
<tr>
<td>Undoped + Level 2</td>
<td>6.03</td>
<td>0.34</td>
<td>34.20</td>
<td>0.52</td>
</tr>
<tr>
<td>Undoped + Level 3</td>
<td>6.40</td>
<td>0.34</td>
<td>35.53</td>
<td>0.53</td>
</tr>
<tr>
<td>Undoped + Level 4</td>
<td>6.76</td>
<td>0.34</td>
<td>36.80</td>
<td>0.54</td>
</tr>
<tr>
<td>Undoped + Level 5</td>
<td>7.11</td>
<td>0.34</td>
<td>38.02</td>
<td>0.55</td>
</tr>
</tbody>
</table>

**Simulation of the influence of the $R_s$ and $R_{sh}$ on the solar cell performance**

In this section is the influence of the $R_s$ and $R_{sh}$ on the solar cell performance of the Cr-doped single heterojunction cell presented. The theoretical background was presented in chapter 2.1.3, and in the following some numerical values for the solar cell performance were found by simulations, including non-ideal series and shunt resistances. In Fig. 5.8 (a), it is shown that an $R_s$ in the range of 5 $\Omega$cm$^2$ to 20 $\Omega$cm$^2$ will reduce the $J_{sc}$ and the $FF$ of the
5.2 Simulation of our Solar Cells

solar cells significantly. Fig. 5.8 (b) shows a large decrease of the FF and $V_{oc}$ for a low $R_{sh}$. In both figures the ideal cases of $R_s = 0 \, \Omega \text{cm}^2$ and $R_{sh} = \infty \, \Omega \text{cm}^2$ are shown as the dashed lines.

![Simulated JV curves for series resistance $R_s$ and shunt resistance $R_{sh}$](image)

**Fig. 5.8 (a)** Simulated JV curves for series resistance $R_s$ in the range 0 to 20 $\Omega \text{cm}^2$, from top to bottom. **(b)** Simulated JV curves for shunt resistance $R_{sh}$ in the range 10 $\Omega \text{cm}^2$ to $\infty \, \Omega \text{cm}^2$, from bottom to top.

In Table 5.5, the cell performance parameters are presented of the JV curves shown in Fig. 5.8. It can be clearly seen that the efficiency of the cell decreased a lot with a small $R_s$ increase. For example, if $R_s = 5 \, \Omega \text{cm}^2$, the efficiency was already reduced by 35 % from the ideal case. The $R_{sh}$ did not influence the performance as much, if it is not very low. The efficiency was only reduced by 12 % for an $R_{sh}$ as low as 70 $\Omega \text{cm}^2$ instead of the ideal infinite high shunt resistance.

| Table 5.5 Cell performance parameters for SH cells with various (a) series resistance $R_s$ and (b) shunt resistance $R_{sh}$. |
|---|---|---|---|---|
| (a) | $R_s$ | $\eta$ (%) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF |
| 0 $\Omega \text{cm}^2$ | 5.40 | 0.34 | 31.40 | 0.51 |
| 5 $\Omega \text{cm}^2$ | 3.40 | 0.34 | 27.58 | 0.37 |
| 10 $\Omega \text{cm}^2$ | 2.23 | 0.34 | 23.12 | 0.29 |
| 15 $\Omega \text{cm}^2$ | 1.62 | 0.34 | 18.40 | 0.26 |
| 20 $\Omega \text{cm}^2$ | 1.25 | 0.34 | 14.76 | 0.25 |
| (b) | $R_{sh}$ | $\eta$ (%) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF |
| $\infty \, \Omega \text{cm}^2$ | 5.40 | 0.34 | 31.40 | 0.51 |
| 70 $\Omega \text{cm}^2$ | 4.58 | 0.33 | 31.40 | 0.45 |
| 50 $\Omega \text{cm}^2$ | 4.28 | 0.32 | 31.40 | 0.42 |
| 30 $\Omega \text{cm}^2$ | 3.67 | 0.31 | 31.40 | 0.38 |
| 10 $\Omega \text{cm}^2$ | 1.94 | 0.23 | 31.40 | 0.27 |
6 Results and Discussion

The main results from this work are presented in this chapter together with a consecutive discussion of the results.

The first section is on initial tests of the setups used for IV and Suns-Voc measurements, contributing to the establishment of good measurement procedures. The second section is about the use of these two measurements for one of our solar cells. It will also cover three different ways to determine the series resistances in a cell, which has influence on both measurement techniques in different ways.

In the third section is the development of our solar cells presented. Three different structures of the cells led to gradually higher efficiencies. In all structures a high increase of the cell performances was seen due to the Cr-doping in the ZnS layer. In the end of this section a summary of the three structures is presented. The following, fourth section, presents a discussion on the cell development.

The fifth and sixth section covers the results and discussion of the observed aging effects in some of our solar cells. Thereby a clearly degradation of the cell performance was seen for SH cells over time, while the DH cells apparently not were effected. The last section in this chapter is about the ideal thickness of the IB-layer in our DH solar cells.

6.1 Testing and Comparing of IV Curves and Suns-Voc Measurements

One goal of this thesis work was to establish good measurement procedures to obtain reproducible result for our ZnS based solar cells, which are very different to ordinary silicon solar cells. However, in the start of this thesis work, the IV and Suns-Voc set-ups were tested, using a silicon solar cell as a known reference. The cell was made and tested at the Institute for Energy Technology (IFE) in Kjeller, Norway.

Test of reproducibility of IV setup

In Fig. 6.1, a comparison between the reference data of the silicon solar cell, with an area of 6.25 cm², and the measured IV curve using our equipment is shown. The procedures of the measurements were described in chapter 4.3. The difference in the \( J_{sc} \) and \( V_{oc} \) was less than 0.5 % and the difference in the maximum power was 3.7 %.
In the following the reproducibility of our measurements was tested. For that purpose a series of 19 measurements was taken on the same cell, at stable conditions (temperature and light intensity), see Fig. 6.2. The first eight measurements were just repeated IV measurements without any changes of the contact between the contacting probe and the metal contact (busbar) on the cell. For these measurements the standard deviation of the maximum power from the mean value was 0.35 %. In the next six measurements, number 9 to 14, the probe was lifted and repositioned on the busbar for each measurement, but in almost the same location. Number 15 to 19 were made after rotating the sample 180°, so that the probe was contacting the busbar in a new area, and again the probe was repositioned in that area before each run. The deviation from the mean value of the maximum power for all these curves (9 to 19) was 5.8 %. Two curves (16 and 17) showed a somewhat lower fill factor, which might have been due to a worse contact between the probe and the busbar than for the other measurements.

The last IV curve, shown in Fig. 6.2, was calculated with an additional contact resistance added to the curve with the highest fill factor, number 13. It is seen that an additional resistance, with $R_s = 0.46 \, \Omega$, added to the best curve results in a good fit to the shape of the curves with the lowest fill factors. For all the measurements on this solar cell, the variation in the $V_{oc}$ was 0.04 %, which is small. The temperature during this measurement series was
very stable. Due to an improper measurement range setting, the measurements for this cell started at 0.1 V and did not contain the $J_{sc}$.

Fig. 6.2 IV curves of a silicon reference cell for different contacts between measurement probe and cell busbar. Measurements 1 to 8 had no changes in the contact position. For measurements 9 to 19 the probe was lifted and repositioned in a new spot on the busbar. In curve ‘13 + Rs=0.46Ω’ a contact resistance of 0.46 Ω was added by simulation to the best curve (number 13).

Current and voltage change for varying size of the illuminated areas

Another test was made by illuminating different areas of one cell. The cell position, contact, temperature and illumination were the same for all measurements, but different areas of the cell were shaded. The shift of the IV curves due to the amount of illumination is clearly seen in Fig. 6.3. For less illumination both the $I_{sc}$ and $V_{oc}$ decreases. The plot shows that the $I_{sc}$ is proportional to the area illuminated for a uniform cell and the $V_{oc}$ is dependent on the IV curve shape and its shift due to photo-generated current.
6.1 Testing and Comparing of IV Curves and Suns-Voc Measurements

Fig. 6.3 IV curve measurements for different illuminated areas (full cell area, left and right half of the cell, and two 5 mm x 5 mm areas on each side).

Fig. 6.4 Suns-Voc measurements for different illuminated areas (full cell area, left and right half of the cell, and two 5 mm x 5 mm areas on each side).
Suns-Voc measurements with the same areas illuminated are shown in Fig. 6.4. The current is shown as current density and is therefore the same for all curves. It is seen that the Voc is decreasing as expected with the same rate than in the IV curves. The difference of the open circuit voltage between the IV and Suns-Voc measurements was less than 1 \%.

**Comparison of IV curve and Suns-Voc measurement**

In the last step of this initial stage, a comparison of the IV curve with the Suns-Voc measurement of the silicon reference cell was made. The Suns-Voc measurement is a way to measure an IV curve without the effect of a series resistance on a solar cell, as described in chapter 4.4. In Fig. 6.5 both curves are plotted, together with a calculated curve. The calculated curve is the Suns-Voc measurement with an added, manually adjusted, resistance of $R_s = 1.6 \, \text{Ωcm}^2$, resulting in a close fit to the measured IV curve.

![Graph showing comparison of IV curve and Suns-Voc measurement](image)

**Fig. 6.5** JV curve compared to Suns-Voc measurement without series resistance effects. In addition the Suns-Voc curve with an added series resistance of 1.6 Ωcm² was calculated and plotted.

The performance of this silicon solar cell was calculated from the IV measurement and compared to the Suns-Voc measurement. The efficiency of the cell was 11.5 % with a fill factor of 0.57. The pseudo efficiency of the Suns-Voc curve was 12.9 % with a pseudo fill factor of 0.64. As shown in the plot the series resistance of this cell was 1.6 Ωcm² and if this series resistance in the cell could be eliminated, the cell efficiency could be increased by 1.4 %-points.
In summary the tests of the IV and Suns-Voc set-ups showed that there is a good correlation within the measurement techniques and to the reference data. For the contact position between the probe and the cell busbar, a deviation of 5.8 % from the mean maximum power was found. For this silicon cell a series resistance of 1.6 Ωcm$^2$ was found with the Suns-Voc measurement.

### 6.1.1 Discussion of Initial Setup Test

The purpose of this initial test was to compare the two measurement methods and to get a better insight in the measurement procedures. A silicon solar cell was used, which was provided by the producer with an exact measured IV curve. This measurement of the IV curve was used as reference data for my measurements. However the time between the measurement used as reference and the actual measurements done in our laboratory is quite long. The exact time span is not known, but it was at least several months. The performance of the solar cell might have decreased slightly in that time. The difference between the two IV curves showed a loss of 3.7 % in the efficiency and changes of the $V_{oc}$ and $I_{sc}$ smaller than 1 %. The accordance of the two curves was close for these circumstances and within the later found error estimations of 6 % for the efficiency in our measurements.

**Test of reproducibility of IV setup**

The next measurement series was made to determine the reproducibility of the measurements according to the contacting of the cell. Thereby some consecutive measurements were made without any changes, and some with new contacts before each measurement. With a new contact it is meant that the probes, contacting the busbar of the solar cell, are removed and replaced on a new point. The results showed that the contact resistance was varying with about 0.5 Ω between the best and worst curve. It is therefore very important to get a “good” contact between the cell and the probe. If the contact is not good, a series resistance is added to the IV curve, decreasing the performance. Without any changes at the contact, the variations in the curves were very small. These small fluctuations might have been due to variations of the light intensity of the lamp or the temperature of the sample. When the temperature not was stable, larger changes in the $V_{oc}$ have been seen. It is therefore important to wait with the measurement until the temperature control has stabilized. Since the contact always might vary a little, as also shown in the results, it is reasonable to use the standard deviation of 6 % around the mean value of the maximum power as error estimation for the power and efficiency in our further measurements.

**Current and voltage change for varying size of the illuminated areas**

To get a better understanding of IV curves, the changes due to illumination were investigated. As described in the theory part, chapter 2.1.3, the IV characteristic is changed by an additional term proportional to the illumination. The results, in Fig. 6.3, followed this shift, with a change of the $I_{sc}$ proportional to the area illuminated. The $V_{oc}$ was additionally
dependent on the shape of the IV characteristic in the dark. The results from the Suns-Voc measurement showed exactly the same trend for the $V_{oc}$ as seen in Fig. 6.4.

**Comparison of IV curve and Suns-Voc measurement**

The last part of this initial study was on the correlation between the IV curves and the Suns-Voc measurements. The result showed a series resistance of 1.6 $\Omega \text{cm}^2$ in the cell, lowering the possible efficiency with 1.4 %-points. In this and the previous measurement with the different areas illuminated, it was seen that the correlation between the $V_{oc}$ of the IV measurements and the Suns-Voc measurements were very close, with a difference smaller than 1 %.

All results in this part with the silicon solar cell proved that the setups for the IV and Suns-Voc measurements are working properly and providing reliable current-voltage characteristics. The comparison between the curves and thus the benefits of the comparison of those two methods, worked for this solar cell as expected and described in the method part. This was a good starting point to use these measurement methods on our samples for characterizations, leading to further improvements. In the next section, both methods will be used on a poor ZnS cell.

### 6.2 Determining Series Resistance in Three Different Ways

In this section a comparison between an IV and Suns-Voc curve for a poor ZnS cell is shown. Additionally the series resistance of this device was determined with three different methods. The sample picked (130510pZnS) was an undoped single heterojunction cell (Si/ZnS) with a very low performance of only 0.009 % efficiency. This sample was the very opposite of the previously used silicon solar cell, because it had a relative large series resistance, as will be seen. As a result of that, the comparisons between the IV curves and the Suns-Voc curves need extra considerations, as presented below. The measurements are presented in Fig. 6.6, together with two simulated curves.

To determine the series resistance in this cell, three different methods were used. The first method was a simple calculation, where it was used that $1/R_s$ is approximately equal to the slope of the IV curve near $V_{oc}$ [8, 63]. For the second method a simulation of the cell was made with SCAPS, varying $R_s$ and $R_{sh}$ so that the simulated curve fitted the measured curve. The last method was using the Suns-Voc measurement in combination with a simulation. A series resistance was added to the measured Suns-Voc curve until the new IV curve matched the measured one. The results for the series resistances found using the three different methods are shown in Table 6.1.
6.2 Determining Series Resistance in Three Different Ways

Table 6.1 Series resistance in sample 130508pZnS determined in three different ways, as described in the text.

<table>
<thead>
<tr>
<th>Method</th>
<th>$R_s$ (Ω)</th>
<th>Average value and standard deviation (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/slope of IV curve at $V_{oc}$</td>
<td>6007</td>
<td></td>
</tr>
<tr>
<td>SCAPS simulation</td>
<td>6000</td>
<td>5902 ± 143</td>
</tr>
<tr>
<td>Suns-Voc-IV curve + $R_s$</td>
<td>5700</td>
<td></td>
</tr>
</tbody>
</table>

All three values of the series resistance in this cell were close to each other, with a standard deviation $\sigma = 2.4\%$. In Fig. 6.6, the measured IV curve is shown together with the SCAPS simulation with $R_s = 6000$ Ω and the Suns-Voc measurement. Also plotted is the Suns-Voc curve with an added $R_s = 5700$ Ω (called ‘Suns-Voc + Rs’). The measured IV curve, the SCAPS simulation, and the ‘Suns-Voc + Rs’ IV curve were all three very similar. To get a match of the ‘Suns-Voc + Rs’ curve and the IV measurement, the $I_{sc}$ entered into the Suns-Voc software has to be higher than the $I_{sc}$ of the IV measurement. This is in correlation with the theory, as a high series resistance may reduce the $I_{sc}$, but not the $V_{oc}$. The $I_{sc}$ had to be increased about 4 times, from 0.02 mA to 0.08 mA for this cell. This emphasizes that the very high series resistance in this cell destroyed the solar cell performance significantly.

![IV curve graph](image)

Fig. 6.6 An IV curve of a low performance cell (black curve) is shown and compared to a SCAPS simulation including $R_s$ (blue curve) and a Suns-Voc measurement with a manually added $R_s$ (red curve). The Suns-Voc measurement without $R_s$ effects (green curve) is also shown as a comparison. The $I_{sc}$ was adjusted due to the large $R_s$ of ca. 5900 Ω.
6.2.1 Discussion of Determination of Series Resistance

The series resistance of a solar cell degrades the output power. It is therefore of interest to reduce this value as much as possible, to keep the power loss low. Three different ways to determine the amount of the series resistance within a solar cell were shown above. The solar cell chosen for this purpose was one with a very high $R_s$, since it also demonstrated an interesting issue for the Suns-Voc measurements.

For all Suns-Voc measurements the $I_{sc}$ has to be set manually, to get a current-voltage characteristic. For “normal” solar cells with a quite low series resistance, like the Si cell in the previous section, this is no problem. The $I_{sc}$ will not be affected by the $R_s$ and therefore be the same for an IV and a Suns-Voc measurement. For solar cells with a high $R_s$, as most of our cells are, this is however a problem, since a high $R_s$ suppresses the $I_{sc}$ of the IV measurement and the value used for the Suns-Voc measurement needs to be higher than for the IV measurement. When a high $R_s$ suppresses the $I_{sc}$ from a solar cell, the curve shape is close to a straight line, with a very low fill factor. This is also predicted and shown in Fig. 2.7 in the theory part and simulated in figure Fig. 5.8.

The sample used in this part showed this behavior very clearly. In Fig. 6.6, it is shown that the $I_{sc}$ value of the Suns-Voc measurement was set about 4 times higher than the $I_{sc}$ value of the IV curve measurement. The value for the $I_{sc}$ of the Suns-Voc measurement was determined by achieving a good fit of the ‘Suns-Voc + Rs’ curve to the IV curve. This emphasizes that the very high series resistance of (5902 ± 143) $\Omega$ in this cell destructed the solar cell performance significantly.

The three methods give a very good correlation in the results for the value of $R_s$ in this cell. The standard deviation around the mean value for these three measurements was about 2.4 %. This will be used as estimation of the error for all $R_s$ determined in the further work. For some cells in section 6.3, the two methods ‘1/slope at $V_{oc}$’ and ‘Suns-Voc + Rs’ were used to determine $R_s$. The simulation with SCAPS was not made for those samples, since it is the most time consuming method. It was however in very good correlation with the other two methods, as the results for the high series resistance cell 130510pZnS showed.

6.3 Improvement of Undoped and Cr-doped ZnS Solar Cells

In this section the development of our solar cells is presented. As described earlier (see chapter 3.2.1) we used a thin ZnS film on top of a Si substrate to create a p-n junction. For all cell improvement stages, always at least one cell with an undoped ZnS film and one with a Cr doped ZnS film were made. The goal was to see the impact on the solar cell performance by introducing chromium. Ideally the Cr atoms should lead to an intermediate band in the ZnS band gap, without introducing too much non-radiative recombination.
6.3 Improvement of Undoped and Cr-doped ZnS Solar Cells

The first large improvement in the performance of the solar cells was made by changing from simple indium dot contacts to aluminum finger contacts on the film. The second major change was the introduction of a third layer, an Al-doped ZnO layer on the top of the cell. For a schematic figure of the different cell structures, see Fig. 3.3.

In the following three subsections, the best doped and undoped cells for each of the three solar cell designs are shown. In the course of the work for this thesis, 7 SH cells with Al finger contacts, and 13 DH cells were processed and investigated. The improvements due to the different cell structures are presented, together with some IV versus Suns-Voc comparisons. The last subsection will give a summary overview of all record cell performances.

The estimated errors in the IV measurements were based on the results from chapter 6.1. For the film thickness measurements, using a profilometer, an uncertainty of 5% was chosen, due to non-uniformities in the film, rather than measurement uncertainties. For all of the presented cells we did not have data on the exact Cr contents, nor the actual absorption coefficients. The Cr contents were aimed to be close to 3 at%, but can vary from 0.5 to 5 at%.

### 6.3.1 First SH Solar Cells with Simple Contacts

The first solar cells with the ZnS/Si structure made of our group at the Department of Physics at the NTNU had a simple contact design. The samples, contacts and measurements for these two cells were made by Xiaodong Yang, Postdoc in our research group. As described in chapter 4.2, an InGa liquid was used as a back contact and a small In ball was pressed onto the front, as a front contact.

In Table 6.2 the solar cell performance parameters are shown for the two best devices with these simple contacts. One device had an undoped ZnS layer and the other device had a Cr-doping in the ZnS film.

<table>
<thead>
<tr>
<th></th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>0.003</td>
<td>0.22</td>
<td>0.03</td>
<td>0.40</td>
</tr>
<tr>
<td>Cr-doped</td>
<td>0.008</td>
<td>0.26</td>
<td>0.08</td>
<td>0.37</td>
</tr>
</tbody>
</table>

A difference was seen in the efficiency between the two samples. The efficiency of the Cr doped device was three times higher than the undoped one. This was mainly due to the difference in $J_{sc}$, the amount of current produced by illumination, since the open circuit voltage and the fill factor of the two samples were quite similar.
6.3.2 Improvement of the Metal Contact on the Cells

The first simple devices, presented in the previous section, proved that a ZnS films on a Si substrates results in a solar cell and that the Cr doping increased the efficiency. To enhance the performance of the cells new contacts were made on the cells. As described in chapter 4.2, a finger pattern was deposited as front contact instead of the point contact. The circumference of the front contact was enlarged about ten times, from estimated 6 mm for the point contact to about 60 mm for the finger contact.

The current-voltage characteristics of the two best cells with finger front contacts are presented in the following (see Fig. 6.7). One sample had a Cr doping of approximately 3 at% in the ZnS layer, while in the other sample the ZnS layer was undoped. Both films were deposited on a Si substrate and had a film thickness of (307 ± 15) nm and (274 ± 15) nm, respectively. The sample names are composed of the date of production, the film deposition method used (p = PLD) and the film material used (Cr doped or undoped ZnS).

![130507pZnS-Cr 130508pZnS](image)

Fig. 6.7 Best Cr-doped and undoped SH solar cells.

In Table 6.3 the cell performance parameters are shown. The solar cells were illuminated in an area of 5 mm x 5 mm in the middle of the cell and the efficiencies were calculated for the illuminated film area, omitting the metal coated area.

<table>
<thead>
<tr>
<th></th>
<th>η (%)</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA/cm^2)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>130508pZnS</td>
<td>0.02</td>
<td>0.34</td>
<td>0.18</td>
<td>0.28</td>
</tr>
<tr>
<td>130507pZnS-Cr</td>
<td>0.28</td>
<td>0.32</td>
<td>2.73</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Table 6.3 The performance parameters for the best SH (ZnS/Si) solar cells with Al-finger front contacts. The estimated uncertainty of η and FF is 6 %, 1 % for the J_{sc}, and 0.1 % for the V_{oc}.

The efficiencies of the cells improved with finger front contacts in comparison to the previous point contacts. The efficiency of the undoped sample increased about 7 times, while the doped sample increased about 35 times. The Cr-doped cell with the finger contact had an about 14 times higher efficiency than the undoped cell. In comparison, the previous difference between the doped and undoped cells was about 3 times. The V_{oc} of both cells
with finger contacts was similar, and higher than for the films with point contacts. The $J_{sc}$ increased significantly for the Cr-doped cell, but the fill factor was only slightly higher. In Fig. 6.8 the JV curves of these two best SH cells with finger front contacts are shown.

![JV curves of the best single heterojunction solar cells with finger front contacts, made with doped (blue curve) and undoped (red curve) ZnS on Si substrates.](image)

**Fig. 6.8 JV curves of the best single heterojunction solar cells with finger front contacts, made with doped (blue curve) and undoped (red curve) ZnS on Si substrates.**

### Comparison of IV and Suns-Voc measurements

The best Cr-doped SH cell with a finger front contact was measured with the Suns-Voc setup and compared to the IV measurement of the same cell. No shading of the cells was used during these measurements, i.e. the complete cell area was illuminated. The area of the film was not measured and therefore the results are presented as voltage versus current, instead of voltage versus current density. For this reason the maximum power produced is shown instead of the efficiency of the cell.

In Fig. 6.9, the IV curve and the Suns-Voc curve are shown. In addition, the Suns-Voc measurement with an added series resistance is shown. A good fit between the calculated “Suns-Voc + $R_s$” curve and the IV curve was achieved for a manually set $R_s = (900 \pm 22) \Omega$. Calculating the $R_s$ with the slope of the IV curve at the $V_{oc}$ gave $R_s = (1015 \pm 24) \Omega$. The $I_{sc}$ of the Suns-Voc curve was set to a value slightly above the $I_{sc}$ of the IV measurement, to get a match between the measured and calculated curves. The actual value for $I_{sc}$ was found by fitting the ‘Suns-Voc + Rs’ curve to the IV measurement.
Fig. 6.9 Comparison of measured Suns-Voc and IV curve of the best SH Cr-doped cell with finger contact (sample 130507pZnS-Cr). Open circuit voltage, (pseudo) fill factor and (pseudo) maximum power are shown for the IV and Suns Voc curve.

The measurements showed the same $V_{oc}$ with both techniques. The pseudo fill factor and the pseudo maximal power of the Suns-Voc measurements, without series resistance effects, were about 3 times larger than for the IV measurement.

6.3.3 Full Structure Double Heterojunction IBSC

To further improve the performance of our cells, a third layer, the n-emitter, was added on top of the ZnS thin film. This third layer completed the cell structure into a full p-i-n junction. The new n-type layer was made out of a $(50 \pm 3)$ nm thick Al-doped ZnO layer. The contacts were made as described in chapter 4.2. Both the front and the back contact were made with $(100 \pm 5)$ nm Al on the cell, covered with $(100 \pm 5)$ nm Au.
6.3 Improvement of Undoped and Cr-doped ZnS Solar Cells

In Table 6.4 are the solar cell characteristics of the two best DH cells (see Fig. 6.10) presented, measured at standard conditions. The efficiencies were calculated for the illuminated cell area of 5 mm x 5 mm, as for the SH cells. The combined film thickness of the Al:ZnO plus the (Cr:)ZnS layer was (603 ± 30) nm for the undoped and (766 ± 38) nm for the doped cell.

<table>
<thead>
<tr>
<th></th>
<th>( \eta ) (%)</th>
<th>( V_{oc} ) (V)</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>140206pDH</td>
<td>0.08</td>
<td>0.33</td>
<td>0.85</td>
<td>0.27</td>
</tr>
<tr>
<td>140131pDH-Cr</td>
<td>2.05</td>
<td>0.31</td>
<td>16.05</td>
<td>0.41</td>
</tr>
</tbody>
</table>

A clear increase in the efficiencies was seen in the results, compared to the single heterojunction cells (see Table 6.3). The increase in efficiency was about 4 times for the undoped and 7 times for the doped samples. This was mainly due to the increase of the \( J_{sc} \), since both the \( V_{oc} \) and the \( FF \) were about the same for both structures. The Cr-doped DH cell had a much higher efficiency than the undoped cell. The efficiency was about 26 times higher for the Cr-doped cell. The IV curves of the two best DH cells measured at standard conditions are shown in Fig. 6.11.
Fig. 6.11 JV curves of the two best doped (blue curve) and undoped (red curve) double heterojunction solar cells.

**Comparison of IV and Suns-Voc measurements**

As in chapter 6.3.2, the IV curve of the Cr-doped sample was compared to a Suns-Voc measurement. Again the full area of the cell was used, and therefore the maximum power is shown instead of the efficiency in Fig. 6.12.

The series resistance of the cell was estimated by fitting the ‘Suns-Voc + Rs’ curve to the IV measurement. The value of the $I_{sc}$ in the Suns-Voc measurement was slightly above the value of the IV measurement. This showed again that the series resistance suppressed the $I_{sc}$ of the cell. The series resistance found with this method was $R_s = (29 \pm 1) \Omega$. Calculating the $R_s$ with the slope of the IV curve at the $V_{oc}$ gave $R_s = (30 \pm 1) \Omega$. 
6.3 Improvement of Undoped and Cr-doped ZnS Solar Cells

For this Cr-doped double heterojunction solar cell the maximum power could be increased up to 2.4 times, if the series resistance was decreased. With $R_s = (29 \pm 1) \Omega$ the series resistance was significantly lower for this p-i-n structure than for the previous presented single heterojunction cells. However, as shown in Fig. 6.12, lowering this series resistance further could more than double the solar cell performance.

6.3.4 Comparison and Overview of all Improvement Steps

The performance parameters of all six previously presented cells are presented in Table 6.5, together with the total thickness of the film(s). In the case of the double heterojunction cells, this means the combined thickness for the ZnS and the Al:ZnO layer.
Table 6.5 Summary of the performance of the best samples for the three development steps described. The estimated error is 6% for $\eta$ and FF, 5% for $t$, 1% for $J_{sc}$, and 0.1% for the $V_{oc}$.

<table>
<thead>
<tr>
<th>Cell design</th>
<th>Sample Name</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>$t$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH cells with point contact</td>
<td>Undoped</td>
<td>0.003</td>
<td>0.22</td>
<td>0.03</td>
<td>0.40</td>
<td>381</td>
</tr>
<tr>
<td>Cr-doped</td>
<td></td>
<td>0.008</td>
<td>0.26</td>
<td>0.08</td>
<td>0.37</td>
<td>332</td>
</tr>
<tr>
<td>SH cells with Al finger contacts</td>
<td>130508pZnS</td>
<td>0.02</td>
<td>0.34</td>
<td>0.18</td>
<td>0.28</td>
<td>274</td>
</tr>
<tr>
<td>130507pZnS-Cr</td>
<td></td>
<td>0.28</td>
<td>0.32</td>
<td>2.73</td>
<td>0.32</td>
<td>307</td>
</tr>
<tr>
<td>DH cells with Al finger contacts</td>
<td>140206pDH</td>
<td>0.08</td>
<td>0.33</td>
<td>0.85</td>
<td>0.27</td>
<td>603</td>
</tr>
<tr>
<td>140131pDH-Cr</td>
<td></td>
<td>2.05</td>
<td>0.31</td>
<td>16.05</td>
<td>0.41</td>
<td>766</td>
</tr>
</tbody>
</table>

In Table 6.6, the efficiencies of the six different cells are shown together with the efficiency increase when adding Cr and/or changing solar cell structure. The differences between the undoped and Cr-doped cells were getting larger for each new cell structure. In addition, the efficiencies of the Cr-doped samples improved more than the undoped cells, when changing the contact and the cell structure. It was very obvious that the Cr-doping in the ZnS layer greatly increased the efficiencies of our solar cells.

<table>
<thead>
<tr>
<th>Efficiency $\eta$ (%)</th>
<th>Undoped cells</th>
<th>Cr-doped cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH (point cont.)</td>
<td>0.003</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>$\times 2.7$</td>
<td>$\times 35.0$</td>
</tr>
<tr>
<td>SH (finger cont.)</td>
<td>0.02</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>$\times 14.0$</td>
<td>$\times 7.3$</td>
</tr>
<tr>
<td>DH (finger cont.)</td>
<td>0.08</td>
<td>2.05</td>
</tr>
<tr>
<td></td>
<td>$\times 25.6$</td>
<td></td>
</tr>
</tbody>
</table>

6.4 Discussion of the Improvement of our Solar Cells

In the previous section, chapter 6.3, was the improvement of our solar cells presented. Three different structures were used and will be discussed in the following three subsections. The effect of the Cr-doping in the ZnS layer on the solar cell performances is discussed in the last subsection.

6.4.1 First Solar Cells with Simple Contacts

The first solar cells made with ZnS on Si had very low efficiencies in the order of 0.005%. This might be out of several reasons. Since the resistivity in the ZnS film was very high, the area, where electrons were collected, was only close to the metal contact. The initial contact was only a small dot on the front side, with a small circumference. The amount of current extracted from the cell was therefore very small.
6.4 Discussion of the Improvement of our Solar Cells

However, the first devices proved that ZnS films on Si substrates resulted in a solar cell, but the power output was very low. It was interesting to see that difference of the doped and undoped cell. As shown in the results the main difference was the amount of current produced in the two cells, since the fill factor and the $V_{oc}$ were quite similar.

6.4.2 Improvement of the Metal Contact on the Cells

As mentioned for the first cell structure, the high resistivity in the ZnS films limited the distance of how far from the contact electrons will be collected. If the distance is too long the electrons created by photons will recombine in the film or at the surface before reaching the contacts. These electrons will never contribute to a current extracted from the solar cell. By increasing the contact circumference a larger area of the film will contribute to the power generation. In our case the circumference of the contact was increased roughly 10 times, using finger contacts instead of simple point contacts. The contact improvement increased the efficiency also roughly about one order of magnitude. The change of the contact material should not show a noticeable difference in the performance, since both In, used for the point contacts, and Al, used for these finger contacts, are known from literature to form ohmic contacts to the cells (see chapter 3.2.3).

For the Cr-doped solar cell, with the metal contacts, also a Suns-Voc measurement was made to see the IV curve without series resistance effects. In this part, the current of the full cell illuminated was used instead of a current density. This method was better for the comparison between the Suns-Voc and IV curve measurements, since exactly the same areas of the cells were considered. It was however not as good for the comparison of cells between each other, because the size of the cells, deposited film areas and metal contact areas can vary.

As discussed in chapter 6.2.1, the $I_{sc}$ of the Suns-Voc curve had to be set higher than the $I_{sc}$ of the IV curve, for cells with high series resistances. This was also the case for this cell. As shown in Fig. 6.8, the value of the $I_{sc}$ was increased by 11% for the Suns-Voc curve in comparison to the IV curve. The $V_{oc}$ was in a very good correlation, supporting that the two measurements were reliable and comparable. The difference between the two measured curves was quite high, since the FF of the Suns-Voc curve was almost 3 times larger than the one of the IV curve. This implies that the power output of this solar cell could be up to 3 times larger, if the series resistance in the cell was reduced. The series resistance found with the Suns-Voc measurement for this cell was $R_s = (900 \pm 22) \Omega$. If this value for example is compared to the undoped cell, disused in chapter 6.2.1, the series resistance was about 6 times lower. This reduction could have been due to the Cr-doping, reducing the resistance in the film.

6.4.3 Full Structure Double Heterojunction IBSC

The next step to improve our cells was the implementation of the Al:ZnO top layer. This layer is a highly n-type doped material, which also is transparent in the visible light range.
The ZnS layer was then sandwiched between two stronger doped materials, resulting in a p-i-n structure for the cell. The intrinsic layer was not really undoped, but in comparison to the other two material just lightly doped. Due to the extra layer the current produced in the cell was increases, as well as the series resistance of the cell was decreased, as discussed below.

For the Cr-doped solar cell again a Suns-Voc measurement was made out of two purposes. First of all, it was to compare the Suns-Voc curve to the IV curve, to identify the $R_s$ of the cell. Secondly it was to compare the $R_s$ of the DH cell to the $R_s$ of the SH cell. The full cell was illuminated in both measurements. The series resistance in this cell was found to be $R_s = (29 \pm 1) \Omega$, and hence much lower than for the SH cell. This was most likely due to a lower contact resistance. However, in Fig. 6.10, this much smaller series resistance still influenced the IV curve significantly. The reason is that the current through the cell was much higher and therefore also a smaller resistance will influence the voltage to a larger amount. The value of the $I_{sc}$ was increased by 9 % for the Suns-Voc curve, in comparison to the value of the IV curve. The maximum power of the solar cell could be increased up to 2.4 times, if the series resistance in the cell was reduced. In terms of efficiency, this could increase the cell from 2.05 % to an efficiency of 4.9 %.

### 6.4.4 Comparison and Overview of all Improvement Steps

A very interesting aspect was the improvements of the cell performances due to the Cr-doping in the ZnS layer. An efficiency difference between the undoped and Cr-doped film was expected due to the formation of the intermediate band within the band gap. The second interesting difference was to see how our solar cells improved with each step described above. Both aspects will be discussed for different solar cell parameters in the following.

There were two different kinds of improvements in the efficiencies of the solar cells. First of all there was an improvement between each of the three structures used. Secondly there was a difference between the undoped and Cr-doped cells.

As shown in the results, the efficiency increase from the first to the second structure (In point contact to Al finger contact) was about 7 times for the undoped cells, and 35 times for the doped cells. The efficiency increase was in correlation with the increase of the contact circumference. The areas of the point contacts are not known and could have been very different for the two considered cells. It was estimated that the increase of the circumference is about 10 times. Another reason for the difference in the improvement might also be the contact quality between the different metals and differently doped ZnS films, resulting in different contact resistances. From the second to the third structure (SH to DH structure) the efficiency of the undoped cells increased 4 times, while the doped cells increased about 7 times. The contacts were the same on all four cells and therefore the difference in the increases was much smaller.
The difference between the undoped and Cr-doped cells was also different for all three structures (from 2.7 times to 25.6 times). The reason might be due to different junction and contact properties within the different three structures for the doped and undoped cells, but was not confirmed. For the SH structure with the Al finger contact, the increase of 14.0 times is discussed in more detail below.

The IB theory predicts that some additionally light with below band gap energy will be absorbed within the solar cell, leading to an increased current generation and hence higher efficiencies. As expected from theory and literature, a clearly increase of the efficiencies was seen for our cells when Cr was introduced in the ZnS layer. The increase of the efficiency might however also have occurred because of changes in the electrical properties within the film and the junctions. The simulation of this solar cell structure with different absorption data was made in chapter 5.2.2. As a result it was seen that the efficiency increased 11 % from the undoped to the doped cell, due to below band gap absorption, as seen in Table 5.4. With arbitrary set below band gap absorption coefficients, the efficiency increased up to 1.5 times. This value was significant lower than the increase of 14 times measured for our cells. As a consequence, the efficiency increase of the Cr-doped cell cannot just be due to the IB generated absorption, but must also be due to changes in the electrical properties. The Cr-doping of ZnS has influences on the transport properties of the charge carriers, increasing the conductivity of the film. The total series resistance in the cells is lower due to the Cr-doping, increasing the overall performance. It is thus not suitable to use the undoped cell as a reference cell to investigate the increase of the solar cell due to below band gap absorption via the intermediate band. A different dopant material in the ZnS layer should be used in a reference cell, to achieve the same conductivity in that layer, but not introducing below band gap absorption.

The $J_{sc}$ of the different cells behaved very similar as the efficiencies. The main improvement in the efficiencies was due to changes in the conductivity in the film and the higher absorption in the Cr-doped films. Both effects will increase the amount of current produced in and extracted from a solar cell.

The $V_{oc}$ showed in contrast only small changes in all structures. It increased somewhat with the Al finger contact. Most likely this was not related to the contact properties, but to the larger amount of current collected. When the collection area is increased, it is similar as if a larger area of the cell is illuminated, resulting in the same shift of the IV curve as seen in Fig. 6.3. With the Al contact it was however seen that the $V_{oc}$ was slightly smaller for the Cr-doped cells with higher currents than for the undoped. This is explainable with a small reduction of the band gap with the introduction of impurity atoms and the reduction of the $V_{oc}$ due to higher recombination losses in an IB cell.

The $FF$ of the cells was better for the Cr-doped cells with Al finger contacts than for the undoped cells. One reason might have been the lower $R_s$ in the Cr-doped films. As presented
in the results and discussed above, the cells showed a decrease of the FF due to high $R_s$ and hence a small reduction of the $R_s$, will increase the FF at once.

### 6.5 Aging of ZnS Based Solar Cells

In some of our solar cells with aluminum finger contacts, a significant decrease of the efficiency was seen over time. Five different cells were monitored up to 152 days. Almost all these cells were measured their whole life span, until they were used for other destructive characterization methods. Only for the three cells with the SH structure and finger contacts, a large decrease was seen. The two DH cells did not show a significant decrease.

The following five samples were investigated, with the further used names in the parentheses:

- 130510pZnS, the undoped SH cell considered in chapter 6.1.1 (SH undoped)
- 130604pZnS-Cr, a Cr-doped SH cell (SH-Cr 1)
- 130507pZnS-Cr, the Cr-doped SH cell considered in chapter 6.3.2 (SH-Cr 2)
- 131107pDH-Cr, a Cr-doped double heterojunction cell (DH-Cr 2)
- 140131pDH-Cr, the Cr-doped DH record cell considered in chapter 6.3.3 (DH-Cr 1)

The effect of aging was found while remeasuring IV curves of some of the first samples produced with the Al contacts. As an example, the IV curves of sample SH-Cr 1 are shown in Fig. 6.13, for all measurements over a time span of 152 days.

![Fig. 6.13 Degradation of IV curves over time for sample SH-Cr 1.](image)
In Fig. 6.13, it is seen that the $I_{sc}$ was affected strongest over time, while the $V_{oc}$ was almost the same. In the following part, each characteristic solar cell parameter (efficiency, short circuit current, open circuit voltage, and fill factor) will be considered separately, in dependency of time, for all five measured cells.

The estimated errors in the IV measurements are the same than in the previous chapters. Based on the results from chapter 6.1, the efficiency and the fill factor have a relative error of 6 %, the $J_{sc}$ an error of 1 %, and the $V_{oc}$ an error of 0.1 %. For some measurements even higher errors are estimated, since the temperature control was inaccurate for some time, after the laboratory was relocated into another room. Experimental tests for this larger range of temperature uncertainty ($25 \pm 3^\circ C$ instead of $\pm 0.3^\circ C$), showed an error of 10.3 %, 8 %, and 3 % for $\eta$ and $FF$, $J_{sc}$, and $V_{oc}$, respectively.

In the following sections, the degradations of the different parameters over time are described by trend lines for each cell. Trend lines with an equation of the form $y = a \cdot x^b$ fitted the data points in the best way, whereby $a$ is the starting value at $x = 1$ (first day of measurement) and $b$ describes the extend of the decrease.

### 6.5.1 Efficiency Degradation over Time

In this section the changes of the efficiencies over time are presented. In Fig. 6.14 the efficiencies of the cells, normalized to their first measurements, are shown as a function of the days since the first measurements. Table 6.7 shows the absolute efficiency values for the first measurements of each cell, with a large spread between the best and weakest cell.

<table>
<thead>
<tr>
<th>Solar Cell Name</th>
<th>Efficiency on first day $\eta_0$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DH-Cr 1</td>
<td>2.05 ± 0.12</td>
</tr>
<tr>
<td>DH-Cr 2</td>
<td>0.51 ± 0.05</td>
</tr>
<tr>
<td>SH-Cr 1</td>
<td>0.30 ± 0.02</td>
</tr>
<tr>
<td>SH-Cr 2</td>
<td>0.28 ± 0.02</td>
</tr>
<tr>
<td>SH undoped</td>
<td>0.009 ± 0.001</td>
</tr>
</tbody>
</table>
In Fig. 6.14, it is clearly seen that the two DH cells, within the error bars, did not decrease in their efficiency over time. In contrast to that, all three SH cells showed a significant efficiency decrease. For the undoped SH cell, two data points were excluded from the trend line, since these two data points showed large aberrations from the trend lines in the $J_{sc}$ and $V_{oc}$ plots, as shown in the two following subsections. Nevertheless, the trend line did not fit the data points very well for the series of the undoped SH cell.

### 6.5.2 Short Circuit Current Degradation over Time

In Fig. 6.15, the normalized $I_{sc}$ of the IV measurements are presented. As for the efficiency results, the currents of the DH cells were just slightly changed over time, while they strongly decreased for the SH cells. One data point (at day 106) of the undoped SH cell was excluded for the trend line, since it was far off from the trend line fitted through the other points.
6.5 Aging of ZnS Based Solar Cells

6.5.3 Open Circuit Voltage Degradation over Time

In Fig. 6.16, the $V_{oc}$ of the IV measurements are presented. Only two samples showed a decrease of the $V_{oc}$ over time. The other samples showed a more or less constant $V_{oc}$ over time. The two decreasing SH samples had been about 20 days in air before the contacts were deposited onto the films. One data point (at day 16) of the undoped SH cell was excluded for the trend line, since it was far off from the trend line fitted through the other points.
6.5.4 Fill Factor Degradation over Time

The last parameter considered was the $FF$ of the IV measurements, presented in Fig. 6.17. Almost all cells showed a very small increase of the $FF$ in the beginning, while they stayed at a constant level over longer time. The only exception was the undoped SH cell, where a large fluctuation of the $FF$ was seen in the beginning and was reduced by half after a longer time. This was also resulting in a very bad fitting trend line for the undoped SH cell.
6.6 Discussion of the Aging of our Solar Cells

The aging effect presented above was only seen for the SH structure cells, while the two considered DH cells did not show any degradation within the measurement uncertainties over the regarded time.

In chapter 3.2.1, it was shown that aging of ZnS in air due to oxygen and moisture is a known phenomenon. This will also explain why the DH cells are not affected. There was no decrease seen, since the DH cells had a top layer of Al:ZnO, which does not oxidize when exposed to air. There were however also different rates of decrease seen for the SH cells. The undoped SH cell had definite the highest relative decrease in all parameters considered. In comparison to the other cells, it had by far the smallest absolute efficiency and was additionally the thinnest of all films. In the following figure (Fig. 6.18), a comparison of all aging processes is shown. The value shown is the trend line exponent \( b \), from the trend line with the form \( y = a \times x^b \), as described earlier.
Between the decreases of SH-Cr 1 and SH-Cr 2 was also a slightly difference seen. The only major property distinguishing these two cells was that the contact for SH-Cr 2 was made 22 days after the film was deposited, while the contact was made on the day after deposition for SH-Cr 1. According to the assumption of the oxidation, this would mean that a ZnO layer was formed on the ZnS film of the SH-Cr 2 before the contact was deposited. The oxidation of the Si before the formation of the back contact should not have had any influence, since the Si was ion-sputtered, to remove the SiO₂ before the Al deposition. The oxide under the finger contacts however, might additionally affect the contact properties over time. For the cell SH-Cr2, a decrease of the $V_{oc}$ was seen over time. The only other cell with a decrease of the $V_{oc}$ was the undoped SH cell, which also had about 20 days between the film and contact production. DH-Cr 1 had as well a longer time between the film and contact production, did however not show any degradation, which was expected due to the top layer of the cell.

From the results it was seen that the Al:ZnO layer was not just increasing the cell performance due to its properties as an n-emitter, but it was also important to preserve the cell performance over a longer time. It contributes as a protective layer on the undoped or Cr-doped ZnS layer, against the influences from the surrounding atmosphere.
6.7 Thickness of Cr:ZnS Layer in DH Solar Cells

A further aspect in the development of our solar cells was the thickness of the ZnS thin film. Solar cells with a film thickness up to about 1 μm were produced and investigated. To find the optimal thickness for our solar cell design, a simulation with film thicknesses up to 10 μm was made.

6.7.1 Experimental test

A series of six samples with different thicknesses was made. All cells were Cr-doped ZnS films with the DH structure. The thinnest ZnS film was about 80 nm thick, while the thickest was about 950 nm. In the following, the combined thicknesses of both the films (ZnS + Al:ZnO) deposited onto the substrate are used, because it was this value that was measured with the profilometer. The Al:ZnO film was for all cells nominally (50 ± 3) nm. Fig. 6.19 shows the solar cell performance parameters for these six DH cells, plotted as a function of the total film thickness. The performance parameters are listed in Table 6.8.

![Graphs showing solar cell performance parameters](image)

Fig. 6.19 Solar cell performance parameters of six DH cells with different thicknesses of the Cr:ZnS layer.
Table 6.8 Performance parameters for DH cells with different film thicknesses (Cr:ZnS + Al:ZnO layer). The estimated error of $\eta$ and $FF$ is 6%, 5% for $t$, 1% for $J_{sc}$, and 0.1% for $V_{oc}$.

<table>
<thead>
<tr>
<th>$t$ (nm)</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$FF$</th>
</tr>
</thead>
<tbody>
<tr>
<td>140219pDH-Cr</td>
<td>127</td>
<td>0.16</td>
<td>0.16</td>
<td>3.80</td>
</tr>
<tr>
<td>131107pDH-Cr</td>
<td>349</td>
<td>0.51</td>
<td>0.25</td>
<td>7.19</td>
</tr>
<tr>
<td>140204pDH-Cr</td>
<td>559</td>
<td>0.74</td>
<td>0.29</td>
<td>8.30</td>
</tr>
<tr>
<td>140131pDH-Cr</td>
<td>766</td>
<td>2.05</td>
<td>0.30</td>
<td>16.05</td>
</tr>
<tr>
<td>140221pDH-Cr</td>
<td>827</td>
<td>0.09</td>
<td>0.28</td>
<td>1.30</td>
</tr>
<tr>
<td>140220pDH-Cr</td>
<td>997</td>
<td>0.87</td>
<td>0.33</td>
<td>9.20</td>
</tr>
</tbody>
</table>

6.7.2 Simulation

As mentioned above, also a simulation for our solar cells was made with the purpose to find the optimal thickness of the ZnS layer. The thickness was varied from about 0.5 μm to 10 μm with a step size of 0.1 μm. In the simulation of the DH cells, the settings presented in Table 5.1, were used. All efficiencies were calculated with the same absorption coefficient (see Fig. 5.6: Cr-doped ZnS). In Fig. 6.20, the result of the simulation is shown. It was found from this result that the optimal film thickness is 3.8 μm (Cr:ZnS + Al:ZnO), for the DH cell structure used in this work.

Fig. 6.20 Simulated efficiencies for different thicknesses of the ZnS layer in our DH solar cells.
6.8 Discussion of the Optimal Thickness of the Cr:ZnS Layer

The thickness of the Cr:ZnS layer is just one parameter out of many, influencing the performance of our solar cells. It might therefore be that other parameters outweigh the effect of the thickness dependency in the experimental results. Such parameters are the Cr concentration in the film and growth parameters like the temperature, growth rate, and laser fluence. The set point for these parameters was the same for the production of the six films, but some deviations cannot be eliminated. The number of pre-ablation pulses varied for the Cr:ZnS film depositions. It was discovered quite late in the project that the amount of Cr in the films depends on the number of pre-ablation pulses, and the effect is currently being investigated by other members in the group. By ellipsometry measurements the absorption coefficient for each cell was obtained, and was found to vary with Cr contents. In contrast to the experimental results, only one parameter was changed in the simulations, which was the thickness of the Cr:ZnS layer.

It was expected that the cell performance will increase with the film thickness, because more of the light will be absorbed in the ZnS layer. However, the low conductivity in the ZnS film will decrease the maximum performance for thick films. It is therefore expected that our solar cells will have their highest possible performance at a certain optimal thickness.

6.8.1 Experimental test

Two of the cells, in Fig. 6.19, did not follow the expected trend for the efficiency in comparison to the other cells. The cell with a thickness of 827 nm showed a very poor cell efficiency and $J_{sc}$. It had also one of the lowest $FF$ and a lower $V_{oc}$ than expected. Although there was no visible damage seen, it is supposed that something abnormally happened to that cell, but exactly what this was, is not determined yet. The other cell, behaving differently than expected, was the cell with a thickness of 766 nm. This cell showed, in comparison, a very high efficiency. This might to some part have been due to a lower series resistance within this cell, because clearly a higher $FF$ was seen than for the other cells. In addition the $J_{sc}$ was higher, while the $V_{oc}$ did not deviate considerably in comparison to the other cells. As known from theory and seen in previous results, a high series resistance affects the IV curve in such a way that the $FF$ and the $J_{sc}$ can be suppressed significantly, but the $V_{oc}$ stays unaffected. It is therefore most likely that this cell had a lower series resistance than the other cells. However, there is no evidence yet on why this cell differed from the others.

In Fig. 6.19 a), the efficiency in dependency of the film thickness, is shown. The highest measured efficiency was at a thickness of 766 nm. If the two cells with 766 nm and 827 nm were omitted, we could see a trend for an increasing efficiency with increasing thickness. The $J_{sc}$ in Fig. 6.19 b), was behaving very similar to the efficiency. This is in correlation with the expected higher current generation in thicker ZnS films. As mentioned above did the sample with 766 nm show a higher $FF$ (see Fig. 6.19 c)) than the other cells. This indicates
that the series resistance in that cell was lower than in the other cells. The $V_{oc}$, in Fig. 6.19 d), was also increasing with thickness. When more light generated current is produced in thicker films, the IV curves will be shifted more from the dark curve and hence increase the $V_{oc}$ up to a certain maximum value, determined by the material properties.

6.8.2 Simulation

In the experimental test, a general trend was seen, showing that the efficiency increases with thickness. No thicker samples than 1000 nm were produced for this work. The simulation was made to see how the efficiency behaves for higher thicknesses and to find the optimal thickness for our cells.

It was found with the simulation that the optimal thickness would be 3.8 μm for our cells, with the absorption coefficient of Cr-doped ZnS shown in Fig. 5.6. This is about 4 times more than the thickest of our cells. The absolute increase in the efficiency, is however not so large, from 1 μm to 4 μm. In the experimental results it was seen that the resistance in the cell, has a high influence on the cell performance. It was also shown in previous simulations that, for example, the carrier density in the semiconductor has a high effect on the cell performance. An improvement of such parameters might have a higher influence on the total cell performance than to further increase the cell thickness. Nevertheless, it would be interesting to produce a cell with that thickness and compare the performance to the other cells.
6.8 Discussion of the Optimal Thickness of the Cr:ZnS Layer
Chapter 7 - Conclusion

7 Conclusion

The focus in this thesis was on the fabrication, testing and improvement of intermediate band solar cells with chromium doped zinc-sulfide as the intermediate band material. The solar cell performance improved from a starting efficiency of $(0.008 \pm 0.001)\%$ to a record efficiency of $(2.05 \pm 0.12)\%$ during the work for this thesis. Two changes in the cell structures led to this performance increase. First of all, the contacts on the solar cells were changed to a reproducible contact pattern with a larger circumference, and secondly an additional n-emitter layer was introduced as top layer on the cell. The best undoped reference cell had an efficiency of $(0.08 \pm 0.01)\%$, which is 25.6 times lower than the efficiency of the doped cell. However, the Cr-doping in the ZnS layer does not just increase the below band gap absorption due to the intermediate band, but does also significantly increase the conductivity in this layer, lowering the resistivity. It is shown in the results that a high series resistance in our cells suppress the performance significantly, which could be increased up to 3 times by lowering this resistance.

Current-voltage measurements were primarily used to characterize the cell performances. Additional Suns-Voc measurements were used to determine the series resistance in the solar cells.

The aging of some of our solar cells was another topic focused on in this thesis. It is presented in the results that the single heterojunction cells showed a performance decrease in the range of 40\% to 90\% in the course of 100 days. In contrast, the double heterojunction cells did almost not show any changes in their performance within the same time span. As a conclusion, it was seen that the Al:ZnO layer not just increases the cell performance as an n-emitter. It is also an important cover layer, protecting the ZnS film from oxygen and water. With this cover layer, the cell performances are maintained over time for our solar cells.

The simulation software SCAPS was used to get a better understanding of our solar cells. Some different aspects regarding our solar cells were simulated. One result, for our cell structures, was that the simulated performance increases up to 50\% when the below band gap absorption is increased. It was also seen that an increase of the donor density in the Cr:ZnS film could improve the cell performance significantly, and that the as-deposited contacts result in Schottky barriers, lowering the cell performances. The optimal film thickness for our solar cells was found to be 3.8 $\mu$m.
8 Further Work

The four main recommendations for further work based on this thesis are:

**Development and improvement of IBSCs**

To further improve the performance of our solar cells, some changes in the structure could be beneficial. One suggestion is to improve the metal contact on the cell. It is recommended to investigate different heat treatments of the contacts, to get better ohmic contacts. Another recommendation is to investigate the use of lithography techniques for the formation of the contacts. With this, a thinner and denser contact pattern could be used, lowering the shading losses and shortening the required collection length. The use of an anti-reflective coating would also reduce the reflective losses and increase the cell performance.

Another question, to investigate further is on the materials used as n and p emitters. Especially for the Si as a substrate, it is suggested to find a suitable material with a more similar band gap to the ZnS film, so that the high band gap can be utilized to get high open circuit voltages. In further work it is also necessary to investigate more on the effect of the Cr concentration on the cell performance and the optical and electrical properties of the ZnS films. From simulations it was seen that the optimal film thickness for our cells is 3.8 μm. It is therefore recommended for future work to increase the film thickness of our cells.

**The use of further characterization methods to prove IB in Cr:ZnS solar cells**

In this work it was shown that the $J_{sc}$ is increased strongly due to Cr doping and a below band gap absorption was observed, as it is expected for IBSCs. However, more additional characterization methods should gradually be used to prove the IB in ZnS cells, due to Cr-doping. Examples for such measurements could be sub-band gap spectral response or quantum efficiency measurements, or measuring a two-photon sub-band gap photocurrent.

**Experimental affirmation of aging in ZnS due to oxygen and moisture**

A further interesting experiment on the aging of the solar cells would be to make long time studies of solar cells in different atmospheres, with enriched oxygen and moisture contents. The effect on the contact quality, for a cell which has been exposure to air a longer time before the contact deposition, could also be investigated in such a long term study.
Simulation of our solar cells

As it was stated, in chapter 5.1 that the large amount of input parameters for the simulations, allows that a different set of parameters could result in the same simulation outcome. Therefore addition measurements on complete and partial cell structures are recommended to select the input parameters. This should be done for both electrical and optical cell properties, to improve the adaption of literature based values.
9 References


