Low-cost Cu(In,Ga)Se₂ absorbers from nanosized precursor materials for thin-film solar cells

A dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of

DOCTOR OF SCIENCES

presented by

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Zurich, 2005
Seite Leer / Blank leaf
Acknowledgements

First of all I would like to express my gratitude to Prof. Ayodhya N. Tiwari and Prof. Sotiris E. Pratsinis for their motivation, advice and supervision of my PhD thesis.

I would also like to thank PD Dr. Hans Zogg for giving me the opportunity to work in his laboratory. Further I acknowledge the help from Dr. Toby Meyer and Andreas Meyer. I profited a lot from the close collaboration.

This work would not have been possible without the contribution and help of my colleagues, former and present members of the Thin Film Physics group:
Dominik Rudmann, David Brémaud, Franz Haug, Alessandro Romeo, Derk Bätzner, the thin-film solar cell makers,
Karim Alchalabi, Dmitry Zimin, Klaus Kellermann, Martin Arnold, the infrared-sensor team,
Fedor Kurdesau, António F. da Cunha, Maxim Ganchev, Gennady Khrypunov, our academic guests during my thesis work,
Christoph Langhammer, having investigated electrospray in his semesterwork in our group,
Thomas Kämpfer, Michael Leopold, our technical staff,
Gaby Strahm, Paulette Pfamatter, the group's secretaries.

Many thanks go to the members of the particle technology laboratory. The fruitful discussions with Olliver Wilhelm, Wendelin Stark, Lutz Mädler und Karsten Wegner led to many new ideas.

I am very grateful for the XPS measurements and their interpretation by Dr. Roland Hauert from the Swiss Federal Laboratories for Materials Testing and Research.

I would also like to thank the workshop of the physical department, Mr. Brühwiler, Mr. Nussberger and co-workers for their advice in construction design and excellence in manufacturing of complicated mechanical parts.
Further, I appreciated very much the company of my good friends, especially Jan-
Marc Lehky and his wife Jaqueline with which I have been sharing a flat for some time
and finally, I would like to thank my family for their support during the whole time.

The financial support by the Commission for Technology and Innovation (KTI) is
kindly acknowledged. This thesis resulted from the work done in the frame of the
TopNano21 Programme (KTI Project 5491).
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Zusammenfassung

Im Rahmen dieser Arbeit wurden kostengünstige Solarzellen basierend auf polykristallinem CuIn_{1-x}Ga_xSe_2 (CIGS oder CIS für x=0) entwickelt. Dabei wurde für die Abscheidung der CIGS Schicht auf die konventionellen, teuren Hochvakuum-Techniken verzichtet und stattdessen einfache Druck- und Sprayverfahren bei Atmosphärendruck eingesetzt. In einem ersten Schritt wird ein Vorläufermaterial in Form eines Nano-Pulvers mit der gewünschten metallischen Zusammensetzung aufgetragen. Im zweiten Schritt wird die Vorläuferschicht in kontrollierter Atmosphäre zu CIGS konvertiert. Dabei werden für die chemische Umwandlung keine gefährlichen Gase benutzt und die Temperaturen so tief gehalten, dass kostengünstige Substrate wie Fensterglas und Metallfolien eingesetzt werden können. Wirkungsgrade bis zu 6.7% konnten mit den entwickelten Techniken aufgezeigt werden.


In Kapitel zwei bis vier wird die Entwicklung von CIGS Schichten mit pulverförmigem Vorläufermaterial beschrieben:

Im zweiten Kapitel werden verschiedene Nano-Pulver (reine Metalle, Legierungen, Metallselelide und Metalloxide) in Bezug auf Partikelgröße, Form, Agglomeration, Zusammensetzung und Kristallinität charakterisiert. Zusätzlich wird ihre Eignung zum Sintern und zur Konvertierung in Selendampf untersucht: Zwar bilden alle Vorläufermaterialien die CIGS-Phase aus, zeigen aber auch Verunreinigungen durch In_2O_3 und Cu_{2-x}Se. Rein metallisches Nano-Pulver (nur Cu und In; Ga wurde wegen dem tiefen Schmelzpunkt nicht verwendet) bildet zwar bis zu 1 μm-grosse Agglomerate eignet sich jedoch von den getesteten Materialien am besten, um grosskörnige, dichte CIS-Schichten herzustellen.
Im dritten Kapitel werden typische Billigdruck-Verfahren wie Rakeln, Siebdruck und eine Spraymethode bezüglich ihrer Eignung zur Abscheidung dünnen Schichten untersucht. Die Herstellung der Druckpasten und die verwendeten Druckmethoden werden beschrieben. Spraybeschichtungen zeigen die beste Homogenität der Schichtdicke.

In Kapitel vier wird der Einfluss verschiedener Selenisierungsbedingungen auf die chemische Umwandlung des Vorläufermaterials und Eliminierung von Verunreinigungen untersucht. Mit drei verschiedenen Reaktortypen (Vakuumkammer, geschlossene Quarzkammer, offenes Quarzrohr) wird der Hintergrunddruck (Stickstoff) und Selen-Partialdruck über mehrere Größenordnungen verändert, um die optimalen Umwandlungsbedingungen zu finden. Es wird gezeigt, dass ein hoher Selendruck nötig ist, um Oxid-Phasen umzuwandeln.

In Kapitel fünf werden die Fertigungsschritte von der CIGS-Schicht bis zur fertigen Solarzelle beschrieben. Die Solarzellen werden anhand der Strom-Spannungs-Kennlinie charakterisiert. Ein maximaler Wirkungsgrad von 1,5% wurde mit dem pulverförmigen Vorläufermaterial erreicht. Die Gründe für die niedrigen Wirkungsgrade werden diskutiert.

Summary

Within the scope of this work, low-cost solar cells based on polycrystalline CuIn_{x}Ga_{x}Se_{2} (called CIGS, or CIS for x=0) absorber layers were developed. The CIGS layer, being the most complex and important part of the solar cell, was deposited with simple non-vacuum equipment. In the first step a thin film of a nano-powder precursor material is deposited, which contains the metals in the desired stoichiometry. The second step converts the precursor material into the CIGS compound in a controlled atmosphere. Conversion conditions were restricted to the use of non-hazardous gases and reaction temperatures compatible with low-cost substrate materials such as soda-lime glass or metal foils. Efficiencies up to 6.7% with techniques scalable to large-area were obtained in this thesis.

The first chapter gives an introduction into the field of photovoltaics. In a brief historical summary the development from the first solar cell to current thin-film solar cells is discussed. The chapter then focuses on the properties of CIGS, which yielded the highest efficiencies in thin-film solar cells to date. Even if thin-film solar modules, compared to wafer based crystalline silicon modules, have the potential for lower production costs, further cost reduction is necessary for photovoltaics to compete with conventional energy sources. The current status of low-cost CIGS deposition techniques is reviewed and targets for the present work are elaborated.

Chapters two to four describe the research and development work of CIGS layers based on particulate precursor materials:

Chapter two describes the precursor materials (pure metals, alloys, metal-selenides and metal-oxides) with respect to particle size, shape, agglomeration, composition and crystalline state. After reacting the precursor materials in selenium vapor, the CIGS phase formation and sintering properties are evaluated. All precursor materials form the CIGS phase but also impurity phases, mainly In_{2}O_{3} and Cu_{2-x}Se form depending on the precursor material and selenization process. Metal precursors (nanopowder containing Cu and In only; Ga was not used due to its low melting point), even though forming agglomerates of ~1 μm, are most suited for dense and large-grained CIS compound formation during selenization.

Chapter three compares important non-vacuum deposition methods, namely doctor-blade, screen-printing and electro-spray and investigates their suitability for
CIGS precursor thin-film deposition. Precursor paste preparation, deposition as well as the used set-up is described. Films resulting from spray deposition show superior homogeneity in thickness but lack of compositional homogeneity if sprayed on a fixed substrate.

Chapter four shows the influence of different selenization processes on the chemical conversion and impurity phase elimination. Testing three different reactor types (vacuum chamber, closed quartz box and an open quartz tube) the background pressure (nitrogen) and selenium partial pressure were varied by several orders of magnitude to find optimal conversion conditions. High selenium pressure is found to be necessary for oxide impurity elimination.

Chapter five describes the cell processing from the CIGS layer to the finished solar cell by depositing the n-CdS part of the heterojunction and the ZnO/ZnO:Al transparent conducting electrical contact. Characterization of the solar cells by recording the current-voltage curve show maximum efficiencies of ~1.5% for the particulate precursor materials. Reasons for the low efficiency are discussed.

Chapter six describes a novel CIGS deposition process based on metal salt precursors. The precursor paste, prepared by dissolution of the salts and organic binder material (ethyl cellulose) in alcohol, is deposited by the doctor-blade method, preheated in air and selenized in selenium vapor. An approximately 600 nm thick CIGS layer is formed on top of an amorphous carbon layer. Solar cells based on this approach have reached efficiencies up to 6.7%. Considering the simplicity, non-toxicity and large-area scalability this is a good efficiency with further potential for improvement and cost-reduction. Further improvements can be reached by increasing the CIGS layer thickness, while reducing the amorphous carbon layer and optimization of the elemental grading profile of the CIGS layer.
1 Introduction

Photovoltaic systems, also called solar cells, present an interesting and clean alternative to fossil and nuclear fuels for energy generation. They work with sunlight, which is freely available for the next 10 billion years, and convert it directly into electrical energy.

Solar cell industry continues to grow at an astonishing pace -- over 35% annually with sales easily expected to reach US $ 8 billion by 2010. With further cost-cutting innovations on the horizon and the effects of economies of scale, there may be a bright future for solar cells. Large scale production with drastic cost reductions could be reached with simple, fast and affordable non-vacuum deposition equipment. Direct manufacturing costs given by typical techniques as printing or spraying are estimated to be in the 50-100 $/m² range, and are well below current industrial production costs (200 $/m²) with vacuum based technology.

The development of such techniques yielding reasonable solar cell efficiencies is therefore required. For targeted energy costs of 0.8 $/Wₚ (Watt peak), a technique capable of producing 6% efficient modules at 50 $/m² does already meet the aim, and high efficiency modules (η>12%) are not mandatory (although higher efficiencies are always desired) as seen in Table 1.1.

Table 1.1 Module cost in $/Wₑ calculated for direct manufacturing costs between 50 and 200 $/m² and produced module efficiencies in the range of 6 to 15% (Zweibel, 1999)

<table>
<thead>
<tr>
<th>Module Efficiency</th>
<th>Manufacturing costs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$ 200/m²</td>
</tr>
<tr>
<td>6%</td>
<td>3.3</td>
</tr>
<tr>
<td>8%</td>
<td>2.5</td>
</tr>
<tr>
<td>10%</td>
<td>2</td>
</tr>
<tr>
<td>12%</td>
<td>1.7</td>
</tr>
<tr>
<td>15%</td>
<td>1.3</td>
</tr>
</tbody>
</table>
1.1 Development of photovoltaics

1.1.1 Historical Background

The photoelectric effect, being the basis of photovoltaics (PV), was first observed in 1839 by Alexander Edmund Becquerel, while experimenting with an electrolytic cell made up of two metal electrodes (Becquerel, 1839). His observation that a voltage developed when light fell on the electrodes was considered very interesting, yet there were neither practical applications nor any theoretical explanations. In the 1870's a similar photovoltaic effect was first studied in a solid, namely selenium (Smith, 1873), and allowed to prove that a solid material can change light directly into electricity without heat or moving parts (Adams and Day, 1877). These findings led to the development of the first photoelectric (or solar) cell by Fritts in 1883. The cell was made of selenium wafers coated with a nearly transparent layer of gold, yielding a conversion efficiency of ~1%. Only in 1905, a revolutionary explanation for the photoelectric effect was given by Einstein (Einstein, 1905) for which he received the Nobel Prize in 1921. Other materials, as thin films of copper oxide, were found to show the same effects as selenium and in 1914 the existence of a barrier to current flow in one direction (rectifying mechanism) in PV cells was reported, where the theory for metal-semiconductor barriers was developed later in 1938 by W. Schottky and F.N. Mott.

1.1.2 Crystalline silicon solar cells (1st generation cells)

In the 1930's selenium and the copper oxide cell still had efficiencies less than 1% and were mainly employed for light-meters in photography. Despite a better understanding of the physics involved, photovoltaic systems did not improve significantly until research started to focus on silicon. By introducing impurities into the silicon that allowed the formation of a p-n junction, Daryl Chapin, Calvin Fuller, and Gerald Pearson at Bell Laboratories produced silicon solar cells with efficiencies up to 6% in 1954 (Chapin et al., 1954). This was a major breakthrough and demand for the technology grew, especially from the US military, which used solar cells to power satellites. During the energy crisis in the early 1970's public sectors became interested in PV energy generation for terrestrial applications. Improvements in technology of manufacturing over three decades led to efficiencies up to 24.7% with single crystal silicon wafers (Green et al., 2004). Researchers began to use polycrystalline silicon in order to provide
a lower cost alternative, but solar cells still remained too expensive for widespread adoption. Crystalline silicon is a relatively poor light absorbing material (Fig. 1.1) with extreme sensibility on impurities. Therefore silicon cells need typically 200-300µm thick absorbers of solar-grade silicon wafers. They have a projected energy payback time (the time a PV system has to operate to recover the energy needed for its production) of 2-3 years and an assumed life expectancy of 20-30 years. Single crystal and polycrystalline silicon cells share about 90% of the current industrial PV market.

1.1.3 Thin-film solar cells (2nd generation cells)

Efforts were initiated to find alternative materials with high absorption coefficients (Fig. 1.1) that could be processed in the form of thin films (<10 µm). In contrast to wafer based technology, thin-film absorber materials can be grown on different substrate materials including flexible foils and allow monolithic module production (series connection of many solar cells on a common substrate) and roll-to-roll processing. Projected energy payback time for thin-film cells is as short as one year.

Requirements for optimal thin-film solar cell materials are:

- Semiconductor with a bandgap of 1.4 eV, however 1.1-1.5 eV are also suitable
- High absorption coefficient (Direct band gap)
- Consisting of abundant and non-toxic materials
- Suitable for large area thin-film deposition with simple methods
- Should yield long term stable and high efficiency cells
A material fulfilling all these criteria has not been discovered yet. However, high efficiency thin-film cells have been developed with different material classes (Figure 1.2): amorphous silicon (a-Si:H), cadmium-telluride (CdTe), gallium-arsenide (GaAs), indium phosphide (InP) and copper-indium-gallium-selenide-sulfide (Cu(In,Ga)(Se₂,S₂)).

Hydrogenated amorphous silicon (a-Si:H) and polycrystalline Cu₂S/CdS solar cells were first developed. Cu₂S/CdS cells showed severe stability problems due to high Cu diffusivity and the development was stopped by the early 1980’s. Amorphous silicon was more successful and devices became commercially available, although these cells have low conversion efficiencies (~6% stabilized).

To increase the efficiency of thin-film solar cells, other materials were investigated and research efforts in polycrystalline CdTe and Cu(In,Ga)(Se₂,S₂), called CIGS, based solar cells led to 16.5% and 19.3% efficiency cells (Wu et al., 2002; Ramanathan et al., 2004).

1.1.4 Future prospects (3rd generation cells)

Even though high efficiency second generation cells are on the spot to enter the solar cell market, new concepts of future PV devices are already theoretically being elaborated. As conventional single band gap solar cells are limited to a theoretical maximum conversion efficiency of ~33%, new concepts to reach conversion efficiencies beyond the Shockley-Queisser limit (Shockley and Queisser, 1961) are being pursued. Such concepts include tandem systems, fluorescent mirrors, impact ionization, impurity level systems, intermediate bands and hot electron collection. Except for stacked multi-junction solar cells other concepts are at an early theoretical stage and suitable materials and structures still have to be found.
1.2 Properties of the CIGS compound

CIGS is a I-III-VI compound material, which can be derived by splitting the bivalent component of II-VI materials into a mono- and a trivalent component and doubling the VI component (Fig. 1.2). The specifically high absorption coefficient (Fig. 1.1) makes the tetragonal chalcopyrite compounds well suited for thin-film solar cells. With an absorption coefficient of the order of $10^5 \text{cm}^{-1}$, CIGS compound layer thicknesses of 1-2 μm are sufficient for complete absorption of light.

![Figure 1.2: Some important semiconducting material classes. CIGS is a I-III-VI, compound derived from II-VI class materials.](image)

The phase composition of the ternary CIS compound is mostly described by the pseudo-binary phase diagram of the binary Cu$_2$Se and In$_2$Se$_3$ phase (Fig. 1.3). In the region of the stoichiometric composition (50% Cu$_2$Se / 50% In$_2$Se$_3$) four different phases are observed: The $\alpha$-phase (chalcopyrite, CuInSe$_2$, Fig. 1.4a), the $\beta$-phase (ordered defect compound, CuIn$_2$Se$_3$), the $\delta$-phase (sphalerite, cation disordered CuInSe$_2$) and Cu$_{2-x}$Se. The existence range of the $\alpha$-phase is limited to 24-24.5% Cu content at room-temperature, not even including the stoichiometric composition of 25% Cu. The Cu content in high efficiency solar cells is typically in the range of 22-24%. At deposition temperatures of $\sim$500°C this composition yields single $\alpha$-phase. At room temperature the equilibrium phase diagram shows a phase separation for these compositions. By the partial replacement of In by Ga and the addition of small quantities of sodium the single phase region can be extended (Herberholz et al., 1999).
Figure 1.3  

Cu$_2$Se and In$_2$Se$_3$ pseudo-binary phase diagram (Stanbery, 2002). The chalcopyrite α-phase shows only little tolerance to stoichiometric distortions at thermodynamic equilibrium. Slightly copper rich compositions form in addition the Cu$_2$Se phase, slightly indium rich compositions form in addition an ordered defect compound (β-phase).

I-III-VI$_2$ compounds containing Cu, In, Ga, Se and S give great flexibility in band gap tailoring. The obtainable band gaps range from 1.04 eV for CulnSe$_2$ to 2.43 eV for CuGaS$_2$ while the lattice constant a changes from 5.78 Å for CulnSe$_2$ to 5.35 Å for CuGaS$_2$ as shown in Fig. 1.4b.

Figure 1.4  

a) Unit cell of chalcopyrite structure (α-phase) with lattice constants a and c, named after the mineral Chalcopyrite (CuFeS$_2$). Cation and Anion arrangements are the same as in the Zincblende mineral (ZnS) and the basic atom arrangement corresponds to the diamond crystal structure. b) Band gap and lattice constants range for CIGS compounds.
1.3 The CIGS solar cell

1.3.1 Formation of the p-n junction

In addition to an efficient light absorbing material, which creates free electrons and holes when illuminated, a charge separation mechanism is required to form two distinct electric poles. In semiconductor materials, charge separation is implemented with an electric field (called built-in field) building up in the junction area of the p and n-semiconductor (Fig. 1.5). The electric field is due to the depletion of charge carriers near the junction and the resulting space charge region (SCR), oppositely charged in the n- and p-semiconductor. Most absorber materials used for solar cells are p-type. This is due to the fact that the electron mobility in semiconductors is higher than hole mobility and efficient transport of light generated minority carriers is important to avoid recombination. Polycrystalline CIGS absorber layers are grown slightly copper deficient and are p-type conductors with carrier concentrations of the order of $10^{15}$ to $10^{17}$ cm$^{-3}$. In order to extend the SCR deep into the absorber layer, higher doping levels are required for the n-type semiconductor. Additionally, the n-type semiconductor must be nearly transparent to allow the light to reach the absorber layer.

![Figure 1.5](image)

**Figure 1.5** Schematic drawing of the p-n junction of a solar cell (in substrate or back-wall configuration) showing light-generated carrier separation due to a built-in electrical field in the space charge region (SCR). An asymmetrical doping profile allows the SCR to extend deeply into the p-type absorber layer. A quasi-neutral region (QNR) remains near the back contact.

The efficiency of CIGS solar cells can be improved by applying thin n-type buffer layers of Cd(S,OH) and i-ZnO between the p-absorber and the n+-front contact TCO (transparent conducting oxide). The mechanisms responsible for the cell
enhancements are not fully understood and they probably serve more than one purpose. They may act as diffusion barriers between the TCO and absorber layer, provide interface passivation, reduce optical reflectivity (although absorbing a part of the solar spectrum at the same time) or establish an inverted region in the absorber and thus lead to the formation of a homojunction. A detailed explanation of the physics of solar cells can be found elsewhere (Nelson, 2003)

1.3.2 Layer structure of a CIGS solar cell

The conventional CIGS solar cell consists of a stack of 5 layers deposited on a substrate material (substrate configuration, Fig. 1.6). A molybdenum back contact is first deposited by dc-sputtering. Thereafter the CIGS layer (p-type, 1-2 μm thickness) is grown typically by vacuum co-evaporation and covered with a Cd(S,OH) layer (n-type, ~50 nm thickness) using a chemical bath deposition process. The front contact is realized by sputtering a thin intrinsic ZnO layer (~50 nm thickness) followed by a thicker ZnO:Al transparent conducting oxide layer (TCO, 0.3-1 μm thickness). In order to increase current collection a Ni/Al grid is deposited on the TCO. Further efficiency enhancement can be obtained by depositing an antireflection layer. Eventually, the cells/modules are protected against environmental impact by encapsulation.

![SEM image showing the cross-section of a conventional CIGS cell. The CIGS layer was deposited by vacuum co-evaporation of the elements.](image.png)
1.3.3 Band diagram and CIGS layer grading

The band diagram of the CIGS solar cell is shown in Figure 1.7a. The front contact (ZnO:Al) is a heavily doped n-type material. It is followed by the buffer layers which are within the space charge region. The band gap of the CIGS compound depends on its Ga/(In+Ga) ratio which lifts the level of the conduction band minima with higher Ga contents while the valence band remains nearly unaffected (Wei, 1995). Therefore the spike height produced between CdS(-OH) and the CIGS depends on the Ga/(In+Ga) ratio of the CIGS layer. Some of the deposition processes (§1.4) lead to graded CIGS layers where Ga accumulation at the back contact is observed. This leads to a higher band gap towards the CIGS/Mo interface, keeping photoelectrons away from this interface where the recombination is supposed to be high. A detailed investigation of grading effects is given by Lundberg (Lundberg et al., 2003).

![Band diagram of the CIGS solar cell with a normal Ga grading increasing the band-gap at the back contact.](image)

**Figure 1.7**

a) Band diagram of the p-n junction of a CIGS solar cell with a normal Ga grading increasing the band-gap at the back contact.

b) Material properties of the layers used in the conventional CIGS solar cell. The refractive index (n_0), band-gap (E_g), conduction type and acceptor and donor doping levels (N_A, N_D) are given for the optically and electrically important layers.

<table>
<thead>
<tr>
<th>layer</th>
<th>material</th>
<th>n_0</th>
<th>E_g</th>
<th>type</th>
<th>N_A, N_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>anti-reflection</td>
<td>MgF_2</td>
<td>1.37</td>
<td>10.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>front contact</td>
<td>ZnO:Al</td>
<td>1.9</td>
<td>3.6</td>
<td>n^+</td>
<td>10^20</td>
</tr>
<tr>
<td>buffer</td>
<td>i-ZnO</td>
<td>1.9</td>
<td>3.3</td>
<td>n</td>
<td>10^16</td>
</tr>
<tr>
<td>buffer</td>
<td>Cd(S,OH)</td>
<td>2.4</td>
<td>2.5</td>
<td>n</td>
<td>10^15</td>
</tr>
<tr>
<td>absorber</td>
<td>CIGS</td>
<td>2.9</td>
<td>1.2</td>
<td>p</td>
<td>10^16</td>
</tr>
<tr>
<td>back contact</td>
<td>Mo</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
1.3.4 Electrical properties

When there is no illumination (dark) the solar cell, being a p-n junction, has the same characteristics as a diode. The rectifying behavior is shown in Fig 1.8, where the characteristic dark current density (\(J_{\text{dark}}\)) is indicated. For an ideal diode the dark current density is given by

\[
J_{\text{dark}}(V) = J_0 \left( \frac{qV}{e^{\frac{qV}{kT}} - 1} \right)
\]  

where \(J_0\) is a constant (reverse saturation current density), \(K_B\) is Boltzmann's constant and \(T\) the temperature in K.

Illumination of the cell generates a photocurrent. The overall current density-voltage characteristic can be approximated as the sum of the short-circuit photocurrent (\(J_{\text{sc}}\)) and the dark current (photocurrent is positive by convention):

\[
J(V) = J_{\text{sc}} - J_0 \left( \frac{qV}{e^{\frac{qV}{kT}} - 1} \right)
\]  

Real solar cells may suffer from power dissipation in parasitic series resistances such as electrical contacts or in parallel resistances created by shorts at pinholes or at the sides of the devices. The influence can be modeled by two resistances in the equivalent
circuit (Fig. 1.9a) and leads to a deteriorated current-voltage characteristic as seen in Fig. 1.9b. The according current density is written as:

\[
J(V) = J_{SC} - J_0 \left( e^{\frac{q(V - R_{series} - J)}{A \cdot k \cdot T}} - 1 \right) - \frac{V - R_{series} \cdot J}{R_{Shunt}}
\]  

(1.3)

Figure 1.9  
(a) Equivalent circuit of solar cell with parasitic parallel (shunt) and series resistances,  
(b) Current density-voltage characteristic of a real solar cell showing a reduced maximum power point \((V_m, J_m)\) due to the influence of series and parallel resistances.

1.3.5 Solar cell efficiency

The solar cell efficiency, defined by the ratio of the electrical output power to the input power of the solar radiation, is the most important characteristic of a solar cell. Standard efficiency measurements use an air mass factor 1.5 (AM1.5) spectrum, which corresponds to standard terrestrial conditions (ASTM 1999) with an integrated irradiance power density of 1000W/m² \((P_s)\). The output power density of a solar cell is given by

\[
P_{out} = J_m \cdot V_m
\]

(1.4)

This value corresponds to the grey rectangular area in the J-V characteristic (Fig. 1.8a). The fill factor \((FF)\) is often used to characterize the quality of a solar cell junction. It expresses the ratio of the areas of the two rectangles drawn in Figure 1.8a:

\[
FF = \frac{J_m \cdot V_m}{J_{SC} \cdot V_{oc}}
\]

(1.5)
Therewith, output power and efficiency can be expressed as:

\[ P_{\text{out}} = J_{SC} \cdot V_{OC} \cdot FF \]  \hspace{1cm} (1.6)

\[ \eta = \frac{P_{\text{out}}}{P_S} = \frac{J_{SC} \cdot V_{OC} \cdot FF}{P_S} \]  \hspace{1cm} (1.7)

1.4 Conventional CIGS deposition techniques

Sophisticated vacuum co-evaporation techniques (Fig. 1.9) give the best control of composition and compositional grading through the films. Maximum CIGS cell efficiencies up to 19.3 % have been obtained by the use of a three-stage co-evaporation process (Ramanathan et al., 2004). The three-stage process has not been implemented in industrial large-area module production. However, other co-evaporation process variants have been used for module production as large as 1.2x0.6 m² at Würth Solar, Germany (Powalla et al., 2003, Figure 1.10 b).

![Figure 1.10](image)

Figure 1.10  High vacuum CIGS deposition systems have high complexity.

- a) Schematic drawing of laboratory-scale equipment based on an MBE system with point effusion cells for each element.
- b) Industrial in-line deposition system at Würth Solar, Germany.

Shell Solar and Showa Shell preferred selenization processes (also called two stage processes) for industrial module production. These processes consist of the deposition of a precursor material and a subsequent thermal annealing in a controlled reactive
atmosphere. Typically, the sputter deposition of a metal-alloy precursor is followed by selenization and sulfurization in reactive \(H_2Se\) and \(H_2\) ambient or by evaporation of a selenium layer on the metal precursor followed by rapid thermal annealing (Palm et al., 2003). A controlled band gap grading (grading of Ga/In ratio) is more difficult to achieve, but the use of a post-sulfurization step to obtain a higher band-gap at the CIGS surface led to module efficiencies above 14\% on 30x30 cm\(^2\) substrates with good process yield, showing the mature status of this technology (Kushiya et al., 2003). Although, low-cost CIGS solar modules can be produced by such vacuum-based deposition techniques, a high initial investment is required for the sophisticated vacuum deposition equipment and module costs will depend strongly on the production volume and - of course - also high efficiencies are mandatory. An overview of the different vacuum methods for CIGS growth is given in Figure 1.11.

![Figure 1.11 Vacuum methods for CIGS growth.](image)

### 1.5 Low cost CIGS deposition techniques

CIGS layer deposition is the most challenging step for low cost cell processing, since it is the most complex layer of the cell. High material utilization efficiencies close to 100\% are important in order to keep material costs and processing waste as low as possible. In general, these low-cost techniques follow the idea of the sequential techniques: A precursor material having defined metal ratios is deposited at low temperature and followed by a chemical reaction or annealing step at higher temperature. The aim is to develop fast processes with technologically simple and
reliable low-cost equipment. Undesired contamination of the precursor materials by the non-vacuum environment have to be avoided by choosing suitable precursor materials and additives. Two different approaches evolved: In one the precursor materials decompose during deposition on the substrate and form the CIGS compound directly (spray pyrolysis, electrodeposition of compound layers) whereas in the second approach, the precursor material is deposited as a thin layer that is subjected to a chemical treatment and selenization thereafter (paste coating, electrodeposition of metal layers). Even if CIGS formation during deposition is an appealing approach, the as-produced material is of poor quality, includes impurity phases and may be amorphous or microcrystalline due to the low deposition temperatures (<400°C). The quality is generally improved with a second processing step, where the material is annealed at higher temperature.

1.5.1 Spray pyrolysis

The spray pyrolysis technique is one of the best-investigated non-vacuum deposition processes for chalcopyrites, but there are only few reports on cell performance. The efficiency record dates back to 1989 (Duchemin et al., 1989) and is of 5% for a small area cell. The spray technique is very well suited for uniform large-area coatings. The process consists of the decomposition and reaction of premixed precursors, generally metal chlorides and a chalcogen compound (typically N,N-dimethyl selenourea or thiourea), on a heated substrate (300-400°C) (Pamplin and Feigelson, 1979; Brown and Bates, 1990). Drawbacks of this technique are impurity phases (binary oxide and chalcogenide phases), traces from the reaction by-products (chlorine and carbon) and the relatively small grain size obtained. However, annealing treatments in controlled atmosphere can reduce the impurity concentration and enhance crystallinity (Krunks et al., 2002; Marsillac et al., 2003).

Alternative precursor solutions based on organic single source precursors have also been investigated. The idea behind the development of single source precursors is to lower the CIGS formation temperature and to avoid the formation of impurity phases, since the synthesis is controlled on a molecular level (Hirpo et al., 1993; Banger et al., 2002). These organic precursors decompose and form the CIGS compound at temperatures below 400°C. However, such precursors are not commercially available and no cell efficiencies have been reported so far.
1.5.2 Electrodeposition

Electrodeposition has been successfully used to deposit quaternary CIGS films, resulting in small area efficiencies above 10% after a subsequent thermal annealing (Guimard et al., 2003). By applying additional In and Ga and a high-temperature annealing treatment in vacuum, an efficiency of 15.4% was obtained (Bhattacharya et al., 2000). The stability of the chemical solution, large-area uniformity and high deposition rates are still a challenge. Electrodeposition of an elemental-layer stack subsequently subjected to a selenization treatment led to 7-10% efficient devices (Kapur et al., 1987; Kampmann et al., 2003).

1.5.3 Paste coating

Typical paste coating techniques are screen printing, doctor-blade coating and curtain coating. Paste coating is a fast process and can be applied in continuous roll-to-roll deposition. The paste is prepared with the precursor materials (e.g. nanoparticles) in the desired stoichiometry and a liquid binder used as a transfer media (US Pat No. 5,985,691, Basol B. M., Nov 1999). Paste rheology can be tailored with material load and additives, which affect the final film thickness and homogeneity. In contrast to liquid atomization (spraying), where valuable portions of the precursor material are wasted, paste coating allows a very efficient use of the material and exhibits higher packing densities (Eberspacher et al., 2003). Material loss minimization is very desirable for precursors containing expensive elements like indium and gallium. After deposition, the precursor layer is sintered and converted to the CIGS layer in controlled atmosphere.

After some preliminary work on high temperature sintering (780°C) of CulnSe₂ (CIS) pellets from a powdered CIS ingot (Gombia et al., 1983), it was quite a challenge to produce homogenous thin layers by sintering of ground material (Arita et al., 1988; Vervaet et al., 1989). The motivation for the approach was the successful development of screen printed and sintered CdTe/CdS solar cells. However, in the case of CIS, the precursor powders used to formulate screen printable pastes had too large particle size (5-50 µm) and did not lead to compact single-phase thin layers. But even chemically synthesized colloidal CIS did not lead to pore-free CIS layers (Schulz et al., 1998). Ball-mill grinding of soft and reactive metals resulted in mechanically alloyed CIS powder, which requires higher sintering temperatures than pure metal powder. A solution to
this problem was presented by using copper-indium-alloyed powder produced by gas atomization (Basol, 2000). The alloy is more brittle than pure In and therefore allows ball milling to produce finer powder. CIS Devices produced by selenization in diluted H₂Se gas yielded efficiencies in the range of 10-11 %, although some porosity remained in the film, which was attributed to the randomly shaped precursor particles. Layers of metal oxide nanoparticles allowed an apparently higher packing density due to smaller particle size and uniformly round shape. Furthermore, gallium could be introduced into the precursor material, which led to a higher open-circuit voltage and devices with maximum efficiencies of 11.7 % (Eberspacher et al., 2002) and 13.6 % (Kapur et al., 2003, US Pat No. 6,127,202 Kapur V.K., Oct 2000). Still higher efficiencies above 15 % may be reached if a better control of the Ga grading is achieved (e.g. optimum Ga concentration near the CdS-CIGS interface for higher Voc). The chemical conversion of the stable metal-oxides to CIGS requires well optimized reactions. Such a two stage process includes a reduction step in diluted hydrogen prior to selenization with diluted H₂Se (Kapur et al., 2003). It is an ongoing discussion if the highly toxic H₂Se gas, though diluted to a small concentration in N₂, or the less hazardous selenium vapour should be used for selenization in industrial production. An experimental comparison study concluded that H₂Se selenization gives more uniform layers with better control, especially at moderate selenization temperatures of 400-500°C (Alberts, 2002). However, there are some restrictions on the use of H₂Se in many European countries and costly security measures are required in industrial production. Figure 1.12 gives an overview of different non-vacuum CIGS deposition processes.

1.6 Completely non-vacuum processed CIGS solar cells

Although all the component layers of the cell (metal back contact, buffer, front contact) can be grown with non-vacuum methods, more research and development is necessary to find suitable low-cost deposition methods and conditions. Some issues on non-vacuum TCO layers from sintered nanoparticles were presented, but the sintering temperature required for low sheet resistances is still too high for the application in efficient solar cells (Ederth et al., 2003; Eberspacher et al., 2002).
1.7 Objectives of this work

The objective of this thesis is to develop solar cells with a low-cost CIGS absorber deposition method using simple non-vacuum equipment and avoiding the use of hazardous chemical agents. The most promising concept is to start with a nanosized precursor powder that is coated on a substrate and subsequently converted into a CIGS layer (Fig. 1.13). The separation into two independent steps allows a better control of the layer properties:

- Deposition of a precursor film with good control of the resulting film composition (and structure to some extent)
- Conversion of the precursor layer to the I-III-VI compound layer by a suitable reaction pathway to control the CIGS phase formation and grain growth
The experimental work for the thesis concentrated on the following aspects:

1) Finding a suitable **precursor material** which fulfills the following requirements:
   - Suitable chemical properties for the conversion into impurity free CIGS
   - Nano-sized material to allow the deposition of homogenous precursor films with a thickness below 5 μm.
   - Economical production in large quantities

2) Evaluating different non-vacuum **deposition techniques** for a specific precursor material, allowing a reliable and fast coating of the substrate.

3) Construction and evaluation of different reactor designs for the **chemical conversion** of the precursor to high quality CIGS layer.

4) Development of solar cells with non-vacuum processed CIGS absorber layers.
2 Precursor material evaluation

In non-vacuum deposition methods, the constituents of CIGS (Copper, Indium, Gallium and Selenium) can not be reacted in their pure form as it is done in high vacuum co-evaporation deposition. As CIGS has to be formed at temperatures above 300°C, the atmospheric environment would instantly lead to oxidation and incorporation of impurities into the layer. Therefore a two-stage process is preferred, which first deposits a film containing the constituents in the correct ratio (at room temperature) and, second, converts that precursor layer into the desired compound at high temperature. Because of the required final layer thickness of only 1-2 μm, precursor material with small particle size (< 1 μm) has to be employed. Particles with a diameter smaller than about 50-100 nm show different properties compared to the bulk material. The high surface to volume ratio is responsible for many new aspects, e.g. lower melting and sintering temperature, increased catalytic activity, modified thermo-physical, electric, magnetic and mechanical properties as plasticity and hardness. Lower melting points and high reactivity will facilitate layer sintering by the used two step process (§1.7). Therefore nanoparticles are well suited as precursor materials.

2.1 Precursor characterization

Nanoparticles can be produced by different physical or chemical methods like e.g. flame aerosol or plasma processes, co-precipitation, sol-gel, high energy ball- or cryogenic milling, etc. Some of the methods are specialized to several kinds of nanoparticles. While milling methods work well with brittle materials they can not be used for ductile materials such as indium. On the other hand, the vacuum co-precipitation method can be applied for a large range of materials.
Four classes of materials were chosen for investigation:

### Table 2.1 Investigated precursor materials.

<table>
<thead>
<tr>
<th>Precursor Material</th>
<th>Supplier</th>
<th>Production Method</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metal</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu and In nanoparticles</td>
<td>Aldrich Co.</td>
<td>gas phase condensation</td>
</tr>
<tr>
<td>CuInGa alloy</td>
<td>EPFL</td>
<td>laser spark ablation</td>
</tr>
<tr>
<td><strong>Metal-Oxide</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu/In/Ga Oxide nanoparticles</td>
<td>NEI (Nanoparticle</td>
<td>gas phase condensation/</td>
</tr>
<tr>
<td></td>
<td>Enterprises Inc.)</td>
<td>oxidation</td>
</tr>
<tr>
<td><strong>Selenide precursor</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed metal selenide nanoparticles</td>
<td>SOLARONIX</td>
<td>wet chemical synthesis</td>
</tr>
<tr>
<td><strong>Salt precursor</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inorganic salts (chlorides and nitrates)</td>
<td>Alfa Aesar</td>
<td></td>
</tr>
</tbody>
</table>

The criteria for evaluation of the resulting layer were:

- uniformity of deposition (smooth and crack-free morphology, homogenous thickness)
- purity of CIS/CIGS phase formation (no binary selenide and oxide impurities)
- CIS/CIGS grain size after selenization (large grains of ~1 µm, dense layer)
- Porosity (elimination of pores by sintering of the precursor layer)

The deposition pastes were all prepared as suspensions of the nanoparticles in alcohol (pentanol). The pastes were deposited with the doctor-blade technique (§ 3.1.1). The deposition and conversion of the salt precursor layers developed during this thesis are described separately in Chapter 6.
2.1.1 Metals

The metal precursors, copper (purity >99.9%) and indium (purity >99.9%) nanoparticles, were obtained as nanosized activated powder with a particle size of ~100nm. As indicated by the vendor (Aldrich Co.), they have a high defect structure and internal energy which should facilitate chemical reaction and sintering processes. The powders are shipped in inert hexanes.

![SEM images of precursor powder](image)

Fig. 2.1 shows SEM micrographs of the Cu and In powder. The particle size is in a range of 100-200nm, but the particles form agglomerates of 1-2μm. The XRD patterns of mixed-powder deposition (§2.2.1) show Cu, In and In$_2$O$_3$ peaks indicating that the deposition in ambient atmosphere already leads to partial oxidation of the indium nanoparticles at room temperature.

Gallium, having a melting point of 29.7°C, is not available as metallic nanosized precursor material. If a pure metallic precursor is needed, it has to be alloyed with In and Cu. Therefore a Cu-In-Ga ingot, prepared by melting appropriate quantities of the metals in an evacuated quartz tube, was pulverized by laser spark ablation (Houriet et
al., 1999). Figure 2.2 shows the Cu-In-Ga precursor material. The particle size is in the range of 100-300nm.

![SEM image of Cu-In-Ga nanoparticle precursor produced by laser spark ablation of a Cu-In-Ga ingot](image)

**2.1.2 Metal-oxides**

The use of oxide precursors is motivated by the high flexibility and good control in (mixed-)metal-oxide nanoparticles production of several available production processes. The metal oxide precursors from Nanoparticle Enterprises Inc. were produced in a vapor phase condensation method. The metals are vaporized in the desired stoichiometry. This vapor is rapidly cooled in the presence of oxygen, causing nucleation and condensation of copper-indium-gallium-oxide particles. Before doctor-blade deposition, the powder was mixed and ball milled in pentanol. Fig. 2.3 shows a SEM picture of this powder.

![SEM image of Cu,In,Ga mixed-oxide nanopowder](image)
The powder from NEI was ordered in three different chemical composition ratios Cu/(In+Ga) (table 2.2) where the In/Ga ratio was fixed to 4:1.

<table>
<thead>
<tr>
<th>Powder; Cu/In/Ga ratio</th>
<th>Group III/I ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEI 1: 0.33/0.8/0.2</td>
<td>3  group III rich</td>
</tr>
<tr>
<td>NEI 2: 0.95/0.8/0.2</td>
<td>1.05 slightly group III rich</td>
</tr>
<tr>
<td>NEI 3: 1.1/0.8/0.2</td>
<td>0.9 group I rich</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD) revealed the main constituent phases of these powders (Fig. 2.4). The very pronounced In$_2$O$_3$ peaks can be detected in the XRD pattern of the oxides precursor. Additionally, there are some minor peaks attributable to other oxide phases, which have their most intense reflections in the 32-34° 2θ region (Cu$_2$In$_2$O$_5$, JCPDS file 30-479; CulnGa$_2$O$_7$, 38-840; CulnGaO$_4$, 38-839). The occurrence of a very pronounced In$_2$O$_3$ peak even in the case of the copper rich precursor may be an indication that the precursor powder mainly is a mixture of amorphous or microcrystalline copper oxide and polycrystalline indium oxide.

![XRD patterns of mixed oxide precursor layers with different Cu/In/Ga ratios. (Joint Committee on Powder Diffraction Standards, ASTM, Philadelphia, PA, 1967, Cards: In$_2$O$_3$, 6-416; Cu$_2$In$_2$O$_5$, 30-479; Mo, 42-1120)](image)

Figure 2.4 XRD patterns of mixed oxide precursor layers with different Cu/In/Ga ratios. (Joint Committee on Powder Diffraction Standards, ASTM, Philadelphia, PA, 1967, Cards: In$_2$O$_3$, 6-416; Cu$_2$In$_2$O$_5$, 30-479; Mo, 42-1120)
2.1.3 Metal-selenides

The formation of CIGS is often reported to be a reaction of binary selenides (Cu₂Se + InSe; Orbey et al., 1998). Therefore, these compounds have the potential to be well suited as precursor materials. A ternary selenide precursor was synthesized by reaction (2.1) at ambient temperature.

\[
\text{H}_2\text{O} \\
2 \text{Cu}_2\text{SO}_4 + 2 \text{InCl}_3 + 4 \text{SeC(NH}_2\text{)}_2 \rightarrow 2 \text{CuInSe}_2 + 2 \text{H}_2\text{SO}_4 + 4 \text{C}_2 \text{H}_2\text{N}_2 + 3 \text{Cl}_2 
\]

The obtained powder did not yield a stoichiometric composition although the reaction chemicals were mixed in stoichiometric quantities. The powder is indium rich and deficient in selenium. Less indium rich precursors are obtained by changing the Cu/In ratio of the reaction chemicals (Table 2.3a and 2.3b). The composition measurements by energy-dispersive X-ray analysis (EDX) are however not very accurate as the deposited porous films were only 1-2 μm thin. By adding GaCl₃ into the solution a Cu-In-Ga-Se powder was obtained. The XRD pattern of the produced powder does not show distinct peaks corresponding to crystalline phases (Figure 2.13) and therefore indicates an amorphous state.

<table>
<thead>
<tr>
<th>Cu/In ratio chemicals</th>
<th>Cu (at%)</th>
<th>In (at%)</th>
<th>Cu/In</th>
<th>Se (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.5</td>
<td>42</td>
<td>0.77</td>
<td>25.5</td>
</tr>
<tr>
<td>1.2</td>
<td>30.5</td>
<td>32.5</td>
<td>0.94</td>
<td>37</td>
</tr>
<tr>
<td>1.4</td>
<td>33.5</td>
<td>30.5</td>
<td>1.1</td>
<td>36</td>
</tr>
</tbody>
</table>

Table 2.3a. Composition of CIS precursors obtained after reaction 2.1.

<table>
<thead>
<tr>
<th>Cu/(In+Ga) chemicals</th>
<th>Cu (at%)</th>
<th>In (at%)</th>
<th>Cu/(In+Ga)</th>
<th>Ga (at%)</th>
<th>Se (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>29.5</td>
<td>29.5</td>
<td>0.88</td>
<td>4</td>
<td>37</td>
</tr>
</tbody>
</table>

Table 2.3b. Composition of CIGS precursors as measured with EDX.

The obtained powder was highly aggregated and therefore ball-milling was used to disperse the brittle powder in an alcoholic suspension paste. Figure 2.5(a) shows a Cu-In-Se precursor powder obtained by the chemical reaction (2.1). After 1.5 h of ball milling the big 1-3 μm agglomerates are reduced to submicron particles, although still some bigger particles are present (figure 2.5(b)).
2.2 Chemical conversion in selenium vapor

To evaluate the suitability of the precursor material, the doctor-bladed precursor layers were annealed at high temperature (500-600°C) in selenium vapor. The used reactor consisted of a two-temperature zone semi-closed quartz box in a vacuum chamber (Chapter 3). The sample is heated in one temperature zone to 450-550°C, while the selenium partial-pressure and selenium-feed is controlled by the second temperature zone. Prior to reaction the chamber is pumped down to $10^{-5}$ mbar.

To investigate the degree of conversion of the precursor, X-ray diffraction patterns were recorded of the precursor layer before and after selenization. The composition was measured by EDX before and after selenization to determine a possible metal ratio distortion.

2.2.1 Metals

The doctor-blade deposited mixed metal precursor layer was selenized at a temperature of 500°C for 25 minutes. The selenium was hold at a temperature of 250°C which corresponds to a selenium partial pressure of $10^{-2}$ mbar. Figure 2.6 shows the morphology of the layer before and after selenization.
Figure 2.6  SEM images showing the morphology of a metal precursor- (a) and selenized layer (b).

The selenized layer shows grains up to 1-2µm in diameter. X-ray diffraction confirms the conversion from Cu and In to the CIS compound (figure 2.7).

![XRD pattern of precursor and selenized layer](Image)

The precursor layer is not only composed of pure In and Cu but also of In₂O₃. The selenized layer contains in addition to CuInSe₂ still some In₂O₃ crystals indicating that the reaction is not complete. As a second impurity phase, Cuₓ₋ₓSe is formed in small quantity. The average composition during selenization changed from indium rich to slightly copper rich as seen in Table 2.4. The compositions in different places varied and therefore the significance of these measurements is limited. Better mixing of the precursor layer is required for a homogenous composition.
Table 2.4 Composition before and after selenization (in atomic percentage).

<table>
<thead>
<tr>
<th></th>
<th>Cu (at %)</th>
<th>In (at%)</th>
<th>Cu/ln ratio</th>
<th>Se (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>48</td>
<td>52</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>Selenized</td>
<td>27.5</td>
<td>27</td>
<td>1.02</td>
<td>45.5</td>
</tr>
</tbody>
</table>

The layers from the alloyed precursor produced by laser spark ablation did not show pronounced grain growth (fig. 2.8). Moreover, they cracked during selenization.

Figure 2.8 SEM images showing the morphology of selenized laserablatted metal-alloy precursor layer at two different magnifications.

The XRD patterns revealed an incomplete conversion to CIGS. Where the precursor layer only shows some Cu and In peaks, the selenized layer contains the CIGS phase as main constituent along with In$_2$O$_3$ and Cu$_{2-x}$Se impurity phases (Figure 2.9).

Figure 2.9 XRD patterns of laserablatted alloyed metal precursor and selenized layer.
2.2.2 Metal-oxides

Selenization was performed at 500°C for a duration of 45 minutes. The selenium temperature was 250°C, corresponding to a partial selenium pressure of $10^{-2}$ mbar. The selenized layer shows very limited grain growth and sintering (Figure 2.10 a). During the selenization reaction the layer is cracked in different parts (Figure 2.10 b), where the crack width scales with the layer thickness. Care had to be taken that the evaporation of the alcohol proceeded slowly, to prevent micro-crack formation in the precursor layer. However, the formation of micro-cracks in the precursor layer could not be completely excluded. Different deposition methods were tested for this precursor (Chapter 3).

Figure 2.10  SEM image of morphology of selenized metal oxide precursor layer at two different magnifications.

![SEM image of morphology of selenized metal oxide precursor layer](image)

Figure 2.11  XRD patterns of metal-oxide precursor (NEI 3) layer before and after selenization.

![XRD patterns of metal-oxide precursor layer](image)
The selenization reaction was investigated by XRD before and after selenization (Figure 2.11). This precursor showed the best conversion results. Whereas the ternary oxide phase \( \text{Cu}_2\text{In}_2\text{O}_5 \) present in the precursor is converted, the \( \text{In}_2\text{O}_3 \) phase is still present in the selenized layer.

Another prerequisite for a precursor material is a controllable metal ratio in the selenized layer (Table 2.5, 2.6).

### Table 2.5 Metal ratios of oxide-precursor layers before selenization.

<table>
<thead>
<tr>
<th>Powder type and Cu/In/Ga ratio</th>
<th>Elemental composition measured by EDX in at% and (elemental fractions)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>NEI1 (0.33/0.8/0.2)</td>
<td>23</td>
</tr>
<tr>
<td>NEI2 (0.95/0.8/0.2)</td>
<td>46</td>
</tr>
<tr>
<td>NEI3 (1.1/0.8/0.2)</td>
<td>53</td>
</tr>
</tbody>
</table>

### Table 2.6 Metal ratios of selenized layers obtained from oxide precursors mentioned in table 2.5.

<table>
<thead>
<tr>
<th>Powder type and Cu/In/Ga ratio</th>
<th>Elemental composition measured by EDX in at% and (elemental fractions)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>NEI1 (0.33/0.8/0.2)</td>
<td>18.9</td>
</tr>
<tr>
<td>NEI2 (0.95/0.8/0.2)</td>
<td>34.5</td>
</tr>
<tr>
<td>NEI3 (1.1/0.8/0.2)</td>
<td>32.3</td>
</tr>
</tbody>
</table>

Taking into account a measurement error of 5\%, it can be concluded that the metal composition is generally retained during selenization of oxide precursors. Only for the copper rich composition there may be a slight tendency for an increase in the indium content. In all three cases the selenium content is below the stoichiometric CIGS composition, indicating that the reaction is not completed, since the reaction proceeds via a replacement of the oxygen by selenium.

The data of Fig. 2.11 was obtained for the NEI3 powder which has a copper rich composition. This composition showed the most intense CIGS peaks of the three oxide precursors and had the highest amount of incorporated selenium (table 2.6). This fact suggests that copper is more easily converted than indium and gallium.
2.2.3 Metal-selenides

The selenide precursor layers were selenized at 500°C for 15 minutes. The selenium temperature was 250°C, which corresponds to a partial selenium pressure of \(10^{-2}\) mbar. Figure 2.12 shows the selenized layer morphology. During the selenization step the layer cracked and grain size remained in the sub-micron range. Therefore only very limited grain growth occurred in the selenized layer compared to the precursor (figure 2.5).

![Figure 2.12 SEM image showing the morphology of selenized CIS precursor showing large cracks and small grains.](image)

The composition of the precursor and the selenized layer is given in table 2.7. The copper to indium ratio is slightly increased during selenization but the change is not significant, given the precision of the measurements. The low selenium content in the precursor material was increased but is still below the values for stoichiometric CIS (~50%). Therefore, it can be concluded that the CIS formation reaction is not complete.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>In</th>
<th>Cu/In ratio</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>32.5</td>
<td>42</td>
<td>0.77</td>
<td>25.5</td>
</tr>
<tr>
<td>Selenized</td>
<td>26</td>
<td>30.5</td>
<td>0.85</td>
<td>43.5</td>
</tr>
</tbody>
</table>

Fig. 2.13 shows the phases formed upon selenization. Beside the desired CIS phase also In\(_2\)O\(_3\) and Cu\(_{2-x}\)Se impurity phases are present. Since the introduction of oxygen during selenization in the vacuum chamber can be excluded, the oxygen must already be present in an amorphous or microcrystalline phase in the precursor material.
The results of this chapter show that all the tested precursor materials (pure metals, alloyed metals, metal selenides, metal oxides) form the CIS/CIGS phase by a simple reaction step in selenium vapor. The metal ratios can change during the CIS/CIGS phase formation, but it is possible to control the composition by choosing appropriate precursor concentrations. However, sintering of dense homogenous films, grain growth, and complete elimination of impurity phases were not achieved. The main impurity phases forming during the reaction in selenium vapor are the indium oxide and the copper selenide phases, which always occurred together. For a complete selenization reaction the indium oxide impurity phase needs to be converted to indium selenides which would react with the copper selenide to form the CIS/CIGS phase.

Cracking of the layers during the heating is another problem encountered. Except for the pure metal precursor, all the layers cracked during the selenization step. One reason for this may be seen in the fact that the layer undergoes a threefold volume expansion during CIGS formation, which is filling out the pores in the precursor layer. Metal-oxides and selenides have a much lower volume expansion and may lead to island and crack formation. Cracking is absolutely detrimental for the subsequent deposition of front contact and buffer layer, because they would short-circuit the cell through the cracks. Table 2.8 shows a summary of the results.
Table 2.8 Layer properties resulting from selenization of various precursor materials in selenium vapour (+ satisfactory; 0 medium; - poor).

<table>
<thead>
<tr>
<th>Nanoparticle Precursor</th>
<th>CIS phase formation</th>
<th>No impurity phases</th>
<th>Large grain size</th>
<th>Crack-free layers</th>
<th>Low porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed metal</td>
<td>+</td>
<td>0</td>
<td>+</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>Alloyed metal</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Metal-oxide</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Metal-selenide</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The mixed metal precursors obviously provide the best properties of the selenized layer and will therefore have the main focus in the following chapters. The introduction of gallium into this precursor material remains an issue. Therefore, the other precursor materials have not been completely abandoned at this point. Cracking of the layers may be linked with the deposition methods and may therefore be eliminated by using an appropriate method (Chapter 3). Grain growth and impurity phase elimination are very much dependent on the conditions of the conversion reaction (Chapter 4).
3 Precursor deposition

The aim of the work in this chapter is to investigate and evaluate different non-vacuum deposition methods for nanoparticle precursor materials.

3.1 Deposition methods

The tested methods are doctor-blade (also known as cup coating or tape casting, Svec et al., 2002), screen printing (Jabbour et al., 2001) and electrospray (Siefert, 1984). Even though these techniques are readily used to deposit thick films (> 10 μm), only few reports on paste formulations are given in the literature. In general, it is agreed that the paste viscosity should be low for spray liquids, higher for doctor-blade and even higher for screen printing. Figure 3.1 shows a schematic illustration of the three methods.

![Figure 3.1 Common non-vacuum deposition methods: doctor-blade (a), screen-printing (b), spraying (c).]

3.1.1 Doctor-blade

Doctor-blade is one of the simplest methods for film deposition. Everything required is a blade and a mechanism that fixes the distance between blade and substrate. The fixed distance can be realized with a spacer that is applied on both sides of the substrate. In this work stripes of adhesive tape (~55 μm thick) were used. The deposition suspensions containing the precursor particles were prepared with alcohol (1,2-propanediol or 1,2-propylene glycol). Suitable viscosity of the precursor paste for doctor-blade deposition was obtained with 5 ml alcohol per gram of precursor powder.
3.1.2 Screen printing

Screen printing is widely used for ceramic layer deposition in dye sensitized solar cells (Späth et al., 2003) and fuel-cells (Weber et al., 1996). This technique consists in printing a high-viscosity material through a mesh that is in contact with the substrate at the moment of paste deposition (fig. 3.1b). The mesh properties such as mesh size and mesh thickness will define the deposited layer thickness for a given paste rheology. Screen printing has been widely used in thick film applications such as printed circuit board (PCB) metallization and color printing where usually layers of several 100 μm are deposited. By a careful control of the paste rheology, especially thixotropy and viscosity, this method is applied to print homogenous layers with submicron thickness. A vast chemistry of additives has been developed to tailor the paste properties for the required results. Most often an organic binder material is used that can be removed by a heating step in air prior to sintering at higher temperature. These processing steps are well suited for oxide layer deposition, but are suspected to introduce oxide impurities into oxygen-free compounds like CIGS. However, there may be a workaround if the introduced impurities can be removed by the subsequent selenization step. To lower the risk of organic contamination pure alcoholic suspensions were used as deposition pastes, where a ratio of 1ml alcohol per gram of powder was chosen. The deposition was done with a manual screen printer set-up using a 250 mesh screen.

3.1.3 Electrospray

The electrospray has recently been developed for chemical spray pyrolysis. The main advantage compared to traditional sprays is the very high droplet deposition efficiency. While pneumatic sprays carry a large fraction of the droplets out of the deposition area, electrospray generates an electric field between nozzle and substrate which attracts the charged droplets to the deposition target. The electric field acts as an atomizing and driving force which also speeds up the droplet transport (Siefert, 1984). Electrospray allows a precise control of the gas phase reaction near the heated substrate, good film adhesion and a very high efficiency of material usage (> 80% even with a carrier gas). In the present work no gas is used for atomization but some vapors are produced during the evaporation of the suspension liquid.

Electrospray has successfully been applied in chemical spray pyrolysis to grow various oxide films such as lithium manganese oxide (Vanzomeren et al., 1994), indium

While chemical spray pyrolysis uses diluted precursor materials, in this work electrospray was investigated for the transfer of solid particles suspended in alcohols. Precursor liquids were prepared with suspensions of ethanol and 1,2 propanediol with approximately 35ml of alcohol per gram of powder.

![Schematic drawing of the used electrospray setup.](image)

Figure 3.2 shows the electrospray setup consisting of an electrified plate-nozzle configuration (Vanzomeren et al., 1994) in normal air ambient. The feed of the suspension is controlled by the hydrostatic pressure between nozzle tip and suspension reservoir. Depending on the applied potential one or several jets are emitted at the nozzle tip. The Taylor cone mode (Taylor, 1964), which is used for the deposition process, is defined by the emission of a single, stable jet, breaking into droplets with nearly monodisperse size distribution. A Hamilton Luer Tip probe (Pt. Style 3, 2.1 mm outer diameter, 1.6 mm inner diameter) was used as nozzle, located 50 mm below the substrate. An evaluation of the material deposition efficiency (MDE, weight ratio of deposited particles on a defined surface to the total sprayed particles) was achieved by spraying 1 ml of the 1,2-propanediol suspension on a heated stainless steel foil of 5x5 cm² in area. The increase in weight of the foil was compared to the weight of the residues after heating and evaporation of the alcohol of 1 ml of the same spray suspension. The MDE measurements yielded an efficiency of nearly 100%. As a comparison, conventional pneumatic spray yields typically a MDE of 25% while for ultrasonic spray ~85% MDE has been reported (Eberspacher et al., 2001).
3.2 Evaluation

3.2.1 Mixed-metal precursor

Typical SEM pictures of as-deposited pastes for doctor-blade, screen printing and electrospray are shown in Fig. 3.3. In the case of doctor-bladed layers (Fig. 3.3a), the formation of clusters of agglomerated particles prevents uniform deposition of thin layers of less than 2 μm. During evaporation of the suspension liquid, the risk of dislocating the deposited particles, which may result in clusters and cracked layers, rises for increased liquid to particle ratios. A better uniformity of the film is obtained with the screen printing method (Fig. 3.3b); such films present a clustered structure as well, but they have a smoother surface due to the mechanical forming by the screen. In electrosprayed layers (Fig. 3.3c) agglomeration was limited to submicron clusters arising from the small droplet size of the spray. It is desirable to evaporate the suspension liquid before or just after the droplets impinge on the substrate, so that the film remains dry and the particles are unable to move after deposition.

![SEM images showing the morphology of mixed metal nanoparticulate precursor films deposited by doctor-blade (a), screen printing (b), and electrospray (c).](image)

The substrate temperatures needed to evaporate the liquid during spray were below the boiling temperatures of the suspension liquids. More precisely, room temperature is enough to evaporate ethanol ($b_p = 78^\circ$C) so that the sprayed film remains dry. Charging prevents the particles from agglomeration after atomization and results in a good adhesion to the substrate. The composition of layers deposited by spraying the ethanol suspension does not correspond to the composition of the suspension. A decrease of the Cu/In ratio, typically from 1 to 0.2 is observed (Table 3.1). The Cu/In ratio distortion increased with increasing deposition times. This may be explained by settling effects of agglomerates in tube and nozzle. In order to avoid the distortion, a alcohol
with higher viscosity (1,2-propanediol) was tested (Table 3.2). At 25°C the Cu/In distortion could be reduced but not eliminated (Table 3.1).

**Table 3.1** Cu/In ratio of sprayed films.

<table>
<thead>
<tr>
<th>Suspension liquid</th>
<th>Suspended powder Cu/In ratio</th>
<th>Sprayed film Cu/In ratio</th>
<th>Selenized film Cu/In ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>1</td>
<td>0.2</td>
<td>0.25</td>
</tr>
<tr>
<td>1,2-Propanediol</td>
<td>1</td>
<td>0.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>

**Table 3.2** Boiling temperature and viscosity of alcohols used for the spray suspension liquid (Lide, 2000).

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Boiling temperature [°C]</th>
<th>viscosity [mPa s] 0 °C</th>
<th>viscosity [mPa s] 25 °C</th>
<th>viscosity [mPa s] 50 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>78</td>
<td>1.8</td>
<td>1.1</td>
<td>0.7</td>
</tr>
<tr>
<td>1,2-Propanediol</td>
<td>184</td>
<td>248</td>
<td>404</td>
<td>113</td>
</tr>
</tbody>
</table>

Electrospray of ethanol suspensions is delicate, as little vibrations and small changes in the electrostatic configuration (charges near spray) lead to instabilities in the spray jet. The voltage used to produce the Taylor cone spray mode was around 5 kV. Using 1,2-propanediol, the jet is more stable and does not get disturbed that easily.

Figure 3.4 compares the morphology of electrosprayed films for ethanol and 1,2-propanediol suspensions. For ethanol suspensions sprayed at room-temperature (Figure 3.4a) the film is composed of uniformly distributed particles. If 1,2-propanediol is used as suspension liquid, bigger agglomerates of several micrometers are deposited, as shown in Figure 3.4b and 3.4c. The thickness of the sprayed films was controlled by the spray time. While ethanol suspensions required nearly one hour spraying time for precursor films with ~2μm thickness, 10 minutes were sufficient with 1,2-propanediol suspensions. This indicates that the higher viscosity of the suspension prevents particles and agglomerates from sinking. The higher boiling point of 1,2-propanediol (184°C) required heating of the substrate to 90°C-100°C to keep the substrate dry during spraying.
Figure 3.4 SEM images showing morphology and cross-section of electrosprayed metal nanoparticle layers. Layer (a) was deposited using an ethanol suspension. Layer (b) and (c) result from 1,2-propanediol suspensions.

The measured composition varied across the sample. Figure 3.5 shows the copper and indium fractions as a function of distance from the sample center. Except for a small offset the composition shows a symmetrical distribution around the sample center. The copper content is decreasing from the sample edge towards the sample center. This problem can be circumvented by using moving substrates, which is common practice in industrial spray processing.
3.2.2 Metal-oxide precursor

Selenization of doctor-blade deposited oxide precursors led to severely cracked layers (Figure 2.10). Figures 3.6 a) and b) compare the morphology of a screen-printed and an electrosprayed oxide precursor layer from 1,2-propanediol suspension. The deposition results for metal-oxide precursors are similar to the metal precursors: The sprayed layer is more homogeneous and shows only small round deepenings, probably due to un-evaporated droplets impinging on the surface. The printed layer shows bigger agglomerated particles and indicates micro-cracks. However, the subsequent selenization of the electrosprayed layer also led to crack formation.

The width and length of the cracks diminish when the deposition method is changed from doctor-blade to screen printing and to electrospray. This may be linked to the high liquid content in the doctor-blade deposited precursor before evaporation of the alcohol. Crack formation in the precursor layer results from evaporation of the alcohol. During the conversion of the precursor the cracks widen. The electrosprayed layer remains dry during deposition. The small cracks appear during the conversion at high temperature probably due to a difference in the expansion coefficient of the substrate and the particulate precursor layer. In the literature (Eberspacher et al., 2000), a volume expansion of a factor of 2-3 times is reported for the conversion of oxides to selenides, which should be sufficient for pore elimination and avoidance of crack formed by tensile stress. However, the conversion reaction is not complete (§2.2.2) and the cracks form probably during heating up and before the chemical conversion reaction.
Figure 3.6 Morphology of screen printed (a) and electrosprayed precursor layer (b). The sprayed layer presents a smoother surface compared to the screen printed layer. Selenization led to cracking of both layers, screen printed (c) and electrosprayed (d) layers. Mechanical compression of the screen-printed precursor layer prior to selenization led to a very smooth layer, but cracking could not be prevented (e).

In order to investigate the influence of higher packing density on crack formation, the precursor layer was mechanically compressed with a manual hand-press. After precursor deposition the sample was covered with a 3mm thick glass plate and put under the press. After selenization, the layer shows a smooth surface, but cracking was not prevented (Figure 3.6e). Figure 3.7 compares the microstructure of a compressed with a normal metal-oxide precursor layer.
In the compressed layer large copper rich crystals (as measured by EDX) are formed on top of a smooth surface. This may be explained by fast diffusion and dewetting properties of the copper selenide phase. Even though the two samples were selenized in the same run (~450°C), the compressed layer contained only 20% of selenium whereas the normal layer had 24%. This may be an indication that denser precursor films require longer selenization times due to more restricted selenium in-diffusion.

3.3 Conclusion

Three non-vacuum deposition techniques commonly used for thick film deposition were tested for thin-film deposition of nanosized precursor materials. The deposition pastes were prepared as suspensions in pure alcohols to prevent pollution by organic additives as fillers or dispersants. Doctor-blade, being the simplest deposition technique, yielded the poorest layers compared with the other techniques. Screen printing gives more control on layer homogeneity by using higher viscosity pastes and by the mechanical forming by the screen. Electrospray deposition yields homogeneous layers at the cost of a much longer deposition time. To improve the spray jet stability and the control of composition higher viscosity alcohols have to be used.

For even better results on layer homogeneity, the deposition pastes have to be improved. The bad results of doctor-blade are mainly due to agglomerated particles which should be better dispersed in the liquid. Ball milling (Figure 2.5) can be used to improve the pastes but the results are still far from being optimum for homogenous
layer deposition. The cracking of oxide and selenide layers during selenization could not be avoided by any of the tested deposition methods.
4 Selenization

The conversion of the precursor material to the CIGS phase is achieved by the selenization reaction. CIGS, being a refractory material with a melting point of 989°C, generally exhibits sintering and grain growth at the same time as the CIGS phase is formed. Low-cost glass substrates do not support temperatures higher than 600°C, therefore reaction and deposition temperatures are limited to this maximum temperature. The most common selenization agent is selenium vapor produced by thermal evaporation.

Selenium is known to produce various allotropie modifications (cyclo-hexaselenium $\text{Se}_6$, cyclo-heptaselenium $\text{Se}_7$, cyclo-octaselenium $\text{Se}_8$, ...) with different crystalline and amorphous structures showing red, grey, and black colors. It melts at 220°C and boils at 685°C. Selenium vapor consists of $\text{Se}_n$ molecules ($n = 2-10$) with a molecular size distribution that depends on the vapor temperature. Higher temperatures shift the distribution to low atomic molecules, which have higher enthalpies of formation than the higher atomic molecules (Steudel and Strauss, 1987). The existence of different vapour compositions is supposed to influence reproducibility. Another commonly used reactant is hydrogen selenide gas ($\text{H}_2\text{Se}$).

Selenium and its compounds are toxic for the human body. Consumption of more than 1 µg Se per g of food leads to poisoning phenomena such as inflammation of the respiratory organs and loss of hair. On the other hand, Se deficiency symptoms appear if less then 0.2 µg Se per g of food is consumed because Se is an essential mineral with powerful antioxidant effects in the body. Se also seems indispensable to appropriate immune response. It can chelate various metals (e.g. Cd and Hg) allowing their detoxication (Dubois and Belleville, 1988). Elemental Se is solid at room temperature and therefore unproblematic to handle. But the use of hydrogen selenide gas requires sophisticated safety precautions and expensive storing and disposal equipment (scrubber).
4.1 Chemical conversion in vacuum reactor

Figure 4.1 shows a schematic drawing of the reactor used for the selenization treatment. The reactor is set up in a stainless steel high vacuum chamber and consists of a heated quartz plate and a heated cap which can be lifted. Two temperature zones allow separate heating of the selenium pellets and substrate. Prior to selenization, the vacuum chamber is evacuated to a pressure below $10^{-5}$ mbar with the lifted cap. Then the cap is lowered onto the plate, which results in a better confinement of the selenium vapor. However, the fitting of the cap on the plate is not tight and the selenium can diffuse out of the reactor and then condenses on the walls of the vacuum chamber.

4.1.1 Conversion reaction

For the formation of CIGS a variety of reaction pathways must be considered depending on the precursor material. The precursors that were best investigated, are stacked layers of metal (evaporated or sputtered) and selenium which are annealed in high vacuum reactors under excess selenium. Time resolved *in-situ* XRD during annealing of a substrate/Cu/In/Se precursor identified the following (crystalline) phase transformations (Brummer et al., 2003):
Table 4.1 Phases and reaction paths investigated by in-situ high energy powder diffraction for stacked vacuum deposited precursors (substrate/Cu/In/Se configuration with composition Cu/In/Se = 1/1/2.5) (Brummer et al., 2003).

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>Phases and Phase transformations</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>Cu, CuIn, CuInIn, Se amorphous</td>
</tr>
<tr>
<td>150-200°C</td>
<td>CuIn + Cu → CuIn</td>
</tr>
<tr>
<td>125-175°C</td>
<td>Se (amorphous) → Se (crystalline)</td>
</tr>
<tr>
<td>208-225°C</td>
<td>Se → Se (liquid)</td>
</tr>
<tr>
<td>225°C</td>
<td>CuIn + Se → InSe + CuSe + CuSe + Cu2xSe</td>
</tr>
<tr>
<td>350°C</td>
<td>InSe + Cu2xSe</td>
</tr>
<tr>
<td>375°C</td>
<td>2 InSe + Cu2xSe + Se → 2 CuInSe</td>
</tr>
</tbody>
</table>

In contrast to vacuum evaporated stacked precursors, nanoparticulate precursors have a porous structure and may react differently. Additionally, the observed In2O3 impurity phase contained in the metal nanoparticle precursors (§2.2.1) may influence the typical reaction path shown in table 4.1.

To investigate the conversion reaction with nanoparticulate metal precursors, a series of selenization treatments was carried out at various temperatures (steps of 100°C between 100 and 600°C). During the annealing at different temperatures the temperature of the selenium source was kept constant at 300°C. The reaction time was 30 minutes. Figure 4.2 shows the XRD patterns of the selenized and quenched samples.

In contrast to \textit{in situ} phase monitoring this \textit{ex situ} method may suffer from phase back transformation (including solidification of liquids) during quenching and storing at room temperature.

In contrast to the observations made on vacuum deposited stacked metal precursors, no intermetallic phases are observed. The phases CuIn and CuInIn are known to form already at room temperature but only elemental Cu and In are observed in the nanoparticle precursor. The fact that the layer is composed of small elemental particles with little contact surface may result in a very slow intermixing. The In2O3 impurity phase, probably present on the surface of the In nanoparticles, may further inhibit the intermetallic phase formation.

Selenization at 100°C does not lead to any detectable reaction. The evaporated selenium is deposited on the precursor and crystallizes in its thermodynamically stable hexagonal structure.
After passing the melting point of indium (156°C) and approaching the melting point of selenium (220°C) a first reaction between selenium and copper to the CuSe₂ phase is detected. In contrast to the vacuum evaporated stacked precursors (Table 4.1), no indium selenide phases could be identified and there is still some metallic indium present that may have been stabilized by the In₂O₃ phase.

At 300°C the indium and the CuSe₂ phase have disappeared and the CIS phase started to form. However, the In₂O₃ impurity phase is still present together with a newly formed Cu₂₋₅Se phase. With higher selenization temperatures the CIS peaks get sharper and the Cu₂₋₅Se peaks diminish indicating higher interdiffusion rates and increased CIS crystallinity (Figure 4.4).
Table 4.2 Phases formed during selenization of metal nanoparticle precursors at various temperatures.

<table>
<thead>
<tr>
<th>Selenization Temperature (°C)</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Cu, In, In$_2$O$_3$</td>
</tr>
<tr>
<td>100</td>
<td>Cu, In, In$_2$O$_3$, Se</td>
</tr>
<tr>
<td>200</td>
<td>In, In$_2$O$_3$, CuSe$_2$</td>
</tr>
<tr>
<td>300-600</td>
<td>CuInSe$_2$, In$_2$O$<em>3$, Cu$</em>{2-x}$Se</td>
</tr>
</tbody>
</table>

The conversion of the oxide precursor material most probably consists of two reactions where first the metal-oxides are converted to their selenides and then react to CIS. However, no data of in situ monitoring of the conversion reaction is available.

4.1.2 Impurities

The previous chapter has shown that it is not possible to eliminate the impurity phases in the metal precursor with the used selenization reactor and temperatures up to 600°C. As presented in Table 4.1, the Cu$_{2-x}$Se phase reacts with indium selenide and selenium to form the CIS compound. But as there is no indium selenide (indium is trapped in the oxide phase) the copper selenide phase cannot be converted. Temperatures higher than 600°C lead to a strong bending of the glass substrate and are therefore of no interest for production. In Figure 4.3 the phase fractions of CIS and In$_2$O$_3$ in the selenized layer are shown. This data was obtained by fitting the XRD patterns with crystal diffraction data of the identified phases (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, ASTM, Philadelphia, PA, 1967, In$_2$O$_3$: Card 6-416; CuInSe$_2$: Card 40-1487). The oxide phase contributes a nearly constant amount of ~18 wt%.

The conversion reaction in the other precursor materials has not been investigated in detail. Similar observations are made for the oxide precursor material (Figure 2.11). Whereas some of the oxide phases can be converted to CIS, the In$_2$O$_3$ phase is not reacted and remains in the layer. Also, the selenide precursor forms the In$_2$O$_3$ phase in small concentration during selenization (Figure 2.13).
Figure 4.3 Phase fractions of In$_2$O$_3$ and CIS in the selenized layer in function of different selenization temperatures calculated by fitting the XRD patterns with the Topas 2.0 software. For the tested temperature range, the selenization temperature has only little influence on the conversion of In$_2$O$_3$ to CIS.

Enthalpy and free energy calculations show that the conversion of In$_2$O$_3$ to selenide is difficult to achieve with the given reaction.

\[
2 \text{In}_2\text{O}_3 + 9 \text{Se} \rightarrow 2 \text{In}_2\text{Se}_3 + 3 \text{SeO}_2 \quad \Delta H^\circ = 490 \text{kJ/mol; 117kcal/mol} \tag{4.1}
\]
\[
\Delta G^\circ = 505 \text{kJ/mol; 121kcal/mol}
\]

The use of higher selenium partial pressures allows a partial conversion of the oxide phases (§2.4).

A more efficient reaction for the conversion of the oxides is reported by Kapur who used hydrogen gas to reduce the oxides to metal and H$_2$Se gas to convert the metal alloy to CIGS (Kapur et al., 2003). Even though this reaction is not energetically favorable either, the conversion is achieved by using non-equilibrium conditions (excess hydrogen and successive removal of the volatile conversion byproduct H$_2$O).

### 4.1.3 Crystallization

The CIS phase starts to form at 300°C (Fig. 4.2). During the thermal treatment, gradual conversion and coalescence of small grains lead to larger grain size. This phenomenon is reflected with sharper and higher-intensity CIS peaks in the XRD patterns for higher selenization temperatures. The average crystallite size has been
extracted with the Rietveld method (Cheary and Coelho, 1998) using the Topas 2.0 software (Bruker AXS, 2000) and the Inorganic Crystal Structure Database for CIS and In$_2$O$_3$ crystal data (CIS: ICSD 6397, In$_2$O$_3$: ICSD 14387). Figure 4.4 shows the average grain size as a function of the selenization temperature. The average CIS crystal size grows from 40 to 170 nm with an increase in selenization temperature from 300 to 600°C. The In$_2$O$_3$ crystals cannot grow much since no further oxygen is provided during selenization.

![Graph showing average crystal size as a function of selenization temperature.](image)

Figure 4.4 Average crystal size of the In$_2$O$_3$ and CIS phases in dependence of the selenization temperature calculated by fitting the XRD patterns with the Topas 2.0 software. Higher temperatures lead to gradually larger CIS crystals, while the In$_2$O$_3$ crystal size remains nearly constant during selenization.

### 4.2 Chemical conversion in non-vacuum reactors

High vacuum equipment is expensive and requires long pumping times. Low-cost solar cell production methods therefore aim for non-vacuum processes. Since atmospheric oxygen would lead to oxide formation during annealing, a suitable non-vacuum process requires an inert atmosphere (typically argon or the considerably cheaper nitrogen) which is then mixed with selenium vapor. For safety precautions the reactor may be designed for sub-atmospheric pressure operation which reduces the risk of out-diffusion of reactants or explosion. A further advantage of a non-vacuum reactor is the use of reactant pressures some orders of magnitude higher than used in vacuum reactors. This allows shifting the chemical equilibrium of a reaction to the desired product.
4.2.1 Reactor design

Figure 4.5 shows a schematic illustration of the employed non-vacuum reactor. The precursor sample is placed in a quartz vessel. It is difficult to construct a closed hot-wall reactor capable of working at temperatures up to 600°C with tight sealing and which can be opened to load samples. This reactor uses quartz-quartz sealing. Two inlets allow purging the vessel with nitrogen. The top and bottom part have independent heaters for independent control of substrate temperature and selenium pressure. A second container around the quartz vessel is pumped to the same base pressure and condenses any selenium vapor diffusing through the sealing. The outer container is water cooled. A membrane pump with a base pressure of 1-5 mbar is used for evacuating the reactor.

![Schematic illustration of non-vacuum reactor](image)

Figure 4.5 Schematic illustration of non-vacuum reactor, allowing the use of higher selenium pressures than the vacuum reactor.

The elimination of the In₂O₃ phase in the precursor has turned out to be very difficult with selenium vapor. In order to improve the efficiency of this reaction, selenium has to be available in large quantities, which is achieved by increasing the selenium partial pressure. Table 4.3 gives an overview of the process parameters of the two reactor systems.
### Table 4.3 Comparison of reactor parameters

<table>
<thead>
<tr>
<th></th>
<th>Vacuum reactor</th>
<th>Non-vacuum reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure</td>
<td>$10^{-3}$ mbar</td>
<td>1 mbar</td>
</tr>
<tr>
<td>Selenium pressure</td>
<td>$10^{-1}$ mbar</td>
<td>100 mbar</td>
</tr>
<tr>
<td>Selenium source temperature</td>
<td>~300°C</td>
<td>~500°C</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>500-550°C</td>
<td>500-550°C</td>
</tr>
</tbody>
</table>

#### 4.2.2 Impurity phases

Precursor layers similar to the ones used in the vacuum reactor were selenized in the non-vacuum reactor. Figure 4.6 compares the selenized layers obtained from the two reactor types. Impurity phases, namely the $\text{Cu}_{2-x}\text{Se}$ and $\text{In}_2\text{O}_3$ are only detected in layers processed with the vacuum reactor. Selenium vapor at higher pressure is therefore advantageous for the conversion of the oxide phase. However, the XRD results do not allow excluding the presence of small concentrations of oxides in the layers because of the detection limit of XRD.

![Figure 4.6 Comparison of XRD patterns of metal nanoparticle precursors selenized in the vacuum and the non-vacuum reactors, where the selenium pressure is 3 orders of magnitude higher in the non-vacuum reactor (Table 4.3). The high selenium pressure allows the conversion of the $\text{In}_2\text{O}_3$ and $\text{Cu}_{2-x}\text{Se}$ impurity phases to the CIS compound.](image-url)
Whereas the metal precursor contained only a small quantity of the oxide phase on the particle surface, the oxide precursor contains only pure oxides and will therefore be more difficult to convert. In addition, the oxide precursor also contained the gallium component which was not possible to incorporate in the pure elemental metal paste. \( \text{Ga}_2\text{O}_3 \) will be even more difficult to convert, having a free energy of formation of \( \Delta H_f^o = -1090 \), which is even higher than that of \( \text{In}_2\text{O}_3 \) (\( \Delta H_f^o = -926 \)). But since the gallium content is rather low it is not detected by XRD. Figure 4.7 compares the XRD patterns of the oxide precursor selenized in different reactors. The non-vacuum reactor converts the oxide precursor much better than the vacuum reactor. But there is still a broad, low-intensity peak of the \( \text{In}_2\text{O}_3 \) phase around \( \theta = 30.5^\circ \).

![XRD patterns comparison](image)

**Figure 4.7** Comparison of XRD patterns of \( \text{NEI}_2 \) oxide nanoparticle precursors selenized in the vacuum and the non-vacuum reactors, the selenium pressure being 3 orders of magnitude higher in the non-vacuum reactor (Table 4.3). The high pressure of selenium allows the conversion of the \( \text{In}_2\text{O}_3 \) and \( \text{Cu}_{2-x}\text{Se} \) to the CIS compound.

Figure 4.8 shows the XRD patterns of the selenized CIS powder from Solaronix. The conversion in the non-vacuum reactor is more efficient than in the vacuum reactor. This is seen in the complete conversion of the oxide phase which is still present in the vacuum selenized layer. In addition to the CIS peaks two large and broad peaks of the \( \text{MoSe}_2 \) phase appeared. This phase must have formed on top of the molybdenum back contact, resulting from reaction of molybdenum with selenium, and was not observed.
in other precursor materials. This can be explained by the different sintering behavior of the precursors: While selenization of metal and oxide precursors leads to densification of the layer by a 2-3 fold volume expansion (Eberspacher, 2000), the selenide precursor does not undergo a chemical reaction and no densification takes place (Figure 4.10). Therefore the porous layer gives the selenium vapor direct access to the molybdenum back contact. This reaction is again much faster in the non-vacuum process.

Figure 4.8 Comparison of XRD patterns of the selenide nanoparticle precursors selenized in the vacuum and non-vacuum reactor, the selenium pressure being 3 orders of magnitude higher in the non-vacuum reactor (Table 4.3). The high pressure of selenium is able to convert most of the In$_2$O$_3$ and Cu$_x$Se, which is still present in large amounts in vacuum selenized layers, to the CIS compound. In addition, peaks indicating the MoSe$_2$ phase are identified. This phase forms at the interface between the Mo back contact and the CIS layer. The remaining porosity in this precursor gives the selenium vapor direct access to the back contact.

### 4.2.3 Crystallization

The morphology of the selenized metal nanoparticle layer indicates a compact and large-grained structure (Figure 4.9a). The in-depth sinter reaction and grain growth of a 5 μm thick sprayed precursor layer was analyzed. Figure 4.9b shows the cross-section of the layer after selenization (550°C for 5 minutes). The layer consists of a large-grained, compact top layer and a porous small-grained bottom layer. As the layer surface is first
exposed to the selenium vapor, the chemical conversion starts on the surface of the precursor. The reaction of the metal to the CIS phase results in a volume expansion which leads to compact, pore free layers. However, the densification stops vapor transport of selenium to the bottom layer. Therefore after sintering of the top layer the further conversion reaction is slowed down. Nevertheless, the formation of a 1.5 to 2 μm thin compact CIS layer is obtained in a short time and the reaction may therefore be suitable for rapid thermal processing of thin precursor layers.

![Figure 4.9](image_url) SEM micrograph of metal precursor layer selenized in non-vacuum reactor showing the morphology (a) and cross-section (b), showing a densified top layer and a porous, small grained bottom layer.

Although the chemical conversion of the oxide precursor could be improved using the non-vacuum reactor, the grain size of the layer remained small. Also cracking of the layer could not be prevented.

![Figure 4.10](image_url) SEM micrograph of a vacuum (a) and a non-vacuum (b) selenized selenide nanoparticle precursor. Although the obtained grain size in the non-vacuum selenized layer is much larger it is still highly porous.
Sintering and densification of the selenide precursors has turned out to be very difficult (Figure 2.12). The use of a non-vacuum process with a high selenium pressure resulted in a markedly changed morphology. Figure 4.10 compares the resulting layers obtained by each method. Whereas vacuum selenization does not change the morphology of the precursor layer, the non-vacuum reaction leads to a coarsening of the layer with larger grains although the layer remains porous.

4.2.4 Open non-vacuum reactor

The design of a closed hot-wall reactor imposed some difficult construction issues. The main problem was the sealing between the two caps of the quartz vessel (Figure 4.1). The two parts were carefully adjusted to fit and to give a nearly tight system. Therefore, after evacuation the system was closed and allowed to maintain a high selenium pressure. The presented results in the last sections were obtained within the first runs after set-up. Subsequent runs were not able to reproduce the same results and the \( \text{In}_2\text{O}_3 \) phase appeared again in the layers. This phenomenon can be explained by two reasons:

- The quartz sealing of the caps started to leak so that the selenium pressure in the vessel dropped. Direct evidence was given by the fact that some selenium vapor condensed on the water-cooled outer walls of the reactor.
- The second reason may be the accumulation of oxide in the reactor. When the impurity phases are converted to the \( \text{CuInS}_2 \) phase the byproducts may condensate in the reactor (e.g. in the form of \( \text{SeO}_2 \)). The oxygen stored in the reactor may then lead to concurrent reactions which favor the formation of oxide phases.

These drawbacks were eliminated by using an open reactor design as shown in figure 4.11.
Nitrogen gas flows over the heated selenium source and carries the selenium vapor to the substrate region. The outlet region of the reactor is cold and the selenium vapor condenses there. In order to keep the selenium consumption low, the selenium evaporation temperature is kept at 350-400°C. This design does not allow as high partial selenium vapor pressures as the closed reactor, and therefore the conversion reaction is less efficient (Figure 4.12).

The open non-vacuum reactor does not produce the Cu$_{2+x}$Se phase but could not convert all the In$_2$O$_3$ crystals. In contrast to the vacuum reactor, some of the oxides could be converted so that the copper selenide reacted to CIS. The Cu$_{2+x}$Se phase is known to be highly conductive and detrimental for solar cells. It is therefore very important to eliminate it in order to avoid shunts in the CIS layer. The influence of the In$_2$O$_3$ phase, being a very stable and less conductive compound leads to increased resistivity and reduced mobility and is also detrimental (Haba et al., 1990).

The open non-vacuum reactor is easy to use and produces reproducible results, but is not efficient for converting the In$_2$O$_3$ compound. In order to characterize this reaction, indium and copper nanoparticle films were deposited and selenized separately for 20 minutes at 550°C (Figure 4.13). The selenized copper layer shows clearly defined large crystals with diameters up to 10µm. However, many pores form between the grains. In contrast to the copper sample, the grains of the selenized indium layer do neither show sharp edges nor a smooth surface.
Figure 4.12 XRD data for metal nanoparticle precursor films selenized under different conditions. Substrate temperature, selenization time, partial selenium pressure and reactor type are indicated on the left-hand side of the diagram.

Figure 4.13 SEM pictures showing the morphology of a selenized copper (a) and selenized indium (b) nanoparticle layer.
Compositional depth profiling by sputtering and XPS surface analysis was performed to investigate the selenization reaction in the two layers (Figure 4.14). The selenized copper layer has a constant selenium content through the measured depth range and no oxygen is detected in the film, except for surface contamination. Therefore the selenization reaction of copper can be considered as complete through the whole film. The selenized indium layer shows complete reaction only for the first 200 nm. Below 200 nm, the oxygen content is increasing while the selenium content decreases and they stabilize after 500 nm. The results indicate that the conversion reaction of indium nanoparticles is much slower than the conversion of copper particles.

![Figure 4.14 XPS depth profile measurements for selenized copper (a) and indium (b) nanoparticle layers.](image-url)
4.3 Conclusions

The selenization treatment is used to convert various precursor layers into CIS/CIGS absorber layers. Different conditions for the conversion reaction were tested and evaluated by means of CIGS phase purity, grain size, cracks and density. The conversion of the metallic nanoparticle precursor was investigated in more detail and showed a distinct behavior from vacuum evaporated, stacked metal precursors. No alloying of the nanoparticle metals prior to selenide formation was observed, which may be due to the limited contact area between the metal surfaces of the particles, since the oxidized surface of the In particles reduces the reactivity for metal alloy formation. Vacuum selenization with selenium vapor pressures up to $10^{-1}$ mbar was not efficient to convert the indium-oxide, hence the reaction to the ternary CIS phase is not complete. A closed non-vacuum reactor was designed to allow higher selenium partial pressures. High partial selenium pressure reactions were very efficient in removing impurity phases during selenization of the metal precursors and even converted most of the oxide precursors to the CIGS compound. The resulting layers selenized under different conditions lead to the conclusion that a high selenium partial pressure during annealing is more efficient for complete conversion than reaction time, substrate temperature or base pressure ($<10^{-3}$ mbar for vacuum reactors, 1 mbar for non-vacuum reactors). As the conversion reaction and layer densification starts from top of the layer, further selenium inclusion and oxygen removal from precursor material near the back contact is much more difficult. Layers with a thickness of 1-2 µm were easily converted. However, the deposition of thin (<1 µm) and homogeneous layers with the used nanoparticles (which include agglomerates up to 1 µm) is an unsolved problem. Metal-oxide and metal-selenide precursors did not yield compact, large grained CIGS layers, even if converted in higher-pressure selenium vapor. Although coarsening resulted in the selenide precursor, the porosity remained and allowed the selenium to directly access the molybdenum back contact, where it formed the MoSe$_2$ phase on top of the molybdenum back contact. Pure CIS phase was only obtained with the metal precursor selenized in the closed reactor.

Despite the promising results with the closed non-vacuum reactor reproducibility to obtain single phase layers in successive runs was not possible. Reaction byproducts remain in the reactor and compete with the selenization reaction unless the reactor is completely cleaned periodically. To overcome this problem, an open non-vacuum
reactor was designed and tested. Due to lower selenium partial pressures, it is less efficient for oxide conversion, but allows non-vacuum processing in a reproducible manner.

The difficulties of homogeneous precursor layer deposition and complete conversion of the oxide impurities motivated the search for a new precursor material, which allows depositing more homogeneous and thinner layers, improved intermixing of the metals and optimal incorporation of gallium in the selenized layer.
5 Solar cell devices from nanoparticle precursor

This chapter describes the processing and characterization of solar cells. Only solar cells based on CIS obtained from selenized metallic Cu and In nanoparticle precursors were characterized in detail, as the other precursor materials did not lead to crack-free CI(G)S layers and the resulting cells were shunted.

5.1 Device processing

The processing of complete CIGS solar cells (Figure 1.4) includes three steps after CIGS deposition:

- CdS buffer deposition in a chemical bath
- TCO front contact deposition (ZnO/ZnO:Al layers deposited by rf-sputtering) optionally a metallic grid (Ni/Al) is applied on top for improved current collection
- Cell area definition by scribing

5.1.1 Chemical bath deposition of Cd(S,OH) layer

The thin n-doped Cd(S,OH) layer forms the p-n heterojunction in conventional CIGS solar cells. The deposition of the buffer by the non-vacuum chemical bath deposition process has yielded the highest-efficient CIGS solar cells so far. The advantages of this deposition method with respect to vacuum evaporation are the etching of the CIGS layer surface prior to deposition and the perfect surface coverage even for very thin layers (< 50 nm). The incorporation of impurities from the bath (namely hydroxides and oxides) results in a material with different properties compared to vacuum deposited CdS.

The recipe used in this work consists in mixing the precursor chemicals cadmium-acetate and thiourea in alkaline ammonium hydroxide solution before immersing the substrate and heating of the bath from room temperature to 65°C. The chemical reaction taking place is written as:

\[
\text{Cd(CH}_3\text{COO)}_2 + \text{SC(NH)}_2 \rightarrow \text{CdS}_\downarrow + 2 \text{CH}_3\text{COOH} + \text{CH}_2\text{N}_2
\] (5.1)
The typical deposition time is 20 minutes during which the bath is heated to 65°C. The thickness is controlled by simultaneous CdS deposition on a Mo coated glass, where the layer thickness can be easily estimated by its color. A dark blue color corresponding to ~50 nm Cd(S,OH) is found to be an appropriate thickness (§1.3).

5.1.2 ZnO/ZnO:Al TCO deposition

As for conventional CIGS solar cells, an rf-sputtered ZnO bilayer front contact was applied. First, a first 50 nm thin, high resistivity intrinsic ZnO layer is deposited on the buffer layer. Then the conductive ZnO:Al with a thickness of 0.3 to 1 μm is sputtered. The thickness of the ZnO:Al layer must be chosen as a trade-off between transparency and conductivity. If a metallic grid is deposited on top of the TCO layer, a sheet resistance of 70 Ω is sufficient for high fill factors and efficiencies (Ramanathan et al., 2003) and the thickness can be optimized for maximum transparency.

5.1.3 Cell scribing

After the complete processing of the CIGS solar cell, the cell area has to be defined by scribing for efficiency measurements. The layer is therefore partitioned into smaller clearly defined cells by scratching through all the layers on the molybdenum. Typically, cells of 0.5 x 1 cm² were defined for laboratory scale characterization.

5.2 Characterization

5.2.1 Contacting

If a metallic grid has been deposited on top of the TCO, it is connected by the probe needles as the front contact. Otherwise the front contact is connected directly on the TCO. The molybdenum back contact is connected at the edge of the sample. Contact resistances are monitored by 4-terminal Kelvin connections.
5.2.2 Current-Voltage characteristic

The current-voltage measurement determines the electrical output performance of solar cells (§1.3.4): open-circuit voltage ($V_{oc}$), short-circuit current ($I_{sc}$), fill factor (FF), the maximum power output of the device, voltage at maximum power ($V_{m}$), current at maximum power ($I_{max}$) and the conversion efficiency ($\eta$). 4-terminal Kelvin connections enable the use of separate channels for voltage and current measurements, which minimizes measurement errors by eliminating voltage-drop losses resulting from resistances due to cables and contacts.

The most efficient cell obtained with nanoparticle precursors was a metal precursor-based cell deposited by electrospraying. The precursor was selenized in the open non-vacuum reactor at a maximum temperature of 600°C. Figure 5.1 shows the current-voltage characteristics of this solar cell.

![Current-Voltage characteristics](image)

**Figure 5.1** Current – Voltage characteristics of a non-vacuum processed CIS solar cell prepared from metallic nanoparticles.

With a FF of 33%, $V_{oc}$ of 219 mV, $I_{sc}$ of 17.3 mA/cm² all the values are about half of the values of good, vacuum-processed CIS cells. The low value of the fill factor, which measures the “squareness” of the I-V curve, indicates a large series resistance and a low shunt resistance.

In order to investigate the layer composition at different depth levels, XPS depth profiling of a CIS layer was done. Material was removed from the surface by argon-ion
sputtering in-between consecutively acquired XPS spectra. The sputter rate is approximately 100 nm/min. Figure 5.2 shows the resulting depth profiles.

![Sputter rate: 100 nm/min](image)

**Figure 5.2** XPS depth profiles of a selenized metal nanoparticle precursor layer.

No clear interface between the CIS and the substrate (soda-lime glass) can be seen. Although the molybdenum concentration was not measured (perturbation by Se3s peak) the binding energies of the oxygen (either In2O3 or to SiOx) allows identifying the start of the substrate material between 10 and 12 min sputter time. With a thickness of about 300 nm for the Mo layer, the average CIS layer is 800 nm thick. Remaining porosity and the inhomogeneous thickness of the film are responsible for the blurred concentration profile. However, the profile shows a clear copper deficiency in the first 500 nm layer thickness. This fact may result partly from the spray process which yielded slight composition deviations due to settling effects in the spray liquid so that the sprayed film was copper deficient in the top part of the layer (§3.2). But similar observations are made for vacuum deposited Cu-In alloy layers where the surface turns copper deficient after selenization (Kurdesau et al., 2004).
5.3 Conclusion

A variety of CIS and CIGS layers from different precursor powders were deposited on molybdenum coated glass substrates and processed to solar cells. Oxide and selenide precursors yielded only resistive devices without photovoltaic behavior. Measurable photovoltaic properties were observed in devices obtained from sprayed and screen-printed copper and indium nanoparticles. These CIS solar cells yielded a maximum efficiency of 1.4%. The cell parameters $I_{sc}$, $V_{oc}$ and FF of the best cell have only half of the values of good vacuum processed CIS cells.

There are different reasons for the low efficiency values obtained. XPS depth profiles and cross-section SEM images have shown that the selenized layers have a rough surface and high porosity which lead in some places to very thin layers where electrical shunting is possible. The mixing of the precursor particles is not perfect and agglomerates are formed which lead to precursor layers with local composition deviations. But single-phase CIS is limited to a narrow composition range of 24-24.5% copper ($\text{Cu}$) and already small deviations with excess copper lead to the formation of the low-resistive $\text{Cu}_{2+x}\text{Se}$ phase which shunts the cell.
6 Inorganic salt precursors and solar cells

Metal salt precursor materials have been used for a long time for non-vacuum CIGS layer deposition in the spray pyrolysis process. Copper-, indium- and gallium-containing salts are dissolved together with a soluble chalcogenide compound in a liquid and sprayed on a heated substrate where they react and form the CIGS compound. Obtained solar cell efficiencies were rather poor, probably due to nanocrystallinity of the CIGS and inclusions of byproducts during the reaction (Krunks et al., 2002).

Within the work of this thesis, inorganic metal salts dissolved in alcohol solvent are used to deposit a mixed salt precursor layer instead of depositing the CIGS compound directly. After precursor layer deposition, the sample is dried to evaporate the solvent and binder materials. The dry precursor material is then converted to CIGS by selenization in selenium vapor.

The use of liquid precursor materials avoids most of the problems encountered in nanoparticle precursor pastes such as agglomeration of particles and non-perfect mixing. Atomic scale-mixing generally increases the reaction rate and lowers the reaction temperature. However, the anion part of the salt, the solvent, and possibly any binder materials introduce further elements into the paste that have to be released and extracted during chemical conversion. Inorganic salts were chosen to prevent carbon contamination.

6.1 Doctor-blade (Paste coating)

The precursor paste should allow the deposition of an amorphous layer consisting of an atomic scale-mixture of the precursor salts. Nitrate and chloride precursors (Table 6.1) were chosen because of their low cost and good availability. The precursors also show good solubility in water and a variety of alcohols such as methanol, ethanol, propanol and others. The advantages of using nitrates include simplicity of the process, exclusion of carbon contamination, and their low decomposition temperatures compared to other inorganic salts.
Table 6.1 Inorganic salts used for precursor paste preparation in this work

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Molecular formula</th>
<th>Purity (%)</th>
<th>³P (°C)</th>
<th>³b (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cupric chloride, anhydrous</td>
<td>CuCl₂</td>
<td>99.999</td>
<td>630/300 dec.</td>
<td>-</td>
</tr>
<tr>
<td>Copper nitrate hydrate</td>
<td>Cu(NO₃)₂ x H₂O</td>
<td>99.99</td>
<td>115</td>
<td>170 dec.</td>
</tr>
<tr>
<td>Indium chloride, anhydrous</td>
<td>InCl₃</td>
<td>99.99</td>
<td>583</td>
<td>500 subl.</td>
</tr>
<tr>
<td>Indium nitrate hydrate</td>
<td>In(NO₃)₃ x H₂O</td>
<td>Techn. grade</td>
<td>100 dec.</td>
<td>-</td>
</tr>
<tr>
<td>Gallium nitrate hydrate</td>
<td>Ga(NO₃)₃ x H₂O</td>
<td>99.999</td>
<td>110 dec.</td>
<td>-</td>
</tr>
</tbody>
</table>

6.1.1 Paste formulation

Dissolved precursor materials can easily be applied to the substrate surface by spin coating, dip coating, or spraying. However, two main problems have to be solved by adjusting the paste chemistry (Schwartz et al., 2004):

- When the solvent is allowed to evaporate, the mixed metal salts lead to local cationic segregation because of their different solubilities and decomposition temperatures/rates.
- Dewetting of the substrate may occur due to the absence of gelation and the extent of hydrogen bonding.

Therefore, an organic binder material, which decomposes upon heat-treatment, is added to the paste. Ethylcellulose is widely used as a binder material for coating applications and was adopted in this approach. Because the ethylcellulose influences the solubility of the metal salts and leads to the precipitation of a white powder after some days (which was not further investigated), the precursor paste was prepared in two components, which are mixed just before deposition:

Precursor pastes were prepared by dissolving appropriate quantities of Cu nitrate, In chloride and Ga nitrate hydrate in methanol. The precursor composition is adjusted to the desired metal ratio with a concentration of 1 mili-mole (mmol) copper atoms per gram methanol. In parallel, a high viscosity cellulose paste is prepared: Ethylcellulose (30-50 mPas) is dissolved in 1-pentanol with a weight ratio of 1/10. The pastes are mixed in a weight ratio of 1/2 to yield a precursor paste with suitable rheology for doctor-blade coating.

Alternative precursor pastes were prepared containing Cu chloride or In nitrate dissolved in methanol or 1,2-propanediol. Resulting layers and cell properties were inferior to those obtained with the above described paste.
6.1.2 Paste deposition

A 1 mm-thick soda-lime glass substrate is coated with a 400 nm thick molybdenum layer by conventional dc-sputtering. For doctor blade deposition, two stripes of scotch tape (~50 μm thickness, 1 cm wide) are applied on each side of the deposition area. In a one-pass movement the precursor paste is evenly distributed on the substrate surface.

By weighing the deposited precursor layer and calculating the metal parts in the layer, it can be estimated that the layer has a copper content of about 10 mmol/m². After complete conversion without metal losses during preheating and selenization, this will yield a CIGS layer thickness of roughly 600 nm. Thicker CIGS films would require higher metal concentrations, but due to adhesion problems encountered for thicker films, the metal concentration was kept low.

6.1.3 Preheating

The as-deposited sample is placed on a hotplate and heated to 250-350°C for a few minutes in ambient atmosphere to evaporate the volatile alcoholic solvent and to burn the cellulose. Depending on the precursor salts used, the heated layer changes its color in different steps. For the paste described in §6.1.1 the color changes from white to brown and then to black. When the layer turns from black to a metallic blue, the sample is removed from the hotplate and allowed to cool down.

Longer heating and higher temperatures lead to fast oxidation of the uncovered molybdenum layer and changes the color of the precursor layer to silver metallic and further to a rough reddish surface. Homogenous film thickness and heating rates are important to avoid the formation of regions where the preheated layer shows different colors.

Depending on the drying conditions, the heated film contains different crystalline phases. Figure 6.1 shows the XRD patterns of the heated films. Common to all heating conditions no crystalline phases containing gallium or indium are detected. It can therefore be concluded that even though the precursor layer was heated to 350°C in air for several minutes the group III metals did not form crystalline oxides which would complicate the chemical conversion (Chapter 4). After heating the sample to 50°C to evaporate the methanol a dry film of ethyl cellulose containing the metal salts is formed. During evaporation of the solvent, crystals of CuCl are formed. This is due to its
Figure 6.1  XRD patterns of precursors layer after drying at different conditions: evaporation of the alcohol at 50°C, heating to 350°C in air, heating to 350°C in nitrogen, heating to 420°C in nitrogen for two to three minutes each. (Joint Committee on Powder Diffraction Standards, ASTM, Philadelphia, PA, 1967, Cards: CuCl, 06-0344; CuO, 05-0661; Cu, 85-1326; Mo, 42-1120)

low solubility and early precipitation in alcohol. If heated in air to 350°C, which is the standard procedure for sample preparation in this work, fumes are produced (burning of the ethylcellulose) until a metallic blue color appears. At this stage the CuCl crystals show a strong texturing in the (111) direction and traces of the CuO phase are detected. If the heating is done in nitrogen atmosphere, the XRD pattern does not show peaks from the CuO phase but elemental Cu crystals form. Heating to 420°C in nitrogen leads to even more pronounced peaks from copper, while the CuCl phase is not detected anymore. The low 2θ region, with its very broad peak, indicates some amorphous phases, containing the rest of the precursor material.
The observations of these experiments do provide a detailed reaction path of the precursor material during preheating. It could nevertheless be shown that the introduced salts may partly change their anionic part and oxidation state (Table 6.2):

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Modified Precursor</th>
<th>Preheating Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{In}^{III}\text{Cl}_3)</td>
<td>(\text{In}^{0}\text{X})</td>
<td>Air, 25°C, Solvent evaporation</td>
</tr>
<tr>
<td></td>
<td>(\text{Cu}^{0}\text{Cl})</td>
<td>Air, 25°C, Solvent evaporation</td>
</tr>
<tr>
<td>(\text{Cu}^{II}(\text{NO}_3)_3)</td>
<td>(\text{Cu}^{0}\text{Cl}, \text{Cu}^{II}\text{O})</td>
<td>Air, 350°C</td>
</tr>
<tr>
<td></td>
<td>(\text{Cu}^{0}\text{Cl}, \text{Cu}(0))</td>
<td>(\text{N}_2), 350°C</td>
</tr>
<tr>
<td></td>
<td>(\text{Cu}(0))</td>
<td>(\text{N}_2), 420°C</td>
</tr>
</tbody>
</table>

### 6.1.4 Selenization of precursor

Chemical conversion of the preheated precursor samples was performed in the open non-vacuum reactor (§4.2.4). The sample temperature is ramped up to 560°C and then held constant for 10 minutes whereas the selenium source is maintained at a temperature of ~350°C during selenization. The mass of the evaporated selenium was measured after each selenization run. Typical amounts of 20-30mg were evaporated and used to convert the 5x5 cm² substrate sample.

To test the conversion of the metal precursors separately, precursor pastes containing only the copper or only the indium precursor were prepared in analogy to the CIGS pastes (§6.1.1). EDX measurements (Table 6.3) suggest a nearly complete conversion to the \(\text{Cu}_{2+x}\text{Se}\) and \(\text{In}_2\text{Se}_3\) phases, respectively.

<table>
<thead>
<tr>
<th>Selenized (\text{Cu(NO}_3)_2), precursor (at %)</th>
<th>Selenized (\text{InCl}_2), precursor (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cu})</td>
<td>(\text{In})</td>
</tr>
<tr>
<td>(\text{Se})</td>
<td>(\text{Se})</td>
</tr>
<tr>
<td>62.3</td>
<td>39.7</td>
</tr>
<tr>
<td>37.7</td>
<td>60.3</td>
</tr>
</tbody>
</table>
Figure 6.2 Morphology Cu$_{2+x}$Se (a) and InSe, (b) thin-films obtained by non-vacuum deposition and selenization of salt precursor materials.

Figure 6.2 shows the morphology of separately selenized Cu and In precursors. The layers show different morphology when compared to selenized metal nanoparticle layers (§4.14). Due to the liquid state of the precursor materials deposition of thin films is facilitated and the selenized layers are smooth, while the copper selenide does not cover all of the substrate and forms large isolated grains, the indium selenide formed a dense and smooth surface with clearly visible grains. However, only poor adhesion of the In selenide layer on the Mo coated glass was obtained and most of the converted layer delaminated during selenization.

Figure 6.3 Morphology of non-vacuum deposited and selenized CIGS precursor layer. The polycrystalline layer has a smooth surface showing large grains.

The morphology of a selenized CIGS layer containing the precursors as described in §6.1.1 is shown in Figure 6.3. The compact layer has a smooth surface with large grains as desired for efficient solar cells. On top of the surface few small grains are formed.
In Figure 6.4 the EDX spectra of the precursor (after heating to 350°C) and the selenized layer are shown. The conversion introduced selenium and reduced the chlorine and oxygen to a level below the detection limit of EDX (1-2 at %) in completely selenized layers (Table 6.3).

Table 6.3 Typical composition of precursor and selenized layer measured by EDX.

<table>
<thead>
<tr>
<th>Element</th>
<th>Precursor paste</th>
<th>Precursor layer % relative to Cu</th>
<th>Selenized layer % relative to Cu</th>
<th>Changes selenized layer/precursor paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1</td>
<td>19.5</td>
<td>22.0</td>
<td>reference</td>
</tr>
<tr>
<td>In</td>
<td>0.85</td>
<td>23.0</td>
<td>21.4</td>
<td>0.97</td>
</tr>
<tr>
<td>Ga</td>
<td>0.4</td>
<td>7.9</td>
<td>5.5</td>
<td>0.25</td>
</tr>
<tr>
<td>Cl</td>
<td>2.55</td>
<td>49.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Se</td>
<td>-</td>
<td>-</td>
<td>51.1</td>
<td>2.32</td>
</tr>
</tbody>
</table>

The Cu/(In+Ga) ratio of 0.8 remained constant during selenization, although the In/Ga ratios changed nearly by a factor 2 from the precursor paste to the selenized layer. This may be explained by the inhomogeneous distribution of In and Ga in the layer (Figure 6.6) and a difference in vapor pressure of intermediate binary phases. The high In content measured in the precursor layer may be explained with a matrix effect.
resulting from the formation of copper chloride crystals in an amorphous In and Ga containing material.

The conversion reaction and incorporation of Ga into CIS was investigated by XRD analysis. Fig. 6.5 compares the XRD patterns of a CIS (Cu/In ratio of 1/1.1) and CIGS (Cu/In/Ga ratio of 1/0.8/0.6) layers.

Addition of Ga leads to broad and asymmetrical peaks with their maxima shifted to slightly higher 2θ values indicating a change in the lattice parameters (Figure 1.4). The peak shift is less than expected for the measured layer composition and the asymmetric, broad peaks suggest non-uniform composition of the precursor film.

For further investigation, Auger electron spectroscopy (AES) depth profiling was performed to determine the elemental distribution in the layer (Fig. 6.6). As seen in Figure 6.6 (a) except for the top part, the layer is not formed of pure CIGS but contains large amounts of carbon. The carbon signal increases towards the back contact. Hence, paste drying and evaporation of the organic binder was not efficient in removing all the organic material (Figure 6.6a and 6.7). Figure 6.6b gives the depth profiles for the metals only. The data suggests a Ga/In graded composition across the layer thickness. The CIGS composition changes from a low Ga content on the surface to a high Ga
content at the back contact. Such a grading can lead to a back surface field which is favorable for thin absorber layers (<1 μm) since it reduces fill factor deterioration (Lundberg et al., 2003). But a low Ga content near the p-n junction of the device is limiting the $V_{oc}$ parameter in solar cells (§6.1.6).

![Figure 6.6](image)

**Figure 6.6** Auger electron spectroscopy depth profile of a selenized precursor layer. After a short sputter time a carbon signal is detected with increasing intensity towards the back (a). Depth profile showing the metal concentrations only, while the C and Se signals are ignored (b).

![Figure 6.7](image)

**Figure 6.7** Cross section of selenized precursor layer showing a double layer structure with the polycrystalline CIGS layer formed on top of an amorphous carbon layer.

The cross-section SEM micrograph picture (Figure 6.7) is taken from a selenized precursor layer. The figure shows a double layer structure, where the bottom-layer is
responsible for the carbon signal in the AES depth profile (Figure 6.6). EDX composition analysis on a focused point in the lower layer showed C, O, Se and Ga signals, which corresponds well to the results of the AES depth profile. Finally, a CIGS layer thickness of about 600 nm in average is very thin compared to 1.5-2 μm which is considered optimal for total light absorption and required for high efficiency solar cells.

6.1.5 CIGS growth mechanisms

Doctor-blade deposition of the precursor paste containing dissolved metal salts in the desired stoichiometry and an organic binder material leads to a thin and homogenous precursor layer upon evaporation of the alcohol solvent. Crystals of CuCl are formed in the layer whereas In and Ga remain in an amorphous state in the organic matrix. When heated to 300-350°C in ambient atmosphere, some of the organic material evaporates although large amounts remain in the precursor layer. In addition to the CuCl crystals, small Cu2O crystals form due to reaction with ambient oxygen. In and Ga remain embedded in the organic matrix. During selenization, the selenium vapor reacts with the metal on top of the layer and forms the CIGS compound. The conversion taking place at a temperature of 500°C allows most of the metal atoms to diffuse to the surface of the organic layer, where they react with in-diffused selenium and are added to the formed CIGS film. Because of the difference in the reaction kinetics of CIS and CGS (Marudachalam et al., 1997), preferably the CIS compound forms in the first phase. This leads to depletion of indium and accumulation of gallium in the remaining precursor layer and the formation of CIGS with a higher Ga content in the back. Complete decomposition of the remaining organic layer which resulted from burning the ethylcellulose could not be achieved with this method. The residual layer with its high carbon content is trapped between the molybdenum back contact and the CIGS layer.

Having an amorphous organic (and therefore possibly an electrically insulating) layer between the CIGS absorber and the back contact may be detrimental for the solar cell device. However, device characteristics have shown encouraging results (§6.1.6).

Spray deposition of the precursor salts in cellulose-free solutions was tested in order to avoid the formation of a carbon layer (§6.2).
6.1.6 Solar cell device characterization

Selenized precursor layers were finished to complete solar cells according to §5.1. To estimate the homogeneity of the selenized layer, a solar cell on a 5x5 cm² substrate was scribed into 21 small cells with an area of 0.6 cm² each (Figure 6.8) and which were individually characterized by I-V measurements under simulated AM1.5 illumination conditions. Figure 6.9 shows the solar cell parameters of the cells. Efficiencies vary between 2.4 and 4.9%. While $I_{sc}$ values are nearly constant over the whole sample (and may only reflect the inhomogeneity of illumination from the centered single-light-source sun simulator) the FF and mainly the $V_{oc}$ show larger variations. The parameters are more consistent in the direction of the blade movement during deposition (from column 1 to column 3) than perpendicularly to it. As differences in paste composition are not probable, the reason may be found in a non-uniform (manual) blade deposition resulting in different layer thicknesses.

Figure 6.8  5x5 cm² substrate with 21 cells of 0.6 cm² area arranged in three columns (11 mm spacing) and 7 rows (5.5 mm spacing).
The cell parameters $V_{oc}$ (a), $I_{sc}$ (b), FF (c) and efficiency (d) show moderate homogeneity over the substrate area. Degradation of the parameters is observed towards the substrate edges.

### Table 6.4 Average values with standard deviation of the cell parameters.

<table>
<thead>
<tr>
<th></th>
<th>$I_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>average</td>
<td>23.5</td>
<td>340</td>
<td>43.6</td>
<td>3.52</td>
</tr>
<tr>
<td>standard deviation</td>
<td>1.1</td>
<td>34</td>
<td>3.5</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Maximum efficiencies above 6% were obtained on smaller area cells. Figure 6.10 shows the IV curve and cell parameters of the best cell with an area of 7.3 mm². The higher efficiency of 6.7% is mainly due to the high FF above 60%. The $V_{oc}$ with 404 mV is low for a CIGS compound containing 6 at % Ga.
External quantum efficiency (EQE) measurements were performed to identify the sensitivity of the device to different wavelengths of the illumination spectrum. A comparison of the EQE diagram of a non-vacuum processed solar cell with a conventional co-evaporated solar cell (Figure 6.11) reveals significant losses in the middle and long wavelength region. The cut-off wavelength of the non-vacuum processed cell is at \(\lambda = 1200\,\text{nm}\) indicating a band gap energy of only \(-1\,\text{eV}\).
medium to long wavelength region (500-1100 nm), which confirms that the CIGS layer is too thin to completely absorb the AM 1.5 solar spectrum. The band gap for a cut-off wavelength of approximately 1200 nm corresponds well to the CIS compound with a band gap of 1.04 eV. The addition of Ga should increase the band gap by 0.2-0.3 eV but the observations indicate inhomogeneous Ga distribution, which is supported by the AES depth profile measurements (Figure 6.6b). The top part of the layer consists of CIGS with a low concentration of Ga and a band gap near to the CIS compound.

6.2 Electrospray

Using the spray method, deposition of low viscosity liquids as metal salts dissolved in methanol is possible. Therefore, the addition of a cellulose binder material is not necessary. The aim is to reduce the carbon content in the paste formulation in order to prevent the formation of a carbon layer between the molybdenum back contact and the CIGS layer.

Carbon free CIGS layers would allow a better contact for CIGS solar cells in substrate and superstrate configuration. In contrast to substrate solar cells, where the CIGS is deposited on the molybdenum back contact and the p-n junction is formed near the surface of the CIGS layer, superstrate cells form the junction between a TCO layer and the thereon deposited CIGS. The formation of an amorphous carbon layer in the junction region would completely deteriorate the cell properties and carbon free CIGS layers are a prerequisite.

Precursor pastes were prepared accordingly to §6.1.1 but only containing the dissolved salt precursor in methanol and 1,2-propanediol (Ga was not added at this stage). In order to prevent incorporation of moisture into the precursor layer, spraying was done on a heated glass substrate (100°C) in inert nitrogen atmosphere. After deposition the sample was quickly transferred to the selenization reactor and selenized at 550°C.

Figure 6.12 shows the XPS depth profile of a selenized precursor layer deposited on a molybdenum coated substrate by electrospray. The precursor paste did not contain the gallium precursor. Because the C1s signal gets perturbed by the selenium LMM Auger signal the carbon content was evaluated by the area of the C KLL Auger peak, which is more difficult to quantify. The resulting carbon concentration may therefore vary up to a factor of three. However, the C KLL peak is very low and the indicated carbon
concentrations are covered by noise (0-2 at %). Hence, the carbon contamination was reduced below the detection limit of XPS.

![Figure 6.12 XPS depth profile: Electrospray deposition of salt precursor and selenization allows carbon free compound formation.](image)

The reduction of the carbon content should also be reflected by elimination of the carbon layer between the CIGS and the substrate which was present in the doctor-blade deposited samples (Fig. 6.7). The morphology is dominated by large grains on top of the layer. Surface and cross-section SEM images (Fig. 6.13) show a 1.5 μm thick small-grained bottom layer with large crystals towering on the surface, which induce a high surface roughness. No distinct carbon layer was formed. Hence the electrospray deposition method is suitable to eliminate the carbon layer which is otherwise formed in the doctor-blade deposited layers.

Compositional analysis of the selenized layers showed non-uniform distribution of the elements across the sample surface. Contrary to electrosprayed metal nanoparticle layers (§3.2.1) the tendency for salt precursors was a copper rich region in the sample center and copper poor composition in the edges. However, this problem of compositional non-uniformity may be overcome by a moving substrate.
Solar cells produced from electrosprayed and selenized salt precursors showed either very poor efficiencies (< 0.1 %) or just an ohmic behavior produced by shunts in the cell. Considering the CIS structure shown in Figure 6.13 it is assumed that the large Cu-rich crystals are responsible for shunting the cells. The formation of such Cu-rich crystals results from non-homogenous precursor layers which may be explained by the growth of large CuCl crystals during precursor deposition. Higher substrate temperatures during electrospray deposition will keep the precursor film completely dry preventing the sprayed layer from recrystallization to larger salt particles. Further investigation of the precursor spray process is necessary to find optimized deposition conditions.
6.3 Conclusions

In spite of the notable cell efficiencies, many aspects of the conversion reaction from the precursors to the CIGS compound remain unclear. For instance, nitrate precursors usually result in metal-oxides upon heating (Beck and Cocivera, 1996). A previous study (Kaelin et al., 2004a) revealed difficulties in converting the stable compound In2O3 and probably Ga2O3 into their selenide phase using selenium vapors. As seen in Figure 6.1, no oxide phases are detected upon preheating the precursor to 250°C in air. The organic matrix may prevent the formation of metal oxides and thus have a beneficial effect by reducing the conversion time.

The addition of cellulose material in the precursor paste allows adjustments in paste rheology for optimal coating results and avoids formation of larger CuCl crystals upon evaporation of the solvent, which otherwise deteriorate local film stoichiometry. However, an amorphous carbon layer forms between the Mo and the CIGS layer. The obtained cell efficiencies demonstrate that the carbon layer is not completely detrimental for cell performance, although it is 1 μm thick, porous, and amorphous and although it increases the series resistance of the cell. Thicker precursor layers deposited by doctor-blade resulted in poor adhesion of the CIGS/carbon structure to the Mo surface; hence further experiments are required to improve the adhesion. Carbon-free structures were prepared by electrospraying cellulose-free pastes in nitrogen ambient on substrates heated to 100°C followed by selenization. Such CIGS layers were extremely rough and had irreproducible compositions.

Ga can be incorporated into the selenized layer but its distribution has to be improved (higher Ga concentration near the CdS buffer layer) to achieve higher Voc values. Better results may be obtained with longer selenization times or an additional annealing step (Marudachalam et al., 1997).

CuCl2 and In(NO3)3 have also been tested as precursors in paste formulations and were successfully converted to the CIGS compound, but the obtained cell efficiencies were lower than for the described paste formulation. However, further investigation is needed to optimize the paste chemistry and conversion processes.
7 Research recommendations

A novel CIGS absorber formation process was developed, which, due to its simplicity and the exclusion of hazardous reactants, allows the manufacturing of low-cost CIGS solar cells. Cost-effectiveness is a trade-off between direct manufacturing costs and the efficiency of the produced solar cells. Optimization of the cell efficiency remains the prior development target.

Comparing the results obtained with metal/metal-oxide/metal-selenide nanoparticles to those with inorganic precursor salts, it results that, under the given conversion conditions, the salt precursor based cells have a higher potential to yield high-efficiency solar cells. The following topics should be considered for further research and development activities:

The chemical conversion reaction of the precursor layer containing chlorides, nitrates and cellulose is not fully clear yet. It is important to know which volatile products form in the selenium atmosphere. An investigation of remaining oxide and chloride impurity traces and their location (in the CIGS crystals, at grain boundaries, or in the carbon bottom-layer) would help to optimize selenization conditions (time, temperature ramps, Se vapor pressure). Electrosprayed layers yielded carbon-free layers but lacked of compositional and structural control. The cellulose binder used in doctor-blade pastes allows good control of the composition and the layer structure but introduces an amorphous carbon layer into the cell structure. Finding a binder material which undergoes controlled decomposition during the selenization treatment would solve this problem.

The CIGS formation process is lacking Ga/In composition control for band gap engineering in the CIGS layer. Selenization processes are known to accumulate gallium near the molybdenum back contact yielding mainly CIS compound in the CdS-CIGS interface region. An additional sulfurization treatment introducing sulfur into the top layer would increase the band gap in the junction region, which leads to higher cell efficiency thanks to a higher Voc. Therefore, the diffusion behavior of sulfur during an additional sulfurization step and resulting band-gap structures should be investigated.

In order to follow the concept of completely non-vacuum processed CIGS solar cells, the sputter-deposited TCO layer has to be replaced by a low-cost, non-vacuum processed TCO layer. Similar precursor paste chemistry as used for CIGS synthesis
should be investigated for TCO deposition processes, using oxidation treatments instead of selenization. The TCO layer is one of the last layers applied (§1.3.2) and therefore the aim would be to bring the reaction temperatures to a minimum (below 250°C, to avoid elemental diffusion between layers and junction degradation) while maintaining good transparency and electrical conductivity of the TCO layer.
References


# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>AM\textsubscript{1.5}</td>
<td>Air mass factor 1.5</td>
</tr>
<tr>
<td>b\textsubscript{p}</td>
<td>Boiling point temperature</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>CIGS</td>
<td>Compound formed by Cu, In, Ga, Se; usually CuIn\textsubscript{1-x}Ga\textsubscript{x}Se\textsubscript{2}</td>
</tr>
<tr>
<td>CIS</td>
<td>Compound formed by Cu, In, Se; usually CuInSe\textsubscript{2}</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray analysis</td>
</tr>
<tr>
<td>E\textsubscript{g}</td>
<td>Band-gap energy</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-voltage</td>
</tr>
<tr>
<td>J-V</td>
<td>Current density-voltage</td>
</tr>
<tr>
<td>J\textsubscript{sc}</td>
<td>Short circuit current density</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>m\textsubscript{p}</td>
<td>Melting point temperature</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>SCR</td>
<td>Space charge region</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SLG</td>
<td>Soda-lime glass</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conducting oxide</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>V\textsubscript{oc}</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>W\textsubscript{p}</td>
<td>Watt peak, unit for indicating the output power of solar cells at 1000 W/m\textsuperscript{2} solar irradiation</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
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Curriculum vitae

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