Development of Cu(In,Ga)Se$_2$ Superstrate Thin Film Solar Cells

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZÜRICH
for the degree of
DOCTOR OF NATURAL SCIENCES

presented by
Franz-Josef Haug
Dipl. Phys. Universität Ulm
born September 27$^{th}$, 1969
Citizen of Germany

accepted on the recommendation of:
Prof. Dr. G. Kostorz, examiner
Prof. Dr. M.-Ch. Lux-Steiner, co-examiner
Prof. Dr. H. Melchior, co-examiner
PD Dr. H. Zogg, co-examiner

2001
Contents

Zusammenfassung 1
Summary 3

1 Introduction 5
1.1 Solar energy conversion 6
1.2 Thin film solar cells 8
  1.2.1 Optical considerations 9
  1.2.2 Electrical compatibility 9
  1.2.3 Structural compatibility 12
1.3 Configurations for thin film solar cells 14
  1.3.1 Substrate solar cells 14
  1.3.2 Superstrate solar cells 15

2 Electrical properties of solar cells 17
  2.1 Current voltage characteristics 17
  2.2 Properties of the illuminated p-n junction 19
  2.3 C-V measurements 20

3 Epitaxy of CGS layers 25
  3.1 Molecular Beam Epitaxy 25
  3.2 Characterization of the crystal quality 27
  3.3 Lattice vibrational properties 28
  3.4 Photoluminescence properties 30
  3.5 Microstructural analysis 31

4 Aluminium doped zinc oxide 33
  4.1 Sputtering of ZnO and ZnO:Al layers 33
  4.2 Electrical properties 35
4.3 Thermal stability of the conduction mechanism ........................................ 38
4.4 Influence of sodium .............................................................................. 42

5 Solar cell absorber layers ........................................................................ 43
  5.1 Influence of the substrate material ....................................................... 43
  5.2 Morphology and structural properties ................................................... 45
  5.3 Optical properties ............................................................................... 48

6 Characterization of the interface ............................................................... 51
  6.1 TEM investigations ............................................................................ 51
  6.2 Chemical analysis .............................................................................. 55

7 Solar cell performance ............................................................................. 61
  7.1 Influence of series and parallel resistance ............................................ 61
  7.2 Influence of the growth procedure ....................................................... 63
  7.3 Influence of trap states ....................................................................... 65
  7.4 Carrier density analysis ...................................................................... 66
  7.5 Light soaking .................................................................................... 68

8 Conclusions and outlook ......................................................................... 73

Bibliography .............................................................................................. 77
Symbols and abbreviations ........................................................................ 91
Acknowledgements .................................................................................... 93
Publications ............................................................................................... 95
Curriculum Vitae ....................................................................................... 99
Zusammenfassung


Solarzellen mit CuGaSe₂ Absorberschichten wären wünschenswert, da sie hohe Betriebsspannungen versprechen. Allerdings ist ihre Effizienz im Vergleich zu Cu(In,Ga)Se₂ Solarzellen gering. In dieser Arbeit wurden epitaktische CuGaSe₂ Schichten auf Si- und GaAs-Substraten hergestellt und mit verschiedenen Methoden charakterisiert, um grundlegende Materialeigenschaften zu untersuchen. Ausserdem wurden Superstrate-Solarzellen mit CuGaSe₂ Absorberschichten hergestellt, die Wirkungsgrade von bis zu 2.8% erreichten.

Die Absorberschicht von Cu(In,Ga)Se₂ und CuGaSe₂ Solarzellen wird mit Vakuumverdampfung bei Substrattemperaturen von 550°C hergestellt. Dies erfordert eine hohe thermische Stabilität der Leitfähigkeit des Frontkon-
taktes, der aus Aluminium-dotiertem ZnO besteht. In dieser Arbeit zeigte sich, dass Kontaktschichten, deren Prozessparameter für Substrat-Zellen optimiert wurden, diese Stabilität nicht aufwiesen. Ihr elektrischer Widerstand verschlechterte sich während des Wachstums der Cu(In,Ga)Se₂-Schicht um bis zu 800%. Deshalb wurde der Depositionsprozess der ZnO:Al Schichten auf eine hohe thermische Stabilität der Leitfähigkeit und auf eine erhöhte Wachstumsrate hin optimiert. Der elektrische Widerstand solcher Schichten steigt während der nachfolgenden Prozessschritte um maximal 25% an. Durch den verringerten Serienwiderstand konnte die Effizienz beträchtlich gesteigert werden.


CuInSe₂ and CuGaSe₂ and their quaternary alloys are important semiconductors for thin film solar cells. In this thesis solar cells in the so called superstrate configuration were developed on the basis of these materials and their properties were investigated. Conventional Cu(In,Ga)Se₂ solar cells are made in the substrate configuration on glass substrates coated with molybdenum. Thus, it is not possible to illuminate the cell through the glass substrate. Rather, it is necessary to illuminate from the opposite side which requires an elaborate transparent encapsulation. In contrast to that, the configuration of superstrate solar cells allows the illumination through the glass substrate. This saves the expensive transparent encapsulation. Currently, substrate solar cells with Cu(In,Ga)Se₂ absorbers yield conversion efficiencies of up 18.8%, the highest published efficiency of Cu(In,Ga)Se₂ superstrate solar cells is 12.8%. In this thesis an efficiency of 9.5% has been achieved.

Solar cells with CuGaSe₂ absorber layers are desired because of their potential of high operation voltage. However, their performance is rather bad compared to Cu(In,Ga)Se₂ solar cells. In this thesis epitaxial CuGaSe₂ layers were prepared on Si and GaAs substrates in order to study their basic material properties with a variety of methods. Polycrystalline CuGaSe₂ superstrate solar cells were prepared on ZnO coated glass, they reached efficiencies up to 2.8%.

The Cu(In,Ga)Se₂ and CuGaSe₂ absorber layers are deposited by vacuum evaporation at substrate temperatures of 550°C. This requires a high thermal stability of the front contact. In this work it was found that ZnO layers whose deposition process was optimized for the contact on substrate solar cells turned out to be unsuitable for superstrate solar cells. Their electrical resistance increased up to 800% during the absorber growth. Therefore, the deposition process of ZnO:Al was optimized to yield thermally stable layers with a higher deposition rate; their resistance increases by not more than 25%. 

Summary
during later process steps. The application of such layers for superstrate solar cells lead to a considerable increase in efficiency due to the reduced series resistance.

High efficiency substrate solar cells need a CdS buffer layer between front contact and absorber layer for electrical and structural matching. For the superstrate structure CdS is not an option because it does not show a sufficient thermal stability and diffuses into the absorber layer. The use of undoped ZnO as alternative buffer layer yielded promising results, however, the performance of substrate solar cells has not been reached. In this work the chemical and structural properties of the interface between ZnO and Cu(In,Ga)Se₂ were investigated. This revealed the accumulation of gallium in the absorber layer close to the interface which results in a bad band alignment. A change in the growth process could not entirely prohibit the Ga accumulation, but it succeeded in an improvement of the diode characteristics. Solar cells with efficiencies of up to 9.5% were achieved.

The presented Cu(In,Ga)Se₂ superstrate solar cells show open circuit voltages between 450 and 550 mV. This is more than 100 mV below substrate solar cells with comparable absorber layer composition. Measurements of the capacitance showed that the low open circuit voltages correlate with low carrier densities. A chemical analysis of different superstrate absorber layers revealed a low concentration of sodium, which is a dopant in Cu(In,Ga)Se₂. The analysis showed that the ZnO front contact acts as diffusion barrier and prohibits a sufficient incorporation of sodium from the glass substrate. Thus, further developments should aim at an increase of the sodium content by external doping.
Chapter 1

Introduction

The development of mankind was always intimately related to the availability of energy and the same will hold true for the future, only with an ever increasing demand. There are countries where the geography allows to produce large amounts of energy from wind and hydro, like, for example, in the Netherlands and in Switzerland. However, worldwide the supply of energy is widely based on fossil fuels like coal, oil, and natural gas and on nuclear energy. While some uncertainties exist about the overall amount of these sources and how long they will be able to meet the growing demand, there cannot be any doubt that alternate sources of energy are needed within a few decades.

Not only the limited resources, also the environmental impact of the present energy production causes serious problems. At the moment mankind is only beginning to feel the consequences of global warming and atmospheric pollution.

The most promising source of clean, safe, and abundant energy is the sun which made possible the life on earth itself. Photovoltaic devices (or simply solar cells) offer the direct conversion of sunlight into electricity. The discovery of the photovoltaic effect dates back to 1839 when Becquerel found a photovoltage between electrodes in electrolyte solutions. In 1877 Adams and Smith discovered a similar effect in selenium which is still used today in exposure meters for photography.

By the year of 1954 light conversion efficiencies of 6% were achieved which made solar cells an interesting means for power generation. Initially intended for the energy supply of satellites, solar cells have also become a very attractive power source for terrestrial applications. Over the last decade
the production of solar modules grew by more than 20% per year and now photovoltaics is on the verge of becoming a cost effective means for energy production.

More detailed presentations of the historical developments are found in review articles [1] and textbooks [2, 3].

1.1 Solar energy conversion

The absorption of light in solids takes place via the excitation of electrons from states at an equilibrium energy into states of higher energy. Eventually the excited electrons distribute their extra energy and the entire system returns to equilibrium again. The absorbed light is used to increase the average energy which corresponds to a higher temperature of the material.

In semiconductors the situation is quite different; owing to the different electronic structure a certain range of states is forbidden for the electrons. Only at some higher energy there are available states again. The allowed states as a total are called bands, the forbidden region in between is the band gap. In terms of energy, the band below the gap is the valence band, the band above the forbidden region is the conduction band.

Absorption of light only happens when the light has sufficient energy to excite electrons across the gap. The excited electrons leave behind free states below the gap, these are called holes. Once an electron is excited into the conduction band, it may take some time until it finds a hole in the valence band to jump into. Appropriate combinations of materials lead to a spatial separation of the electrons from the holes. Electric contacts direct them into an external circuit where they may power an electric device.

The outlined absorption mechanism shows that the excitation of an electron in a semiconductor is closely related to the energy of the irradiation. If the incident light does not have enough energy to excite the electron across the band gap, it cannot be absorbed. Light with higher energy can excite electrons, but the obtainable electric potential does not exceed a value corresponding to the band gap. Thus, for a given irradiation there are restrictions for the choice of semiconductors whose properties are suitable for a solar cell:

- There must be sufficient absorption of light in the semiconductor
- The band gap of the semiconductor must match the irradiation
The transport of the charge to the external circuit must be ensured

The entire solar cell must be cost effective

The spectral irradiation density of the sun is presented in figure 1.1. AM means Air Mass and AM0 corresponds to the irradiation of the sun without any absorption in the atmosphere. AM1 would correspond to the irradiation at the equator and AM1.5 is the irradiation in Central Europe because of the inclined path through the atmosphere.

Theoretical calculations show that the ideal band gap of the absorber layer is about 1.4 eV for AM1.5 irradiation. However, the curve of maximum performance is quite broad and band gaps of the entire range from 1.0 to 1.8 eV are considered suitable for solar energy conversion. Generally, high
band gaps result in high operation voltages but low current and vice versa.

The most conventional solar cells are produced from the standard electronic materials, Si and GaAs. These cells are quite advanced because they benefit from the experience of the electronic industry. Their record efficiencies are 24.7% and 25.1% [4], respectively, which is close to the theoretical limit which is between 25 and 28%, depending on the underlying models [5]. These solar cells are obtained from expensive single crystal materials and they require complicated fabrication steps. Obviously, such cells can only serve for special applications (e.g. space applications and concentrator cells), where the cost of the individual cell is not an issue.

Silicon solar cells are also produced from lower grade material but the integration into modules still requires a large amount of manual work which makes them expensive. Under the present circumstances it is unlikely that they are able to penetrate the market of large scale energy production. An analysis revealed that the present cost of Si-based photovoltaic modules is about 3 € per Wp, where Wp means the peak power output of the module under ideal conditions. However, module costs of less than 0.8 € per Wp are mandatory for competitive energy prices [6].

1.2 Thin film solar cells

Thin film solar cells have several striking advantages over crystalline Si (c-Si) and GaAs solar cells because they are not produced from single crystal material. The deposition of amorphous or polycrystalline thin films onto a low cost substrate material at moderate temperatures not only lowers the required input of energy and material but, more important, it offers the possibility of easier module interconnection by scribing with a hard stylus or laser light between the different growth steps.

Historically, the development of solar cells entirely based on thin film processes started with the Cu2S/CdS cell [1]. In 1954 the development was already quite advanced; 6% cells were realized, the same efficiency as silicon solar cells at that time. Even several pilot productions came into operation but it was noticed that the degradation of the cells due to the inherent instability of Cu2S could not be avoided.

A search for more suitable thin film materials revealed three possible candidates; amorphous silicon, CdTe and Cu(In,Ga)Se2 are promising for the production of low cost thin film solar cells. The experience gained in the
1.2. THIN FILM SOLAR CELLS

operation of pilot plants [7, 8] allows to project costs of about 0.6 € per Wp for thin film solar modules which enables them to compete with conventional sources of energy even under the present conditions [9].

1.2.1 Optical considerations

In order to ensure sufficient absorption of the solar irradiation, the band gap of the absorber should be in the range of 1.0 to 1.8 eV with an optimum around 1.5 eV [5]. For amorphous silicon (a-Si) the band gap is 1.8 eV, but it can be lowered by alloying with Ge. CdTe has a band gap of 1.44 eV which is very close to the optimum and in the Cu(In,Ga)Se₂ system (often also called CIGS) the band gap can be varied from 1.04 to 1.68 eV, depending on the Ga/(Ga+In) ratio. Of all these thin film materials, Cu(In,Ga)Se₂ yields the highest efficiency of up to 18.8% with a Ga/(In + Ga) ratio of approximately 0.25. In CdTe cells the efficiencies are up to 16.0%. The highest reported efficiency for a-Si solar cells is 12.7% for an unstabilized cell [4].

These three materials have a high absorption coefficient for visible light which is in the order of $10^5$ cm$^{-1}$. Thus, thin absorber layers with a thickness of only about 1 to 2 μm are sufficient for a complete absorption of light. In contrast, Si solar cells need a thickness of about 300 μm or elaborate light trapping structures for the absorption.

Usually thin film solar cells require a transparent conducting contact material which effectively carries the current to the electric contacts. Conductivity and transparency at the same time is only obtained in semiconductors. They are transparent for photons with energy less than the band gap and the conductivity depends on mobility and carrier density which can be controlled by doping. In order to transmit the entire solar spectrum to the absorber material, the band gap of the transparent front contact should exceed 3 eV (c.f. figure 1.1). This condition is met by transparent conducting oxides (TCOs) like ZnO doped with group III elements, SnO₂ doped with In (ITO) or F (FTO), CdO and Cd₂SnO₄ [10, 11].

1.2.2 Electrical compatibility

In most semiconductors the mobility of electrons is high compared to holes. Thus, in solar cell designs usually p-type absorber layers are used for an efficient transport of the minority carriers generated by the absorbed light.
Additionally, an asymmetric doping profile with a higher carrier concentration in the n-type semiconductor is used to extend the built-in field into the absorber region, where it enhances the carrier collection.

The electrical description of a heterojunction between two semiconductors is based on their band gaps $E_g$, electron affinities $\theta$, work functions $\Phi$, and dielectric constants $\epsilon$ [12]. Theoretically, when two semiconductors are brought into contact, the Fermi levels align. Electron affinity and work function are defined as the energies which are required for the removal of an electron from the conduction band edge and from the Fermi level, respectively, to a position just outside the material, the vacuum level. Different work functions result in an electric potential $V_b$, and the bands bend according to the band offsets and carrier concentrations. The presence of interface charges results in discontinuities of the electric field, which can interfere with the calculated band alignment.

Experimentally, the discontinuities of the valence bands between two semiconductors are measured by photoelectron spectroscopy. Additionally, the band alignment between different semiconductors can be estimated from a common reference by using the transistivity rule [13]. However, the estimate fails to describe the real behaviour of the junction because its accuracy is often limited.

Figure 1.2 illustrates two types of band alignments between a CIGS absorber layer with a Ga to (In + Ga) concentration ratio of 0.25 and typical transparent conducting oxides. Two possible kinds of alignments are referred to as “cliff” and “spike” type, respectively, because of the shape of the conduction bands. The values have been calculated from reported data on CIS/CdS/ZnO heterostructures [14] and the interfaces between CdS and SnO$_2$ [15]. Once the band offsets are known, the junction built-in potential $V_{bi}$ is calculated by the difference in work functions. The work function of CuIn$_x$Ga$_{1-x}$Se$_2$ does not change significantly for a wide range of Ga-contents [16, 17] which limits the built-in voltage despite the increasing band gap. The combination of CIGS and ZnO results in a junction with a cliff-type alignment whereas the combination of CIGS and FTO yields a spike in the conduction band.

Little data is available on the band alignment with ITO. The combination of values from the interfaces of CdTe/CdS [18] and CdTe/ITO [19] indicates a spike shaped conduction band offset of about 0.9 eV. In contrast, an estimate based on the work functions and band gaps [20] yields a much smaller spike
1.2. THIN FILM SOLAR CELLS

Figure 1.2: Schematic band alignment between p-type Cu(In,Ga)Se₂ absorber material and typical front contact materials. The lower part illustrates the band bending under open circuit conditions. The use of a ZnO front contact leads to a “cliff” shaped alignment, the SnO₂ window layer results in a “spike” shaped conduction band offset.

Owing to the inconsistencies in the literature, the values can only be given within accuracies of 0.2 to 0.4 eV. Furthermore, simulations showed that spikes of up to 0.3 eV in the conduction band are tolerable for reasonable solar cell operation, assuming carrier concentrations of typical solar cells [21]. Thus, the experiment must tell whether a chosen combination yields a suitable solar cell or not.

Buffer layers between the p- and n-type semiconductors can be helpful for the improvement of the band alignment. For example, the CdS layer in CIGS substrate solar cells results in a spike shaped band diagram [14], nevertheless, it is essential for high efficiency solar cells [22].
Figure 1.3: Unit cell of the ZnO crystal. Zinc atoms are denoted by small circles, large circles represent oxygen atoms.

1.2.3 Structural compatibility

Zinc oxide is frequently used as transparent contact material in Cu(In,Ga)Se₂ solar cells. It occurs in nature as a mineral called Zn-cite which crystallizes in the hexagonal wurtzite structure with lattice constants of $a = 3.24 \, \text{Å}$ and $c = 5.19 \, \text{Å}$. A schematic drawing of the unit cell is presented in figure 1.3. It has an optical bandgap of about 3.3 eV which makes it transparent over the entire visible range [11]. Polycrystalline ZnO deposited on glass by rf-sputtering grows with a preferred [0001] texture, thus the c-axis is directed perpendicular to the glass substrate. Details on the deposition of ZnO layers and their electrical properties are presented in chapter 4.

The most commonly used contact in CdTe solar cells is F- or In doped SnO₂ with an optical band gap of 3.6 eV. It has a tetragonal rutile structure, the lattice parameters are $a = b = 4.737 \, \text{Å}$ and $c = 3.185 \, \text{Å}$ [11]. A schematic drawing of the unit cell is shown in figure 1.4. The texture of these layers is preferentially in the [110] direction with additional contributions of the [221] and [200] orientations.

The quaternary system Cu(In,Ga)ₓSeᵧ exhibits a large variety of structures, depending on the composition. Phase diagrams are usually restricted to quasi binary cuts in the ternary systems of CuInₓSeᵧ [23, 24] and CuGaₓSeᵧ [25, 26]. The lattice constants vary between $a = 5.61 \, \text{Å}$ and $c = 11.03 \, \text{Å}$ for
1.2. THIN FILM SOLAR CELLS

Figure 1.4: Unit cell of the SnO\textsubscript{2} crystal. Tin atoms are denoted by small circles, large circles represent oxygen atoms.

Figure 1.5: Unit cell of the tetragonal chalcopyrite structure of stoichiometric CuInSe\textsubscript{2} and CuGaSe\textsubscript{2}.
CuGaSe$_2$ and $a = 5.789$ Å and $c = 11.612$ Å for CuInSe$_2$.

All Cu-rich compositions are mixtures of binary Cu$_{2-x}$Se phases and stochiometric CuInSe$_2$ and CuGaSe$_2$ phases, respectively. The stoichiometric materials have the chalcopyrite structure shown in figure 1.5, group III-rich compositions are either single phase or mixtures of different ternary phases, but no binary segregations are observed.

From the differences of the crystal structures and the lattice constants some degree of incompatibility exists between window and absorber. In case of layer growth, crystallographic defects due to nucleation phenomena and dangling bonds at the interface result in trap states which may enhance the undesired interface recombination. Investigations of the electrical and structural properties are presented in chapters 6 and 7, respectively.

1.3 Configurations for thin film solar cells

1.3.1 Substrate solar cells

Thin film solar cells with Cu(In,Ga)Se$_2$ absorber layers are mostly grown in the substrate configuration. A cross-section of a substrate solar cell is presented in figure 1.6. The growth sequence starts with the deposition of a metallic contact on the glass substrate. Molybdenum is frequently used as contact material because it forms a good Ohmic contact to CIGS. The second step is the growth of the p-type absorber layer. This can be done by coevaporation from elemental sources or by the deposition of metal precursor
layers and subsequent selenization. The best performance is achieved if the heterostructure is continued with CdS buffer layer grown by a chemical bath process [27]. Alternate materials and deposition methods like In(OH)$_x$S$_y$ [28], (In,Ga)$_x$Se$_y$ [29], and ZnSe [30] have also been proposed. Finally, the transparent front contact is deposited. Usually it consists of two layers; one is undoped ZnO for band matching, the second is doped ZnO layer for good conductivity. The layers are grown by sputtering or chemical vapour deposition. The combination of buffer and front contact is frequently referred to as window layer.

### 1.3.2 Superstrate solar cells

The name frontwall or superstrate solar cell refers to a configuration where the glass substrate is not only used as mechanical support but also as part of the transparent encapsulation. This configuration is commonly used for solar cells based on CdTe and a-Si absorber layers and was also successfully employed for solar cells with Cu(In,Ga)Se$_2$ absorber layers [31, 32, 33]. An efficiency of 10.2% has been reported for cells with extrinsic Na doping [34]. In this thesis efficiencies of up to 9.5% were obtained without the addition of Na as dopant.

A cross-section image of a Cu(In,Ga)Se$_2$/ZnO superstrate solar cell and a schematic drawing of the configuration are shown in figure 1.7. The growth sequence for superstrate solar cells starts with the deposition of the trans-
parent front contact on glass, followed by a ZnO buffer layer and the growth of the absorber layer. Finally, a metal layer is applied for the Ohmic back contact.

The superstrate configuration offers some technological advantages; the substrate glass acts as reliable encapsulation against environmental impacts and no second glass is needed on the back. Rather, any low cost encapsulation can be applied because it needs not to be transparent. This facilitates production and lowers the overall cost.
Chapter 2

Electrical properties of solar cells

From the electrical point of view, solar cells can be considered as p-n junctions; two semiconductors of different carrier type are in contact and the recombination of charge carriers across the interface leads to the formation of a space charge region (or depletion layer) and a built in potential. The junction shows rectifying behaviour [35] and the depletion region gives rise to a junction capacitance [12].

2.1 Current voltage characteristics

In its most basic form a solar cell is described by the Shockley model of p-n junctions with a current density prefactor \( j_{00} \) [35]. Details of the current transport are accounted for by a diode quality factor \( A \):

\[
j = j_{00} \left( \exp \left\{ \frac{qV}{AkT} \right\} - 1 \right)
\]

In eq. (2.1) \( k \) denotes the Boltzmann constant, \( T \) the absolute temperature. All physical constants are also listed in the appendix. In real junctions often parallel (or shunt) and series resistances \( R_p \) and \( R_s \) (resistance area products) are present. Thus, eq. (2.1) is modified to:

\[
j = j_{00} \left( \exp \left\{ \frac{qV - qjR_s}{AkT} \right\} - 1 \right) + \frac{V - jR_s}{R_p}
\]
The exact form of the current prefactor and the value of the diode quality factor are determined by the underlying transport mechanism of the junction.

Ideally, the charge transport is governed by diffusion. In forward bias, the term in the round brackets may be simplified, and the value of the band gap $E_g$ can be incorporated into the exponent. For a p-n+ junction the diffusion length $L_D$ and the diffusion constant $D_n$ of the electrons in the p-material govern the behavior.

\[
J_{\text{diff}} = \frac{qN_CN_VD_n}{N_A L_D} \exp\left\{\frac{qV - E_g}{kT}\right\} \tag{2.3}
\]

$N_C$, and $N_V$ are the effective densities of states of the conduction band and the valence band, respectively. $N_A$ is the acceptor density. The diode quality factor is 1.

A different transport mechanism considers recombination via levels in the band gap. It is often found in polycrystalline material because the diffusion lengths are usually quite low and recombination centers are likely to exist. The occupation of such levels is governed by their position with respect to the Fermi level. An applied bias splits the Fermi level in the space charge region and increases the probability for recombination in this region. This is illustrated by the dependence on the space charge width $w$

\[
J_{\text{rec}} = \frac{D_n \sqrt{N_CN_V}}{L_D^2 V_{bm}} \cdot w \cdot \exp\left\{\frac{qV - E_g}{2kT}\right\} \tag{2.4}
\]

The carrier density is contained the band bending $V_{bm}$. The trap density $N_T$ enters the relation via the diffusion constant $D_n$ and the diffusion length $L_D$. The diode quality factor is 2.

A third important transport mechanism is related to recombination via interface states. States at the interface are expected for heterojunctions because of structural incompatibility of the materials or different lattice constants or orientations. The recombination is governed by the interface recombination velocity $S_P$ and the barrier height for holes $\Phi_B^P$ [16].

\[
J_{\text{int}} = qS_P N_V \exp\left\{\frac{qV - \Phi_B^P}{kT}\right\} \tag{2.5}
\]

Frequently the characteristics of a junction are not governed by one transport mechanism but by a combination, because different mechanisms may become dominant at different voltages. For example, the two diode model is used for Si solar cells [36, 37]. Temperature dependent diode quality factors
2.2 Properties of the illuminated p-n junction

Under illumination the characteristics of the p-n junction are modified because incident light generates electron hole pairs which are separated by the built-in field of the junction. If the description is again restricted to the simple case of the ideal p-n junction, the photocurrent \( j_{\text{photo}} \) is superimposed to the current characteristics of the junction:

\[
j = j_{\text{junction}} - j_{\text{photo}}
\]

in Cu(In,Ga)Se\(_2\) thin film solar cells have been described by a distribution of states extending from the conduction band into the band gap [38]. Recently, this model was further refined by the consideration of tunnelling enhanced recombination [39].

Figure 2.1: Schematic \( j-V \) characteristics of a solar cell. Under illumination the exponential relationship between current density and voltage is shifted by the short circuit current density \( j_{\text{sc}} \).
Figure 2.1 schematically shows the characteristics for the dark and the illuminated case. Important parameters of the solar cell are the intercepts with the axes; on the voltage axis this is the open circuit voltage $V_{oc}$, on the current axis it is the short circuit current density $j_{sc}$ which is identical to the photocurrent. The dark grey rectangle defines the point of maximum output power $P_m$ which is important for solar cell operation. The form of the curve is described by the fill factor ($FF$) which is the ratio of the rectangle areas $V_{oc} \cdot j_{sc}$ and $V_m \cdot j_m$. Finally, the efficiency of the cell is determined by the ratio of the maximum output power of the device (corresponding to the dark rectangle in figure 2.1) to the incident illumination.

Of course, the simple shift along the $j$-axis is not always observed in illuminated thin film solar cells. Carriers which are created deep in the absorber only add to the photocurrent, if they feel the influence of the built in field and gradients in the carrier density. When the depletion layer shrinks under forward bias they may be lost due to their short diffusion lengths. Another example where the superposition is not valid is the cross over of the dark and light $j-V$ characteristics which is attributed to photoconductivity of the CdS layer [40].

### 2.3 C-V measurements

Close to the junction of two semiconductors with different conduction types the carriers move towards each other and recombine. This forms the depletion region. An applied forward bias injects carriers and shrinks the depletion region, reverse bias withdraws carriers and widens it. A higher carrier density in the window material compared to the absorber results in an asymmetrical p-n$^+$ junction and causes the depletion region to extend mainly into the absorber. A relation between depletion layer capacitance $C_D$ (with respect to unit area) and voltage $V$ of such ideal single sided heterojunctions is described by the Anderson model [12].

\[
C_D = \frac{1}{\sqrt{\frac{2}{\varepsilon \sigma N_A}}(V_{bi} - V)} \tag{2.7}
\]

A plot of $1/C_D^2$ versus $V$ is called Mott-Schottky plot. Ideally it yields a straight line whose intersect with the voltage axis gives the junction built in potential. The slope determines the acceptor density of the absorber material. In reality, however, deviations are observed frequently.
2.3. C-V MEASUREMENTS

Figure 2.2: Schematic drawing of the band alignment between n-type window and p-type absorber including a hole trap level in the p-material. Open circles represent ionized doping levels. Additionally, in region III, the hole traps are empty.

$C - V$ measurements are performed by applying a dc bias in order to widen or shrink the depletion layer and a small superimposed ac signal voltage for probing the actual capacitance at a given bias. Often the junction capacitance shows a dependence on the measurement frequency which the simple Anderson model cannot account for. More detailed models of the junction include trap levels in the band gap or at the interface whose charging and discharging adds to the depletion layer capacitance which explains the observed frequency dependence. Typically, the trapping processes take place on timescales in the order of $10^{-6}$ s.

$$C(\omega) = C_D + C_T(\omega)$$

(2.8)

Figure 2.2 illustrates the band diagram of a p-n junction including a single trap level in the absorber layer. If required, the treatment is easily extended to more than one level or even distributions of trap levels. Five regions are
distinguished:

- Regions I and V are the neutral areas of the window layer and the absorber, respectively. The charge density is zero, the solution of the Poisson equation yields constant potentials corresponding to flat bands.

- In Region II the free electrons have moved towards the absorber and recombined with holes. The charge density is \(-q \cdot N_D\), the number of ionized donor states. The solution of the Poisson equation yields a parabolic band which bends upwards.

- In Region III all states (acceptors and trap states) below the Fermi level are ionized, all holes have recombined. The charge density is \(q \cdot N_A\), the band bending is downwards.

- In Region IV the trap states are above the Fermi level, thus they are occupied with holes. The charge density is \(q \cdot (N_A - N_T)\), the density of ionized acceptors reduced by the concentration of trap states. Because of the reduced charge density the band bending is less than in region III.

At low measurement frequency the trap levels at the boundary between regions III and IV as well as the acceptors at the boundary between the regions IV and V change their occupancy with the measurement signal. At high measurement frequencies, however, the charging processes of the traps are too slow to follow the signal and only the depletion layer capacitance is probed. Two different expressions for the capacitance at low and high frequency are obtained [41, 42, 43]:

\[
C_{lf} = \frac{1}{\sqrt{\frac{2}{q \varepsilon_0 \varepsilon_N} (V_{bi} - V) - \frac{2N_T}{q^2 \varepsilon_0 \varepsilon_N} \Delta E}} 
\]  
\[
C_{hf} = \frac{1}{\sqrt{\frac{2}{q \varepsilon_0 \varepsilon_N} (V_{bi} - V) - \frac{2N_T}{q^2 \varepsilon_0 \varepsilon_N} \Delta E + \frac{N_T}{qN_A \sqrt{\varepsilon_0(N_A - N_T)}} \Delta E}} 
\]

\(\Delta E = E_F - E_T\) represents distance of the trap level from the Fermi level or simply the “depth” of the trap. Eqns (2.9) and (2.10) indicate that the linear dependence in the Mott-Schottky plot is only obtained at low measurement frequencies below the inverse trapping time, while at high frequency \((\omega > \)
2.3. C-V MEASUREMENTS

1/τ) the behaviour is only asymptotically linear for high reverse bias. At intermediate frequencies small signal theory yields a dispersion law with the time constant τ of the capture and re-emission process [44]:

\[
C(\omega) = C_{\text{hf}} + \frac{1}{1 + \omega^2 \tau^2} (C_{\text{hf}} - C_{\text{hf}}) \tag{2.11}
\]

Thus, a comparison with eq. (2.8) identifies the depletion layer capacitance with \( C_{\text{hf}} \) and the trap related capacitance with \( C_{\text{hf}} - C_{\text{hf}} \). The treatment reveals a junction conductance \( G \) as a further important consequence of trap states:

\[
G(\omega) = \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} (C_{\text{hf}} - C_{\text{hf}}) \tag{2.12}
\]

Very similar to the presented approach, the consideration of traps located at the interface results in an additional interface state capacitance \( C_{\text{is}} \) and the same frequency dependence [45]:

\[
C(\omega) = C_{\text{D}} + \frac{C_{\text{is}}}{1 + \omega^2 \tau^2} \tag{2.13}
\]

Then, the density of interface states \( N_{\text{is}} \) is obtained by:

\[
N_{\text{is}} = \frac{C_{\text{is}}}{q} \tag{2.14}
\]

Which one of relations (2.11) and (2.13) applies to a measured dispersion in capacitance is discussed together with the experimental data in chapter 7.
Chapter 3

Epitaxy of CuGaSe$_2$ layers

Photovoltaic modules with high voltages are desired because of lower resistive loss in operation. Therefore, cells with a higher operation voltage are desired. CuGaSe$_2$ (CGS) with its band gap of 1.7 eV is interesting for photovoltaic devices because it should allow open circuit voltages exceeding 1 V. Advanced tandem solar cells in combination with low band gap CuInSe$_2$ are also a promising option. Current state of the art CGS thin film solar cells reached efficiencies of up to 8.7% [46] but the performance is still quite low compared to Cu(In,Ga)Se$_2$ solar cells.

Studies of single crystal material and epitaxial layers of CGS may contribute to a deeper understanding of the intrinsic material properties and eventually contribute to the improvement of solar cells on the basis of CGS. In this thesis, epitaxial layers of CuGaSe$_2$ were prepared on 3" Si wafers. The structural and electrical properties of the layers were investigated with a variety of characterization methods.

3.1 Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) is a form of physical vapour deposition for the growth of layers with high crystal quality on single crystal substrates. The growth of the epitaxial layers was performed in a home made ultra high vacuum (UHV) system [47] with background pressures of less than $10^{-7}$ Pa. Pressures in this range are necessary to avoid contamination of the growing layers and ensure the formation of molecular beams from the evaporation sources because the mean free path of particles at this pressure is in the order
of kilometers. The evaporation sources were Knudsen-type cells rather than open boat crucibles. This guarantees thermodynamical quasi-equilibrium conditions for the vapour and ensures constant and reproducible flux.

The crystal structure of the substrate is chosen to match with the grown layer in order to establish a defined relationship between the crystal orientation of the two materials. During the growth the substrate is kept at a temperature which ensures a sufficient amount of surface diffusion for high crystal quality of the growing layer.

Differences in lattice constants and thermal expansion coefficients between substrate material and epitaxial layer can give rise to structural defects. Reactions at the interface and diffusion can influence the electrical properties. In this thesis, mostly Si substrates were chosen because of their similar crystal structure. The lattice mismatch between CGS and Si is about 3%. The thermal expansion coefficients are $13.1 \times 10^{-6} \text{ K}^{-1}$ for CGS and $3.0 \times 10^{-6} \text{ K}^{-1}$ for Si.

The Si substrates were cleaned with the Shiraki method. Before the growth the oxide layer of the Si substrates was removed thermally at $1000^\circ \text{C}$ in a separate UHV. Reflection high energy electron diffraction (RHEED) was used to confirm the formation of a clean surface.

Figure 3.1 shows RHEED images of epitaxial CGS layers on Si(111) substrates at $570^\circ \text{C}$. The patterns indicate the formation of islands and 3D growth due to the high lattice mismatch between CGS and Si. All layers were cooled down in Se ambient at a rate of $5^\circ \text{C}$ per minute. Only Ga rich layers showed good adhesion to the Si substrate and could be grown epitax-
ially. It was not possible to grow Cu-rich epitaxial layers on Si, they were always polycrystalline and peeled off the substrate.

Similar to epitaxial CuInSe₂ layers [48], at substrate temperatures between 520 and 550°C the formation of twins was observed in the initial phase of the growth. Growth at higher substrate temperatures between 570 and 600°C or a short annealing step helped to reduce the twinning.

### 3.2 Characterization of the crystal quality

The crystal quality of epitaxial layers with 800 nm thickness was investigated with X-ray diffraction. Linewidths of 430 arcsec of the (336) reflection were achieved for Ga-rich layers on Si(111) substrates. The values compare well to linewidths between 700 and 900 arcsec for the (336) reflection epitaxial CuInSe₂ layers on Si [49].

An alternate method for the determination of the crystal quality is the ion channelling with Rutherford back scattering spectrometry (RBS)¹. Figure 3.2 shows the scattering yield of experiments with a 2 MeV ⁴He⁺ ion beam. The minimum channelling yield \( \chi_{\text{min}} \) is defined as the ratio of the backscattered intensities in aligned and random direction. A high crystal quality allows the incident ions to penetrate into the lattice along directions of high crystal symmetry. Defects in material with low crystal quality scatter the incident ions. This results in a high yield of of backscattered ions and, therefore, high values of \( \chi_{\text{min}} \).

The minimum channelling yields for CGS/Si(111) were between 12 and 15% for layers with a thickness of 900 nm. Layers grown at lower temperatures exhibited higher channelling yields of about 20%. Similar values have been reported for CuInSe₂ on Si(111) [49]. The channelling yields for bulk single crystals are between 3 and 5%.

RBS additionally allows to determine the thickness and absolute composition of the layers. For this purpose the shape of the spectrum was fitted with the RUMP simulation program [50]. The values of the layer thickness were found to be consistent with profilometer measurements. The signals of Cu, Ga and Se correspond to the steps in the high energy tail of the spectrum in figure 3.2. The evaluated compositions are consistent with results from energy dispersive X-ray spectroscopy (EDS) in the electron microscope.

¹The RBS measurements were performed by Dr. M. Döbeli, ETH Zürich.
Figure 3.2: Back scattered ion intensities of a CGS/Si(111) in aligned and in random orientation. The incident beam consists of $^4\text{He}^+$ ions accelerated to 2 MeV.

### 3.3 Lattice vibrational properties

RBS measurements give no evidence whether the layers consist of single phase material or not. The backscattered ions could be collected from different domains or segregations, thus the resulting compositions could be averaged values. In XRD low intensity reflections of segregations of similar crystal structure could be hidden in the dominant peaks.

The study of lattice vibrational properties offers the possibility to detect segregations because of their different vibration modes. Figure 3.3 shows Raman measurements of an epitaxial CuGaSe$_2$ layer\textsuperscript{2}. The dominant feature is a peak at 185 cm$^{-1}$ which is attributed to the vibration of Se against

\textsuperscript{2}The Raman and IR-transmission measurements were performed by Dr. V. Vorlicek, Institute of Physics, Prague.
3.3. LATTICE VIBRATIONAL PROPERTIES

The cation lattice (A$_1$ vibrational mode) in the chalcopyrite structure. Two peaks at 247 and 273 cm$^{-1}$ are attributed to TO and LO phonon modes and correspond to E$^1$ and B$_2^2$ vibrations, respectively. The peak positions are consistent within 3 cm$^{-1}$ to published values of single phase material [51].

The use of a Si substrate also allows the investigation of the vibrational properties with IR transmission because the Si substrate is transparent in this range of wavelengths. Figure 3.4 compares the IR absorption of epitaxial CuGa$_x$Se$_y$ layers with different compositions. Stoichiometric CuGaSe$_2$ shows a small dip at 154 cm$^{-1}$ and distinct dips at 187 and 248 cm$^{-1}$. These E and B modes are related to vibrations of the Ga-Se bonds. The upper two spectra in the figure were recorded from Ga rich compositions. The absorption peaks are wider and small shifts are observed in all peaks, also a new absorption at 220 cm$^{-1}$ is observed.
Figure 3.4: IR absorption was used to investigate the vibrational modes of the Ga-Se bonds (B and E modes). Ga-rich samples show an additional absorption at 220 cm$^{-1}$.

3.4 Photoluminescence properties

The photoluminescence properties of the epitaxial layers were investigated at 10 K with irradiation from a laser diode at 672 nm and at output powers between 0.02 and 20 mW$^3$. Figure 3.5 shows spectra of a typical Ga-rich epitaxial layer. The spectra are dominated by a broad emission peak located at 1.57 eV. The peak energy of this emission shifts to higher energies with increasing excitation power which is typical for donor-acceptor (D-A) transitions. Position and shape is similar to a reported peak at 1.58 eV which is attributed to an electronic transition from a selenium vacancy ($V_{Se}$) to a copper vacancy ($V_{Cu}$) [52, 53]. This transition shows no significant change in shape or position for different Ga rich compositions. Excitonic or deep level

$^3$The PL experiments were performed by Dr. M. Saad, HMI, Berlin.
Figure 3.5: Photoluminescence spectra of an 800 nm thick Ga-rich epitaxial CGS layer on Si(111). The blue shift with higher excitation power is typical for D-A transitions.

related transitions were not observed.

3.5 Microstructural analysis

The microstructural properties of the CGS layers were studied with a Philips CM30 ST transmission electron microscope (TEM) at an acceleration voltage of 300kV\(^4\). For the investigations of the interface to Si samples were cut into stripes and glued into metallic tubes. Small slices were cut from these tubes with a wire saw and mechanically polished to a thickness of 100 \(\mu\)m. In the center these slices were thinned further to 20 \(\mu\)m with a dimple grinder and finally polished in an ion mill.

\(^{4}\)The possibility to use infrastructure and know-how of the Institute of Applied Physics (IAP), ETH Zürich, for TEM investigations is thankfully acknowledged.
Figure 3.6: High resolution TEM image of the interface between CGS and the Si(111) substrate. Twinned regions (a) and dislocations reduce stress in the layer. The boundary of the twinned region along the (112) growth planes is not coherent. Stacking faults (b) extend into the layer.

High resolution micrographs show twins and stacking faults on \{112\} planes at the interface to Si. Strain caused by thermal and lattice mismatch between layer and substrate is partly relaxed by these faults. Figure 3.6 shows an image of the interface region between CGS on Si(111). Twins in epitaxial CGS on Si(111) are frequently observed on \{11\bar{2}\} planes but not on (112) growth planes as it is the case for CuInSe2 on Si(111) [48]. Like twins, stacking faults form on (112) planes and extend from the interface into the layer. The number of twins and stacking faults decreases with the thickness of the layer which explains the better crystal quality of thicker layers.
Chapter 4

Properties of aluminium doped ZnO layers

Aluminium doped ZnO (ZnO:Al) is frequently used as front contact in thin film solar cells with Cu(In,Ga)Se₂ absorbers because it combines good electrical conductivity with high optical transparency. ZnO is a low cost and abundant material, which is easily doped with group III elements for high conductivity. A variety of methods have been used for the deposition of ZnO, such as MOCVD [54], laser ablation [55], spray pyrolysis [56], sol-gel techniques [57], reactive evaporation [58], and sputtering [59].

In this thesis it was found that the front contact of sputter deposited ZnO:Al layers deteriorated during the subsequent growth of an absorber layer. This seriously limited the performance of superstrate solar cells because of a high series resistance. Therefore, the electrical properties of ZnO:Al layers were investigated and the influence of annealing on these properties were studied. This investigation yielded conditions for a high rate deposition of layers whose resistivity increased by less than 20% upon annealing. Additionally, Na which is a constituent of the glass substrate and is essential for the operation of Cu(In,Ga)Se₂ solar cells, was found to have small influence on the electrical properties of ZnO:Al layers.

4.1 Sputtering of ZnO and ZnO:Al layers

The sputter process employs a glow discharge in the pressure range of $10^{-2}$ to 10 Pa. Positive ions of the discharge are accelerated towards the cathode
where they sputter neutral atoms or clusters of atoms. The impact of the ions provides the sputtered material with enough kinetic energy to cross the region of the glow discharge and travel towards a substrate where it sticks and forms the desired layer.

Sputtering processes are distinguished by the kind of electric field which is required to drive the glow discharge. Conducting cathode material can transport the charge which is delivered by the incident positive ions, but insulating material would accumulate the charge and eventually cancel out the applied field. Thus a dc-plasma is suited only for the sputter deposition of metals whereas insulating cathode materials require an ac-driven field for sustaining the discharge process. The rf sputtering process uses a standard operation frequency of 13.65 MHz and is a widely used and established method for the deposition of dielectric and insulating materials.

Intrinsic ZnO layers were deposited from a target of pure ZnO, doped layers from a compound target consisting of ZnO with 2 wt% Al2O3. Both targets have a diameter of 100 mm and a purity of 99.999%. The substrate holder is positioned 40 mm below the targets, it is electrically grounded and equipped with radiation heating up to substrate temperatures of 400°C. All layers are deposited at an argon pressure of 0.3 Pa.

The electrical conduction of pure ZnO is due to intrinsic defects, i.e. oxygen vacancies (Vo) and zinc interstitials (Zn_i) which act as shallow n-type donors [60, 61]. The incorporation of electrically active defects in sputtered ZnO layers depends critically on the sputter parameters. Oxygen depletion of the sputter plasma leads to the deposition of metallic zinc along with zinc oxide. In order to obtain transparent layers, oxygen is added to the sputter gas or the layers are deposited on heated substrates where the free zinc is re-evaporated. However, the use of too much oxygen or too high temperatures prevents the formation of the defect related donors and results in highly resistive layers [62]. Thus, the addition of oxygen needs precise controlling. Heating of the substrate is not always an option, especially if ZnO layers are deposited as front contact on substrate solar cells with a CdS buffer layer because the electrical properties of the p-n junction may suffer from interdiffusion effects.

Another possibility to introduce charge carriers into ZnO is extrinsic doping, for example with group III elements such as such as B, Al, Ga, or In [63, 64]. Annealing experiments up to 400°C showed that ZnO layers doped with indium or aluminium additionally exhibit a thermally more stable con-
4.2. ELECTRICAL PROPERTIES

Figure 4.1: The specific resistivity of Al-doped ZnO layers increases when the substrate temperatures approaches 400°C, irrespective of the sputtering power.

duction mechanism compared to intrinsic ZnO layers. In extrinsically doped layers the resistivity increased by less than one order of magnitude [65, 66], whereas it increased by several orders of magnitude in intrinsic ZnO layers [67]. TCOs with a thermally stable conductivity are particularly desirable for the use in CIGS superstrate solar cells because the absorber layer requires a high deposition temperature.

4.2 Electrical properties of sputtered ZnO:Al layers

Figure 4.1 shows that the resistivity of ZnO:Al layers increases as the substrate temperature approaches 400°C. This behaviour has been attributed to
a thermally activated migration of the aluminium dopant towards the grain boundaries, where it reacts with adsorbed oxygen and forms $\text{Al}_2\text{O}_3$ segregations. Thus the potential barrier for charge transport across the grains is increased which lowers the mobility and increases the resistivity [68].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{znoal.png}
\caption{Grain size and roughness increase with substrate temperature and power density (AFM image size 2×2 μm²).}
\end{figure}

Figure 4.2 presents AFM morphologies of ZnO:Al layers grown under different conditions\footnote{The AFM measurements were performed by Dr. C. Vignali, University of Parma}. The images a) to c) show that grain size and roughness increase with increasing substrate temperature. The layers are less compact
which could also limit the charge transport across the grain boundaries and therefore the mobility. A comparison of images c) and d) shows that higher sputtering power also increases the grain size.

![Figure 4.3: Electrical properties of layers deposited with different rf power densities and substrate temperatures.](image)

The influence of the rf power density on the resistivity is displayed in figure 4.3. At all substrate temperatures the rf power density defines three regimes in the resistivity (I, II, and III); ZnO:Al layers with a resistivity of $9 \times 10^{-4} \ \Omega \text{cm}$ are deposited at low power densities (regime I), at intermediate power density the resistivity of the layers is observed to increase to values between 1.3 and $1.5 \times 10^{-3} \ \Omega \text{cm}$ (regime II). This is also in agreement with
reported data [69]. At still higher power density a second regime for the deposition of layers with a resistivity of $9 \cdot 10^{-4} \, \Omega \text{cm}$ is identified (regime III).

Hall measurements of carrier density and mobility show that the behaviour of the resistivity to a large extent is influenced by the carrier density and only little by the mobility; low resistivity corresponds to high carrier density and vice versa.

The mobility, however, is influenced rather by the temperature than by the power density. Films grown at room temperature have mobilities in the range of 15 to 20 cm$^2$/Vs, at 200°C the mobility is increased to 20 cm$^2$/Vs. At still higher temperatures of 400°C the mobility is decreased to 10 to 15 cm$^2$/Vs which leads to the increased resistivity which is observed in Figure 4.1.

Mobilities in the range of 10 to 30 cm$^2$/Vs are typical for rf sputtered ZnO doped with aluminium [70, 71], gallium [72] and indium [63]. Higher values between 40 and 60 cm$^2$/Vs are obtained on boron doped layers [63, 64].

4.3 Thermal stability of the conduction mechanism

The previous section showed that low resistivity layers are deposited under certain conditions. However, for the superstrate solar cells the initial resistivity is less important than the final resistivity of the TCO in the complete device. In order to simulate the conditions of the growth of an absorber layer the ZnO:Al layers were annealed at 550°C in vacuum. The changes of the electrical parameters after the annealing showed which deposition conditions yield layers with a themally stable conduction mechanism, and only such layers were used for subsequent superstrate solar cell processing.

The validity of this simulation was checked on completed superstrate solar cells. After the removal of the absorber layer the resistivity of the TCO indeed showed the same behaviour like vacuum annealed ZnO:Al layers.

Figure 4.4 shows how the layers grown under different conditions respond to annealing in UHV. The thermal stability of the resistivity is governed almost entirely by the rf power density. At the low rf power (regime I) the resistivity is observed to increase up to 800%. In contrast, highly stable layers with increments of less than 20% are observed in the intermediate range of power densities (regime II). Annealing of layers deposited at high
4.3. THERMAL STABILITY OF THE CONDUCTION MECHANISM

Figure 4.4: Relative changes of the electrical properties after vacuum annealing at 550°C.

power density leads to increments between 40 and 200% (regime III).

The increments of the resistivity are attributable mostly to losses in the carrier density. The mobility is affected by the annealing only in the case of room temperature deposited layers. At low rf power density these layers exhibit a loss of more than 80%, whereas the films grown at high rf power density actually show an increase of the mobility of up to 60%. This increase compensates the effect of the charge carrier loss which leads to the moderate increase in resistivity of 20-40% for layers grown at high power density. Different from the layers grown at room temperature, all the layers deposited at elevated temperatures show a uniform loss in mobility of about 30%.
Figure 4.5: X-ray diffraction in $\theta - 2\theta$ configuration of ZnO:Al films grown at different power densities.

The figures 4.3 and 4.4 show that the electrical properties as well as their relative changes are distinguished by three different regimes of the rf sputtering power; the regimes of low and high rf power density yield layers with low resistivity but their conduction is not thermally stable. The regime of intermediate power density, on the other hand, yields a slightly higher initial resistivity but the resistivity changes only marginally after annealing at 550°C. Eventually the layers of this deposition regime were used for superstrate solar cells. The beneficial effect of a low resistive front contact is displayed in figure 7.1.

The dependence of the electrical properties as well as the thermal stability of the conduction mechanism are explained by the effects of ion bombardment. Impinging ions from the plasma are reported either to damage the growing film [73] or to enhance the surface mobility of adatoms, thereby leading to an improved crystal quality [74, 75, 76]. Exactly this trade-off...
between damaging and beneficial effects of the ion bombardment is reflected in the three regimes of the electrical properties.

At low rf power only little energy is transferred to the substrate by argon ions. Also the energy in the plasma is not sufficient for a complete dissociation of Al₂O₃. Sputtered particles move to the substrate and stay at whatever place they arrive, surface diffusion and reorganization is limited. Thus in the layer small grains and defects like zinc interstitials and oxygen vacancies are formed. The conduction mechanism is governed by a high concentration of donor type intrinsic defects which results in low resistivity. Upon annealing the donor type defects recombine with oxygen which is desorbed from the grain boundaries and that leads to a large increase in the resistivity [67].

At intermediate powers a higher flux and higher energies of argon ions provide enough energy for the dissociation of Al₂O₃ and for the enhancement of surface diffusion of adatoms. Since larger grains with less defects are formed, the conductivity is no longer governed by a high concentration of intrinsic defects but by extrinsic donors (aluminium on the zinc site); thus the resistivity is slightly increased. However, extrinsic donors on substitutional sites show a higher thermal stability than intrinsic donor type defects [66]. Thus the resistivity increases only marginally upon annealing. The obtained improvements in the front contact of superstrate solar cells illustrated in figure 7.1

At high power density the growth rate is high and donor type defects are produced due to impinging ionized species which lower the resistivity. Like in the case of low power density annealing of these layers removes the defect type donors which gives rise to increased resistivity.

Figure 4.5 compares X-ray diffraction measurements on layers grown at different rf power densities. The loss of the preferential [0001] texture in layers grown at high rf power density indicates a change in the growth kinetics. At low energy of the incident ions the grain growth is dominated by the surface with the lowest free surface energy which is the (0001) surface. Grains with other orientations like [10\overline{1}0] and [10\overline{1}1] can only grow if the surface diffusion is facilitated by incident ions with higher kinetic energy [77, 78].

The average grain size determined from the full width at half maximum (FWHM) is approximately 30 nm for layers grow at 1.3 to 2.6 W/cm² and 40 nm at 3.9 W/cm². The width of the (0001) reflection at higher sputtering power has not been evaluated because of the superimposed reflections but it appears to be smaller again.
Table 4.1: Comparison of different glass substrates. The layers are deposited at two different power densities and temperatures. Values of the electrical properties are given in initial (i) and annealed (a) state.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Substrate</th>
<th>Carrier density [10^20 cm⁻³]</th>
<th>Mobility [cm²/Vs]</th>
<th>Resistivity [10⁻³Ωcm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( n_i ) ( n_a ) ( \mu_i ) ( \mu_a ) ( \rho_i ) ( \rho_a )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>Float</td>
<td>2.2</td>
<td>1.7</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Na-free</td>
<td>2.1</td>
<td>1.6</td>
<td>19</td>
</tr>
<tr>
<td>400°C</td>
<td>Float</td>
<td>2.8</td>
<td>1.6</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Na-free</td>
<td>3.4</td>
<td>1.7</td>
<td>17</td>
</tr>
</tbody>
</table>

4.4 Influence of sodium

Thin film solar cells are usually fabricated on low cost Na-containing glass substrates. Na diffuses from the substrate into the absorber layer and in case of Cu(In,Ga)Se₂ absorbers it improves the performance. In ZnO, Na is expected to form an acceptor which compensates the material [79]. Therefore, the influence of Na on the electrical properties of ZnO:Al was investigated by comparing layers grown on Na-containing float glass and Na-free glass.

Table 4.1 shows the resistivity and Hall data of layers grown at room temperature and at 400°C. Samples grown at room temperature show no difference, neither in the as-deposited state nor after annealing. Layers deposited at high temperature show a lower initial resistivity on the Na-free glass which is due to higher mobility as well as carrier density. The increase of the resistivity of high temperature grown samples due to annealing is the same for layers on Na-free and Na-containing glass.

The behaviour suggests that sodium is incorporated into the layer only during growth at high temperatures where it forms an acceptor. The change in resistivity of the high temperature grown layers after annealing in vacuum at 500°C is the same on both types of substrates. This indicates that the increase in resistivity during annealing is not related to incorporation of Na into the film but rather due to the saturation of donor type defects as discussed earlier.
Chapter 5

Solar cell absorber layers

The deposition of the absorber layer is the most important step in the preparation of solar cells. Two major kinds of deposition processes for Cu(In,Ga)Se₂ and CuGaSe₂ are distinguished: These are selenization of precursor layers and co-evaporation. The deposition of precursor layers and the subsequent selenization is suited for large area processing because the individual steps are straightforward and compatible with thin film technology [80]. Co-evaporation of the elements offers a precise control of the source fluxes and generally it results in more homogeneous absorber layers. The operation of pilot plants showed that the process can also be adopted to large area manufacturing [8].

For the superstrate solar cells presented in this work a precise control of the deposition process is particularly important because the initial stage of the deposition forms the p-n junction. Na, which is an important dopant in Cu(In,Ga)Se₂, is incorporated by diffusion from the glass substrate. Unfortunately, the layers of the transparent front contact inhibit the diffusion of Na. Grain size and shape of the absorber layer depend mostly on the Cu-content, the bandgap can be adjusted by the ratio of the group-III elements.

5.1 Influence of the substrate material

Common to all thin film solar cells is the choice of a low cost and abundant material for the transparent conducting oxide (TCO). Doped ZnO is frequently used as front contact in thin film solar cells, in Cu(In,Ga)Se₂ substrate cells it is mostly a double layer of undoped ZnO and aluminum doped
ZnO [81, 82]. In principle, for superstrate solar cells other TCOs can be applied. FTO and ITO have been tried with and without ZnO buffer layers, but the use of ZnO:Al or a ZnO/ZnO:Al double layer emerged as the most promising window layer and was usually used in this thesis.

For Cu(In,Ga)Se₂ solar cells it is of particular interest how the TCO interferes with the diffusion of Na from the substrate into the absorber layer. Na is known to improve the structural properties of the absorber layer and it passivates grain boundary effects. Most important, it is an acceptor and increases the carrier density in Cu(In,Ga)Se₂ [83].

Figure 5.1 compares SIMS (Secondary Ion Mass Spectroscopy) count rates of sodium in Cu(In,Ga)Se₂ layers on different TCOs. The average rates for all other constituents in the absorber layer are summarized in table 5.1. SIMS

\footnote{The SIMS measurements were performed by Dr. G. Bilger, University of Stuttgart}
5.2. MORPHOLOGY AND STRUCTURAL PROPERTIES

Table 5.1: SIMS count rates of the elements of Cl(G)S layers on different substrates. The Na counts are similar for layers on glass and Mo/glass, but in layers on TCO/glass they are lower by orders of magnitude.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>t [nm]</th>
<th>Cu</th>
<th>In</th>
<th>Ga</th>
<th>Se</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>glass</td>
<td>-</td>
<td>1 \cdot 10^6</td>
<td>2 \cdot 10^5</td>
<td>5 \cdot 10^6</td>
<td>4 \cdot 10^4</td>
<td>3 \cdot 10^5</td>
</tr>
<tr>
<td>Mo</td>
<td>500</td>
<td>1 \cdot 10^6</td>
<td>3 \cdot 10^5</td>
<td>7 \cdot 10^6</td>
<td>3 \cdot 10^4</td>
<td>2 \cdot 10^5</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>400</td>
<td>2 \cdot 10^1</td>
<td>-</td>
<td>3 \cdot 10^7</td>
<td>2 \cdot 10^4</td>
<td>5 \cdot 10^3</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>600</td>
<td>1 \cdot 10^5</td>
<td>3 \cdot 10^1</td>
<td>1 \cdot 10^6</td>
<td>1 \cdot 10^4</td>
<td>1 \cdot 10^3</td>
</tr>
<tr>
<td>FTO</td>
<td>300</td>
<td>1 \cdot 10^5</td>
<td>8 \cdot 10^4</td>
<td>1 \cdot 10^6</td>
<td>1 \cdot 10^4</td>
<td>8 \cdot 10^1</td>
</tr>
<tr>
<td>ITO</td>
<td>300</td>
<td>4 \cdot 10^4</td>
<td>1 \cdot 10^5</td>
<td>1 \cdot 10^6</td>
<td>1 \cdot 10^4</td>
<td>1 \cdot 10^2</td>
</tr>
</tbody>
</table>

Count rates are not directly related to the composition of the samples, but they can still give an impression of the content of the elements throughout the samples. The counts for In, Ga, and Se vary within one order of magnitude, Cu by a factor of 30, which is related to differences in composition and to differences in the measurement procedure on metals, TCOs and glass. However, the differences in the counts of Na are much more pronounced and depend on the substrate; the comparison between layers on glass and on Mo shows that the Mo back contact does not notably inhibit the diffusion of Na. The Na count rates in the layers on ZnO are lower by two to three orders of magnitude, depending on the thickness of the ZnO layer. The Na count rates in the layers on FTO and ITO are comparable, compared to ZnO they are yet lower by one order of magnitude. Obviously, all TCO materials are effective barriers for the diffusion of Na from the glass substrate.

An analysis of the junction capacitance showed that the prohibited diffusion of Na into the absorber layer results in a low carrier concentration which seriously limits the performance of the solar cells (see chapter 7).

5.2 Morphology and structural properties

The growth of the absorber layers was usually started at a substrate temperature of 450°C in order to ensure a good coverage of the substrate. During the growth it was ramped up to the desired deposition temperature which was in the range from 550 to 600°C. Figure 5.2 presents morphologies of Cu-
rich and Cu-poor layers grown at 570°C, the layers are easily distinguished by the typical size and shape of the grains.

The composition of the layer has also large impact on the carrier density of the material. Cu-poor layers have low carrier concentration, it can be as low as $10^{12}$ cm$^{-3}$ for Cu(In,Ga)$_3$Se$_5$ layers [17] which is no longer suitable for solar cells. For Cu-rich material the carrier density is in the range of $10^{18}$ cm$^{-3}$, resulting in depletion layer widths which are so small that the performance is limited due to tunnelling [84].

Additionally, in Cu-rich layers segregations of binary Cu$_{2-x}$Se phases are expected from the phase diagrams of CIS and CGS. A KCN treatment is necessary for removing such segregations from the surface, otherwise the devices are shunted. Still, remaining Cu$_{2-x}$Se precipitates within the CIGS grains limit the open circuit voltage [85, 86].

Segregations of binary Cu$_{2-x}$Se phases are undesired because they shunt the devices. Nevertheless, they have a beneficial effect on the grain size because at the growth temperature of the absorber layers Cu$_{2-x}$Se acts as fluxing agent for Cu(In,Ga)Se$_2$ and CuGaSe$_2$. The increased grain size of Cu-rich layers is clearly visible in figure 5.2. This lead to the development of the two stage process which involves a Cu-rich stage for the growth of large grains followed by a Cu-poor growth regime to adjust the overall composition [87]. Figure 5.3 illustrates the beneficial effect of the two stage process on the grain size for two CIGS layers with very similar composition. The behaviour
5.2. MORPHOLOGY AND STRUCTURAL PROPERTIES

Figure 5.3: Morphologies of CIGS layers grown with a “one stage process” (left) and a “two stage process” (right). Both layers show the typical triangular grains of Cu-poor, near stoichiometric layers, however, the grain size is notably different at the same growth temperature.

of binary Cu$_{2-x}$Se phases in CGS layers is very similar.

A further improvement of the solar cell performance was achieved by the three stage process [88]; in a first stage In, Ga, and Se are deposited, followed by the deposition of only Cu and Se to yield a Cu rich layer with large grains. Finally, in the third stage the composition is adjusted by another deposition of In, Ga, and Se. Solar cells with these absorber layers reached efficiencies of up to 18.8%. This is the highest efficiency for any kind of thin film solar cell at this time [27, 4].

X-ray diffraction in the $\theta - 2\theta$ mode was used for the investigation of the crystal quality of the layers and in order to check for the presence of binary phases. Figure 5.4 compares diffractograms of different C(I)GS layers which show strong preferential [112] texture. The intense reflections at higher angles correspond to the (220)/(204) and (312)/(116) doublets. They are resolved only for CGS because the $c/a$ ratio notably differs from 2 ($c/a = 1.97$). In CIS the $c/a$ ratio equals 2.006.

Cu-rich layers are distinguished by an additional reflection which can be attributed to binary Cu$_{2-x}$Se impurity phases. Due to the peak shift of the (112) reflection in material with a high In-content this peak is only visible in CGS layers.
48 CHAPTER 5. SOLAR CELL ABSORBER LAYERS

20 30 40 50 60
Diffraction angle [deg]

Figure 5.4: X-ray diffraction patterns of a slightly group-III rich CuIn0.7Ga0.3Se2 and a Cu-rich CuGaSe2 layer on ZnO/ZnO:Al. The position of the (112) reflection of CGS allows to resolve a reflection at 27.1° which corresponds to binary copper selenide segregations in the Cu-rich material.

5.3 Optical properties

The evaporation from individual sources allows to vary the composition of the layers by adjusting the Ga/(In+Ga) ratio between the values of CuInSe2 (1.04 eV) and CuGaSe2 (1.68 eV). Figure 5.5 shows transmission measurements of absorber layers with different compositions, the corresponding band gaps can be roughly estimated by extrapolating the wavelength of the absorption edge. The figure shows that the band gap also depends on the Cu/(In+Ga) ratio, CuGaSe2 layers have a band gap of approximately 1.9 eV.

Theoretically, the highest photovoltaic energy conversion of a single semiconductor under AM1.5 irradiation is expected for band gaps of 1.4 eV. However, the optimum performance of CIGS thin film solar cells is obtained for
Figure 5.5: Transmission spectra of ZnO and different absorber layers. The different absorption edges of the CIGS layers correspond to different compositions.

Ga/(In+Ga) ratios between 0.2 and 0.3 corresponding to band gaps between 1.15 and 1.25 eV. At higher Ga content the open circuit voltage saturates and lower current densities limit the efficiency [89, 90].
Chapter 6

Characterization of the interface between absorber and window/buffer layer

At the interface between absorber layer and ZnO some degree of structural disorder is expected due to the different crystal properties. Interdiffusion of Cd was reported for superstrate solar cells with CdS buffer layers [33]. The diffusion of Cd and Zn was observed in Cu(In,Ga)Se₂ substrate solar cells with buffer layers of CdS and ZnS, respectively [91, 92].

In this work high resolution transmission electron microscopy (HR-TEM) was used to investigate the influence of different growth procedures on the interfacial properties. The interdiffusion of Cu and Zn across the metallurgical junction was studied with microprobe energy dispersive X-ray spectroscopy (EDS) in the scanning mode of the TEM and with secondary ion mass spectroscopy (SIMS). These chemical analyses could not resolve an interdiffusion of Cu or Zn across the interface but they revealed an unfavourable accumulation of Ga at the interface. Studies with X-ray photoelectron spectroscopy (XPS) showed that the accumulated Ga stems from an interfacial layer consisting of Ga₂O₃.

6.1 TEM investigations

For TEM investigations of the interface samples were prepared in a similar way like the cross section samples of epitaxial layers in chapter 3. The inves-
CHAPTER 6. CHARACTERIZATION OF THE INTERFACE

Figure 6.1: Cross section image of the interface between CGS and ZnO. There are five columnar grains of ZnO overgrown by one single grain of CGS. Under lower magnification the dark contrast in the CGS grain was attributed to two stacking faults rather than a grain boundary. At the interface light areas are distinguished (see arrows).

Investigations showed that the grain structure and the interfacial properties for CGS and CIGS layers on ZnO are very similar. Figure 6.1 shows an overview of the interfacial region between ZnO and CuGaSe$_2$. Typical for room temperature deposited ZnO, the surface roughness is small and the grain size is approximately 30 nm which is in good agreement with the grain size determined by XRD in chapter 4. The size of the CGS grains varies between 500 nm and 1 μm. At the interface an approximately 10 nm thick layer is distinguished by its different contrast. Apart from this region the nucleation of the absorber layer takes place undisturbed by the grain boundaries of the underlying ZnO film.

Figure 6.2 presents a high resolution image of the interfacial region. The
Figure 6.2: High resolution image of the interfacial region. Most of the light area exhibits the lattice spacing of ZnO. The interfacial layer in the upper part of the image shows a layered structure which is neither coherent to the ZnO nor to the CGS layer.

The whole interfacial layer shows a layered structure with a planar spacing of about 4.8 Å. The spacing of the ZnO layers in the [0001] direction is 2.60 Å, the distance between two planes of the CGS layer in the [112] direction is 3.22 Å, thus the interfacial layer is incoherent to both.

In figure 6.1 light areas with a size of about 5 nm are observed whenever a grain boundary of the ZnO meets the interfacial layer. The high resolution image in figure 6.2 shows that the lattice of the ZnO is distinguished almost throughout the light area and it reveals a heavily distorted lattice in the nucleating CGS layer. This could be caused by inclusions or segregations of a different material. The different contrast most probably originates from a different sample thickness which is caused by inhomogeneous etching during the final thinning in the ion polishing system.
Figure 6.3: High resolution image of the interface between Cu(In,Ga)Se₂ and ZnO. The ZnO surface is corrugated due to deposition with high sputter power. The arrows indicate positions of misfit dislocations.

The interface between Cu(In,Ga)Se₂ and ZnO is presented in figure 6.3. The ZnO layer of this sample was prepared at a temperature of 250°C which results in larger grains and a more corrugated surface compared to ZnO grown at room temperature (c.f. chapter 4). The image shows an area where the interface is not perpendicular to the growth direction, thus misfit dislocations mark the region where the growth of the absorber layer started. The observed density of dislocations can account only for approximately one half of the lattice mismatch between Cu(In,Ga)Se₂ and ZnO. The nucleation layer shows a similar disordered region like the interface between CuGaSe₂ and ZnO which indicates similar incompatibilities between the hexagonal ZnO lattice and the tetragonal chalcopyrite structure of the absorber layer.
6.2 Chemical analysis

SIMS is a straightforward and frequently used method for compositional depth profiling of multilayer stacks. Its most serious drawback on polycrystalline material is preferential etching along grain boundaries which leads to inaccuracies, particularly on thick samples. A second problem arises from the different sputtering yields of different elements which cause accumulation at the investigated surface. An upper limit for the accuracy of depth profiles is given by approximately 50 nm.

An alternate method for depth profiling is microprobe EDS in the scanning mode of the TEM on cross section samples. The spot size of the electron beam is approximately 2 nm but the lateral resolutions of the measurement is limited to about 10 nm due to secondary excitation by X-ray fluorescence and drift of the samples in the microscope. SIMS and EDS can provide complementary information and the combination of the two allows a detailed chemical study of the interface.

Figure 6.4 compares SIMS spectra of the interfaces between two different absorber layers and the underlying ZnO layer. Both spectra show an accumulation of Cu at the interfaces. Ga also tends to accumulate at the interface, but more pronounced in case of the group III-rich absorber layer. Also the interfaces differ considerably; the transition from the absorber layer to the ZnO is quite sharp for the group III-rich layer, whereas the Cu- and Ga-signals show a broad overlap with the Zn-signal in the case of the Cu-rich absorber layer.

Figure 6.5 presents EDS linescans across the p-n junction of solar cell structures. The diagrams do not show an accumulation of Cu, whereas the accumulation of Ga is confirmed. Thus, the accumulation of Cu in SIMS measurements is thought to be an artefact of the sputtering process, whereas the EDS linescans clearly show that an accumulation of Ga takes place during the deposition of the absorber layer.

A higher content of Ga in a part of the absorber layer leads to an increased band gap in that region. Accumulation of Ga has been observed frequently as an unintended result of the growth processes and was reported for absorbers prepared by evaporation [93] as well as sequential deposition [94, 95]. In the case of substrate cells the grading promotes the carrier collection and is even intentionally enhanced by the choice of the evaporation flux [96, 97]. For

---

1 The SIMS measurements were performed by Dr. G. Bilger, University of Stuttgart
Figure 6.4: SIMS spectra of the interface between Cu(In,Ga)Se$_2$ and ZnO. The absorber layers deviate slightly from stoichiometry towards group III-rich (left) and the Cu-rich (right) compositions.

superstrate solar cells it is rather detrimental because it forms a barrier which acts against the separation of charge carriers in the space charge region. In order to avoid the accumulation a Ga-depleted step in the initial stage of the growth was introduced. The discussion of the cell characteristics in chapter 7 show that a Ga-depleted layer of 150 nm thickness indeed resulted in a considerable improvement of the solar cell performance. However, the comparison of the EDS linescans in figure 6.5 clearly reveals that the Ga-accumulation is not completely prohibited by the modified growth sequence. It is possible that a more favourable interface is formed between CIS and ZnO which would explain the improvements in cell performance, but figure 6.5 shows that the Ga-depleted step did not yield the expected result of a uniform composition throughout the absorber layer.

The accumulation of Ga seems to stem from an astoundingly strong driv-
6.2. CHEMICAL ANALYSIS

Figure 6.5: EDS linescans across the junction between CIGS and ZnO. The left scan is obtained from a sample which was grown with constant source fluxes, the preparation of the sample corresponding to the right profile was started with a Ga-depleted layer of 150 nm. Both samples show an accumulation of Ga at the interface (upward triangles).

ing force; solar cells where the thickness of the Ga-depleted layer was increased to as much as 1.5 \( \mu m \) still showed the accumulation of Ga at the interface, despite a marginal Ga content in the adjacent region of the absorber layer. Apparently, the mechanism at work can even deplete the adjacent layer in order to accumulate Ga at the interface.

Additional experiments on different substrates showed that the accumulation at the interface occurs also when the CIGS layers are deposited on glass. In contrast to that, on glass coated with a Mo layer an accumulation of Ga is at the detection limit. On glass with a doped SnO\(_2\) front contact it could not be found [98].

In order to learn more about the interfacial layer and its origin a special
Figure 6.6: Ga-LMM XPS depth profiling from the ZnO layer into the absorber. The lowest spectrum corresponds to a measurement through a thin remaining ZnO layer, thus the low intensity. The uppermost spectrum represents the interfacial layer and the remaining spectra are recorded from positions proceeding into the bulk. The chemical shift is observed to change from the oxide level to a bulk level.

superstrate solar cell was prepared. The ZnO:Al was deposited on a water soluble buffer layer, analogous to flexible lift-off solar cells [99]. After removal from the glass the structure was dipped into HCl in order to remove the ZnO. In order to avoid undesired etching in the interfacial region the etching time was carefully chosen to leave a thin layer of ZnO. This process should allow a very accurate depth profiling because the formation of sputtering artifacts should be much lower in comparison to conventional depth profiles through 3 μm of the absorber layer.

Figure 6.6 presents X-ray Photoelectron spectroscopy (XPS) spectra of
6.2. CHEMICAL ANALYSIS

Figure 6.7: A deconvolution of the Ga-2p3 peak into contributions of the oxide and the bulk related shift allows to give a depth profile of the Ga-bonding. At the interface bonding to O prevails, towards the bulk there is a transition to a bulk binding state, presumably the bond to Se.

The Ga-LMM Auger transition\(^2\). As the position of the recording proceeds from the ZnO into the bulk of the absorber layer the binding energy is lowered. In the spectra recorded from positions in the remaining ZnO and in the interfacial layer the chemical shift corresponds to the bond between Ga and O. The energy shift in the bulk is distinctly different and presumably corresponds to the bond between Ga and Se.

This indicates the presence of Ga\(_2\)O\(_3\) at the interface and explains the increased signals of Ga which have been found with SIMS and microprobe EDS measurements.

Figure 6.7 presents the depth profiles extracted from the XPS spectra. It shows that there is a region of approximately 10 to 20 nm thickness where

\(^2\)The XPS measurements were performed by Dr. R. Hauert, EMPA Dübendorf
Ga$_2$O$_3$ forms the major constituent of the structure.

An increased Ga content was reported for substrate solar cells on Mo-coated glass. It is argued that the formation of CIS is preferred over CGS in absorber layers deposited by sequential processes. Thus, in the initial stage of the recrystallization under Se flux CIS is formed at the front while Ga is driven towards the back contact where it forms a more and more Ga-rich material during later stages of the selenization [94].

In Cu(In,Ga)S$_2$ substrate solar cells, where Se is replaced by S, the explanation for a Ga-rich part is exactly opposite [100]: The formation of CuGaS$_2$ should be favoured over CuInS$_2$ when the growth involves Cu-rich material which is thought to be liquid. Thus the Ga-rich material is preferentially grown close to the back contact and only later CuInS$_2$ is formed towards the front.

Apparently, the arguments given for the accumulation of Ga in substrate cells cannot explain the formation of Ga$_2$O$_3$ in superstrate cells. The accumulation was found in the case of constant fluxes and in the case of a Ga-depleted initial step. In the first case the material is group III-rich, in the second case the missing Ga-flux results in a Cu-rich composition which only later becomes group III-rich.

The observations suggest that the accumulation of Ga takes place regardless of the composition of the growing layer. A layer of Ga$_2$O$_3$ has been reported to form on Cu(In,Ga)Se$_2$ in the presence of oxygen at temperatures of approximately 470°C [101]. Possible sources of oxygen in the cases where the accumulation was found are the substrates themselves. In glass the availability of oxygen is obvious. In ZnO oxygen is adsorbed on the grain boundaries. It desorbs at temperatures of about 400°C [65, 102], approximately the temperature where the growth of the absorber layers was started. The absence of the Ga-accumulation on SnO$_2$ and Mo remains to be clarified but compared to the other oxides ZnO has the lowest formation enthalpy. Thus, a reduction of ZnO and the formation of Ga$_2$O$_3$ seems possible.
Chapter 7

Solar cell performance

The most important electrical characterization methods for solar cells are the measurements of the $j-V$ and the $C-V$ characteristics. The $j-V$ characteristics were measured under approximated AM1.5 conditions at room temperature. These measurements were performed routinely on all processed solar cells which offered an immediate feedback, whether changes in the growth process lead to improvements of the efficiency or not. The investigation of the parameters $j_{sc}$, $V_{oc}$, and fill factor allowed to address specific problems like interface properties or the series resistance due to the front contact.

The analysis of the junction capacitance is used to determine the carrier density of the absorber layer. The capacitance of superstrate solar cells indicated low carrier concentrations in the absorber layer. This explains the low open circuit voltages found in $j-V$ measurements.

7.1 Influence of series and parallel resistance

According to eq. (2.2) the $j-V$ characteristics of real cells in high forward bias become linear because of the series resistance. For high values of $R_s$ this asymptotic behaviour becomes already significant at voltages below $V_{oc}$ and lowers the fill factor.

The investigation of ZnO:Al which is presented in chapter 4 shows that the high series resistances in earlier cells were caused by the transparent front contact: Initially, it was deposited with the parameters employed for the contact on substrate cells. This is done at room temperature and low
CHAPTER 7. SOLAR CELL PERFORMANCE

Figure 7.1: Under forward bias the $j - V$ characteristics are dominated by the series resistance $R_s$. The solid and the dotted lines represent superstrate solar cells on different ZnO:Al front contacts, the dashed line corresponds to a superstrate cell on commercially available ITO.

rf power density. However, exactly these conditions result in a very poor thermal stability of the electrical properties as shown in chapter 4.

Figure 7.1 compares $j - V$ characteristics of superstrate cells at various stages of TCO optimization. The cell with the lowest performance had a fill factor of 26% due to a series resistance of 25 $\Omega \text{cm}^2$ (resistance area product). The use of an improved ZnO:Al front contact reduced the series resistance to about 4 $\Omega \text{cm}^2$ which is even lower than the series resistance of a superstrate cell prepared on commercially available ITO.

A necessary requirement for high efficiency solar cells are series resistances below 1 $\Omega \text{cm}^2$ [37]. The resistivity of TCOs can be lowered by the application of metal contact fingers. However, this leads to a trade-off between better conductivity and photocurrent losses due to shadowing.
7.2. INFLUENCE OF THE GROWTH PROCEDURE

Figure 7.2: Current voltage characteristics of solar cells grown with constant fluxes (dashed) and with a Ga-depleted initial step (solid).

In the shown cells the parallel resistance $R_p$ varies between 250 and 500 $\Omega \text{cm}^2$ which is sufficient for reasonable performance.

7.2 Influence of the growth procedure

Initially, the absorber layers were grown without variations in the evaporation fluxes during the deposition time which resulted in efficiencies between 1.5 and 2%. The introduction of a two stage deposition process and changes in the growth temperature resulted in a gradual improvement of the efficiencies to values of about 5% and eventually up to 7% with the use of an improved ZnO:Al front contact. All these superstrate solar cells exhibited a more or less pronounced shoulder in their current voltage characteristics, which is frequently called double diode [103]. The double diode indicates a voltage dependent carrier recombination due to a barrier in the conduction band.
Figure 7.3: Frequency dispersion of the junction capacitance at different bias voltages. The curves represent fits according to the single trap capacitance of eq. (2.11). At different voltages the time constant $\tau$ of the trapping process varies between 1.0 and 1.2 $\mu$s.

[104]. Frequently, the double diode disappears after prolonged illumination which is also called light soaking. Effects of light soaking will be discussed in more detail later in this chapter.

Investigations of the interface between ZnO and the absorber layer in chapter 6 revealed the formation of an interfacial Ga$_2$O$_3$ layer. Due to its low carrier concentration and mobility and its high band gap of 4.6 eV [105] Ga$_2$O$_3$ forms a barrier for the current transport between ZnO and the absorber layer.

In order to avoid this undesired layer at the interface the growth sequence was modified and a Ga-depleted step was introduced. Figure 7.2 shows that this procedure succeeded in inhibiting the formation of the double diode.
7.3 Influence of trap states

The carrier density of the absorber layer has a large impact on the performance of the solar cell. In principle, capacitance measurements offer a straightforward method to determine the carrier concentration, only the measurement is complicated by the presence of series and parallel resistances $R_S$ and $R_P$, respectively. Measurements of the $j-V$ characteristics yield values for $R_S$ between 4 and 25 $\Omega$cm$^2$ and $R_P$ between 250 and 500 $\Omega$cm$^2$. This limits the measurements of the capacitance to the frequency range between 40 and 400 kHz, assuming a junction capacitance in the order of $10^{-8}$ Fcm$^{-2}$.

The measurements are complicated further by the influence of trap states. They cause a significant frequency dispersion in the capacitance and the

---

**Figure 7.4**: Trap levels give rise to a junction conductance. The data points were fitted according to the conductance dispersion of eq. (2.12). Due to the superimposed dc-conductance of the junction the measurement is complicated and trapping time constants between 1 and 4 $\mu$s had to be assumed.
conductance of the junction as shown in figures 7.3 and 7.4, respectively. Theoretical fit curves according to the frequency dispersion of eqns. (2.11) and (2.12) are added in the figures. The model with a deep trap state in the band gap seems to fit well to the recorded capacitance and conductance data. However, charging and discharging of states at the interface yield exactly the same frequency dependence and could also be used to explain the dispersion [44, 45]. In this case the difference between the capacitance at low and high frequency gives an estimate of the interface state density. According to eq. (2.13) it is in the range of $10^9 \text{ cm}^{-2}$ which is roughly in agreement with reported data [45].

An investigation of the dispersion at different voltages can be used to decide which of the two models is applicable. In the case of interface states the inflection point of the dispersion curves depends on the position of the trap level relative to the Fermi level at the interface. An applied bias shifts the Fermi level and therefore changes the position of the inflection point [106]. Only at a very high density of interface states the bias dependence of the inflection point is lost due to Fermi level pinning at the interface [107]. An analysis of the data shown in figures 7.3 and 7.4 does not show a consistent change of the inflection point with applied bias. This favours the model of trap levels in the band gap but due to the limited frequency resolution of the measurement equipment it cannot definitely be distinguished.

### 7.4 Carrier density analysis

Figure 7.5 compares $C - V$ characteristics of two typical superstrate solar cells. A substrate solar cell is included for comparison; low capacitance is observed in group III-rich absorbers. The capacitance is increased in a cell with near stoichiometric Cu(In,Ga)Se$_2$ layer, but it is still low compared to the substrate solar cell.

Figure 7.5 includes the trap related capacitance for one of the cells. It has been estimated according to eqns. (2.11) and (2.12). Based on figures 7.3 and 7.4 a time constant of the trapping process of 2 $\mu$s was assumed. The figure illustrates that the trap related capacitance increases considerably for bias voltages between -1 and 0 V.

Thus, the measurement of the capacitance for the carrier density analysis was restricted to the range of high reverse bias between -2 and -1 V. With the carrier densities from this range the junction capacitance has been
7.4. CARRIER DENSITY ANALYSIS

Figure 7.5: C-V characteristics of different solar cells. Cells (A) and (B) are superstrate solar cells with different compositions, cell (C) is a substrate solar cell for comparison. The dotted curve (D) corresponds to the trap related capacitance of cell (B). The solid lines represent the calculated capacitance according to the Anderson model.

extrapolated according to eq 2.7. Figure 7.5 compares the measured capacitance with the simulations for three typical cells. Between -1 and 0 V the superstrate cells (A) and (B) deviate from the model. Good agreement is observed for the substrate cell (C) because of a much better junction.

The carrier densities of the three representative cells (A), (B), and (C) are listed in table 7.1, together with data of the solar cell performance. The correlation between open circuit voltage and carrier density is explained by the current transport models (see chapter 2). For diffusion and recombination dominated transport a change in the carrier density of one order of magnitude changes the $V_{oc}$ by approximately 60 mV [84]. Cell (A) has a very low carrier concentration because the absorber layer consists of Cu-poor material.
Table 7.1: Parameters of the investigated solar cells in the initial state (i) and after light soaking (ls). The carrier density was always measured in darkness, cell C was not subjected to light soaking.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{oc}$ [mV]</th>
<th>$J_{sc}$ [mA/cm²]</th>
<th>Efficiency [%]</th>
<th>Carrier Density [$10^{15}$ cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>i</td>
<td>ls</td>
<td>i</td>
<td>ls</td>
</tr>
<tr>
<td>(A)</td>
<td>340</td>
<td>430</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>(B)</td>
<td>490</td>
<td>530</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>(C)</td>
<td>620</td>
<td>33</td>
<td>11.1</td>
<td>20.7</td>
</tr>
</tbody>
</table>

However, the absorbers in cells (B) and (C) are close to stoichiometry but the carrier densities still differ by one order of magnitude.

In chapter 5 it was shown that the TCO front contacts act as effective barriers against the diffusion of Na from the glass. The differences in carrier concentration between superstrate and substrate solar cells despite comparable compositions of the CIGS layers support the idea that the prohibited incorporation of Na leads to a low concentration of acceptors which in turn is responsible for the poor open circuit voltage of superstrate solar cells.

### 7.5 Light soaking

Figure 7.6 shows the response of Cu(In,Ga)Se$_2$ and CuGaSe$_2$ superstrate solar cells to light soaking; usually the open circuit voltage increases and on some cells short circuit current density decreases. The shown Cu(In,Ga)Se$_2$ cell with the modified absorber layer growth does not show the double diode (c.f. figure 7.2), but still the open circuit voltage and fill factor increases. Typical changes of Cu(In,Ga)Se$_2$ solar cells are summarized in table 7.1, CuGaSe$_2$ cells have not been subjected to capacitance measurements.

The changes of the performance of superstrate solar cells were attributed to the saturation of trap levels in the ZnO layer or at the interface [89, 108]. In order to investigate the influence of light soaking on the carrier density of superstrate solar cells, the following sequence of $C-V$ measurements was performed: The cells were kept in darkness for several days and measured in this relaxed state. Then, they were exposed to light for 30 minutes. Im-
mediately after the illumination they were put to dark again and measured repeatedly until the $C-V$ characteristic relaxed to the initial state. Between the measurements the cells were kept under open circuit conditions.

Changes in carrier density due to the light soaking are shown in figure 7.7. The bias range where little influence of trap states is expected is indicated by linear fit curves. The carrier density is $7 \cdot 10^{15}$ cm$^{-3}$ in the relaxed state and increases to $2 \cdot 10^{16}$ cm$^{-3}$ after the illumination. The increase is accompanied by a decrease of the depletion layer width. After three minutes in darkness the carrier density decreased to $1 \cdot 10^{16}$ cm$^{-3}$ and within 60 minutes it relaxed to the initial value. This effect of light soaking is fully reversible.

The beneficial effect of light soaking was also observed in substrate solar cells. There the explanation of the effect is based on the saturation of deep
Figure 7.7: Capacitance voltage characteristics during a light soaking sequence. The smaller slope is related to an increased carrier density due to the saturation of trap states. In darkness it gradually relaxes to its initial values.

trap levels, but two mechanisms are distinguished; the first one takes place in the buffer layer, the other in the absorber [84, 109]. The light induced saturation of deep electron traps in CdS is thought to increase the positive charge and the density of electrons in the window layer (blue-illumination effect). Consequently, the built in potential and the depletion layer width are increased [103].

The second light soaking effect saturates hole traps in the absorber layer (red-illumination effect). This increases the negative charge and the number of free holes. Consequently, the built in potential is increased and the space charge width decreases. In $C - V$ measurements it was clearly visible that the capacitance increased after light soaking. In dark it gradually relaxed to the initial values.
Figure 7.8: Comparison of cross sections of Cu(In,Ga)S\(_2\) substrate (left) and superstrate (right) solar cells. In substrate solar cells the p-n junction is in a region where large grains dominate (a), whereas in superstrate solar cells it is formed between ZnO and the nucleation region of the absorber (b).

Thus, the decrease of the short current density and the increase of the open circuit voltage which is displayed in figure 7.6 is explained as follows: Traps are saturated due to the illumination and the carrier density increases. Consequently, the open circuit voltage increases. The reduction of the current density is a result of the small diffusion length of electrons; carriers created more than a diffusion length away from the space charge region no longer contribute to the photocurrent [110]. As the depletion layer shrinks due to higher carrier concentration fewer carriers from deep inside the bulk contribute to the photocurrent.

These observations clearly favour the second light soak model. Saturation of trap levels in the absorber increases the free carrier concentration and lowers the depletion layer width.

The different amount of trap levels in substrate and superstrate solar cells is explained by the different configurations. Figure 7.8 compares cross section images of superstrate and substrate solar cells. It is clearly visible that the nucleation of the absorber layer takes place very much in the same way on ZnO and Mo; many small grains nucleate and eventually some grains with a preferred orientation dominate.
In substrate solar cells the p-n junction is formed between large grains and
the n-type material. Contrary to that, in superstrate cells, the junction is
formed between ZnO and the small grains of the nucleation region. Thus, the
influence of recombination centres should have larger impact on superstrate
rather than on substrate cells. The performance data of the best superstrate
solar cells obtained in this thesis are summarized in table 7.2.

Table 7.2: Parameters of the best CuGaSe₂ and Cu(In,Ga)Se₂ superstrate
cells. The entries indicate values in the initial stage (i) and after light soaking
(ls).

<table>
<thead>
<tr>
<th>Absorber</th>
<th>( V_{oc} ) [mV]</th>
<th>( j_{sc} ) [mA/cm²]</th>
<th>fill factor [%]</th>
<th>( \eta ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuGaSe₂</td>
<td>525</td>
<td>745</td>
<td>16</td>
<td>9</td>
</tr>
<tr>
<td>Cu(In,Ga)Se₂</td>
<td>265</td>
<td>440</td>
<td>36</td>
<td>34</td>
</tr>
</tbody>
</table>
Chapter 8
Conclusions and outlook

In this thesis the properties of epitaxial layers of CuGa_xSe_y deposited on silicon and the development of superstrate solar cells based on Cu(In,Ga)Se_2 are presented.

Molecular beam epitaxy was successfully used to prepare hetero-epitaxial layers of CuGaSe_2 on Si(111) substrates despite a large mismatch of the thermal expansion coefficient and the lattice parameters. Different Ga-rich compositions were grown epitaxially, while Cu-rich layers were polycrystalline and showed bad adhesion to the substrate. The lattice vibrational properties of the epitaxial layers are in good agreement with reported bulk properties. Photoluminescence experiments showed a broad donor-acceptor transition due to the presence of copper and selenium vacancies.

Polycrystalline superstrate solar cells were formed by the combination of sputter deposited n-type ZnO/ZnO:Al window layers and evaporated p-type Cu(In,Ga)Se_2 absorbers. Light conversion efficiencies of up to 9.5% were achieved by several improvements of the growth processes and the interface properties:

- The rf magnetron deposition process of the Al-doped ZnO front contact layer was developed for high thermal stability of the electrical conduction mechanism. Initially only ZnO:Al layers with a low thermal stability of the conductivity were available. During the growth of the absorber layer at 550°C losses in carrier density and mobility increased the resistivity by up to 800%, resulting in high series resistance and poor fill factor of the completed solar cells. A systematic investigation of the sputtering conditions identified parameters for the deposition of
ZnO:Al layers with high growth rate and a thermally stable conduction mechanism. In these layers the remaining increase in resistivity during absorber layer growth amounts to less than 25%.

The achieved improvements of the ZnO:Al layers resulted in a resistivity which stabilizes at $1.5 \times 10^{-3}$ Ωcm. Thus, a rather thick layer is required for a low resistance of the front contact which results in optical transmission losses. Therefore, future developments of the doped ZnO layer should be directed towards lower specific resistivity. In order to maintain a high transmission in the near IR region an increase of the free carrier density is not advantageous. Rather, the mobility should be increased, either by an improved crystal quality [111], by doping with B instead of Al [33] or by using the potential of layered stacks [112].

- An investigation of the interface between ZnO and the Cu(In,Ga)Se$_2$ absorber layer with transmission electron microscopy showed little interdiffusion of Zn or Cu across the interface. However, it revealed an accumulation of Ga. X-ray photoelectron spectroscopy showed that it is due to the formation of a thin layer of Ga$_2$O$_3$ which has a detrimental effect on the photovoltaic performance. Changes in the growth process successfully reduced the accumulation, unfortunately it was not possible to completely avoid it. Nevertheless, a limitation of the fill factor, the so called double diode, disappeared with the modified process. This lead to a substantial improvement of the diode characteristics and the solar cell efficiency.

Additional investigations of the interface should clarify the origin of the Ga$_2$O$_3$ formation. If it is due to a reaction with oxygen adsorbed at the grain boundaries of ZnO it would be desirable to know whether oxygen can be desorbed from ZnO before the absorber deposition, e.g. by annealing in vacuum. The inclusion of oxygen free buffer layers to the structure is also an interesting option. Therefore, materials like ZnS or ZnSe should be investigated. Such layers could have the additional benefit of a better matching to the structural and electrical properties of the Cu(In,Ga)Se$_2$ layer.

- A basic limitation of the solar cell performance was identified, which is related to the carrier density of the absorber layers. Na, which diffuses from the glass substrate into the absorber layer, increases the effective
carrier concentration in Cu(In,Ga)Se₂. SIMS measurements showed that the content of Na in the absorber layer of superstrate solar cells is lower by several orders of magnitude compared to substrate solar cells on Mo-coated glass. This is due to the different diffusion properties of Na in Mo compared to transparent conducting oxides.

For future improvements it is essential to increase the carrier concentration of the absorber layers because it determines the open circuit voltage of the solar cells. This can be achieved either by the deposition of Na-containing precursor layers [83] or by co-evaporation of such materials during the growth [113].

The development of superstrate solar cells which is presented in this thesis lead to high efficiencies of up to 9.5%. In addition to the achieved progress it was possible to identify factors which limit the efficiency of the superstrate configuration. With further work it should be possible to improve the performance of this interesting solar cell and to exploit its promising technological advantages for the production of low cost solar cells.
Bibliography


## Symbols and abbreviations


<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Diode quality factor</td>
</tr>
<tr>
<td>$a, c$</td>
<td>Lattice constants</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacitance with respect to area</td>
</tr>
<tr>
<td>$D_n$</td>
<td>Diffusion constant of electrons</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band gap</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Dielectric constant</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Dielectric permittivity of free space</td>
</tr>
<tr>
<td>$\Phi_b^p$</td>
<td>Interface barrier for holes</td>
</tr>
<tr>
<td>$\Phi_b^e$</td>
<td>Interface barrier for electrons</td>
</tr>
<tr>
<td>$j$</td>
<td>Current density</td>
</tr>
<tr>
<td>$j_{00}$</td>
<td>Current density prefactor</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of the incident light</td>
</tr>
<tr>
<td>$L_D$</td>
<td>Diffusion length</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Electrical mobility of charge carriers</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Density of acceptors</td>
</tr>
<tr>
<td>$N_D$</td>
<td>Density of donors</td>
</tr>
<tr>
<td>$N_C$</td>
<td>Effective density of states in the conduction band</td>
</tr>
<tr>
<td>$N_V$</td>
<td>Effective density of states in the valence band</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
</tr>
<tr>
<td>$R_{S, P}$</td>
<td>Series and parallel resistance area products</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Specific resistivity</td>
</tr>
<tr>
<td>$q$</td>
<td>Elementary charge</td>
</tr>
<tr>
<td>$S_P$</td>
<td>Interface recombination velocity</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Transition time of trapping</td>
</tr>
<tr>
<td>$V$</td>
<td>Applied bias voltage</td>
</tr>
<tr>
<td>$w$</td>
<td>Depletion layer width</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>a-Si</td>
<td>amorphous silicon</td>
</tr>
<tr>
<td>c-Si</td>
<td>crystalline silicon</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AM</td>
<td>Air Mass (for solar spectral irradiation)</td>
</tr>
<tr>
<td>CGS</td>
<td>CuGaSe₂</td>
</tr>
<tr>
<td>CIGS</td>
<td>Cu(In,Ga)Se₂</td>
</tr>
<tr>
<td>CIS</td>
<td>CuInSe₂</td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction Band Minimum</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine doped Tin Oxide</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum (of XRD reflection peaks)</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>LO</td>
<td>Longitudinal Optical (vibration mode)</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>PL</td>
<td>Photo Luminescence</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford Back Scattering</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency (for sputter processes)</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection High Energy Electron Diffraction</td>
</tr>
<tr>
<td>SCR</td>
<td>Space Charge Region</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SMS</td>
<td>Secondary Ion Mass Spectroscopy</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent Conducting Oxide</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TO</td>
<td>Transverse Optical (vibration mode)</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence Band Maximum</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
Acknowledgements

I would like to express my gratitude to Prof. Dr. Gernot Kostorz for agreeing to become my “adoptive” doctor father and to Prof. Dr. Martha-Christine Lux-Steiner for taking the efforts of an external co-examiner.

My thank goes also to Prof. Dr. Hans Melchior and Prof. Dr. Hans-Rudolf Ott for accepting the Thin Film Physics Group in their institutes.

I am grateful to PD Dr. Hans Zogg, head of the Thin Film Physics Group, for offering me a position in his group and for many helpful discussions.

I am very much indebted to Dr. Ayodhya Nath Tiwari for his continuous encouragement. This thesis was made possible due to his skills of fund raising and project management and, what’s more, to his profound knowledge of solar cells. Thank you for the frequent discussions in our office, admittedly, some of them were a bit off-topic.

Special thanks go to my fellow group members, former and present, who took part in my work by creating an unique and encouraging atmosphere: Dr. Joachim John, Dr. Yordan Athanassov, Dr. Qun Lai, Dr. Silke Schöen, Dr. Martin Krejci, Karim Alchalabi, Alessandro Romeo, Derk Bätzner, Dominik Rudmann, Dmitri Zimin, Marc Kaelin, Klaus Kellerman, Thomas Werner, Michael Leopold, Thomas Kämpfer, Gerhard Schreiber, and Paulette Pfammatter. I may add Mathias Terheggen, my link to the Institute of Applied Physics. I particularly appreciated the social life organised by Joachim and the late (and all-) night events with Martin, Karim and Mathias.

I am also very grateful for the possibility to conduct this work within the Wide Gap CPV and Flexis Projects of the European Union. All the people involved in these collaborations were very generous with their support and hospitality whenever I visited them at their institutes.

I would like to express my thanks to my friends, most of all to Stefanie. Without their permanent encouragement it would not have been possible!
Publications


Curriculum Vitae

Name: Franz-Josef Haug
Adress: Hofwiesenstrasse 235
        8057 Zürich/Switzerland
Date of Birth: September, 27th, 1969
Place of Birth: Oberstdorf, Germany
Nationality: German

1976 - 1980 Grundschule Oberstdorf
1980 - 1989 Gymnasium Oberstdorf
1990 - 1996 Study of Physics
        University of Ulm, Germany
        University of Waikato, Hamilton, New Zealand
        Diplomarbeit: Scanning Tunneling Microscopy of
        Epitaxial Layers on Silicon
        Graduation as Dipl. Phys.
1996 - 1997 Teaching Assistant in the
        Institute of Microwave Technology, University of Ulm
        Training at MHH Solartechnik GmbH, Ulm
1997 - 2001 Doctoral Study at the
        Swiss Federal Institute of Technology (ETH), Zürich
2001 Young Scientist Award (Symposium P) of the
        European Materials Research Society