Preparation and Characterization of Heteroepitaxial CuIn$_x$Se$_y$ Layers and Cu(In,Ga)Se$_2$ Substrate Solar Cells

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SUMMARY

Cu-In-Ga-Se is used as an absorber layer in high efficiency thin film solar cells. In this thesis CuIn$_x$Se$_y$, CuGaSe$_2$ and Cu(In,Ga)Se$_2$ layers are studied. The growth of epitaxial CuIn$_x$Se$_y$ layers, their crystal quality and the microstructure of the layers and interfaces are described. A process for the preparation of Cu(In,Ga)Se$_2$ substrate solar cells and a microstructural characterization of the CdS/CuGaSe$_2$ interfacial region are presented.

Epitaxial CuIn$_x$Se$_y$ layers were grown by molecular beam epitaxy (MBE) on Si(111) and GaAs(001) substrates. In-situ monitoring of the growth by reflection high energy electron diffraction (RHEED) showed that the layers predominantly grow by the formation of islands (3-d growth). Streaky RHEED patterns of CuIn$_x$Se$_y$ deposited at high substrate temperatures indicated a smooth surface. The compositions of the epitaxial layers were measured by Rutherford backscattering spectroscopy (RBS) and ranged from slightly Cu-rich CuInSe$_2$ to CuIn$_3$Se$_5$. Infrared absorption, Raman scattering and x-ray diffraction (XRD) measurements were performed on CuIn$_x$Se$_y$/Si(111) samples to distinguish different phases. Single phase layers had the compositions of CuInSe$_2$ (α-phase), CuIn$_3$Se$_5$ (β-phase) and CuIn$_{2.5}$Se$_4$. Other epitaxial layers (e.g. CuIn$_{1.6}$Se$_{2.9}$) consisted of two or more ternary CuIn$_x$Se$_y$ phases.

Electron channeling patterns of CuIn$_x$Se$_y$ layers grown at high substrate temperatures exhibit sharp and clear Kikuchi lines indicating a good crystal quality. Three-fold symmetry of CuIn$_x$Se$_y$/Si(111) patterns gave evidence of no or only little twinning. Diffuse channeling patterns of CuIn$_x$Se$_y$/GaAs(001) were related to a high density of stacking faults and nanotwins. RBS ion channeling experiments of
CuIn\textsubscript{x}Se\textsubscript{y}/Si(111) layers with different compositions resulted in minimum channeling yield ($\chi_{\text{min}}$) values of 7-13\% indicating the growth of "good" crystal quality layers.

Planar defects were characterized by transmission electron microscopy (TEM). Stacking faults and nanotwins were observed on \{112\} planes. Rotational twins form in CuIn\textsubscript{x}Se\textsubscript{y}/Si(111) layers. Six twin variants rotated by $\pm 120^\circ$, $\pm 60^\circ$ and $180^\circ$ about the [221] growth direction were identified. Coherent twin boundaries as well as partly coherent boundaries of twin variants rotated by $\pm 60^\circ$ and $180^\circ$ were imaged by high resolution TEM (HRTEM). The boundaries can be formed by inserting partial dislocations with Burgers vectors $\frac{a}{6}(11\bar{1})$ into the CuIn\textsubscript{x}Se\textsubscript{y} structure. This suggests that the annealing of the samples induces the annihilation of these partial dislocations and consequently reduces the density of twins in the CuIn\textsubscript{x}Se\textsubscript{y} layers.

High resolution TEM of the interfacial regions revealed a high density of planar defects near the layer-substrate interface. Misfit dislocations split into two Shockley partial dislocations which create extended stacking faults by gliding on \{112\} planes. Microprobe energy dispersive x-ray (EDX) analysis and RBS showed that an about 6 nm thick CuSe\textsubscript{x}Si\textsubscript{y} layer is formed at the interface of CuIn\textsubscript{x}Se\textsubscript{y}/Si(111) owing to interdiffusion of Cu and Se. For CuIn\textsubscript{x}Se\textsubscript{y}/GaAs(001) diffusion of Ga into the layer was observed. X-ray $\Theta - 2\Theta$ diffractographs showed that Ga is incorporated in the lattice and a CuIn\textsubscript{x}Ga\textsubscript{y}Se\textsubscript{z} compound is formed.

A process for the preparation of Cu(In,Ga)Se\textsubscript{2} substrate solar cells was established. The Cu(In,Ga)Se\textsubscript{2} absorber layers were deposited by the co-evaporation of the elements on Mo-coated sodium-containing glass. The growth parameters were adjusted in such a way that a Cu-depleted surface was formed. A 30-60 nm thick n-type CdS buffer layer was deposited on top of the absorber layer by a chemical bath deposition. The window layer, a stack of ZnO and Al-doped ZnO is used as the transparent front contact. These layers were deposited by rf sputtering having an
optical transparency of about 90% and a sheet resistance\(^1\) of less than 20 \(\Omega_{\square}\). Using this process solar cells with efficiencies up to 16% were prepared.

The microstructure of the CdS/CuGaSe\(_2\) interface region in Cu-rich CuGaSe\(_2\)-based wide band gap solar cells was characterized. Coherent Cu-Se precipitates were observed in the grains of the absorber layer. The formation of these precipitates seems to be a principal limitation for the performance of Cu-rich CuGaSe\(_2\)-based thin film solar cells. The interaction of the CdS buffer layer with the absorber layer surface depends on the temperature of the deposition bath. For bath temperatures of 80°C the interaction is much stronger and Cu-S inclusions are found in the buffer layer. These inclusions may be responsible for shunts across the p-n junction. There are no Cu-S inclusions in CdS deposited at 60°C. The microstructure the CdS layer depends on the the bath temperature and the growth orientation of the CuGaSe\(_2\) grains. CdS(80°C) crystallizes predominantly in the zincblende structure and contains less linear defects whereas CdS(60°C) tends to incorporate hexagonal regions in the cubic matrix. The investigations showed that “an optimum” CdS buffer layer for the Cu-rich CuGaSe\(_2\) absorber layers could not be obtained by CBD because of either the low crystal quality (CdS(60°C)) or the formation of Cu-S inclusions (CdS(80°C)).

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\(^1\) sheet resistance = (specific resistivity)/(thickness of layer).
ZUSAMMENFASSUNG

Cu-In-Ga-Se-Verbindungen werden für die Absorberschicht von Dünnschichtsolarzellen verwendet. In der vorliegenden Arbeit wurden CuInₓSeᵧ-, CuGaSe₂- und Cu(In,Ga)Se₂-Schichten untersucht. Wachstum und mikrostrukturelle Charakterisierung von epitaktisch auf Si(111) und GaAs(001) gewachsenen CuInₓSeᵧ Schichten werden beschrieben. Ferner wird ein Prozess für die Präparation von Cu(In,Ga)Se₂-Substratzellen vorgestellt, und die chemischen und mikrostrukturellen Eigenschaften von CdS/CuGaSe₂-Grenzschichten werden aufgezeigt.

Epitaktische CuInₓSeᵧ-Schichten wurden mittels Molekularstrahlepitaxie (MBE) auf Si(111)- und GaAs(001)-Substraten gewachsen. Das Wachstum wurde mittels Beugungsbildern hochenergetischer Elektronen (RHEED) verfolgt. Die Beugungsmuster zeigen, dass vorwiegend Inselwachstum vorliegt. Die Zusammensetzung der Schichten, bestimmt mit Hilfe der Rutherfordrückstreuspektroskopie (RBS), variierte zwischen leicht Cu-reichem CuInSe₂ und CuIn₃Se₅. Infrarotspektroskopie, Ramanstreuung und Röntgenbeugung dienten dazu, einzelne Phasen zu unterscheiden. Einphasige Schichten hatten die Zusammensetzungen CuInSe₂, CuIn₂,₅Se₄ und CuIn₃Se₅.

Scharfe Kikuchilinien in Elektronenchannelingmustern und Halbwertsbreiten von Rockingkurven der epitaktischen Schichten, die bei hohen Substrattemperaturen gewachsen wurden, deuten auf eine gute Kristallqualität hin. Die dreizählige Symmetrie in Channelingmustern von auf Si(111) gewachsenen Proben zeigte von unverzwillingten oder nur leicht verzwillingten Schichten. RBS-channeling (χₘᵢₙ) - Werte, gemessen mit Ionenchanneling an CuInₓSeᵧ/Si(111)-Proben mit verschiedenen Zusammensetzungen, lagen zwischen 7 und 13%. Dies deutet auf eine gute kristalline
Qualität der Schichten hin.

Die Transmissionselektronenmikroskopie (TEM) wurde unter anderem dazu verwendet, planare Defekte in den epitaktischen Schichten zu untersuchen. Stapelfehler und Nanozwillinge wurden in {112}-Ebenen gefunden. Ein besonderes Interesse galt Rotationszwillingen, die sich in CuInxSex/Si(111) Schichten an (112)-Wachstums-ebenen bilden. Die sechs verschiedenen Zwillingsvarianten können über Drehungen um ±60°, ±120° oder 180° um die [221]-Wachstumsrichtung ineinander übergeführt werden. Die kohärenten Zwillingsgrenzen sowie teilweise kohärente Grenzen zwischen 60°/180°-Zwillingen wurden mit hochauflösender Transmissionselektronenmikroskopie (HRTEM) abgebildet. Die Grenzen können gebildet werden, indem Partialversetzungen mit Burgersvektoren vom Typ \( \frac{2}{6}(11\bar{1}) \) in das perfekte Gitter eingefügt werden. Deshalb wird vermutet, dass beim Auslagern der Proben die Zwillingsdichte über Vernichtungsreaktionen zwischen diesen Versetzungen reduziert wird.

HRTEM-Untersuchungen von Grenzregionen wiesen eine hohe Defektdichte in Substratnähe auf. Fehlpassungsversetzungen spalten sich in Shockley-Partialversetzungen auf, die dann in {112}-Ebenen gleiten und ausgedehnte Stapelfehler hervorrufen. Eine etwa 6 nm dicke CuSe_{x}Si_{y}-Schicht wurde mittels energiedispersiven Röntgenfluoreszenz- (EDX) wie auch RBS-Untersuchungen an der CuInxSex/Si(111)-Grenzfläche nachgewiesen und mit der Diffusion von Cu und Se in Verbindung gebracht. Für CuInxSex/GaAs(001) wurde mit EDX die Diffusion von Cu und vor allem Ga beobachtet. Röntgenbeugung zeigt, dass sich aufgrund der Diffusion von Ga quaternäre CuInxGaySez-Verbindungen in den Schichten bilden.

Ein Verfahren für die Präparation von Cu(In, Ga)Se_{2}-Substratzellen wurde entwickelt. Die Cu(In, Ga)Se_{2}-Absorberschicht wurde mittels Koverdampfen der Elemente auf Mo-beschichtetes Glas aufgebracht. Die Wachstumsparameter wurden so eingestellt, dass eine kupferverarmte Oberfläche entstand. Die CdS-Pufferschicht wurde im chemischen Bad bei verschiedenen Badtemperaturen abgeschieden. Als Fensterschicht wurde ZnO und Al-dotiertes ZnO auf die Pufferschicht rf-gesputtert.
Die Transparenz betrug etwa 90% bei einem Flächenwiderstand\(^2\) von weniger als 20 Ω\(_{\text{cm}}\).


\(^2\) Flächenwiderstand = (Spezifischer Widerstand)/(Schichtdicke).
Chapter 1

INTRODUCTION

1.1 Cu(In,Ga)Se₂-Based Thin Film Solar Cells

Since the environmental and energy resource concerns have increased in the last years, renewable energy sources such as solar cells have become more important. Although the photovoltaic contribution to the world’s energy demand is still negligible, solar cells have the potential to cover a notable share of the worldwide energy production. The total power of the modules sold worldwide increased within the last ten years from about 30 MW_p \(^1\) to 120 MW_p, and the tendency shows an exponential yearly growth of 15-20% [Sch98]. It is expected that in the year 2010 the number of sold modules will reach 4500 MW_p, and that photovoltaic modules with an overall capacity of 16700 MW_p will be installed worldwide [oE96].

Until now most of the commercially available photovoltaic modules are made of crystalline silicon. The production of mono- and polycrystalline silicon solar cells is very well established because it is closely related to the production processes used for microelectronic devices. However, the high production costs related to the complex manufacturing procedure, high purity requirements for Si wafers and the necessity of about 250-300 μm thick wafers for the absorption of the sun light, have limited a wide application of conventional Si cells.

Thin film solar cells are a valuable alternative to the conventional Si solar cells since they have the potential for the production of cheap solar electricity. In thin film solar cells absorber layers as thin as about 2 μm are sufficient for the absorption

\(^1\) 1 MW_p=1 MW at standard test conditions [Com89].
the visible part of the light, because they are characterized by a high absorption coefficient. The requirement of less material and advantages of thin film deposition processes to grow layers over large areas are responsible for low production costs and a short energy payback time (2-5 months). The most common thin film solar cells are amorphous silicon (a-Si), dye sensitized TiO₂, CdTe and the Cu(In,Ga)(Se,S) solar cells. An overview of the different technologies and the status (1997) of photovoltaic thin film technologies can be found in [SS97, THZ98].

CuInSe₂, CuGaSe₂ and Cu(In,Ga)Se₂ are attractive p-type semiconductors for absorber layers in thin film solar cells because of their band gaps (1.01-1.67 eV) near the optimum of 1.5 eV and their high absorption coefficients (10⁵ cm⁻¹). Starting in 1970, the continual development of the processes used for the preparation of CuInSe₂-based solar cells resulted in highest efficiencies of 15.4% [JOB+93] obtained with CdS/CuInSe₂ heterojunctions. Problems of the CuInSe₂-based solar cells are their low open circuit voltage (less than about 550 mV) due to the low band gap of 1.01 eV and the necessity of a stringent control of the stoichiometry. For high efficiency cells only small deviations from the stoichiometric CuInSe₂ composition are tolerable. Solar cells with Cu-rich layers are shorted (shunts) because of Cu-Se precipitates, and In-rich layers do not form a reasonable p-n junction with CdS since In acts as an n-type dopant in CuInSe₂. Therefore, high efficiency cells are made with a “bi-layer” approach: the deposition conditions are adjusted in such a way that a Cu-rich bulk CuInSe₂ layer with an In-rich n-type surface region (e.g. CuIn₃Se₅) is formed. The overall composition of the layers is close to CuInSe₂. The p-n junction then is located in the absorber layer [Sch94, SRS96a]. The necessity of an exact composition control is a major obstacle to a cheap and large area production of CuInSe₂ modules. The addition of Ga, forming a Cu(In,Ga)Se₂ absorber layer not only increases the open circuit voltage from 550 to about 640 mV, it also solves the composition control problem since p-type conductivity with a high free carrier concentration (10¹⁷ cm⁻³) was observed for group III-rich Cu(In,Ga)Se₂ layers [Sch94]. The highest reported
efficiency of Cu(In,Ga)Se$_2$ solar cells is 17.7% [SS97]. A process which was used for the preparation of 13-16% Cu(In,Ga)Se$_2$ substrate solar cells is described in chapter 8.

A further increase in the open circuit voltage of solar cells can be obtained with CuGaSe$_2$ absorber layers (theoretically up to about 1.2 V). The highest reported efficiency obtained with a Ga-rich CuGaSe$_2$ absorber layer is 9.3% with an open circuit voltage of 870 mV [NHS97]. This comparably low efficiency is related to Fermi level pinning and the observation that the p-n junction is located directly at the CdS/CuGaSe$_2$ interface [NHS97] and not, as reported for CuInSe$_2$ and Cu(In,Ga)Se$_2$ cells, inside the absorber layer. Therefore the chemical and microstructural properties of the CdS/CuGaSe$_2$ interfacial region have a direct impact on the diode behavior. In this thesis the chemical and microstructural properties of the CuGaSe$_2$/CdS interfacial region are characterized by transmission electron microscopy. The CuGaSe$_2$ absorber layers were grown under Cu-rich conditions in order to obtain a higher free carrier concentration. Based on the results the limitations of the cell are explained.

1.2 Epitaxial CuIn$_x$Se$_y$ Layers

Polycrystalline CuInSe$_2$, CuGaSe$_2$ and Cu(In,Ga)Se$_2$ absorber layers have been prepared by different techniques. An overview of different methods is given by Jayachandran et al. [JCML93] for CuInSe$_2$. Cells and modules with the highest efficiencies have been obtained by co-evaporation of the elements and the selenization of metal precursors [Sch94].

The growth and characterization of single crystal material is important for the understanding of the basic structural, optical and electronic properties of CuIn$_x$Se$_y$. These properties are influenced by the technique employed for the preparation of the material. Therefore epitaxial CuIn$_x$Se$_y$ layers are in many aspects better suited than single crystals for the fundamental research necessary for the characterization of CuInSe$_2$ absorber layers:
• Both epitaxial and polycrystalline absorber layers are deposited on a substrate. Therefore the physical (e.g. thermal mismatch) and chemical (e.g. interactions and diffusion) compatibility of substrate and layer can be studied by the growth of epitaxial layers.

• The growth kinetics of the polycrystalline absorber layers deposited by co-evaporation is similar to the kinetics of epitaxial growth. Therefore similarities in the structural (e.g. formation of different phases) and microstructural properties (e.g. defects, formation and distribution of precipitates) are expected.

• Electronic and optical properties of thin films and bulk crystals often are fundamentally different because of the different thermodynamical conditions of the growth. For example, Schmid et al. [SRS96a] reported n-type conductivity for CuIn₅Se₃ layers with \([\text{In}] / ([\text{In}]+[\text{Cu}]) > 0.5\), while Ashida et al. [ASS*98] observed for bulk single crystals p-type conductivity up to compositions near CuIn₅Se₃.

• The growth of CuIn₅Se₃ bulk crystals with controlled compositions is difficult. In contrast the composition of epitaxial layers is easily controlled by adjusting the fluxes of the elements during the co-evaporation process.

Molecular beam epitaxy (MBE) is preferred for the growth of epitaxial CuIn₅Se₃ layers, because it is very similar to the deposition of CuInSe₂ absorber layers by a co-evaporation of the elements widely used for the preparation of high efficiency solar cells:

• In both methods Cu, In and Se are evaporated as elements in a vacuum chamber, and the ternary compound is formed on the surface of the heated substrate.

• The substrate temperature in both cases ranges from 450 to 600°C.
• The growth rate of MBE grown CuIn$_x$Se$_y$ layers, usually about 0.5-1 µm/hour, is comparable to the growth rates used for the deposition of CuInSe$_2$ absorber layers (about 2 µm/h).

In this thesis the growth of epitaxial CuIn$_x$Se$_y$ layers on (111)-oriented Si and (001)-oriented GaAs substrates is presented. Si and GaAs were chosen as substrate material since they are structurally compatible with the chalcopyrite structure of CuInSe$_2$. Table 1.1 lists some properties of Si, GaAs and CuInSe$_2$. Si is less suited than GaAs as far as lattice mismatch and thermal properties are concerned. However, CuIn$_x$Se$_y$ is expected to be chemically more compatible with Si than with GaAs. Because of the generally observed chemical instability of GaAs at temperatures above about 500°C chemical interactions between layers and substrate are more likely for GaAs than for the chemically inert Si substrates. The CuInSe$_2$ absorber layers in thin film solar cells preferably grow in the [221] direction. Therefore [111] oriented substrates are preferred for the epitaxial growth as [221]$_{\text{CuInSe}_2}$ is almost parallel to [111]$_{\text{Si}}$. Si(111) wafers are inexpensive and easily available which is not the case for GaAs(111).

The direct growth of epitaxial CuInSe$_2$ and CuIn$_x$Se$_y$ layers on Si(111) substrates has been demonstrated by Tiwari et al. [TBK+94, TBF+94]. The crystal quality of the about 0.5 µm thick layers was characterized by x-ray rocking curve widths ($\approx$ 900 arcsec) and ion channeling yields (13-30%). The epitaxial growth of CuIn$_x$Se$_y$ layers on GaAs(001) has been described by different research groups [NHSB94, NMH+95, TLGC95]. An aim of this thesis was to grow epitaxial CuIn$_x$Se$_y$ layers with different compositions and to improve the crystal quality of the layers by optimizing the deposition parameters. Another task was the characterization of the microstructural defects in the layers and at the interfaces. Only a few microstructural studies of the complicated Cu-In-Se system have been presented. A detailed investigation of CuInSe$_2$ single crystals and polycrystalline layers [KPKR91] revealed twins and stacking faults using transmission electron microscopy (TEM). Diffuse extra spots in
Table 1.1: Some properties of CuInSe$_2$, Si and GaAs

<table>
<thead>
<tr>
<th></th>
<th>CuInSe$_2$</th>
<th>Si</th>
<th>GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>structure</td>
<td>chalcopyrite</td>
<td>diamond</td>
<td>zincblende</td>
</tr>
<tr>
<td>(space group)</td>
<td>(I$42d$)</td>
<td>(Fd$3m$)</td>
<td>(F$43m$)</td>
</tr>
<tr>
<td>lattice constants</td>
<td>$a = 0.5789$ nm</td>
<td>$a = 0.5431$ nm</td>
<td>$a = 0.5653$ nm</td>
</tr>
<tr>
<td>thermal expansion</td>
<td>$a : 8.6 \times 10^{-6}$ K$^{-1}$</td>
<td>$2.5 \times 10^{-6}$ K$^{-1}$</td>
<td>$6.9 \times 10^{-6}$ K$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$c : 11.0 \times 10^{-6}$ K$^{-1}$ [BNPK81]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

electron diffraction patterns were related to anti-site defects in the cation sublattice. Tseng et al. [TLGC95] observed antiphase boundaries in CuInSe$_2$/GaAs(001) layers and showed that they can be eliminated by annealing the layers at 400°C. Tseng and Wert [TW89] identified defect ordered phases in bulk single crystals using electron diffraction and high resolution TEM. Xiao et al. [XYR94] compared the experimental and calculated electron diffraction patterns of CuIn$_3$Se$_5$/GaAs(001). Wada et al. [WNN94a, WNN94b] observed five-fold multiple twins in polycrystalline CuInSe$_2$ layers.
1.3 The Cu-(In,Ga)-Se System

1.3.1 Phase Diagrams

Figure 1.1: Part of the quasi-binary phase diagram CuSe$_2$-In$_2$Se$_3$ proposed by Haalboom et al. [HGE+98].

Within the Cu-(In,Ga)-Se system binary, ternary (and quaternary) compounds with a large variety of compositions and structures have been observed (see handbooks of the International Center for Diffraction Data (ICDD) (formerly Joint Committee on Powder Diffraction Standards (JCPDS)) or [HGE+98, Mik81, SW75, PBF58] and citations therein). This demonstrates the difficulty to obtain accurate and complete phase diagrams of these systems. Fig. 1.1 shows the most recent CuSe$_2$-In$_2$Se$_3$ phase diagram proposed by Haalboom et al. [HGE+98] for the Cu-In-Se system. It displays five different phases in the range of 15-30 at.% Cu between 20 and 900°C. At room temperature there are two composition regions where ternary single phase compounds are found:

- 24-24.5 at.% Cu: There is only a very narrow single phase region for the chal-
copyrite CuInSe$_2$ α-phase. Earlier phase diagrams [KBK82, Fea86, BK87] suggest a broader region (up to 25 at. % Cu) of the stoichiometric CuInSe$_2$ phase.

- 15-16 at.% Cu: Single phase region of the In-rich β phase. Fearheiley [Fea86] as well as Boehnke and Kühn [BK87] showed that the region is extended to about 12 at.% Cu including the compound CuIn$_3$Se$_5$. There is a controversy about the crystal structure. Two different structures, a stannite [HYN+96] and a defect chalcopyrite [HK88] structure, have been suggested for the β-phase.

Binary CuSe$_2$ co-exists with the α-phase at room temperature, and a high temperature (HT) modification occurs. Another ternary phase, the high temperature δ-phase is observed at temperatures above 600°C, but it is of minor interest for photovoltaic applications. Its structure can be described by the zincblende structure (with space group $F\bar{4}3m$), Cu, and In being distributed homogeneously in the cation sublattice. The structural and physical properties of the chalcopyrite α- and β-phase are described below. Different phase diagrams [Mik81, PB67] have been suggested for the Cu-Ga-Se system. At room temperature three ternary phases, the stoichiometric CuGaSe$_2$ and two Ga-rich phases, have been reported. No publication has been found on the quaternary Cu-In-Ga-Se phase diagram.

1.3.2 Chalcopyrites

The Unit Cell

The chalcopyrite structure is based on the zincblende structure. Fig. 1.2 shows the unit cells of ZnSe and CuInSe$_2$. The unit cell of CuGaSe$_2$ can be obtained by replacing In by Ga. The transformation from the zincblende structure to the chalcopyrite structure can be described by an ordered substitution at the zincblende cation sites by two metal atoms with the same average valence. For example, Zn atoms (valence 2) in ZnSe are replaced alternately by Cu (valence 1) and In (valence 3) atoms. This
ordered substitution of the cation sublattice causes a doubling of the unit cell in the [001] direction, as shown in Fig. 1.2. The chalcopyrite structure belongs to the space group $I\bar{4}2d$ (No. 122) with Wyckoff positions a (Cu), b (In) and d (Se) [HL69]. The lattice constants of CuInSe$_2$ at room temperature are $a = b = 0.5769$ nm and $c = 1.1612$ nm, and $c/a = 2.006$.

![ZnSe (Zincblende) and CuInSe$_2$ (Chalcopyrite) unit cells](image)

Figure 1.2: Zincblende and chalcopyrite unit cells of ZnSe and CuInSe$_2$. A well defined substitution of the Zn cations in the zincblende lattice by Cu and In leads to the tetragonal chalcopyrite structure.

*Crystallographic Notation*

For the description of directions, planes and coordinates in the real and the reciprocal space, the following notations will be used throughout this thesis:
• **Real space:**

- abc: Coordinates in real space
- $\mathbf{a} = [abc]$: Vector in real space
- $\langle abc \rangle$: Set of equivalent directions. This includes all combinations of a, b and c:
  
  $\langle abc \rangle = \{[abc], [cab], [bca], [acb], [cba], [\bar{a}bc]...\}$.

- $(hkl)$: Planes in real space with Miller indices $h$, $k$, and $l$
- $\{hkl\}$: Set of equivalent planes. This includes the planes having all possible combinations of the Miller indices $\pm n \cdot h$, $\pm n \cdot k$ and $\pm n \cdot l$ ($n \in \mathbb{Z}$):
  
  $\{hkl\} = \{(hkl), (lkh), (khl), (hlk), (kh\bar{l}), (\bar{h}k\bar{l}), ... , (10h \ 10k \ 10l), ...\}$

• **Reciprocal space:**

- $hkl$: Coordinates in reciprocal space
- $\mathbf{\hat{h}} = (hkl)$: Vector in reciprocal space
- $\{hkl\}$: Set of equivalent directions in reciprocal space. This includes all possible combinations of $\pm h, \pm k$ and $\pm l$:
  
  $\{hkl\} = \{(hkl), (lkh), (khl), (hlk), (kh\bar{l}), (\bar{h}k\bar{l}), ...\}$

**Distances and Angles in the Tetragonal CuInSe$_2$ System**

A basis of the real space of CuInSe$_2$ is given by

$$
e_a = [a \ 0 \ 0], \ e_b = [0 \ a \ 0], \ e_c = [0 \ 0 \ c]$$

(1.1)

This basis is not orthonormal, since $c \neq a$. Therefore, for measuring absolute distances and angles in real space and having the possibility to compare the chalcopyrite space with e.g. the cubic real space, a metric $g$ is introduced. In order to keep it as
simple as possible it is normalized to $a$. With respect to an orthonormal basis of real space, $g$ is described by the matrix

$$
g = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{c}{a} \end{pmatrix} \approx \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{1.2}$$

The basis of the reciprocal cell is given by

$$
e_a^* \equiv 2\pi \frac{\vec{e}_b \times \vec{e}_c}{\vec{e}_a \cdot (\vec{e}_b \times \vec{e}_c)} = \begin{pmatrix} \frac{2\pi}{a} \\ 0 \\ 0 \end{pmatrix}$$

$$
e_b^* \equiv 2\pi \frac{\vec{e}_c \times \vec{e}_a}{\vec{e}_b \cdot (\vec{e}_c \times \vec{e}_a)} = \begin{pmatrix} 0 \\ \frac{2\pi}{a} \\ 0 \end{pmatrix} \tag{1.3}$$

$$
e_c^* \equiv 2\pi \frac{\vec{e}_a \times \vec{e}_b}{\vec{e}_c \cdot (\vec{e}_a \times \vec{e}_b)} = \begin{pmatrix} 0 \\ 0 \\ \frac{2\pi}{c} \end{pmatrix}$$

Again, a metric for the reciprocal space normalized to $2\pi/a$ is introduced. It is given by $g^{-1}$, the inverse of the matrix in (1.2):

$$
g_{\text{rec}} = g^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{a}{c} \end{pmatrix} \approx \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix} \tag{1.4}$$

The metrics defined above are needed for transformations between the cubic and the chalcopyrite systems. Transformations in real space are described by

$$
\vec{a}_{\text{cubic}} = g \cdot \vec{a}_{\text{chal}}
$$

$$
R_{\text{cubic}} = g \cdot R_{\text{chal}} \cdot g^{-1}, \tag{1.5}
$$

where $\vec{a}$ is a vector and $R$ a linear operation (e.g. rotation, mirroring, translation) in real space. A vector with [221] orientation in the CuInSe$_2$ lattice has the orientation $[2 2 c/a]= [2 2 2.006]$ in a cubic lattice. Its angle to the [111] direction of the cubic lattice is 0.08°. In reciprocal space the transformations are given by:

$$
\vec{h}_{\text{cubic}} = g^{-1} \cdot \vec{h}_{\text{chal}}
$$

$$
R_{\text{cubic}} = g^{-1} \cdot R_{\text{chal}} \cdot g, \tag{1.6}
$$
where \( \vec{h} \) is a vector and \( \mathcal{R} \) a linear operation. Therefore a tetragonal CuInSe\(_2\) (112) plane has the Miller indices \((1\ 1\ 2(a/c))=(1\ 1\ 0.997)\) with respect to a cubic basis. The angle between a cubic (111) plane and a chalcopyrite (112) plane is about 0.08°. The transformations of linear operations will be used for the description of rotational twins in epitaxial CuIn\(_x\)Se\(_y\) grown on Si(111) and the tetragonality of the lattice in the interface region (see chapters 6.2 and 7).

Assuming \( c/a = 2 \) for CuInSe\(_2\), the following conversions between the cubic and the chalcopyrite notations are valid:

- real space: \([abc]_{\text{cubic}}=[ab\ c/2]_{\text{chal}}\)
- reciprocal space: \((hkl)_{\text{cubic}}=(hk\ 2l)_{\text{chal}}\)

All notations used in this thesis are related to the chalcopyrite system if not stated otherwise.

The transformations and notations described above are not only valid for CuInSe\(_2\) but for all tetragonal ternary and quaternary Cu-In-Ga-Se compounds.

The Reciprocal Space

The extinction rules of the chalcopyrite system are defined by the following conditions [HL69]:

\[
\begin{align*}
hkl : h + k + l &= 2nhhl : 2h + l &= 4n \quad (1.7)
\end{align*}
\]

for the Se atoms and

\[
\begin{align*}
hkl : 2k + l &= 2n + 1 \text{ or } 4n \quad (1.8)
\end{align*}
\]

for Cu and In atoms, where \( n \) is an integer.

Fig. 1.3 displays a unit cell of the chalcopyrite structure in reciprocal space. Positions which distinguish the chalcopyrite from the zincblende reciprocal lattice (i.e. positions with \( h + k, \ h + l/2 \neq 2n \)) are marked by black dots.
Therefore the zincblende and the chalcopyrite structures can be easily distinguished in electron diffraction patterns. Fig. 1.4 shows a TEM selected area diffraction pattern (SADP) of CuInSe$_2$ taken along [111] together with the calculated pattern. The calculation of the pattern is based on the kinematical theory of electron scattering. The spots at the positions \{011\} give evidence that the structure of the sample is chalcopyrite (\(\alpha\)-phase) and not sphalerite (\(\delta\)-phase).

1.3.3 The In-rich \(\beta\)-Phase of CuIn\(_x\)Se\(_y\)

Because of the large composition range of the \(\beta\)-phase [Fea86] and the difficulty to grow CuIn\(_x\)Se\(_y\) single crystals the structure of the \(\beta\)-phase has been a controversial topic in the CuIn\(_x\)Se\(_y\) research community. Hönle and Kühn [HK88] suggested a
Figure 1.4: SADP (a) and calculated (b) diffraction patterns of CuInSe₂ taken along [111]: ● kinematically allowed reflections, ○ extra spots due to multiple diffraction of the electron beam.

defect chalcopyrite structure which they named _P-chalcopyrite_. The unit cell of the structure is shown in Fig. 1.5(a). The positions and occupancy of the anions and cations were determined by a refinement of the crystal structure using x-ray powder diffraction data from a CuIn₃Se₅ single crystal. In order to maintain the valence neutrality a statistical distribution of vacancies and antisite defects was suggested. The probability of these "defects" was determined by site occupancy factors calculated by the structural refinement. The lattice constants of CuIn₃Se₅ determined by Hönle and Kühn are _a_ = 0.5755 nm and _c_ = 1.1520 nm (_c/a_ ≈ 2.002)

Hanada et al. [HYN+96] investigated the structure of CuIn₃Se₅ bulk single crystals using x-ray powder diffraction and TEM (selected area and convergent beam electron diffraction). From the extinction rules they concluded that the space group of the β-phase is _I̅42m_. This space group is not a subgroup of the chalcopyrite _I̅42d_ group.
Therefore the structure of the \(\beta\)-phase is not a defect chalcopyrite structure since it cannot be produced by a partial ordering or local substitution of cations in the CuInSe\(_2\) lattice. The defect-stannite unit cell of the \(I\overline{4}2m\) structure proposed by Hanada et al. is shown in Fig. 1.5(b). The valence neutrality is again maintained by site occupancy factors, and the lattice constants are \(a = 0.5754\) nm and \(c = 1.1518\) nm \((c/a \approx 2.002)\).

The chalcopyrite structure of CuInSe\(_2\) can be distinguished from the structure of CuIn\(_3\)Se\(_5\) in electron diffraction patterns. Fig. 1.6 shows the experimental and the calculated TEM electron diffraction pattern of an epitaxial CuIn\(_3\)Se\(_5\) layer grown on Si(111). Considering only the position of the spots the calculated pattern belongs to both, the stannite and the P-chalcopyrite structure. Spots at the positions of type...
Figure 1.6: Selected area (a) and calculated diffraction pattern (b) of CuIn$_3$Se$_5$ taken along [021].

\{100\} and \{0\bar{1}2\} are not allowed in the chalcopyrite [021] pattern (see Fig. 1.3). In some CuInSe$_2$ patterns taken along [021] these spots have been observed, but their intensity was very weak, and they were related to rotational twins (see section 6.2).

Ashida et al. [ASS+98] measured the conduction type of CuIn$_x$Se$_y$ bulk single crystals with different compositions and reported an inversion from p- to n-type conductivity at the composition ratio [In]/[In+Cu]=0.75 at\% which corresponds to CuIn$_3$Se$_5$. A similar inversion was observed by Schmid et al. [SRS96a] in Cu-depleted CuInSe$_2$ absorber layers (see also chapter 8) with the difference that the inversion was observed for In-rich composition in general, i.e. for [In]/[In+Cu]>0.5. Suzuki et al. [SUW+98] explained the inversion as well the anomalous high band gap of CuIn$_3$Se$_5$ (1.23 eV) [NKNW97] by estimating the band structure of CuIn$_3$Se$_5$. The calculations were based on the stannite structure as described above.
Chapter 2

DEPOSITION METHODS

2.1 Molecular Beam Epitaxy (MBE) of CuIn$_x$Se$_y$ Layers

2.1.1 The Cu-In-Se MBE System

MBE is a special physical vapor deposition technique for high quality epitaxial layers to be grown in ultra high vacuum (UHV) [HS89, VK91, Smi95]. Fig. 2.1 shows the home-built MBE system as it was used for the growth of epitaxial CuIn$_x$Se$_y$ layers on Si(111) and GaAs(001) [Blu92]. Cu, In and Se are evaporated from thermally stable effusion cells, and the CuIn$_x$Se$_y$ layer is formed at the surface of the heated substrate. The background pressure, obtained using a turbomolecular pump in combination with a prevacuum pump, was in the low $10^{-9}$ mbar region. This inhibited a contamination of the substrate and sources. At such low pressures the mean free path of the evaporated particles is about 50 km so that the particles form a well defined and homogeneous "beam" after being evaporated from the stabilized effusion source. In order to absorb particles during the growth the walls of the chamber were cooled with water and liquid nitrogen. In addition, the hot sources were protected from contamination during the growth by a liquid nitrogen cold trap. Because of its high vapor pressure ($\approx 10^{-3}$ mbar at 250°C) the evaporation of Se in a well defined particle beam is not possible. The divergence of Se into the chamber lead to an increase of the background pressure to $10^{-7} - 5 \times 10^{-6}$ mbar. At such pressures the mean free path of the evaporated material is still about 50 m. The growth of the layers was monitored in-situ by reflection high energy electron diffraction (RHEED).
Figure 2.1: Schematic drawing of the Cu-In-Se MBE system.
2.1.2 Substrate Cleaning

In order to obtain epitaxial growth a clean substrate surface is required. The Si(111) wafers were cleaned using a Shiraki process [Blu92]. The surface layer was removed by chemical etching, and the clean Si surface was covered by a well defined oxide layer. Before the growth the oxide was removed from the wafer by a heat treatment in an UHV chamber at about 1000°C. The observation of the 7 x 7 surface reconstruction [TTTT85] in the RHEED pattern during the cooling down of the Si(111) wafer gave evidence of a clean surface (Fig. 2.2(a)). After the removal of the oxide the substrate was transferred through an UHV tunnel into the Cu-In-Se chamber.

"Epi-ready" GaAs(001) wafers were purchased for the epitaxial growth. Before the growth of the CuIn_xSe_y layer the substrates were heated to about 600-700°C to remove the protective oxide layer. In order to avoid the formation of Ga clusters on the surface, the heat treatment was performed in Se atmosphere (immediately before the start of growth). The expected 2x1 reconstruction of the cleaned surface was difficult to observe in the RHEED patterns owing to the Se flux impinging on the wafer. However, the spots in the diffraction pattern are sharp and form a semi-circle, as it is expected for a smooth and clean surface (Fig. 2.2(b)).
2.2: RHEED patterns of (a) a Shiraki cleaned Si(111) and (b) a GaAs(001). The 7\times7 reconstruction in (a) and the sharp reflections located on semi-circles in (b) indicate smooth and clean surfaces.
2.1.3 The Growth Process

![Schematic drawing of epitaxial CuIn$_x$Se$_y$ layers grown on (a) Si(111) and (b) GaAs(001) substrates.]

Figure 2.3: Schematic drawing of epitaxial CuIn$_x$Se$_y$ layers grown on (a) Si(111) and (b) GaAs(001) substrates.

Fig. 2.3 shows a schematic drawing of CuIn$_x$Se$_y$ grown on Si(111) and GaAs(001). Because $c/a \approx 2$ the [221] growth direction of CuIn$_x$Se$_y$/Si(111) is almost parallel to the [111] orientation of surface. The growth of the layers was divided into several steps:

1. Heating of the Cu, In, and Se sources:
   - $T_{Cu}=1010-1040^\circ C$
   - $T_{In}=770-830^\circ C$
   - $T_{Se}=240-260^\circ C$

   Because of the high vapor pressure of Se the substrate was kept at $\approx 200^\circ C$ during the heating of the Se source to avoid the deposition of Se on the substrate.

2. Heating of the substrate to $T_{sub}=610-650^\circ C$. 

3. Opening of the Se source shutter and the main shutter. The substrate was exposed to Se vapor for about 2 min.

4. Simultaneous opening of the Cu and In source shutters.

5. Growth of CuIn$_x$Se$_y$ for about 3 min (10-20 nm of thickness).

6. Decreasing the substrate temperature to $T_{\text{sub}}=530-610°C$ (growth temperature).

7. End of the growth after about 60 min.

8. Cooling down of the sample to 200°C at about 5 K/min. In order to avoid condensation of Se, sample and sources were kept at temperatures above 200°C until the background pressure decreased to about $10^{-8}$ mbar.

The substrate temperatures mentioned in this thesis are reference values because the thermocouple used for the temperature measurement was not in contact with the substrate.

The growth rate under these conditions was in the range of 0.5 to 1 $\mu$m/hour. The composition of the layer was regulated by $T_{\text{Cu}}, T_{\text{In}}$ and $T_{\text{sub}}$. No major influence of the Se flux on the composition was observed. Since the source used for the evaporation of Se was not a cracker cell, mainly Se$_8$ instead of elemental Se or Se$_2$ was evaporated. Therefore a high Se flux was needed for the elemental reaction at the substrate involving Cu, In and Se to form epitaxial CuIn$_x$Se$_y$ layers. The treatment of the substrate with Se before the growth was necessary to obtain epitaxial layers. The influence of Se on the growth is not understood. It is believed that some of the evaporated Se$_8$ molecules are cracked at the hot surface to Se atoms which then terminate Si dangling bonds. This behavior has been observed by Metzner et al. [MHJHBS98] for S in the epitaxial growth of CuInS$_2$ on Si(111). In addition the opening of the Se
source before the growth supplies enough Se at the surface for the formation of the ternary CuIn$_x$Se$_y$ compound. The substrate temperature was raised to about 650°C during the first few minutes of the growth. Higher substrate temperatures lead to an improved crystal quality, and the effect of the large thermal mismatch resulting from such high temperatures is marginal for layers thinner than about 20 nm. The substrate was not rotated during the growth, and the resulting lateral inhomogeneity was an advantage for the investigation of different compositions. Slow cooling down of the samples after the growth helped to improve the crystal quality.
2.2 Chemical Bath Deposition (CBD)

In Cu(In,Ga)Se₂ substrate solar cells an about 30-60 nm thick CdS layer is deposited by a CBD method to form the heterojunction with the Cu(In,Ga)Se₂ absorber layer (see chapters 8 and 9). The deposition is carried out from an aqueous basic solution (pH≈11) containing a Cd salt (e.g. cadmium acetate, Cd(ActO)₂), ammonia (NH₃) and thiourea (SC(NH₂)₂). At temperatures above about 30°C cadmium acetate is dissociated in the solution and cadmium ammonia complex ions (Cd(NH₃)₄⁺) are formed. These ions then react with S from the thiourea:

\[
\text{Cd(NH₃)}₄⁺ + \text{SC(NH₂)}₂ + 2\text{OH}⁻ \rightarrow \text{CdS} + \text{CN₂H₃} + 4\text{NH}_₃ + 2\text{H₂O} \tag{2.1}
\]

In the associated reaction mechanisms sulfide ions are formed by the hydrolysis of thiourea in the basic solution, and Cd²⁺ ions are released from the unstable cadmium ammonia complex (decomplexation reaction). CdS then starts to precipitate after the ionic product has exceeded the solubility product of CdS. The mechanism of the reactions involved during the CdS deposition process are discussed in full detail by [OBL94]. Investigations of the growth kinetics of CdS on InP [FBC+95] and GaP [LMCF96] single crystals support the theory that the layer is formed by a controlled atom by atom reaction on the surface. This explains why continuous layers with very small thicknesses are obtained by CBD.

For the deposition of CdS the samples were inserted in an aqueous solution (74 ml) of cadmium acetate (2 × 10⁻³ M) and ammonia (≈1.4 M) which had been prepared using high purity (>8 MΩcm) water. The solution then was heated to the deposition temperature (50-80°C). A solution (30 ml) containing thiourea (0.24 M) was heated separately and added to the solution containing Cd(ActO)₂ and NH₃ after both solutions had reached the deposition temperature. After 1-3 minutes the layers started to grow and the solution became yellow indicating the formation of CdS. Immediately after the deposition the sample was rinsed thoroughly first with warm (60°C) and then with cold clean water in order to remove CdS particles originating from the
solution. The growth rate of the CdS layers on the Cu(In,Ga)Se$_2$ absorber layers varied between 5-20 nm/min depending on the deposition temperature. The thickness of layers grown at different bath temperatures was measured with Rutherford Backscattering Spectroscopy (see chapter 3.3).

2.3 Radio Frequency (rf) Sputtering

ZnO and Al-doped ZnO (ZnO:Al) layers were used for the window layer of Cu(In,Ga)Se$_2$ substrate solar cells (see chapter 8). The layers were deposited by rf sputtering [VK91, Smi95] in a commercial system. ZnO and ZnO+Al$_2$O$_3$ (2 weight%) targets of 6" diameter with 99.999% purity and a density of more than 85% were used. In order to avoid O-depleted ZnO layers the Ar plasma was mixed with oxygen (concentration less than 0.1%). The plasma was created and sustained by applying 120-150 V to electrodes in the discharge chamber and powered with a 140-180 W rf generator (standard frequency 13.56 MHz). The coupling of the power to the plasma was controlled by two tunable capacitors and a fixed inductor. The layers were deposited at a pressure of 1.5-3 µbar without heating the substrate. The deposition conditions were similar for ZnO and for Al-doped ZnO and resulted in a growth rate of about 50 nm/min.

ZnO:Al, a transparent conductive oxide (TCO), was used as the ohmic front contact of the Cu(In,Ga)Se$_2$ solar cells. A higher Al concentration increases the conductivity but results in a lower transparency. Therefore the optimization of the deposition parameters was governed by the trade-off between the conductivity and the transparency of the layers. ZnO:Al layers of 0.5-1 µm thickness with an optical transmission of about 90%, a sheet resistance of less than 15 Ω and carrier concentrations of about 10$^{21}$ cm$^{-3}$ have been obtained on glass substrates. These characteristics are comparable to the values reported by other research groups [SMT93, LWR+97, MHG93, DMTTIV98]. Because of the Cu(In,Ga)Se$_2$ absorber
layer it was not possible to determine the transparency of the window layer of the solar cells. The sheet resistance of the front contact was in the range of 5-20 $\Omega_{\square}$.
Chapter 3

CHARACTERIZATION METHODS

3.1 Transmission Electron Microscopy

3.1.1 Investigation Methods

Transmission electron microscopy (TEM) was the main method used for the characterization of the microstructure of epitaxial and polycrystalline layers. It provides information on the scale of a few micrometers down to the Ångström region and therefore is suited for local microstructural investigations. In a transmission electron microscope electrons are accelerated by a potential difference (typically $10^5$-$10^6$ V) and form a coherent electron beam which then is focused or defocused by electromagnetic lenses on the sample less than 200 nm thick. On its way through the sample, the beam is scattered mainly by the electric potential in the crystal lattice. The objective lens focuses the outgoing beam in its image plane and a projection image of the sample is formed. The electron diffraction pattern is located in the back-focal plane of the lens. Using an appropriate configuration of magnification lenses, either the projection or the diffraction pattern is magnified on a fluorescent screen (or a photographic film or TV camera). An introduction to TEM and more detailed descriptions of the method can be found in [BCE88, Cow84, GH88, HHN77, Rei84, Hor94].

The following TEM techniques have been used for the investigation of the samples:

- Selected Area Electron Diffraction (SAED): Using the selected area aperture located in the image plane of the objective lens electron diffraction patterns of selected areas can be imaged. With this method the structures of the $\alpha$-, $\beta$-
and δ-phases of CuInxSe2 layers were distinguished because of their different reciprocal lattice. The diffraction patterns were compared with simulated patterns which were calculated using the theory of kinematical electron diffraction [HHN+77]. Extra spots in the patterns were related to stacking faults and twins (see chapter 6). In addition SAED was used for the exact orientation of the sample needed for high resolution imaging (see below).

- **Bright Field (BF) imaging**: Selecting the (undeflected) zero beam with the *objective aperture* located in the back-focal plane of the objective lens the contrast of the projected image of the sample can be increased, since the image is formed only by the undeflected part of the electron beam.

- **Dark Field (DF) imaging**: Defects can be imaged and separated by choosing a deflected beam for the image formation. E.g., in a DF image formed using a beam diffracted only by a twin, the contrast of the twin is bright while the matrix is dark.

- **High Resolution Transmission Electron Microscopy (HRTEM)**: HRTEM microscopy images the projection of the electric potential in the crystal lattice. Since there is a strong correlation between potential and position of the atoms in the lattice, HRTEM is a good method to characterize interfaces between layers. Planar and linear defects but not point defects can be imaged, because the image gives only information on atomic columns. Therefore, in order to obtain a high resolution image, the sample with maximum thickness of 10 nm has to be precisely oriented along a zone axis.

For the SAED as well as for the BF and DF studies a JEOL 200 (200 kV acceleration voltage) was used. The HRTEM investigations were performed using Philips CM-30 ST microscope (300 kV acceleration voltage), equipped with a LaB6 cathode and a
Super-Twin (spherical aberration $C_s = 1.1$ mm, chromatic aberration $C_c = 1.4$ mm) objective lens. The point resolution resulting in this configuration is limited to about 0.19 nm. A Ge detector for energy dispersive x-ray analysis (EDX) is attached to the microscope. Microprobe EDX measurements were performed to describe the intermixing of layers and to detect precipitates in the polycrystalline layers (see chapters 7 and 9). The EDX investigations were performed in the scanning TEM (STEM) mode of the microscope. Linescans across interfaces and elemental mappings of regions revealed the distribution of elements. The spatial resolution of the EDX measurement was limited by the spot size of the electron beam and by the drift of the sample. The highest resolution achieved was in the range of 5-10 nm.

### 3.1.2 Sample Preparation

A standard mechanical process consisting of three steps was used for the thinning of plane-view and cross-sectional samples:

1. Mechanical polishing down to a thickness of about 100 $\mu$m.

2. Dimple grinding (30-40 $\mu$m thickness).

3. Ion milling.

A Gatan PIPS ion mill was used for the ion milling. $Ar^+$ ions were accelerated by 3.5-4.5 kV and hit the sample at an angle of 2-4°. For the cross-sectional samples the preparation was more complicated and delicate than for the plane-view samples. The samples were first embedded in tubes made of Cu or Ti. The tubes were cut by a diamond saw to about 250 $\mu$m thick slices which then were polished, dimple ground and ion milled. The preparation of an undamaged interface was difficult, especially for the heteroepitaxial CuIn$_x$Se$_y$/Si(111) layers which were strained at the interface because of the large thermal mismatch of layer and Si substrate and therefore easily
peeled off. It was important that forces acting perpendicular to the interface were minimized during the cutting and the polishing processes. Low incident angles (2°) and acceleration voltages (3 kV) were used for the ion milling.

3.2 Reflection High-Energy Electron Diffraction

Reflection High-Energy Electron Diffraction (RHEED) is an important method used for the in-situ monitoring of the growth of epitaxial layers and for the study of the growth kinetics. A detailed description of the method can be found in [Spr93]. An electron beam accelerated at typically 5-20 kV is diffracted from the surface at angles of less than about 3° and forms a diffraction pattern on a fluorescent screen. At such low angles exclusively elastic diffraction of the electrons takes place only from the first few monolayers below the surface. Therefore, for a perfectly smooth surface the diffraction of the electrons can be described by the diffraction theory from a 2-dimensional lattice, and the spots in the RHEED pattern lie on semi-circles (Laue zones). Diffraction patterns with this feature characterize 2-dimensional (layer-by-layer) growth [Smi95]. A pattern containing spots which are arranged in the same way as in TEM diffraction patterns is related to electron diffraction from a three dimensional lattice. The electron beam passes trough islands which have formed at the surface. In this case a 3-dimensional (island) growth [Smi95] is observed. Steps and mosaicity of the surface lead to a streaky RHEED pattern. Electrons penetrating deeper into the surface are scattered elastically and inelastically. Some of the inelastically scattered electrons with a low energy are scattered elastically before leaving the sample. Such electrons form Kikuchi bands in the diffraction pattern. Clear and sharp Kikuchi lines indicate a good crystal quality.
3.3 Rutherford Backscattering Spectroscopy (RBS)

3.3.1 Determination of Composition and Thickness

Rutherford backscattering spectroscopy is an important method for the exact composition determination of epitaxial CuIn$_x$Se$_y$ layers. A monoenergetic and collimated ion beam (e.g. $^4$He$^+$ accelerated at 2 MeV) impinges perpendicular to a target surface and is scattered by the nuclei of the atoms in the target. A detector is placed at an angle of about 170° with respect to the incoming beam, and the elastically backscattered ions are counted for a range of energies. The counts versus energy are plotted. The energies of the elastically backscattered ions depend on the atomic masses of the elements in the target, e.g. collisions with heavy elements result in a smaller energy loss of the projectiles. Most of the projectiles are scattered forward losing some of their energy as they push their way through the target. Therefore an ion scattered back by an atom with mass M inside of the target will have a smaller energy than an ion which collided with an atom of the same mass M but located at the surface of the target. Each signal in a RBS spectrum belongs to a specific mass and the shape of the signal is related to the depth distribution of the corresponding element or isotope. A detailed description of RBS and its physical concepts can be found in [CMN78, FM86]

Fig. 3.1 shows the spectrum of a CuIn$_x$Se$_y$/GaAs(001) layer measured with 2 MeV $^4$He$^+$ ions. The signals of In (atomic number 49), Se (34) and Cu(29) overlap because the layer is quite thick, and their atomic numbers differ not very much. The signals of Ga and As cannot be separated because their atomic numbers (Ga (31) and As (33)) are almost same. The Ga and As signals are located at lower energies because the $^4$He$^+$ ions are scattered in the CuIn$_x$Se$_y$ layer and therefore lose energy on their way to and from the substrate. The spectrum was fitted using the Rump and Pert programs. The algorithms are described in [Doo85, Doo86]. The simulation suggested a 700 nm thick CuInSe$_2$ layer with a vertically homogeneous composition. In this way
thickness and composition of CuIn$_x$S$_y$ layers were determined with an uncertainty of 5% or less. The precision was estimated by fitting the experimental data with slightly different compositions and thicknesses. For the composition and thickness measurements the sample was tilted in such a way that the incident beam was not parallel to a crystallographic orientation (random alignment). Otherwise, channeling effects (see below) would lead to wrong results. The composition measurements were performed using $^4$He$^+$ accelerated at 2 and 3 MeV. A higher energy offers a better mass resolution but the depth resolution decreases.

3.3.2 Ion Channeling

Ion channeling is used to determine the crystal quality of epitaxial layers and bulk single crystals. For single crystals the backscattering yield will decrease if the planes of the crystal are aligned with respect to the beam direction. A channeling effect arises because some of the ions are not scattered back. They are kept by small-angle
collisions in channels between planes and rows of the aligned atoms. An introduction to ion channeling is given in [FM86]. Applications of channeling techniques are described in [CMN78, FM86].

The RBS channeling minimum yield $\chi_{\text{min}}$, defined as the ratio of the yield in an aligned direction and a random orientation is a measure of the crystal quality. Impurities, planar defects as well as misaligned planes (e.g. observed in twinned CuIn$_x$Se$_y$/Si(111) layers, see chapter 7) contribute to the dechanneling and therefore to an increase of $\chi_{\text{min}}$. The $\chi_{\text{min}}$ value depends on the material system and the crystal orientation used for the alignment. For epitaxial layers the defect density generally decreases with increasing thickness. Therefore the $\chi_{\text{min}}$ values in such cases also depend on the region in the spectrum chosen for the calculation of the spectrum. The spectra were measured using 2 MeV $^4$He ions and the $\chi_{\text{min}}$ value was calculated for the energy region ranging from about 1.65 to 1.75 MeV. Therefore the $\chi_{\text{min}}$ value provided information on the top 100-200 nm of the 650-750 nm thick layers.

The backscattering experiments were performed at the Paul Scherrer Institut and the facilities of the Institute for Particle Physics of the ETH Zürich.

3.4 Further Characterization Methods

Other methods used for the characterization of the epitaxial and polycrystalline layers were scanning electron microscopy (SEM), light microscopy and atomic force microscopy (AFM) for morphology studies. The AFM investigations were performed at the Institute for Nonmetallic Inorganic Materials, ETH Zürich. Compositions of layers were determined by EDX in the SEM, but the values were inaccurate compared with the RBS results. Electron channeling experiments in the SEM performed at the Laboratory of Solid State Physics of the ETH Zürich were important for the distinction between epitaxial CuIn$_x$Se$_y$ layers with higher and lower crystal quality. The crystal quality of epitaxial layers was also characterized with the full width of half
maximum value of x-ray diffraction rocking curves. $\Theta - 2\Theta$ x-ray diffractograms were used to identify phases in epitaxial CuIn$_x$Se$_y$ layers. Lattice vibrational properties of epitaxial CuIn$_x$Se$_y$ layers were investigated by Raman and Infrared spectroscopy. The results obtained from the measurements performed at the Institute of Physics (Academy of Sciences of the Czech Republic) in Prague were used together with $\Theta - 2\Theta$ x-ray diffractograms for the identification of different phases. X-ray photoelectron spectroscopy (XPS) measurements performed at the Institut für Physikalische Elektronik of the Universität Stuttgart were used for elemental linescans across CdS/CuGaSe$_2$ interfaces.
Part I

Epitaxial CuIn$_x$Se$_y$ Layers
Seite Leer / Blank leaf
Chapter 4

GROWTH AND EPITAXY

4.1 Growth

The growth of epitaxial CuIn$_x$Se$_y$ layers by MBE was monitored in-situ by RHEED (see chapter 3.2). The diffraction patterns provided information on the surface quality of the substrate (see section 2.1.2) and the growth kinetics. Furthermore the RHEED investigations gave a first estimation of the crystal quality and formation of phases in the layer.

Because of its sensitivity to the morphology of surfaces, RHEED is a possible method to distinguish between 2-dimensional layer-by-layer (2-d) and 3-dimensional island (3-d) epitaxial growth modes [Spr93, Smi95]. The layer-by-layer growth is related to the structural compatibility of of layer and substrate material. Therefore a lower defect density is expected if the layer grows in the 2-d rather than in the 3-d mode. Fig. 4.1 shows the RHEED patterns of CuIn$_x$Se$_y$ grown on Si(111) and GaAs(001) substrates. The pattern (a) was taken along a $\langle 110 \rangle$ azimuth while the orientation in (b) is either $[100]$ or $[010]$. The layers were grown at “low” substrate temperatures ($\approx 540^\circ$C). The spot-like patterns indicate that the layer grows by the formation of islands. Consequently the morphology of the layers was rough as shown in Fig. 4.2(a) for CuIn$_x$Se$_y$/Si(111). An increase of the substrate temperature to $\approx 580^\circ$C (“high” temperature) leads to streaky RHEED patterns as shown in Fig. 4.3(a) indicating a smoother surface.

The RHEED pattern of a perfect 2-d surface consists of sharp spots as shown in Fig. 2.2 for the cleaned Si(111) and GaAs(001) substrates. The pattern displayed
Figure 4.1: RHEED pattern of CuIn$_x$Se$_y$ layers on (a) Si(111) along a (110) azimuth and (b) GaAs(001) grown at "low" substrate temperatures ($\approx 540^\circ$C) taken along [100] or [010].

in Fig. 4.3(a) consists of streaks with intensity maxima lying on a semi-circle. This corresponds to the RHEED pattern of a surface with steps or mosaicity. Fig. 4.4 shows a SEM micrograph displaying steps on a smooth surface of a high temperature grown CuIn$_x$Se$_y$ layer. Such steps were not observed in every high-temperature grown CuIn$_x$Se$_y$/Si(111) layer. Fig. 4.2(b) shows the morphology of a high temperature CuIn$_x$Se$_y$/Si(111) layer. The steps are missing, and the roughness is higher. The step like growth was most enhanced on miscut (less than 3%) Si(111) substrates. Since the thermal expansion coefficient of CuIn$_x$Se$_y$ is about 3-4 times as large as the one of Si, the layers grown on Si(111) at high substrate temperature (above $\approx 580^\circ$C) cracked and peeled off the substrate during the cooling down process.

The RHEED pattern of CuIn$_x$Se$_y$/GaAs(001) displayed in Fig. 4.3(b) seems to be a superposition of a 2- and a 3-dimensional pattern. Fig. 4.5 shows an AFM micrograph displaying the morphology of the CuIn$_x$Se$_y$/GaAs(001). Small sharp
islands with a size of about 200 nm or less are observed on top of a few micrometers large islands. The roughness of the layer was estimated to be 20-30 nm. The AFM micrograph shows that the growth mode of CuIn$_x$Se$_y$/GaAs(001) is in the 3-d mode not only for low but also for high substrate temperatures. A possible explanation for the 2-d like RHEED pattern in Fig. 4.3(b) is that the islands on top of the smooth layer are so small so that the intensity contribution from the 2-dimensional scattering of the electrons from surface planes is high enough to be seen in the diffraction pattern.

The RHEED patterns provided first information on planar defects as well as whether the layer has an In-rich or the stoichiometric composition of CuInSe$_2$. The pattern of CuIn$_x$Se$_y$/Si(111) shown in Fig. 4.1(a) contains two types of reflections which are forbidden for diffractions from a perfect CuInSe$_2$ lattice. Reflections marked with (a) are caused by rotational twins on (112) growth planes (see chapter 6.2) and spots as the one marked with (b) at the \{110\} positions are related to the ordered vacancy structure of In-rich CuIn$_x$Se$_y$ layers (see section 1.3). The light streaks in the (11\overline{2}) direction are related to stacking faults on the (11\overline{2}) planes. Extra spots related
to twins often disappeared during the growth. This means that for some layers the density of twins decreased strongly with increasing thickness. The RHEED pattern of CuIn$_x$Se$_y$/GaAs(001) taken along either the [100] or [010] azimuth shown in Fig. 4.1(b) contains no other spots than the ones expected in the CuInSe$_2$ patterns along these azimuths. Planar defects such as twins and stacking faults form on \{112\} planes and are therefore not visible in diffraction patterns along \{100\}. Spots at the positions \{011\} are characteristic for the chalcopyrite structure of CuInSe$_2$. Missing reflections of the type \{310\} which result from the tetragonality of the CuInSe$_2$ unit cell indicate that the layer grows mainly in the [001] (and not the [100] or [010]) direction. The microstructure of CuIn$_x$Se$_y$ layers is described in more detail in chapter 6.
Figure 4.4: SEM micrograph of "high" temperature grown CuIn$_x$Se$_y$ on a miscut Si(111) substrate displaying steps on a smooth surface.

Figure 4.5: AFM micrograph of CuIn$_x$Se$_y$/GaAs(001) grown at a "high" substrate temperature.
The samples were not rotated during the growth in order to obtain a lateral composition and thickness gradient. The composition of the 0.5-1 μm thick layers was determined from the fitting of RBS data. Fig. 4.6 shows the experimental and calculated spectra of CuInSe$_2$/Si(111) (slightly Cu-rich) and CuIn$_3$Se$_5$/GaAs(001). The spectra were measured using 2 MeV (Fig. 4.6(a)) and 3 MeV (Fig. 4.6(b)) MeV $^4$He ions. The increase of the acceleration voltage leads to a better mass resolution, but the depth resolution decreases. For the curve fitting in the low energy regions straggling was taken into account. Various compositions of epitaxial CuIn$_{x}$Se$_y$ layers on Si(111) and (GaAs(001) ranging from slightly Cu-rich CuInSe$_2$ to CuIn$_3$Se$_5$ have been measured.

A result of the composition measurements was that all epitaxial CuIn$_{x}$Se$_y$ layers had compositions with a copper to indium ratio smaller than about 1.1. Layers with higher Cu concentrations were always polycrystalline. This correlates with the phase diagram proposed by Haalboom et al. [HGE+98] (see chapter 1.3)) which negates the existence of single phase Cu-rich CuIn$_{x}$Se$_y$. For Cu concentrations larger than 24.5 at% the α-CuInSe$_2$ phase coexists with Cu$_2$Se. Niki et al. [NMH+95] reported the growth of epitaxial Cu-rich CuIn$_{x}$Se$_y$ layers on GaAs(001). In a subsequent study [NFY+97] they found that a KCN treatment of the layers changes the overall composition to In-rich. This result was related to an etching of Cu-Se precipitates formed near the surface of the layer. Cu-Se precipitates in Cu-rich layers grown on GaAs(001) were also reported by Okada et al. [OSoY+94].

The presence of Cu-Se precipitates in epitaxial CuIn$_{x}$Se$_y$ layers grown under Cu-rich conditions illustrates the composition problem of CuInSe$_2$-based solar cells. The precipitates already form at [Cu]/[In] $\lesssim$ 1.05, as was observed from the composition measurements. Therefore it is difficult to obtain an absorber layer with a high free carrier concentration and without Cu-Se precipitates.
(a) CuInSe$_2$/Si(111) Thickness: 770 nm $^4$He at 2 MeV

(b) CuIn$_3$Se$_5$/GaAs(001) Thickness: 640 nm $^4$He at 3 MeV

Figure 4.6: Experimental RBS (×) spectra of CuIn$_x$Se$_y$ grown on (a) Si(111) and (b) GaAs(001). The spectra were fitted with a calculated spectrum (—): (a) CuInSe$_2$/Si(111), thickness 770 nm and (b) CuIn$_3$Se$_5$/GaAs(001), thickness 640 nm.
### 4.2 Crystal Quality

The crystal quality of the epitaxial CuIn$_x$Se$_y$ layers was characterized by ion and electron channeling, and by XRD rocking curves. Fig. 4.7 shows SEM electron channeling patterns of CuInSe$_2$/Si(111) and CuIn$_3$Se$_5$/GaAs(001) grown at low ($\approx 540^\circ$C, Figs (a) and (c)) and high ($\approx 580^\circ$C, Figs (b) and (d)) substrate temperatures. For the high temperature grown samples sharp Kikuchi lines are visible indicating a good crystal quality. The threefold symmetry in the pattern displayed in Fig. 4.7(b) shows that the CuInSe$_2$ layers are type A grown on Si(111) and that the density of twins on (112) growth planes is negligible. The channeling pattern of Fig. 4.7(a) of the low temperature grown CuInSe$_2$ layers however has a sixfold symmetry. This indicates a mixture of type A and B growth on the Si(111) substrate and twinning on (112) planes. The lower crystal quality of the low temperature grown sample is also observed from the Kikuchi lines which are not as clear and sharp as the ones shown in Fig.4.7(b). The patterns of the CuIn$_x$Se$_y$ layers on GaAs(001) substrates exhibit a fourfold symmetry which shows that the growth was in a (100) direction. Only the low-index Kikuchi bands are observed in the channeling pattern of the CuIn$_3$Se$_5$/GaAs(001) grown at a low substrate temperature. Electron channeling is very sensitive to planar defects and the roughness of the surface. TEM investigations of this sample showed a high density of stacking faults on (112) planes (see chapters 6 and 7). The faults which often are formed at the interface and propagate towards the surface, disturb strongly the [001] oriented channels.

The improvement of the crystal quality by increasing the substrate temperature was also observed in rocking curve measurements. Fig. 4.8 shows the (224)$_\alpha$ peak of an about 750 nm thick CuInSe$_2$/Si(111) layer grown at $T_s \approx 570^\circ$C. The full width at half maximum (FWHM) of 775 arcsec is considerably smaller than the values of about 1600 arcsec obtained for low temperature grown CuIn$_x$Se$_y$/Si(111).

RBS channeling investigations provided a quantitative estimation of the crystal
Figure 4.7: Electron channeling patterns of CuInSe₂/Si(111) and CuIn₃Se₅/GaAs(001) grown at \( \approx 540^\circ C \) ((a) and (c)) and \( \approx 580^\circ C \) ((b) and (d)) substrate temperatures.

quality. Fig. 4.9 shows the aligned and random oriented RBS spectra of CuInₓSeᵧ/Si(111) layers with different compositions. The samples were grown at high substrate temperatures. For the channeling experiments the crystals were aligned along the [221] direction and the \( \chi_{\text{min}} \) values were evaluated near the surface (In-related step), in the 1.65 to 1.75 MeV range. The \( \chi_{\text{min}} \) values obtained from the channeling experiments were 7\% for CuIn₂.₅Se₄, 11\% for CuIn₁.₆Se₂.₉ and 13\% for CuInSe₂. They are lower than the values obtained for CuInₓSeᵧ/Si(111) layers grown at low substrate
temperatures (13-30\%) [TBK$^+$94], but slightly higher than the values reported for CuInSe$_2$ bulk single crystals (5\%) [YTN94]. For CuIn$_x$Se$_y$/GaAs(001) $\chi_{\text{min}}$ values of 20\% for high temperature grown and 40-50\% for low temperature grown samples were obtained. These results establish that CuIn$_x$Se$_y$ layers with large compositional variations towards In-rich compositions and good crystal quality can be grown.

Figure 4.8: XRD rocking curve of the (224)$_a$ peak of CuInSe$_2$ with a full width at half maximum (FWHM) of 775 arcsec.
Figure 4.9: RBS channeling spectra of CuIn$_x$Se$_y$/Si(111) samples with different compositions.
Chapter 5

PHASE IDENTIFICATION

Infrared absorption, Raman scattering and XRD measurements were performed on CuIn$_x$Se$_y$/Si(111) samples to distinguish different phases and identify if the layer is a "single phase compound" or a "mixture of different binary or ternary compounds". In XRD $\Theta - 2\Theta$ scans only peaks corresponding to the (112)-oriented CuIn$_x$Se$_y$ and Si are observed. There is no extra peak corresponding to the binary (such as In$_x$Se$_y$ and Cu$_x$Se$_y$) phases. However, a careful analysis of the peaks at high diffraction angles, such as the (336) diffraction peak, provides useful information on the composition of phases.

Fig. 5.1 shows $\Theta - 2\Theta$ XRD scans of CuIn$_x$Se$_y$/Si(111) layers with different compositions measured by RBS; CuInSe$_2$, CuIn$_{1.6}$Se$_{2.9}$, CuIn$_{2.5}$Se$_4$ and CuIn$_3$Se$_5$. Unfiltered x-rays, containing $\alpha$ and $\beta$ lines from the Cu anode are used and the peaks of CIS(336)$\beta$ and Si(333)$\beta$ are shown. Additional (satellite) peaks belonging to Si are marked with (a). The peaks for CuInSe$_2$, CuIn$_{2.4}$Se$_4$ and CuIn$_3$Se$_5$ are at 77.48°, 77.78° and 78.09°, and the calculated lattice constants are (assuming $c/a=2$) $a_{\text{CuInSe}_2} = 0.5783$ nm, $a_{\text{CuIn}_{2.4}\text{Se}_4} = 0.5762$ nm and $a_{\text{CuIn}_3\text{Se}_5} = 0.5744$ nm. The reflections are singular (i.e. only one peak) and the FWHM values of the peaks are in the range of 0.14° to 0.17°. The position and the FWHM of the peaks show that the (336)$\beta$ peak of CuIn$_{2.5}$Se$_4$ is not due to a mixture of CuInSe$_2$ and CuIn$_3$Se$_5$ compounds. The layer mainly consists of a single phase compound with the composition of CuIn$_{2.4}$Se$_4$. For CuIn$_{1.6}$Se$_{2.9}$ however, the (336)$\beta$ peak is a doublet with a FWHM value of 0.57°. This peak in fact is a superposition of two peaks at 77.50° and 77.75° belonging to CuInSe$_2$ and CuIn$_{2.5}$Se$_4$. Therefore the CuIn$_{1.6}$Se$_{2.9}$ is a mixture of two
Figure 5.1: X-ray diffractograms of CuIn$\text{x}$Se$_y$/Si(111) with different compositions using Cu-K$_\beta$ radiation.

compounds. It should be mentioned that no peak shifts due to thermal strain in the layers can be detected. Assuming that the thermal expansion coefficient of CuIn$_x$Se$_y$ is same for all compositions (about four times higher than Si, see table 1.1 in section 1.2) the strain $\Delta d/d$ due to thermal mismatch is limited to about $10^{-3}$, which causes a maximal shift of the (336) peaks by about 0.05°. Moreover, the strain can be assumed to be the same in all the CuIn$_x$Se$_y$/Si(111) layers. Therefore, the positions of the peaks are mainly related to the lattice constants of the layers.

The lattice vibrational properties of CuInSe$_2$ and CuIn$_3$Se$_5$ were measured at the Institut of Physics in Prague. It has been demonstrated that the Raman scattering and infrared absorption measurements may be effectively used to identify chalcopyrite and defect-chalcopyrite phases [TBS+96]. Unpolarized Raman spectra of different CuIn$_x$Se$_y$ layers are shown in Fig. 5.2. The frequency of the most intense $\Gamma_1$ vibrational mode is 174 cm$^{-1}$ for CuInSe$_2$ and 149-151 cm$^{-1}$ for CuIn$_3$Se$_5$. Two peaks (152
Figure 5.2: Polarized Raman scattering spectra of CuIn$_x$Se$_y$/Si(111) layers with different compositions. The spectra were measured at room temperature in backscattering geometry using an Ar$^+$ laser.
and 175 cm\(^{-1}\)) and a shoulder for CuIn\(_{1.8}\)Se\(_{2.9}\), and three peaks (152, 175, 184 cm\(^{-1}\)) for CuIn\(_{2.4}\)Se\(_4\) are observed. Small peaks at 212 and 231 cm\(^{-1}\) due to the \(\Gamma_4\) and \(\Gamma_5\) modes are present in all the cases. It is clear that the most important features (peaks) are in the range of 149 to 189 cm\(^{-1}\). The \(\Gamma_1\) vibrational mode is due to the bonding of Se with the cations (Cu and In). A change in the occupancy of cation sites such as vacancies and antisites (In at Cu site) will shift the frequency of the \(\Gamma_1\) mode. Hanada et al. [HYN\(^+\)96] have specified the space group of CuIn\(_3\)Se\(_5\) as \(I\bar{4}2m\) and they have proposed that its structure can not be produced by partial ordering of cations in CuInSe\(_2\) lattice (see section 1.3).

Space groups of CuInSe\(_2\) and In-rich CuIn\(_x\)Se\(_y\) belong to the \(D_{2d}\) point group. Therefore some similarities are expected in the lattice vibrational properties. Because of the lack of structural information on In-rich phases, the Raman spectra were qualitatively explained in comparison with CuInSe\(_2\). Recently, Nomura et al. [NOE97] have performed polarized and nonpolarized Raman scattering measurements on CuIn\(_{2.3}\)Se\(_{3.5}\) and assigned the broad peak at about 154 cm\(^{-1}\) to the modes due to \(\Gamma_1, \Gamma_3\) and \(\Gamma_5\) symmetries. In our case, based on the nonpolarized Raman scattering measurements on epitaxial layers, peaks cannot be assigned to the symmetries. However, it should be emphasised that the Raman peaks in the frequency range of 145 to 190 cm\(^{-1}\) are different for the \(\alpha\) and \(\beta\) phases and the frequencies depend on the cation distribution (stoichiometry of the layer).

Fig. 5.3 shows the IR absorption spectra of CuIn\(_x\)Se\(_y\)/Si(111) layers with different compositions. The Si substrate does not interfere with the measurements because it is transparent in this wavelength range. In the IR absorption measurements transverse optical modes due to the In-Se bonds are characterized and inhomogenities in the bulk of the layer can be observed. The spectra of CuInSe\(_2\), CuIn\(_{2.4}\)Se\(_4\), and CuIn\(_3\)Se\(_5\) are clearly different. However, the spectrum of CuIn\(_{1.6}\)Se\(_{2.9}\) appears to be a superposition of the CuInSe\(_2\) and CuIn\(_{2.4}\)Se\(_4\) spectra suggesting that the layer is a mixture of two compounds. This is also supported by the XRD measurements of the (336) reflection,
Figure 5.3: IR absorption spectra of CuIn$_x$Se$_y$/Si(111) with different compositions.

where twin peaks for CuIn$_{1.6}$Se$_{2.9}$ and single peaks for other layers are observed.

The phase identification discussed above is in agreement with the phase diagram proposed by Haalboom et al. [HGE+98] shown in Fig. 1.1. At room temperature the compound CuInSe$_2$ is located in the $\alpha$ while CuIn$_{2.5}$Se$_4$ (15.3 at.% Cu) and CuIn$_3$Se$_5$ (12.5 at.% Cu) belong the $\beta$ single phase region. CuIn$_{1.6}$Se$_{2.9}$ however has a Cu content of 22.2 at.%, and, according to the room temperature phase boundaries it is a mixture of the $\alpha$- and the $\beta$-phase.
Chapter 6

PLANAR DEFECTS

6.1 Defect Stacking Sequences

Planar defects, i.e. twins and stacking faults, were the most common defects observed in epitaxial CuIn$_x$Se$_y$ layers grown on Si(111) and GaAs(001). Since the structures of CuIn$_x$Se$_y$ are based on the zincblende structure the planar defects form on the close packed \{112\} planes. For cubic f.c.c. based structures (e.g. the zincblende structure) planar defects can be characterized by irregularities in the stacking sequence \ldots-A-B-C-A-B-C-\ldots of the \{111\} planes. If a stacking error occurs (e.g. \ldots-A-B-C-A-C), the next layer determines the nature of a stacking fault:

- For \textit{intrinsic stacking faults} the atoms of the following \{111\} plane are located on A sites and the subsequent planes are stacked in the correct sequence: \ldots-A-B-C-A-C-A-B-C-\ldots. The defect corresponds to a missing B-plane.

- For \textit{extrinsic stacking faults} the atoms of the following \{111\} plane are located on B sites and the subsequent planes are stacked in the correct sequence: \ldots-A-B-C-A-C-B-C-A-\ldots. The defect corresponds to an extra C-plane.

- For \textit{twins} on \{111\} planes the atoms of the following \{111\} plane are located on B sites and the subsequent planes are stacked in the reverse stacking sequence: \ldots-A-B-C-A-C-B-C-A-B-C-A-\ldots

For the diamond or the zincblende structures one stack in the sequence corresponds to two planes, a \{111\} anion plane and its neighboring cation plane (or vice versa).
The CuIn$_x$Se$_y$ structures are all characterized by a cation superlattice which leads to a more complicated stacking sequence, and therefore to more possible types of stacking fault. For example, the stacking sequence of chalcopyrite \{112\} planes is defined by 6 cation-anion stacks: \ldots-A-B-C-A'-B'-C'-\ldots. The stacking faults were investigated by HRTEM. The resolution of the CM-30 ST Philips microscope used for the investigation is limited to about 0.19 nm (see chapter 3.1) so that neighboring cation and anion planes cannot be resolved when imaging planar defects. Therefore no distinction between e.g. A and A' stacks was made and the stacking sequence was treated similar as for cubic structures. Reverse stacking sequences involving a small number of stacks (less than about 100) were related to so-called nanotwins. Rotational twins in CuIn$_x$Se$_y$/Si(111) are described in the next section.

![HRTEM micrograph](image)

Figure 6.1: HRTEM micrograph taken along [110] displaying stacking faults on \{112\} planes in CuIn$_x$Se$_y$/GaAs(001). The faults are formed at the interface and propagate towards the surface.

The stacking faults and nanotwins in CuIn$_x$Se$_y$/Si(111) as well as in CuIn$_x$Se$_y$/GaAs(001) were observed for all possible \{112\} planes. Fig. 6.1 shows a HRTEM micrograph of stacking faults in a CuInSe$_2$/GaAs(001) layer grown at low substrate
temperature. The high density of these defects is responsible for the bad electron channeling of these layers as shown in chapter 4. Stacking faults ending in the layer are terminated by partial Shockley dislocations with Burgers vectors of type $a/6 \cdot (111)$. The situation is the same as for partly coherent boundaries between twinned regions (see section 6.2). Fig. 6.2 shows a HRTEM micrograph of a stacking fault in CuIn$_3$Se$_5$/Si(111) of (112) growth planes. A reversed stacking sequence is changed into an intrinsic stacking fault. Dislocations can be observed at the end of the defect stacking sequence. Except for the presence of stacking faults and nanotwins formed at the interface because of the lattice mismatch between substrate and layer (see chapter 7) the faults are comparable to those observed in bulk single crystals and polycrystalline layers. A detailed description of stacking faults can be found in the publication by Kiely et al. [KPKR91].

Figure 6.2: HRTEM micrograph taken along [110] displaying a defect stacking sequence of (112) planes in CuIn$_3$Se$_5$/Si(111). The transition zone between a reverse and an intrinsic stacking fault contains partial Shockley dislocations.
One explanation for the high density of planar defects in CuIn$_x$Se$_y$ is the low stacking fault energy which is also related to the observation that these materials appear to have a certain tendency towards hexagonal structures. Fig. 6.3 shows HRTEM images of two regions of a CuIn$_x$Se$_y$ layers grown on Si(111). The stacking sequences, ...-A-B-A-B-... in (a) and ...-A-B-A-C-... in (b) of the (112) growth planes belong to a closed packed hexagonal structure and a double-hexagonal structure, respectively. A microprobe EDX analysis in the TEM proved that the regions consist of a Cu-In-Se and not a binary compound (e.g. Cu-Se). Hexagonal stacking sequences in CuIn$_x$Se$_y$ bulk single crystals have also been observed by Tseng et al. [TW89]. The hexagonal region was related to a new phase.

Another explanation for the high density is illustrated in Fig. 6.1 and discussed in chapter 7. Many of the stacking faults result from the lattice mismatch between layer and substrate. Depending on the growth conditions (high or low substrate temperature) they can be terminated near the interface, or they grow to the top part or even surface of the layer.

Figure 6.3: HRTEM micrograph of a CuIn$_x$Se$_y$/Si(111) layer displaying (a) hexagonal and (b) double-hexagonal stacking sequences of (112) growth planes.
6.2 Rotational Twins in CuIn$_x$Se$_y$/Si(111) Layers

As already mentioned, planar defects on (112) growth planes are very common defects in CuIn$_x$Se$_y$ layers grown on Si(111). Fig. 6.4 shows the selected area diffraction pattern (SADP) and the calculated pattern along [221] of CuInSe$_2$. The sharp extra spots at \{110\} and \{2\4\4\3\3\3\} positions in the SADP are related to the presence of rotational twins. Two types of rotational twins are expected to form in chalcopyrite type materials on (112) planes:

- Twin variants rotated by $\pm 120^\circ$ about the [221] axis with respect to the reference matrix.

- Twin variants rotated by $180^\circ$ about the [221] axis with respect to the matrix.

Combination of both types leads to twin variants rotated by $\pm 60^\circ$ with respect to the matrix.
Figure 6.4: Experimental and calculated diffraction patterns of CuInSe$_2$/Si(111) along [221]. The filled circles in the calculated pattern are at kinematically allowed positions (the radius of the circles is proportional to the logarithm of the intensities). The open circles represent spots which are caused by multiple diffraction. The positions \{134\} characterize the chalcopyrite lattice. Extra spots are due to multiple diffraction (\{110\} and \{1\bar{1}4\} reflections) and to rotational twins of type $\pm 120^\circ$ (\{110\} reflections) and $\pm 60^\circ/180^\circ$ (\{2\bar{4}1\} reflections) on (112) growth planes.
6.2.1 Rotational Twins of Type ±120°

Other than for all cubic crystal systems, ±120° rotations about a (221) (or cubic (111)) axis are not symmetry operations for the tetragonal structures of CuIn\textsubscript{x}Se\textsubscript{y}. Fig. 6.5 shows the arrangement of the unit cells belonging to three ±120° twin variants (marked as “matrix”, “+120°” and “-120°”) for a projection along [221].

![Figure 6.5: The three equivalent orientations the CuIn\textsubscript{x}Se\textsubscript{y} on the (111) oriented Si wafer. The unit cells represent the orientations of ±120° twin variants which are rotated about the growth direction.](image)

With respect to a basis \{[000], [000], [000]\} of real space with c/a ∼ 2 the rotations are described by the matrices

\[
R_{+120°} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 2 \\ \frac{1}{2} & 0 & 0 \end{pmatrix}, \quad R_{-120°} = \begin{pmatrix} 0 & 0 & 2 \\ 1 & 0 & 0 \\ 0 & \frac{1}{2} & 0 \end{pmatrix}.
\] (6.1)

These are permutation matrices which in the cubic system with respect to an or-
thonormal basis are described by

\[
P_+ = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \quad P_- = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}.
\] (6.2)

Therefore, rotations by ±120° about [221] correspond to permutations of equivalent ⟨abc⟩ directions, e.g. the ⟨200⟩ directions. Fig. 6.6 shows four chalcopyrite unit cells viewed along [221]. Three {100} cation planes are displayed. Since CuInSe₂ has a tetragonal unit cell, the stacking sequence of the cations is not the same along the three ⟨200⟩ directions, as can be seen in Fig. 6.6. The sequences are given by

- ⟨001⟩: \(...–\text{Cu}–\text{In}–\text{Cu}–\text{In}–\text{Cu}–\text{In}–...
- ⟨200⟩: \(...–\text{X}–\text{X}–\text{X}–\text{X}–\text{X}–\text{X}–...
- ⟨020⟩: \(...–\text{X}–\text{X}–\text{X}–\text{X}–\text{X}–\text{X}–...

where X is either only Cu or In. For the [200], [020] and [001] directions the following permutation takes place under the rotation by ±120° about [221]:

- [200] \(\rightarrow\) [001] \(\rightarrow\) [020] \(\rightarrow\) [200]

Thus a permutation of these directions in the domain rotated about [221] by ±120° of the lattice causes an exchange of Cu and In atoms at the cation sites (see Fig. 6.6) that is periodic in the ⟨200⟩ directions over the range of the rotated domain. This change in the occupancy of the cation sites results in sharp extra spots at {100} positions in the [021] SADP shown in Fig. 6.7.

The [220], [201] and [021] directions can be treated in the same way. The permutation of these directions resulting from a rotation by +120° about [221] is given by:

- [220] \(\rightarrow\) [201] \(\rightarrow\) [021] \(\rightarrow\) [220]
Figure 6.6: Four CuInSe$_2$ unit cells oriented along [221]. Rotations by ±120° about [221] are not symmetry operations but change the site occupancy in the cation sublattice as shown by the rotations 1 → 2 (+120°), 1 → 3 (-120°) and 1→III (-120°) where In atoms are rotated to Cu sites.

The sequence of the cations of CuInSe$_2$ along the three ⟨110⟩ directions is

- [220]: ...–Cu – In – Cu – In – Cu – In–...
- [201]: ...–Cu – Cu – In – In – Cu – Cu–...
- [021]: ...–Cu – In – In – Cu – Cu – In–...

Again the permutation of the directions changes the occupancy of the cation sublattice of the rotated domain with respect to the original lattice along the three ⟨110⟩ directions, and sharp extra spots appear at {012} positions in the SADP along [021] (Fig. 6.7). Extra spots at {100} and {012} positions in CuInSe$_2$ bulk single crystal
and polycrystalline thin films were also observed by Kiely et al. [KPKR91]. However the spots were diffuse, and they were related to the repetitive formation of smaller clusters with antisite defects in the cation sublattice causing a slight disordering of Cu and In. The presence of rotational twins on (112) growth planes by ±120° can be explained on the basis of symmetry: the rotation about [221] by ±120° causes defects in chalcopyrite, but not in zincblende or diamond lattices (threefold symmetry along [111] in fcc lattices). The growth of CuIn\textsubscript{x}Se\textsubscript{y}/Si(111) starts in three dimensional growth mode [TBK+94] (island growth, see chapter 4.1). The threefold symmetry of the Si substrate along [111\textsubscript{cubic}] leads to three preferred orientations of the overgrowing islands, giving rise to twinned domains rotated about the [221] growth axis by ±120° with respect to each other.
Figure 6.8: Rotational twins on (112) planes of type ±60°/180°. The three unit cells marked with +60°, -60° and 180° represent twin variants which are rotated about the [221] growth direction by ±60° and 180° with respect to a chosen “matrix”.

6.2.2 Rotational Twins of Type ±60°/180° on (112) Growth Planes

The positions {110} in the [221] SADP shown in Fig. 6.4(a) are not only related to ±120° twins, but also to twin variants rotated about [221] by ±60° and 180° with respect to a chosen reference cell as shown in Fig. 6.8. For each chosen “matrix” there are three twin variants which are rotated by ±120° with respect to each other. They can be distinguished only because the cation sites are occupied by In or Cu atoms (see above) and are therefore characteristic for the tetragonal structure of CuInₓSeᵧ. The twins are a result of ± 120° and 180° twinning on the (112) growth planes. In real space 180° rotations about the [111]-oriented axis in a cubic system are described
with respect to the basis \{[a00], [0a0], [00a]\} by the matrix

\[
D = \frac{1}{3} \begin{pmatrix}
-1 & 2 & 2 \\
2 & -1 & 2 \\
2 & 2 & -1
\end{pmatrix},
\]  

(6.3)

For the transformation into the chalcopyrite system with the basis \{[a00], [0a0], [00c]\} \(D\) has to be multiplied by the metric matrix \(g\) and its inverse:

\[
R_{180^\circ} = g^{-1} \cdot D \cdot g,
\]

(6.4)

It is assumed that \(c/a = 2\). Therefore,

\[
g = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 2
\end{pmatrix}, \quad g^{-1} = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & \frac{1}{2}
\end{pmatrix}
\]

(6.5)

\(g^{-1}\) denotes the metric of the reciprocal chalcopyrite space with respect to a basis \{((2\pi)/a 00), (0 (2\pi)/a 0),(00 (2\pi)/c)\}(see chapter 1.3). This leads to

\[
R_{180^\circ} = \frac{1}{3} \begin{pmatrix}
-1 & 2 & 4 \\
2 & -1 & 4 \\
1 & 1 & -1
\end{pmatrix}
\]

(6.6)

The matrices belonging \(\pm 60^\circ\) rotations about a [221]-oriented axis are obtained by multiplying the \(180^\circ\) matrix with the \(\pm 120^\circ\) matrices which is nothing else but a permutation of the rows of the matrix adjusting the metric to the chalcopyrite system:

\[
R_{+60^\circ} = R_{180^\circ} \cdot R_{-120^\circ} = \frac{1}{3} \begin{pmatrix}
2 & 2 & -2 \\
-1 & 2 & 4 \\
1 & -\frac{1}{2} & 2
\end{pmatrix},
\]

(6.7)

and

\[
R_{-60^\circ} = R_{180^\circ} \cdot R_{+120^\circ} = \frac{1}{3} \begin{pmatrix}
2 & -1 & 4 \\
2 & 2 & -2 \\
-\frac{1}{2} & 1 & 2
\end{pmatrix}
\]

(6.8)
Rotations about the [221]-oriented axis in real space result in corresponding rotations about the (112)-oriented axis in reciprocal space.

Figure 6.9: SADP of $\bar{1}$10 zone axis. Extra spots can be obtained by rotating the reciprocal CuIn$_x$Se$_y$ lattice by $\pm 60^\circ$ or $180^\circ$ about an axis along $g = 112$, and by multiple diffraction (spot marked with e).

The presence of $\pm 60^\circ/180^\circ$ twins is most obvious in the cross-sectional $\bar{1}$10 diffraction pattern shown in Fig. 6.9. The SADP contains extra spots which can be obtained by rotating the chalcopyrite $\bar{1}$10 pattern about the (112) direction in reciprocal space by $180^\circ$. Extra spots of this type were not found in the [110], [201] and [021] patterns, and therefore no rotational twins were observed for CuIn$_x$Se$_y$/Si(111) on (112), (112) or (112) planes. $180^\circ$ rotational twins on {112} planes in polycrystalline CuIn$_x$Se$_y$ have been discussed in several papers [TR$^+$90, KPKR91, WNN94a, WNN94b]. The twins are expected to be caused by growth accidents, i.e. changes in the growth conditions owing to poor control of growth parameters. The twinning can occur at the interface of substrate and layer (type B growth) as well as inside
the layer. Fig. 6.10 shows a high resolution transmission electron micrograph of a CuInxSey/Si(111) cross-sectional sample where the twin is located inside the layer. The figure displays two regions separated by a coherent [221] oriented twin boundary (a) and a partly coherent boundary (b) with orientation [111]. The boundary marked with (b) is related to the three-dimensional growth of the layer. It was formed during the growth when two islands with a different twin orientation met. This boundary is similar to symmetric Σ3 type (112) boundaries in fcc lattices [Hof94]. The (112) planes, which are not in the region of the junction of the coherent twin boundary, are discontinuous at the partly coherent boundary. The discontinuity is due to atomic relaxation at the boundary [II85]. The twins and the partly coherent boundary can be simulated by periodically inserting partial dislocations with Burgers vectors \( \frac{2}{6}[111] \), \( \frac{2}{12}[421] \) and \( \frac{2}{12}[241] \) into the perfect lattice as shown in Fig. 6.11. It was reported that rotational twins on \( \{112\} \) planes in chalcopyrite Cu-In-Se compositions can be eliminated by thermal annealing [XYR94]. The annealing obviously activates the movement of the partial dislocations mentioned above on \( \{112\} \) glide planes. The dislocations either glide to the surface of the crystal or they annihilate with a partial dislocation from another partly coherent boundary.

In addition to the reflections at positions \{1\overline{1}0\} extra spots in the CuInSe\(_2\)/Si(111) [221] SADP (Fig. 6.4(a)) are observed at the positions \{\overline{3}33\}. There are two reasons why these spots are caused by ±60°/180° twins on (112) planes. Firstly, based on a publication by Pashley and Stowell on face-centered cubic gold films [PS63], \{\overline{3}33\} reflections can arise from multiple diffraction of beams passing through "matrix" and rotated domain. \( \frac{2}{3}44 \overline{3}33 \) for example can be written as

\[
\frac{2}{3}44\overline{3}33 = 1\overline{1}2 - \frac{1}{3}10 \overline{3}33
\]

(6.9)

\( 1\overline{1}2 \) ("matrix") and \( \frac{1}{3}10 \overline{3}3 \) ("60°", indexed with respect to the "matrix") are the primary spots. Spots can be generated by double diffraction only if the primary spots are present in the diffraction pattern. The \{1\overline{1}2\} and the \{\overline{1}10\overline{3}3\} spots belong to
Figure 6.10: High resolution transmission electron microscopy image of CuIn_xSe_y taken along [\bar{1}10] showing a coherent twin boundary (a) and a partly coherent boundary (b) separating twinned regions. The (11\overline{2}) planes are discontinuous at the partly coherent boundary because of relaxation in the lattice.

the first Laue zone of the [221] zone axis and only appear in the [221] diffraction pattern if the sample is bent or tilted away from the [221] orientation. The reflection in Fig. 6.4(a) marked with an arrow is at a position of \{1\overline{1}2\} and \{\overline{1}1\overline{1}6\} spots, and the bending of the samples was obvious during the tilting experiments in the SADP mode. The second reason is related to the change in the stacking sequence of (112) planes caused by the ±60°/180° twins. The CuIn_xSe_y stacking sequence of (112) planes is ...A-B-C-A-B-C-... when combining one cation and one anion plane, and when neglecting the cation superlattice. At the twin boundaries this stacking sequence is reversed: ...A-|B-C-B|-A-.... The sequence |B-C-B| corresponds to the stacking se-
Figure 6.11: The insertion of a sequence of partial dislocations with Burgers vectors $b_1 = \frac{a}{6}[1\bar{1}]$, $b_2 = \frac{a}{12}[4\bar{2}1]$, and $b_3 = \frac{a}{12}[241]$, into a perfect chalcopyrite lattice (left side) causes rotational twinning on (112) planes by ±60° and 180° (right side). The twinned regions are separated by a coherent twin boundary and by a partly coherent boundary containing the inserted dislocations (⊙ anion, • cation).

Figure 6.11: The insertion of a sequence of partial dislocations with Burgers vectors $b_1 = \frac{a}{6}[1\bar{1}]$, $b_2 = \frac{a}{12}[4\bar{2}1]$, and $b_3 = \frac{a}{12}[241]$, into a perfect chalcopyrite lattice (left side) causes rotational twinning on (112) planes by ±60° and 180° (right side). The twinned regions are separated by a coherent twin boundary and by a partly coherent boundary containing the inserted dislocations (⊙ anion, • cation).

sequence of (0001) planes of materials with wurtzite structure. The structure around coherent twin boundaries is therefore similar to the wurtzite structure for which reflections at $\{\frac{2}{3}\frac{4}{3}\frac{4}{3}\}$ positions are characteristic. Calculations of electron diffraction from a supercell containing ±60°/180° twins separated by coherent twin boundaries on (112) planes showed that spots at $\{\frac{2}{3}\frac{4}{3}\frac{4}{3}\}$ positions are related to these twins. The calculations are based on the kinematical theory of electron diffraction. For the same reason stacking faults on {112} planes as they were observed in CuIn$_x$Se$_y$/Si(111) layers also contribute to the intensity of these spots. Dark field images taken with $\{\frac{2}{3}\frac{4}{3}\frac{4}{3}\}$ showed that both explanations are applicable for the investigated samples.
6.2.3 Separating Twin Variants and Twin Boundaries

The easiest way to separate twins is by TEM dark field images. For this purpose the [131] zone axis was chosen because

- it contains the (112) direction, and therefore rotations about (112) are visible in SADPs along [131],

- it is a low symmetry zone axis, and therefore the presence of rotational twins will result in extra reflections needed for the dark field imaging,

- rotations by ± 120° can be detected by the presence or absence of chalcopyrite spots, and

- the [131] zone axis is located near the [221] zone axis and is therefore suited for plane-view investigations.

For twinned regions superpositions of diffraction patterns along the following zone axes are expected in the [131] SADP:

\[
\begin{align*}
[131] & \equiv \overline{m} \\
[\overline{6}41] & = R_{+120^\circ} \cdot \overline{m} \\
[423] & = R_{-120^\circ} \cdot \overline{m} \\
[311] & = R_{180^\circ} \cdot \overline{m} \\
[4\overline{6}1] & = R_{+60^\circ} \cdot \overline{m} \\
[243] & = R_{-60^\circ} \cdot \overline{m}
\end{align*}
\]

(6.10)

The SADP taken along [131] is shown in Fig. 6.12(a). The calculated pattern in Fig. 6.12(b) illustrates that the SADP is a superposition of the diffraction patterns of up to six different zone axes belonging to regions which are rotated about [221] with respect to the "matrix" as described in 6.10. Additional spots in the [131] diffraction
Figure 6.12: (a) Experimental diffraction pattern of CuIn$_x$Se$_y$/Si(111) oriented along [131]. The pattern is the superposition of patterns belonging to six different zone axes as shown in Fig. (b): [131] ("matrix") pattern (●), [641] (+120°) and [423] (-120°) patterns (△), [311] (180°) pattern (○), [461] (+60°) and [243] (-60°) patterns (□). Extra spots in (a) (e.g. the one marked with e) are due to multiple diffraction. Patterns (for example the one marked with "e") in Fig. 6.12(a) can arise from multiple diffraction. Regions belonging to different twin variants are distinguished in the dark field images shown in Fig. 6.13(a)-(d). Each dark field image was taken using a reflection marked in Fig. 6.12(a) with letters a-d. The relation of the bright regions to twin variants is described in Table 6.1. The size of the domains in the lateral direction is about 0.1 to 1 μm. This explains the sharpness of the extra spots in the SADPs. The distribution of the twinned domains seems to be random. The reference domains ("matrix") and the domains rotated by ±120° occupy about the same area as the ones rotated by ±60° and 180°, as can be seen when comparing Figs. 11(a) and (b). This indicates that ±60°/180° rotational twins are common in CuIn$_x$Se$_y$/Si(111).
Figure 6.13: Dark field images (a)-(d) taken along [131] and formed using the beams marked in Fig. 6.12(a) with the same letter. Different twin variants are distinguished by bright regions (see Table 6.1). Black regions are holes caused by the preparation of the TEM sample.
Table 6.1: Separation of twin variants. Bright regions belonging to twin variants are responsible for the appearance of the spots a-d.

<table>
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<th>Matrix</th>
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<th>+60°-120°</th>
<th>120°-180°</th>
<th>180°-240°</th>
<th>240°-300°</th>
<th>300°-360°</th>
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<tr>
<td>Spot c</td>
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</tbody>
</table>
Chapter 7

INVESTIGATION OF INTERFACES BETWEEN SUBSTRATE AND EPITAXIAL CuIn$_x$Se$_y$ LAYER

7.1 Defects at the Interface

In order to investigate linear and planar defects at the interface of CuIn$_x$Se$_y$ and the substrate, cross-sectional high resolution transmission electron microscopy (HRTEM) studies have been performed. Fig. 7.1 shows a HRTEM micrograph displaying an interfacial region of a CuIn$_x$Se$_y$ layer and the Si(111) substrate. The ion milling process used for the TEM sample preparation may cause some damage at the interface (see chapter 3.1).

7.2 Defects at the Interface

In order to investigate linear and planar defects at the interface of CuIn$_x$Se$_y$ and the substrate, cross-sectional high resolution transmission electron microscopy (HRTEM) studies have been performed. Fig. 7.1 shows a HRTEM micrograph displaying an interfacial region of a CuIn$_x$Se$_y$ layer and the Si(111) substrate. The ion milling process used for the TEM sample preparation may cause some damage at the interface (see chapter 3.1).

The displayed region of the CuIn$_x$Se$_y$ layer in Fig. 7.1 is divided into two parts; one is untwinned with respect to the substrate and the other is twinned by a rotation of ±60° or 180° about the [221] growth direction. The twins are separated by twin boundaries (tb) on (112) growth planes and partially coherent Σ3-type boundaries (Σ3) on (114) planes (see chapter 6.2). The 'untwinned' part is overgrown by the
Figure 7.1: HRTEM micrograph of a CuIn$_x$Se$_y$/Si(111) interfacial region displaying twins and stacking faults. The arrow marks a stacking fault starting at the interface.

'twinned' part after a thickness of about 10 nm. Twins like the ones shown in Fig. 7.1 are islands which had been formed because of the 3-d growth. The islands join during the growth, forming partly coherent boundaries like the $\Sigma 3$-type boundary displayed in Fig. 7.1. With increasing thickness some of the islands are overgrown by neighbors which lead to a reduction of twins. Extrinsic (on (112) planes) and intrinsic (on (112) planes) stacking faults (SF) are also displayed in Fig. 7.1.

Strain in the layers induced by lattice and thermal mismatch between Si and CuIn$_x$Se$_y$ is compensated by misfit dislocations with Burgers vectors of type $a/2 \cdot [110]$ at the interface (Fig. 7.2). Such a dislocation can split into two partial dislocations with Burgers vectors of type $a/6 \cdot [11\bar{1}]$. The splitting of a misfit dislocation with a
Burgers vector $a/4 \cdot [021]$ into two partial dislocations with Burgers vectors $a/12 \cdot [241]$ and $a/6 \cdot [111]$ possibly gives rise to the growth of a stacking fault on the $(11\bar{2})$ glide planes. The stacking fault is created by the gliding of one of the partial dislocations along the $(11\bar{2})$ plane. In Fig. 7.1 a stacking fault on a $(11\bar{2})$ plane starting from the interface is marked with an arrow.

The presence of misfit dislocations is not sufficient for the compensation of the thermal mismatch between CuIn$_x$Se$_y$ and Si. Layers with fewer twins grown at substrate temperature of about 600°C cracked and peeled off during the cooling process after the growth (see section 4.1). Sridhar et al. [SRS96b] showed - using equilibrium conditions for the stress in layer and substrate - that twins formed on the growth planes contribute to the relaxation of strain in thin layers. Therefore the presence of twins similar to the ones shown in Fig. 7.1 supports the growth of crack free CuIn$_x$Se$_y$ layers on Si(111).

The most common defects observed in HRTEM images of CuIn$_x$Se$_y$/GaAs(001)
are nanotwins (or defect stacking sequences) on \( \{112\} \) planes (see section 6.1). Similar to CuIn\(_x\)Se\(_y\)/Si(111), these faults are related to the gliding of partial dislocations on 112 planes as described above. Fig. 7.3 shows a HRTEM image displaying two nanotwins (nt) starting at the interface. Assuming [110] for the direction of the electron beam, one of the nanotwins is formed on a (112) and the other on a (112) planes. The expansion of stacking faults and nanotwins into the layer can be inhibited by the interaction of two faults as shown in Fig. 7.3. For each plane involved, this interaction can be described by the reaction of two partial dislocations with Burgers vectors \( a/6 \cdot \langle 111 \rangle \). One or both stacking faults will be terminated if the partial
dislocations annihilate one another, or if the resulting dislocation has a different glide plane.

7.3 Interaction between Layer and Substrate

The interdiffusion of elements between layer and substrate and the presence of interfacial layers were investigated by RBS using $^{4}$He ions accelerated with 2 MeV, microprobe EDX performed in the scanning mode of the transmission electron microscope (STEM) and XRD.

Figure 7.4: RBS spectra of CuIn$_x$Se$_y$/Si(111): (+) experimental data, (—) one-layer simulation, (—-—) two layer simulation including the diffusion of Cu and Se into the substrate.

Fig. 7.4 shows a RBS spectrum of a CuIn$_x$Se$_y$/Si(111) layer. A fitting of the thicknesses of the peaks is only possible using two layers, an about 60 nm thick Cu-
In-Se top layer and an about 7 nm thick In-free bottom layer. There are two equivalent possibilities to adjust the peak positions. One is a homogeneous incorporation of Si into the bottom layer, the other a roughening of the interface layer surface.

![Diagram](image)

Figure 7.5: Microprobe EDX elemental mapping of CuIn$_x$Se$_y$/Si(111). Bright regions correspond to higher concentrations. The boundaries of the CuIn$_x$Se$_y$ layer are marked with a dashed line.

In order to distinguish these two possibilities elemental mappings of the same sample were measured using microprobe EDX. Maps of the Cu-K, In-L, Se-K and Si-K EDX signals are displayed in Fig. 7.5. The size of the fluorescent region in the sample limits the lateral resolution to about 5 nm (see chapter 3.1). The overlapping of Cu-K (Fig. 7.5(a)) and the Se-K (Fig. 7.5(c)) signals with the Si-K signal (Fig. 7.5(d)) within an 5-10 nm thick region indicates an interaction between Cu and Se on one side and Si on the other side. No interdiffusion between Si and In is observed from the maps of the In-L signal in Fig. 7.5(b) and the Si-K signal. Therefore, the RBS spectrum and the EDX maps indicate the presence of an about 10 nm thick bottom
layer containing Cu, Se and Si. Assuming a smooth surface of the layer the RBS spectrum shown in Fig. 7.4 can be fitted using a 60 nm thick top CuInSe₂ layer and a 7 nm thick bottom layer with the composition ratios Cu:Se:Si=3:2:5.

![HRTEM image of CuInₓSeᵧ/Si(111) displaying the CuInₓSeᵧ interfacial layer.](image)

Figure 7.6: HRTEM image of CuInₓSeᵧ/Si(111) displaying the CuInₓSeᵧ interfacial layer.

A continuous 6 nm thick interfacial region corresponding to the CuSeₓSiᵧ bottom layer was also visible in HRTEM images. Fig. 7.6 shows a twinned region at the interface. Cu-Si compounds are expected to form when heating a Cu layer deposited on Si to about 600°C. The bottom layer was possibly formed during the growth, but not at an early stage. This would explain that twin boundaries marked as (tb) in Fig. 7.6 were observed at the interface of top and bottom layers but never at the interface to Si. A similar interfacial layer was observed by Wada [Wad98] for polycrystalline Cu(In,Ga)Se₂ grown on Mo-coated glass. A 50-100 nm thick MoSe₂ layer was identified by XRD and HRTEM between Mo and the Cu(In,Ga)Se₂ absorber layer.

The Cu and Se peaks of the RBS spectrum shown in Fig. 7.4 are characterized by wings at the back of the peaks. These wings are due to strong diffusion of Cu and Se
in to Si. The wings were fitted assuming diffusion coefficients of about $2 \times 10^{-13} \text{ cm}^2/\text{s}$ for Cu and $8 \times 10^{-14} \text{ cm}^2/\text{s}$ for Se.

Figure 7.7: EDX spectra of different regions in a cross-sectional CuIn$_x$Sey/GaAs(001) sample: (a) GaAs substrate, 500 nm away from the interface, (b) substrate, 50 nm away from the interface, (c) CuIn$_x$Sey, 50 nm away from the interface.

CuIn$_x$Sey/GaAs(001) interfacial interactions were studied by microprobe EDX. Fig. 7.7 shows EDX spectra of the cross-sectional sample. Three different regions; (a) GaAs substrate (far away from the interface), (b) substrate (near to the interface) and (c) CuIn$_x$Sey layer (near to the interface) were investigated. While no other elements than Ga and As were detected in the substrate far away from the interface (Fig. 7.7(a)) the diffusion of Cu in to the substrate was observed near the interface (Fig. 7.7(b)). On the other side Ga diffuses from the the substrate into the layer (Fig. 7.7(c)).
Figure 7.8: X-ray diffractograph of CuIn$_x$Se$_y$/GaAs using Cu-K$_\beta$ radiation. The splitting and the position of the (400) peak belonging to the layer indicates the presence of a CuIn$_x$Ga$_y$Se$_z$ phase.

Schroeder et al. [SBR96] performed a detailed study of the diffusion of Ga in CuIn$_x$Se$_y$ layers grown on GaAs at high substrate temperatures (725°C) and observed a strong dependence of the diffusivity on the Cu/In ratio. For Cu- and In-rich layers the diffusion constant was more than ten times larger than for stoichiometric CuInSe$_2$ layers, which indicates that the diffusion of Ga is enhanced by a diffusion mechanism involving either In or Cu vacancies. This would mean that Ga diffused into the layer is incorporated in the lattice of CuIn$_x$Se$_y$. Fig. 7.8 shows a x-ray diffraction $\Theta - 2\Theta$ scan of an In-rich CuIn$_x$Se$_y$/GaAs(001) layer. The reflections with peak positions 58.14° and 58.50° belong to the layer which therefore consist of two phases. A rough estimate of the lattice constants from the peak leads to lattice constants $a = 0.573$ nm for the peak at 58.14° and $a = 0.570$ nm for the peak 58.50°. The Cu/In ratio - measured
by EDX in a scanning electron microscope - was about 1:3. The lattice constant of CuIn₃Se₅ is about 0.575 nm [HYN+96]. This difference as well as the high 2Θ value of the peak at 58.50° indicate that the layer consists of a CuInₓSeᵧ β-phase with [Cu]:[In]< 1 : 3 and an additional CuInₓGaᵧSeₓ compound.
7.4 Tetragonality of CuIn$_x$Se$_y$/Si(111) near the Interface

The deviation $\delta$ from the "ideal" tetragonality $c/a = 2$ can be defined by

$$\delta = \frac{c - 2a}{2a}$$

where $a$ and $c$ are the lattice constants of CuIn$_x$Se$_y$. For CuIn$_x$Se$_y$ bulk single crystal with $a = 0.5789$ nm and $c = 1.1612$ nm the tetragonality is 0.3-0.6% [SCS86, MDM+98, OSoY+94]. For CuIn$_x$Se$_y$/Si(111) the tetragonality of the layer results in a growth direction slightly off the (111) orientation of the substrate. The angle between $\langle 111 \rangle_{\text{Si}}$ and the $\langle 112 \rangle_{\text{cis}}$ growth planes depends on the $c/a$ ratio of the CuIn$_x$Se$_y$ unit cell. The transformation between the chalcopyrite and the cubic coordinate system is described in section 1.3 by the expressions 1.2, 1.4, 1.5 and 1.6. The [221] chalcopyrite direction corresponds in the cubic system to the direction $[1 1 c/(2a)]$ or $[1 1 (1+\delta)]$. The angle $\phi$ between the vectors $\vec{a}$ and $\vec{b}$ is described by

$$\cos \phi = \frac{\vec{a} \cdot \vec{b}}{||\vec{a}|| \ ||\vec{b}||}$$

In the cubic system, the angle $\phi$ between the cubic $[111]$ planes of the substrate and the chalcopyrite $[221]$ planes of the layer is therefore given by

$$\cos \phi = \frac{[111] \cdot [1 1 (1+\delta)]}{\sqrt{3} \cdot \sqrt{2 + (1+\delta)^2}}$$

For $c/a \approx 2.006$ (0.3% tetragonality) $\phi$ is 0.16°. Fig. 7.9 a displays HRTEM image of a CuInSe$_2$/Si(111) interface. The angle $\phi$ between the $(112)$ planes of the layer and the $(111)$ cubic planes is about 0.3±0.1° which shows that the deviation from $c/a = 2$ is increased near the interface. For the calculation of $\delta$ from the angle between planes of layer and substrate the expression 7.3 is used. Solving the scalar product in the numerator and bringing the denominator under one square root leads to

$$\cos \phi = \frac{3 + \delta}{\sqrt{9 + 6\delta + 3\delta^2}}$$
Taking the square of the whole equation and reducing the fraction then gives

\[
\cos^2 \phi = \frac{(3 + \delta)^2}{9 + 6\delta + 3\delta^2} = \frac{9 + 6\delta + \delta^2}{9 + 6\delta + 3\delta^2} \\
= 1 - \frac{2\delta^2}{9 + 6\delta + 3\delta^2} \\
\approx 1 - \frac{2\delta^2}{9},
\]

(7.5)

or

\[
\delta \approx \sqrt{\frac{9}{2}} (1 - \cos^2 \phi)
\]

(7.6)

For \( \phi = 0.3^\circ \) the deviation from \( c/a = 2 \) is about 1%.

Another way to estimate the tetragonality is by measuring the angle between the (112) planes of a type A and a type B grown island. Fig. 7.10 shows a HRTEM micrograph displaying the partly coherent boundary between two such islands, twin\(_A\) and twin\(_B\). The distance to the interface is about 30-60 nm. The angle \( \phi \) between the (112) of their planes is about 0.6°. Twin\(_A\) is type A grown and twin\(_B\) is twinned by 180° with respect to the substrate. Since the twin was formed in the interface the axis of rotation is the cubic [111] axis and not the [221] axis of the layer. The rotation of the [221]\(_A\) \( \hat{\Delta} [1 1 (1 + \delta)]_{\text{cubic}} \) direction about the cubic [111]-oriented axis by 180° leads to the new direction [221]\(_B\)

\[
\frac{1}{3} \begin{pmatrix}
-1 & 2 & 2 \\
2 & -1 & 2 \\
2 & 2 & -1
\end{pmatrix}
\begin{pmatrix}
1 \\
1 \\
1 + \delta
\end{pmatrix}
= 
\begin{pmatrix}
1 + \frac{2\delta}{3} \\
1 + \frac{2\delta}{3} \\
1 - \frac{\delta}{3}
\end{pmatrix} \sim [221]_{\text{B,chal}}
\]

(7.7)

The angle \( \phi \) between \( [1 1 (1 + \delta)] \sim [221]_{\text{A,chal}} \) and \( [(1 + \frac{2\delta}{3}) (1 + \frac{2\delta}{3}) (1 - \frac{\delta}{3})] \sim [221]_{\text{B,chal}} \) is given by 7.2. Similar transformations as the ones performed in 7.4 and 7.5 lead to

\[
\cos \phi \approx 1 - \frac{4\delta^2}{9},
\]

(7.8)
or

\[ \delta \approx \frac{3}{2} \sqrt{1 - \cos \phi} \]  

(7.9)

The measured angle \( \phi = 0.6^\circ \) corresponds again to a deviation from \( c/a = 2 \) by about 1\% which is again about by a factor 2-3 higher than in a relaxed layer or a bulk single crystal.

The large \( \delta \) value is possibly due to the anisotropic thermal expansion of \( \text{CuIn}_x\text{Se}_y \). It is larger at the high deposition temperatures because of the difference in the thermal expansion coefficients along the \( a \)- and the \( c \)-axis. During the cooling down of the sample the contraction of the interfacial \( \text{CuIn}_x\text{Se}_y \) region is determined by the isotropic thermal expansion coefficient of the Si substrate. Consequently the high \( \delta \) value is conserved. The lattice constants of \( \text{CuIn}_x\text{Se}_y \) at the interfacial region were estimated by measuring the lattice spacings of (112) and (100) planes in Fig. 7.9, and the values \( a = 0.55 \pm 0.01 \) nm and \( c = 1.12 \pm 0.01 \) nm were obtained. This shows that near the interface the \( \text{CuIn}_x\text{Se}_y \) lattice is adjusted to the Si substrate. Both, the reduced lattice constants and the enhanced deviation from \( c/a = 2 \) illustrate the strain in the \( \text{CuIn}_x\text{Se}_y \) lattice near the interface to Si.
Figure 7.9: HRTEM micrograph displaying a CuInSe$_2$/Si(111) interfacial region. The angle between the (111)$_{\text{Si}}$ and (112)$_{\text{CIS}}$ planes of about 0.3° is due to a deviation from $c/a = 2$ of 1%.
Figure 7.10: HRTEM micrograph displaying the angle between (112) planes of type A ($twin_A$) and type B ($twin_B$) grown islands on Si(111).
Part II

Cu(In,Ga)Se$_2$ and CuGaSe$_2$
Substrate Solar Cells
Chapter 8

PREPARATION OF Cu(In,Ga)Se$_2$ SUBSTRATE SOLAR CELLS

In this chapter the preparation of Cu(In,Ga)Se$_2$ substrate thin film solar cell is described. A general introduction to solar cells (including thin film solar cells) can be found for example in [LJ95].

Fig. 8.1 shows the typical structure of a substrate Cu(In,Ga)Se$_2$ (CIGS) based solar cell. The choice of substrate material - either sodium free glass like Corning 7059 or sodium containing glass like standard soda-lime glass as used for architectural applications - strongly affects the electrical properties of the solar cells (see below).
The back contact consisting of an about 1 μm thick Mo layer was deposited by electron beam evaporation at the Institut für Physikalische Elektronik in Stuttgart.

The most important layer of the solar cell, the \emph{p-type Cu(In,Ga)Se_2 absorber layer}, was deposited in our MBE system (see chapter 2.1) by simultaneous thermal evaporation of the elements. The substrate temperature was about 500-600°C. The growth of the absorber layer is based on a “bi-layer growth process” similar to the process described by Bodegård [Bod96]. The growth was started under Cu-rich and finished under (In,Ga)-rich conditions. The Cu-rich growth was important to obtain Cu(In,Ga)Se_2 layers with large grains. The flux of Cu was decreased towards the end of the growth to adjust the overall composition of the absorber layer which helped to avoid the segregation of Cu-Se at the surface. Therefore a chemical treatment of the surface (e.g. with KCN) was not necessary. Another consequence of this process is the formation of a Cu-depleted surface [SRS96a] which can result in an intrinsic p-n junction. The energy band gap of the Cu(In,Ga)Se_2 absorber layer is controlled by the [In]/[Ga] ratio. Depending on the Ga concentration the band gap is between 1.05 and 1.68 eV. The increase in the open circuit voltage ($V_{OC}$) of cells with Ga-rich absorber layers is partly compensated by a low short circuit current ($I_{SC}$). Cells with the highest efficiencies (17.7%) were obtained with [In]/[Ga]\textasciitilde 3 : 1 which results in a band gap of about 1.2 eV [SGN+95, Bod96].

Because of the high absorption coefficient of Cu-In-Ga-Se compounds ($10^5$ cm$^{-1}$) a layer thickness of 1.5 to 2 μm is sufficient to absorb the useful part of the sunlight. Therefore good transport properties of absorber layers will be obtained if the size of the grains in the polycrystalline layer is larger than about 1-2 μm. Fig. 8.2 shows a SEM micrograph displaying the morphology of a Cu(In,Ga)Se_2 absorber layer grown with large grains (> 2μm). The absorber layer was grown on Mo-coated soda lime glass. Sodium diffuses during the growth from the substrate into the absorber layer [SHK+93, GSB+97] and enhances the crystal growth of Cu(In,Ga)Se_2. As a result the grain size is increased significantly. This behavior is illustrated in Fig. 8.3 which
shows a SEM morphology of another Cu(In,Ga)Se$_2$ absorber layer grown on Mo which was deposited on a "polymer substrate with a high sodium concentration". The Mo layer cracked during the heating of the substrate to 500°C. Fig. 8.3 shows that the grain size is significantly larger for the grains located on top of a crack because of the enhanced diffusion of sodium through the crack in the Mo layer. Apart from enhancing the grain growth sodium acts as a p-type dopant in the absorber layer increasing the carrier concentration. The effect of sodium on the microstructure of the absorber layer and on the cell performance is described in several publications [BHG+95, HFU+96, NIOK97, NHS97].

As mentioned above the conductivity of the Cu-depleted surface region in p-type CuInSe$_2$ and Cu(In,Ga)Se$_2$ (with $[\text{In}]/[\text{Ga}] \approx 3$) layers is inverted (n-type), and therefore a p-n homojunction is formed inside the absorber layer. Nevertheless high efficiency solar cells have been obtained only with an about 50 nm thick CdS buffer layer deposited by CBD (see chapter 2.2). CdS is an n-type semiconductor with a band gap of 2.4 eV. Because of the wide energy gap most of the visible light is transmitted. The absorption losses can be further minimized by reducing the
Figure 8.3: SEM micrograph showing Cu(In,Ga)Se₂ deposited on a cracked Mo layer. The large size of the grains on top of the crack is related to the strong diffusion of Na through the crack.

thickness of the layer. The deposition in the chemical bath has, compared to e.g. the physical vapor deposition (PVD) of CdS, beneficial effects which are important for the cell performance [WHH⁺98]:

- For thin CdS layers the transmission of light is higher. Continuous CdS layers can be obtained by CBD with smaller thicknesses than PVD grown layers [LV91].

- The surface of the Cu(In,Ga)Se₂ absorber layer is etched in the chemical bath [NHS⁺99], and therefore the CdS deposition starts on a clean surface free of adsorbed and surface oxides.

- Investigations by Wada et al. [WHH⁺98] and Ramanathan et al. [RWA⁺98] revealed the presence of Cd in the Cu(In,Ga)Se₂ absorber (see also chapter 9) and related it to a chemical reaction between the bath and the absorber layer. It was suggested that Cd acts as an n-type dopant in the Cu-depleted surface region.
CdS was deposited on the Cu(In,Ga)Se₂ absorber layer at different bath temperatures (see chapter 2.2), but no influence on the efficiencies was observed. This behavior is different for CuGaSe₂ solar cells as shown in chapter 9. For the industrial production of Cu(In,Ga)Se₂ thin film solar cells the CBD method is undesirable since it interrupts the vacuum process. Therefore efforts are being made to investigate the role of Cd in the absorber layer and eventually develop a high efficiency cell without a CdS buffer layer.

The window layer consisting of a double layer of ZnO was deposited by rf sputtering: a thin, not extrinsically doped layer (50-100 nm) and an Al-doped conducting layer (1 μm) have been deposited by rf sputtering (see chapter 2.3). The purpose of the thin n-doped ZnO layer is to increase the electric field across the cell for a better transport of the free carriers. n⁺-doped ZnO (ZnO:Al) is used as the transparent conducting front contact of the cell. The samples were mechanically scribed to prepare cells with an area of 0.1-0.2 cm². These small areas were chosen to separate pin holes which destroy the cell.

With the processes described above small area cells with efficiencies of 13-16% were prepared. The I-V-curve and the characteristics of a 15.7% efficiency cell are displayed in Fig. 8.4. Compared with the Cu(In,Ga)Se₂ cells with the highest efficiencies of 17.7% [SGN+95, Bod96] the open circuit voltage V_{OC} is about 40 mV smaller which is due to a lower Ga content in the absorber layer. However, the fill factor FF describing the quality of the diode and the short circuit current I_{SC} are comparable. An anti-reflecting coating and a metal grid on top of the cells would lead to an increase of the efficiencies by about 0.5%.
Figure 8.4: $I$-$V$ curve of a 15.7% efficiency cell. $V_{OC}$: open circuit voltage, $I_{SC}$: short circuit current (density), $FF$: fill factor, $\eta$: efficiency [LJ95].
Chapter 9

MICROSTRUCTURAL STUDY OF THE CdS/CuGaSe₂ INTERFACIAL REGION

9.1 CuGaSe₂-Based Substrate Cells

CuGaSe₂ with a bandgap of 1.68 eV is a member of the Cu chalcopyrite family which has been investigated as an absorber layer for solar cells for more than 20 years [RST77]. The structures of CuGaSe₂ and Cu(In,Ga)Se₂ substrate cells are the same (Fig. 8.1). It is well known that the Cu/(In+Ga+Cu) ratio has a strong influence on the properties of the absorber layers and the solar cells. Cu-rich CuGaSe₂ contains free carrier concentrations which are about three orders of magnitudes higher (10¹⁸ cm⁻³) than in Ga-rich material, and was therefore (in the case of Na-free substrate glasses) more suitable for applications in solar cells. On the other hand, Cu₅Se is formed if the film composition deviates slightly towards Cu-rich compositions. These binary selenides segregate mainly on the film surface or at the grain boundaries as was shown by x-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray (EDX) analysis [Kle93]. This behavior is similar for CuInSe₂, CuInS₂ and CuGaSe₂ [KSS93, KWSC94, WBD+96, NFY+97, FNYT97] and in agreement with the phase diagrams which predict the formation of the copper selenides for small deviations from the 1-1-2-stoichiometry or even for stoichiometric compositions [HGE+98, Mik81]. Cu₅Se is a degenerate p-type semiconductor and causes shunts in the p-n junction. Therefore it has to be removed by etching with KCN [KMCS90, ea94] before the deposition of the buffer layer. Only with the help of this treatment can solar cells
based upon Cu-rich CuGaSe₂ be prepared, although the open circuit voltage is still limited to about 750 mV.

Recent investigations based on a new preparation method of CuGaSe₂-based thin film solar cells resulted in a new record efficiency of 9.3% [NHS97]. In this case the absorber layer consists of Ga-rich CuGaSe₂ on sodium-containing glass. The lower doping concentration of the Ga-rich material is partly compensated by the presence of sodium which acts as a p-type dopant in CuInSe₂, Cu(In,Ga)Se₂ and CuGaSe₂. During the deposition process at 600°C sodium diffuses from the glass substrate through the Mo back contact into the absorber layer (see chapter 8). The doping concentration is in the range of 5x10¹⁶ cm⁻³ [NHS+99]. Owing to the presence of a Ga-rich absorber, the KCN treatment is obsolete. A third major change in the solar cell preparation recipe is the application of elevated bath temperatures for the CBD of the CdS buffer layer in order to adjust the process to the needs of the very sensitive surface of the CuGaSe₂ films. With the recent progress in efficiency the idea conceived earlier of tandem solar cells consisting of a CuInSe₂ bottom cell and a CuGaSe₂ top cell seems to be realistic for a further increase of efficiency.

The efficiencies of CuGaSe₂-based devices, however, still lag behind the values achieved for the lower-gap chalcopyrites. Losses are mainly caused by a low open circuit voltage when compared with the band gap of the absorber layer. The decisive differences between CuInSe₂ and CuGaSe₂ are due to the position of the Fermi level at the absorber surface and the band alignment of the heterojunction to the CdS buffer layer. For CuGaSe₂ solar cells there is no inversion of the conduction type at the surface and therefore the p-n junction is located at the CuGaSe₂/CdS interface [NBS98]. The second important difference is the band offset in the conduction band between CdS and the absorber layer. For CuInSe₂ the conduction band offset is positive while for CuGaSe₂ it is negative [HNR+97]. Both, the position of the p-n junction at the CdS/CuGaSe₂ interface as well as the negative offset of the conduction band, cause a more pronounced dependence of the electrical parameters of the solar
cell on the quality of the CuGaSe2/CdS interface because of interface-related and tunneling-assisted recombination mechanisms. Electronic states in the interfacial region are due to absorber oxidation and crystal defects in CdS at the interface. These defects are caused by the lattice mismatch between CuGaSe2 and CdS and are influenced by the growth conditions of the buffer layer. In order to achieve high-quality devices, careful treatment of the absorber surface and a recipe for the deposition of CdS by CBD (as mentioned above), adapted to the properties of the CuGaSe2 surface, are needed.

In this chapter the principal limitations of solar cells based on Cu-rich absorber layers, the interactions between absorber and buffer layers and the microstructure of the CdS films with respect to device properties are described. The depositions and treatments of the layers were performed at the Institut für Physikalische Elektronik in Stuttgart. In the following the term "Cu-rich" will be used for films with a Cu/Ga ratio of about 1.1, measured by EDX before the KCN treatment. All these films were etched in a KCN solution (10 mol%) [LH87]. The term "Ga-rich" will be used for films with a Cu/Ga ratio of 0.9-0.95, no KCN treatment is applied in this case.

As mentioned above, the treatment of the absorber surface and the deposition method of the CdS layer are critical for the device performance. The absorber surface oxidizes very quickly, which results in the degradation of the solar cell parameters [NHS97]. Immediate deposition of the CdS layer on the absorber layer helps to avoid these losses. The standard bath temperature for the CdS layer deposition is 60°C. This process is well established for applications on CuInSe2 and Cu(In,Ga)Se2 with low Ga content [KVR+92] (see chapter 2.2). Layers deposited according to this recipe will be cited as "CdS(60°C)" in the following. Another recipe for CdS deposition from the aqueous solution, which is optimized for CuGaSe2, uses elevated bath temperatures at 80-85°C. Layers grown with this recipe will be called "CdS(80°C)". Ammonia (NH3) controls the reaction speed by adjusting the pH-value. In order to slow down the reaction which is accelerated at higher temperatures, the NH3 concentration is
increased in the 80°C recipe. Nevertheless the growth rate is higher for the 80°C recipe. The deposition time at 60°C is 5 min, whereas 3 min are sufficient at 80°C. Table 9.1 compares both recipes.

9.2 Precipitates in the Absorber Layer

As mentioned above, as a consequence of deviations from stoichiometric CuGaSe₂ towards Cu-rich compositions, copper selenides are formed in addition to the CuGaSe₂ phase according to the phase diagram [Mik81]. Copper selenides are found at the grain surfaces, i.e. at grain boundaries or on the top of the film. Therefore it is possible to remove them by a chemical treatment like KCN or NaCN [LH87]. Tuttle et al. [TAN91] performed XRD investigations on polycrystalline Cu-rich CuInSe₂ layers. In diffraction patterns measured before the KCN treatment extra XRD peaks were attributed to orthorhombic Cu₂Se and cubic Cu₂₋₄Se. The latter phase could be removed by the KCN treatment, but the peaks of the orthorhombic phase were still present in the XRD patterns obtained after the treatment. Based on these results, Tuttle et al. [TAN91] postulated a model for an intragranular microstructure of polycrystalline CuInSe₂ films with inclusions of Cu₂Se inside the grains, but this was not verified by microstructural studies.

Fig. 9.1 shows a cross-sectional TEM bright-field micrograph displaying a ZnO/-CdS/CuGaSe₂ region of a slightly Cu-rich (26 at% Cu, 24 at% Ga) solar cell. Before the deposition of CdS the absorber layer was treated with KCN. The micrograph shows the presence of precipitates in a CuGaSe₂ grain. Microprobe EDX analysis of the precipitates revealed a Ga-free composition. The constituents of the segregations are copper, selenium and sulfur, with Cu as the major component. Sulfur is not a constituent of the matrix. The reasons for its presence in the precipitates are not clear. The decomposition of the CdS layer during the ion milling process could be a source of the sulfur which replaces Se in the CuₓSe segregations. Walter et al.
Table 9.1: Comparison of the deposition conditions for CdS layers.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Cd salt</th>
<th>S(^2)- source</th>
<th>Additive</th>
<th>T(_{\text{End}}) (°C)</th>
<th>Duration (min)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>(\text{Cd(ActO)}_2) 0.0013</td>
<td>((\text{H}_2\text{N})_2\text{CS}) 0.12</td>
<td>NH(_3), 1.0 M, pH=11</td>
<td>60</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>80</td>
<td>(\text{Cd(ActO)}_2) 0.0013</td>
<td>((\text{H}_2\text{N})_2\text{CS}) 0.12</td>
<td>NH(_3), 1.5 - 3.0 M, pH=11-12</td>
<td>80</td>
<td>3</td>
<td>50</td>
</tr>
</tbody>
</table>
Figure 9.1: Bright field TEM image showing Cu-(Se,S) precipitates in the CuGaSe\textsubscript{2} matrix.

[WS93] have shown that this exchange of selenium is possible and highly favorable for Cu-rich CuInSe\textsubscript{2} and CuGaSe\textsubscript{2}, and even more pronounced for copper selenides. The observations of precipitates inside of CuGaSe\textsubscript{2} grains confirms that the model proposed by Tuttle et al. [TAN91] is in principle also applicable to CuGaSe\textsubscript{2} thin films.

The average diameter of the inclusions is about 30 nm and the total volume fraction of the precipitates in the absorber layer is about 2%. The high contrast of the inclusions in the bright-field images is strongly reduced in high-resolution images. As shown in Fig. 9.2, the boundary between matrix and precipitate is coherent. Electron diffraction studies along different orientations show that matrix and precipitates have similar structures and that their lattice constants differ by less than 2%. Below
1000°C the CuGaSe$_2$ matrix crystallizes in the chalcopyrite structure [GP80, Mik81]. This is a tetragonal structure based on the zincblende structure with Cu and Ga located at the cation and Se at the anion sites. A reduction of symmetry caused by the arrangement of Cu and Ga atoms in the cation sublattice is responsible for the tetragonality. The lattice constants determined by Grzeta-Plankovic [GP80] by x-ray powder diffraction are $a = b = 0.5612$ nm, $c = 1.1032$ nm. Since $c/a \approx 2$, the following conversions between the chalcopyrite and the cubic notations are valid: $[abc]_{\text{cubic}} = [ab\frac{c}{2}]_{\text{chal}}$ (real space) and $(hkl)_{\text{cubic}} = (hk2l)_{\text{chal}}$ (see chapter 1.3). Because of the structural similarities between matrix and precipitates there are two possible phases for the Cu-Se inclusions. One is the mineral Berzelianite (Cu$_{1.85}$Se),
which is also found on top of the films, the other is Cu$_7$Se$_4$. The structural properties of these phases are listed in table 9.2. The lattice mismatch between CuGaSe$_2$ and Cu$_{1.85}$Se is about 2.2%, for Cu$_7$Se$_4$ 1.6%, and both phases have the zincblende structure and are therefore suited to form - irrespective of the orientation - coherent boundaries with the CuGaSe$_2$ matrix.
Table 9.2: Structural properties of CuGaSe$_2$, Cu$_{1.85}$Se, Cu$_7$Se$_4$ and CdS

<table>
<thead>
<tr>
<th>composition</th>
<th>structure</th>
<th>space group</th>
<th>lattice constants</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuGaSe$_2$</td>
<td>chalcopyrite</td>
<td>$I\bar{4}2d$</td>
<td>$a = b = 0.5612$ nm</td>
<td>$[abc]<em>{\text{cubic}} = [ab^2]</em>{\text{chalc}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$c = 1.1032$ nm [GP80]</td>
<td>$(hkl)<em>{\text{cubic}} = (hk2l)</em>{\text{chalc}}$</td>
</tr>
<tr>
<td>Cu$_{1.85}$Se</td>
<td>zincblende</td>
<td>$F\bar{4}3m$</td>
<td>$a = 0.5739$ nm</td>
<td>JCPDS #6-680</td>
</tr>
<tr>
<td>Cu$_7$Se$_4$</td>
<td>zincblende</td>
<td>$F\bar{4}3m$</td>
<td>$a = 0.5706$ nm</td>
<td>JCPDS #26-557</td>
</tr>
<tr>
<td>CdS</td>
<td>zincblende</td>
<td>$F\bar{4}3m$</td>
<td>$a = 0.5818$ nm [TB55]</td>
<td>Stack. seq.: ..-A-B-C-A-..</td>
</tr>
<tr>
<td></td>
<td>wurtzite</td>
<td>$P6mm$</td>
<td>$a = 0.4.136$ nm</td>
<td>Stack. seq.: ..-A-B-A-B-..</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$c = 0.6713$ nm [PBF58]</td>
<td></td>
</tr>
</tbody>
</table>
Figure 9.3: Linescan (EDX) across the CdS/CuGaSe₂ interface. CdS deposited at 60°C: Weak interaction between Cu and the CdS layer. CdS deposited at 80°C: Strong interaction between Cu and the CdS layer and presence of Cd in CuGaSe₂ absorber layer.
9.3 Interaction Between Absorber- and Buffer Layers

The fact that the p-n junction is located directly at the interface between the absorber (CuGaSe₂) and buffer (CdS) layers implies the importance of interfacial interactions between these two layers. It is of interest to study the correlation between deposition temperature, interfacial interaction and solar cell performance. Fig. 9.3 shows two EDX linescans across the interface of CdS. In (a) CdS was deposited at 60°C (CdS(60°C)), in (b) the bath temperature of the solution was 80°C (CdS(80°C)). The overlapping of the Cd-L and S-K with the Ga-K and Se-K curves around the position at 130 nm is not related to any interaction processes, but is due to the limited resolution (see chapter 3.1). Both linescans show that there is an interaction between Cu and the CdS buffer layer, which is much stronger for CdS(80°C). Furthermore, the Cd-L signal in the linescan of CdS(80°C) indicates an incorporation of Cd in the CuGaSe₂ absorber layer as it has been observed by Wada et al. [WHH+98] and Ramanathan et al. [RWA+98] (see chapter 8). Fig. 9.4 shows the elemental mapping of a CdS(80°C)/CuGaSe₂ interface. Maps of the Cd-L, S-K, Cu-K and Ga-K EDX signals are displayed. The Se-K signal was also mapped, but the map showed no significant differences from that of the Ga-K signal. Fig. 9.4(c) reveals the presence of Cu in the buffer layer. The interaction of Cu and the buffer layer is not local, but it takes place along the CdS/CuGaSe₂ interface. Linescans and elemental mapping give no evidence of any interaction of Ga or Se with the buffer layer. Fig. 9.5 shows the elemental mapping of another interfacial region of CdS(80°C)/CuGaSe₂. Regions with no or little Cd (dark regions in Fig. 9.5(a)) are present in the buffer layer. At the same positions a high Cu concentration was measured (white regions in Fig. 9.5(c)). This suggests the formation of binary Cu-S compounds in the buffer layer. Elemental mappings and linescans (Fig. 9.3) indicate only little interaction between Cu and the buffer layer. The large difference in the behavior of Cu shows that the interaction is not related to any diffusion process but to chemical reactions between the surface
of the absorber layer and the solution used for the deposition of CdS. Obviously this reaction is much more pronounced for CdS(80°C).

![Diagram of CdS and ZnO layers](image)

Figure 9.4: Elemental mapping (EDX) of CdS(80°C)/CuGaSe₂ interfacial region of the Cu-K, Ga-K, Cd-L and S-L signals. Figure (c) shows the presence of Cu in the CdS layer.

Differences of the interfaces for the cases CdS(60°C) and CdS(80°C) were also observed in the microstructures. Figs. 9.6 and 9.7 show HRTEM micrographs of CdS(60°C)/CuGaSe₂ and CdS(80°C)/CuGaSe₂ interfaces. For CdS(60°C)/CuGaSe₂ the two layers are separated by a sharp interface whereas for CdS deposited at 80°C the transition between CuGaSe₂ and CdS is not abrupt. For the 80°C recipe the surface etching of the absorber layer is probably enhanced by the higher NH₃ concentration and the higher bath temperature. Surface steps are created during the etching, which explains the transition region at the CuGaSe₂/CdS(80°C) interface.
The density of planar and linear defects in the CdS layer at the interface is much lower for CdS(80°C) than for CdS(60°C). This is partially due to a higher mobility of the atoms at the higher bath temperature.

The enhanced interaction between the CuGaSe₂ absorber layer and the CdS(80°C) buffer layer is not only limited to Cu-rich, KCN treated films. Also for slightly Ga-rich compositions both CdS recipes behave differently with respect to the interface formation. Slightly Ga-rich CuGaSe₂ films show a Cu-depleted surface [NHS97]. Therefore, the interaction of Cu with the CdS bath is very limited in this case.
growth of the buffer layer was monitored by XPS. Repeated measurement of the photoelectron spectra and a subsequent deposition of very thin CdS layers show the evolution of the buffer layer starting from the interface. The depth information of XPS is limited to about 10 nm. Therefore, without any interaction between buffer and absorber layer, the photoemission signals of the substrate elements (Cu, Ga, Se) disappear after a deposition time corresponding to a CdS film thickness of about 10 nm, and only the Cd- and S-lines remain present.

XPS spectra of Ga-rich samples show this behavior for CdS(60°C), but not for CdS (80°C). Fig. 9.8 shows the normalized intensity of the Ga 3d, Cd 4d and Se 3d photoemission signals during the growth of the CdS(80°C) film. After a deposition time of about 70 s, the Ga 3d signal disappears and the Cd 4d signal becomes dominant. But in contrast to the results observed for the 60°C recipe, the Se 3d signal remains visible until the end of the deposition process, though with a significantly reduced intensity. This means that in the case of the 80°C recipe, Se of the absorber surface reacts with the solution and is incorporated in the buffer layer. This explains the presence of the Se 3d emission even at the end of the CdS deposition. The measurements on Cu-rich and Ga-rich layers suggest that the chemical reactions are much more pronounced in the 80°C recipe.
Figure 9.6: HRTEM image of the CdS(60°C)/CuGaSe₂ interfacial region.

The boundary between the two layers is clearly visible because of the high defect density in the CdS layer. The arrows mark the interface.
Figure 9.7: HRTEM image of the CdS(80°C)/CuGaSe₂ interfacial region. Owing to the reaction of the chemical bath solution with the absorber layer, the boundary is not abrupt.
Figure 9.8: Normalized intensity of the Cd 4d, Se 3d and Ga 3d photoemission lines measured by x-ray photoelectron spectroscopy (XPS) during the evolution of the interface between slightly Ga-rich CuGaSe₂ and CdS(80°C). The Se signal is still detectable after deposition of the full CdS-film thickness (50 nm), which is much more than the information depth of XPS, indicating a reaction between Se and CdS.
9.4 Microstructure of CdS Buffer Layers

The structural compatibility of absorber and buffer layers is the basis for a relaxed interfacial region with a low defect density and therefore for a junction without recombination losses. The structures reported for CdS are zincblende \( (a = 0.5818 \text{ nm}) \) \cite{TB55} and wurtzite \( (a = 0.4136 \text{ nm}, c = 0.6713 \text{ nm}) \) \cite{PBF58}. Table 9.2 lists some structural properties of CuGaSe\(_2\) and CdS. The lattice mismatch between the CuGaSe\(_2\) and the CdS zincblende phases is about 3.5\%. For the wurtzite CdS phase the lattice mismatch depends on the orientations of the CuGaSe\(_2\) and the CdS lattices. For \((112)_{\text{chal}}\) oriented CuGaSe\(_2\) and \((0001)\) oriented CdS the lattice mismatch is about 4\%. Zincblende and wurtzite structures in the CdS lattice can be distinguished by the stacking sequence of \{111\} planes:

- Zincblende: ...-A-B-C-A-B-C-A-...
- Wurtzite: ...-A-B-A-B-A-...

The deposition of CdS layers with both, zincblende and wurtzite structures, on chalcopyrites by CBD has been described by different authors \cite{KVR92,Cho93,OBL94,FFB98,FL95}. Figs. 9.6 and 9.9 show HRTEM micrographs displaying a region of CdS\((60^\circ\text{C})\) layers. Images of the CdS\((80^\circ\text{C})\) layers are shown in Figs. 9.7 and 9.10. The growth direction of the CuGaSe\(_2\) grains in the absorber layer is \[221\] (Fig. 9.6, 9.7, 9.10), some grains have a different orientation, e.g. \[001\] (Fig. 9.9). Because of the similarity of the zincblende and chalcopyrite structures the zincblende CdS phase will take on the equivalent growth orientation of the CuGaSe\(_2\) substrate. On \((112)_{\text{chal}}\) oriented CuGaSe\(_2\) wurtzite CdS will always grow in the \[0001\] direction. For other substrate orientations the growth direction of CdS is not predictable. The growth direction in that case is \[0001\]. The CdS\((80^\circ\text{C})\) layers consist of grains or domains (10 to 40 nm in size) separated by small-angle grain boundaries and coherent twin boundaries. The formation of such domains is related to the colloidal growth of CdS as described by Froment \cite{FL95}. The twin boundaries are located
at \{111\} planes and the twinned domains are rotated with respect to each other by 180° (or 60°) about a \langle111\rangle axis (rotational twins on \{111\} planes). The stacking sequences of \{111\} planes within a domain of the investigated regions were always ...-A-B-C-A-B-C-.... Therefore it can be said that the zincblende phase is dominant in the CdS(80°C) layers. Fig. 9.10 shows the boundary region of two twinned domains, separated by coherent twin boundaries on \{111\} growth planes and by partially coherent boundaries on \{112\} planes which correspond to symmetric Σ3 boundaries in the face centered cubic lattice [Hof94]. The lattice planes within one domain are straight and parallel which shows that there is not much strain in the CdS(80°C) lattice. The relaxation of the lattice mismatch strain between CuGaSe₂ and CdS can be achieved by twinning [SRS96b] as well as by the presence of the small angle-grain boundaries, e.g. the partially coherent boundary shown in Fig. 9.10. Each plane contains a partial dislocation with Burgers vector \( b = \frac{a}{6}\langle112\rangle \) which contributes to the strain relaxation in the CdS(80°C) layer. In contrast to the CdS(80°C) layers, domains with a defined structure and well resolved domain boundaries were not be observed in CdS(60°C) layers. Fig. 9.7 shows the lattice of CdS(60°C) grown on a (112) chalc-oriented CuGaSe₂ grain. The lattice is strongly disordered and the stacking sequence is uniform only within the range of a few nanometers where it is preferably ...-A-B-C-A-... and therefore favoring the zincblende structure. Stacking faults similar to those shown in Fig. 9.6 were observed in CdS grown on epitaxial CuInSe₂ [FFB+98]. They were related to an “incorporation of hexagonal CdS into the cubic base plane”. In Fig. 9.9 the structure of the lattice of CdS(60°C) grown on \{001\} oriented CuGaSe₂ grains is even less clear. The lattice planes are bent, and in most cases no stacking sequence can be defined. An exception is shown in the inset which is displayed on a magnified scale at the top of the figure. The stacking sequence A-B-A-B-A-B-C-A shows the presence of both, wurtzite and zincblende structures, in the layer. The bent lattice planes - suggesting a continuous change of the lattice structure between wurtzite and zincblende - indicate a large strain in the CdS(60°C)
layer on (001) oriented CuGaSe$_2$.

The results described above show that the crystal quality of the CdS layer depends strongly on growth orientation and temperature. Similar results - as far as the dependence of crystal quality on the deposition temperature is concerned - were obtained by Furlong et al. [FFB+98] for CdS grown on (112)$_{\text{chalc}}$ oriented epitaxial CuInSe$_2$. There, epitaxial growth of cubic CdS was established on a KCN-treated CuInSe$_2$ surface with deposition temperatures above 70°C. For low temperature growth on epitaxial absorber layers, polycrystalline growth of cubic CdS with some hexagonal inclusions was observed (see above).
Figure 9.9: HRTEM image of a CdS layer deposited at 60°C demonstrating that the lattice is highly strained. By looking at the stacking sequence of \{111\} (cubic) or \{0001\} (hexagonal) planes it is not possible to determine the crystal structure of the region (see inset).
Figure 9.10: HRTEM micrograph of a CdS layer deposited at 80°C. The relaxed lattice consists of two domains with zincblende structure separated by coherent twin boundaries (\cdots\cdots) and partially coherent $\Sigma 3$-type boundaries (\cdots\cdots).
9.5 Discussion of the Results

As stated above two major changes in the preparation of CuGaSe₂-based thin film solar cells lead to significant improvements in the energy conversion efficiency; (i) deposition of slightly Ga-rich absorbers layers instead of Cu-rich grown layers with subsequent KCN treatment and (ii) a new CdS recipe for CBD at elevated temperatures. Both topics have been addressed above.

CuGaSe₂-based thin film solar cells with a Cu-rich absorber layer do not achieve a higher open circuit voltage than 750 mV so far, whereas Ga-rich devices exhibit open circuit voltages up to 950 mV. Temperature and illumination intensity dependent measurements of the open circuit voltage of the devices showed an open circuit voltage of \( \approx 1.25 \text{ V} \) (extrapolated to 0 K) for the cells based on Cu-rich absorbers. The open circuit voltage is expected to extrapolate to the value \( V_{\text{OC}} = E_g/q \) at 0 K for thermally activated recombination mechanisms. The value of 1.25 eV is far below the bandgap of the CuGaSe₂, but close to the bandgap of the copper selenides. Thus, the Cu-Se precipitates described above seem to dominate the electrical properties of the solar cell and therefore limit the open circuit voltage. This is quite understandable because the precipitates are also located very close to the interface to the CdS layer, which means in the space-charge region. Extremely high carrier concentration will lead to strong local fields.

Devices based on Ga-rich absorbers show extrapolated open circuit voltages up to 1.68 V.

The influence of the different recipes for the CdS deposition on the device performance is summarized in table 9.3. It is clear that the 60°C recipe is the better choice for Cu-rich and KCN-treated absorber layers although the CdS crystal quality is poor. As shown in Fig. 9.5 high Cu concentrations and even Cu-S precipitates are detected in the 80°C CdS layer. These are highly conductive and will disturb the p-n junction. Therefore the efficiency of the Cu-rich devices is reduced by application of
Table 9.3: Influence of the CdS-buffer layer recipe on device performance

<table>
<thead>
<tr>
<th>Solar Cell Parameters</th>
<th>Composition</th>
<th>Chemical bath temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>60°C</td>
</tr>
<tr>
<td>(V_{OC}) (mV)</td>
<td>Cu-rich</td>
<td>742.0</td>
</tr>
<tr>
<td></td>
<td>Ga-rich</td>
<td>805.0</td>
</tr>
<tr>
<td>(J_{SC}) (mA/cm^2)</td>
<td>Cu-rich</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>Ga-rich</td>
<td>14.7</td>
</tr>
<tr>
<td>FF (%)</td>
<td>Cu-rich</td>
<td>50.6</td>
</tr>
<tr>
<td></td>
<td>Ga-rich</td>
<td>61.3</td>
</tr>
<tr>
<td>(\eta) (%)</td>
<td>Cu-rich</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>Ga-rich</td>
<td>7.2</td>
</tr>
</tbody>
</table>

On the other hand it was found for Ga-rich absorber layers that the 80°C recipe is advantageous [NHS97]. The open circuit voltage of the as-grown devices is much higher than for devices made with the 60°C recipe. The gain of performance during a short anneal in air at 200°C is also much more pronounced.

These improvements are based on a change in the dominant recombination mechanism. For all devices based on Cu-rich KCN-treated absorber layers and also for the Ga-rich layers with the 60°C recipe, recombination at the interface is dominant [Rau97]. For the Ga-rich devices with CdS(80°C), recombination in the space-charge region becomes dominant. This change is probably related to the interface characteristics presented in section 9.3. The spatially enlarged interfacial region leads to a decrease of the density of interfacial states, and the density of linear and planar defects at the interface is smaller for CdS(80°C). The lattice mismatch is also reduced owing to the dominant cubic CdS phase for the 80°C recipe. It is expected that the strain in the CdS(60°C) interfacial region as well as the local disturbance of the zincblende
structure affect the band structure and cause potential fluctuations. Therefore the effective barrier height is reduced [WG91].

As shown by XPS measurements (Fig. 9.8) a chemical reaction between the Ga-rich absorber layer and the CdS occurs. The selenium dissolved from the absorber layer is probably replaced by sulfur from the solution. The incorporation of sulfur results in a decrease of the valence band energy of the absorber layer. The valence band bending close to the interface creates a front surface field, which pushes the holes back into the absorber layer. Therefore the number of carriers contributing to interfacial recombination is reduced.
Chapter 10

CONCLUSIONS AND OUTLOOK

10.1 Epitaxial CuIn_xSe_y Layers on Si(111) and GaAs(001) Substrates

Based on the results discussed in part I the following conclusions can be made:

- Heteroepitaxial layers with good crystal quality have been grown by MBE on Si(111) and GaAs(001) substrates although the growth of the layers is predominantly in the 3-d (island) growth mode.

- The composition of the epitaxial layers varied from CuInSe_2 to In-rich compositions such as CuIn_3Se_5. Layers with a distinct Cu-rich composition were polycrystalline. Based on the phase diagram proposed by [HGE+98] it can be concluded that these layers are a mixture of ternary CuIn_xSe_y and Cu-Se compounds. Single phase CuInSe_2, CuIn_2.5Se_4 and CuIn_3Se_5 layers have been obtained, and various methods were used to evaluate whether a layer is a single phase compound or a mixture of compounds. Lattice vibrational properties of the chalcopyrite and the defect chalcopyrite/stannite structures are different.

- Sharp Kikuchi bands in electron channeling patterns and low FWHM values of XRD rocking curves (700-900 arcsec) indicate a high crystal quality of the epitaxial layers. Low RBS \( \chi_{\text{min}} \) values were measured for CuIn_xSe_y/Si(111) layers with different compositions, and the lowest \( \chi_{\text{min}} \) values are comparable to values reported for CuInSe_2 single crystals [YTN94]. The enhanced crystal quality is related to higher substrate temperatures (570-610°C) during the deposition of
the layers. It is also believed that the slow cooling process of the samples after the growth had a positive annealing effect on the crystal quality.

- A higher substrate temperature is not only beneficial but also causes some problems. Because of the thermal mismatch between CuIn$_x$Se$_y$ and Si, layers deposited at temperature above about 580°C cracked or even peeled off the Si(111) substrate. The large strain in the layers near the interface to the Si(111) substrate is documented by an increase of the deviation from $c/a = 2$ near the interface by a factor of about 3. The diffusion of Ga from the GaAs substrate and the subsequent formation of quaternary CuIn$_x$Ga$_y$Se$_z$ in the layer was observed for CuIn$_x$Se$_y$ deposited at temperatures ($\approx 600°C$) on GaAs(001).

- Planar defects on $\{112\}$ planes (stacking faults, twins) are common in CuIn$_x$Se$_y$ layers. The observed density of such faults usually is high at the interface and decreases with increasing thickness of the layer. There is a direct relation between some of these defects and the mismatch between layer and substrate. For example, stacking faults on $\{112\}$ planes which were formed at the interface and which are directed into the layer originate from misfit dislocations which split into partial dislocations. The island growth of CuIn$_x$Se$_y$/Si(111) often leads to the formation of rotational twins on (112) growth planes. Rotational twins by $\pm 60/180°$ correspond to the usual twins observed in f.c.c. based structures. For samples grown at lower substrate temperatures (about 540°C and lower), both, twinned type-b as well as type-a grown islands seem to have a similar probability of formation. The slightly different orientation of twinned and untwinned islands related to the tetragonality of CuIn$_x$Se$_y$ contributes to higher $\chi_{\text{min}}$ values obtained for twinned layers [CMN78]. On the other hand $\pm 60/180°$ twins are important for the relaxation of strain in the layer [SRS96b]. Rotational twins in CuIn$_x$Se$_y$/Si(111) by $\pm 120°$ on (112) growth planes are related to the missing of the three-fold symmetry of CuIn$_x$Se$_y$ along [221].
The knowledge on the growth of epitaxial CuIn₅Se₅ layer forms the basis for future investigations concerning the structural, optical and electrical properties of CuInₓSeₙ and Cu(In,Ga)Se₂ layers. Still an important topic is e.g. the verification of the structures suggested for In-rich compounds. A possible approach is the comparison of measured Raman spectra with calculations (based on suggested structures) of the vibrational modes in the CuIn₃Se₅ lattice. For the Raman measurements epitaxial single phase CuIn₅Se₅ layers grown on (111) and (001) oriented substrates can be used. As far as the conduction type of CuInₓSeₙ compounds is concerned there is a difference between the results reported on bulk single crystals and layers which needs to be clarified. As was already mentioned in section 1.3 Ashida et al. [ASS⁺98] reported a change from p- to n-type conductivity at [In]/[In+Cu]=0.75 for bulk single crystals while Schmid et al. [SRS96a] observed the change in conductivity in the Cu-depleted surface zone of absorber layers already for compositions with [In]/[In+Cu]>0.5. Conduction measurements performed on epitaxial CuInₓSeₙ layers could contribute to the solution of this problem.

The growth and characterization of Cu(In,Ga)Se₂ epitaxial layers finally are needed for the understanding of the growth and properties of polycrystalline Cu(In,Ga)Se₂ which in the last few years has replaced CuInₓSeₙ as the compound used for the absorber layer in solar cells. Especially the impact of sodium acting as a fluxing agent for an enhanced grain growth and as a dopant in polycrystalline layers can be studied by investigating the microstructural and electrical properties of epitaxial Cu(In,Ga)Se₂ layers grown on Si or GaAs. The doping of epitaxial Cu(In,Ga)Se₂ layers can be obtained by the co-evaporation of Cu, In, Ga, Se and a Na-precursor (e.g. Na₂Se, NaCl, NaF).
10.2 Cu(In,Ga)Se$_2$ and CuGaSe$_2$ Substrate Solar Cells

A process for the preparation of Cu(In,Ga)Se$_2$ substrate solar cells with stable efficiencies between 13-16% was established. The cells will be used for similar investigations as the CuGaSe$_2$ cells described and discussed in chapter 9. TEM has proven to be a suitable method for the characterization of the microstructural properties of the cells and the interfaces between the absorber and the buffer layer. HRTEM investigations have shown that a better crystal quality of the CdS layer and the CdS/CuGaSe$_2$ interface is achieved using high bath temperatures. Cu-(Se,S) precipitates were detected in the CuGaSe$_2$ absorber layer, and an interaction between the absorber layer and the CdS buffer layer was observed. Both results were obtained using microprobe EDX.

Microstructural investigations of the region around the p-n junction shall be performed also for cells prepared with the process described in chapter 8. One important topic is the detection of Cd in the absorber layer. If Cd is found in the absorber layer the CBD process of CdS can be avoided without reducing the performance of the cell. The n-type doping of the surface region of the absorber layer can be obtained by a coevaporation of Cd along with the other elements at the end of the Cu(In,Ga)Se$_2$ deposition process. A first indication that Cd is incorporated into the CuGaSe$_2$ absorber layer during the CBD process was obtained by microprobe EDX, but the resolution (about 5-10 nm) is not high enough for the analysis to be used as a reliable detection method. A more suitable method for this investigation is energy filtered imaging which offers a spatial resolution of about 2 nm. A possible way to study the impact of sodium on the growth and the conductivity of the absorber layer is by a controlled doping of the Cu(In,Ga)Se$_2$ layer. This can be achieved by the co-evaporation of a sodium precursor along with the other elements during the growth of the absorber layer. The dependence of the microstructure on the sodium flux can be investigated by bright and dark field imaging as well as HRTEM. Energy filtered imaging can be
used for the determination of the spatial distribution of sodium in the absorber layer. A comparison of the results obtained for polycrystalline and epitaxial Cu(In,Ga)Se$_2$ layers might help to explain the importance of sodium for the growth and the doping of Cu(In,Ga)Se$_2$ absorber layers.
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