Electrodeposition of CuInSe$_2$ and doped ZnO thin films for solar cells

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Academic Dissertation

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Abstract

CuInSe\textsubscript{2} is one of the most promising absorber materials for thin film solar cells. CuInSe\textsubscript{2}-based solar cells have shown long-term stability and the highest conversion efficiencies of all thin film solar cells, above 18\%. In this study, Cu\textsubscript{2-x}Se, CuInSe\textsubscript{2}, and doped ZnO thin films were electrodeposited potentiostatically from aqueous solutions. The films were studied by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, ion beam analysis methods, and photoelectrochemical and capacitance-voltage measurements.

For the deposition of Cu\textsubscript{2-x}Se and CuInSe\textsubscript{2} films, a new approach was developed that utilizes induced co-deposition. Suitable conditions for induced co-deposition were achieved by complexing the Cu\textsuperscript{+} ions by thiocyanate ions that shifted the reduction potential of Cu\textsuperscript{+} to the negative direction. Under these conditions, Se reduced at more positive potentials than Cu, and induced the formation of Cu\textsubscript{2-x}Se at more positive potentials than where the deposition of metallic Cu began. Cu\textsubscript{2-x}Se, in turn, induced the formation of CuInSe\textsubscript{2} at the same potential range, i.e., at more positive potentials than where metallic Cu or In deposited. The electrochemistry of the Cu-Se and Cu-In-Se systems was studied by cyclic voltammetry and electrochemical quartz crystal microbalance measurements that verified the deposition mechanisms.

Induced co-deposition allowed the formation of almost stoichiometric CuInSe\textsubscript{2} films (Cu\textsubscript{1.30}In\textsubscript{1.00}Se\textsubscript{2.20}) over wide potential and concentration ranges. The as-deposited CuInSe\textsubscript{2} films were amorphous and contained hydrogen, oxygen, sulfur, carbon, and nitrogen as impurities. Hydrogen and oxygen originated apparently from the aqueous deposition solution and the other impurities from the thiocyanate ligands. Annealing at 400 or 500 °C under nitrogen made the films crystalline and decreased their impurity contents substantially. Etching in KCN solutions and addition of an In\textsubscript{2}Se\textsubscript{3} overlayer enhanced the photoactivities of the films and shifted their compositions towards more stoichiometric values. Also the high carrier concentrations of the annealed films decreased to more favorable values upon these treatments.

Solar cells were prepared using the electrodeposited CuInSe\textsubscript{2} films. The ZnO top electrodes were prepared either electrochemically, by atomic layer deposition (ALD), or by sputtering. For the first time, Al and In doped ZnO films (ZnO:Al and ZnO:In) were prepared by electrodeposition. The cells with electrodeposited ZnO films showed good diode characteristics in the dark. The photoresponses were generally higher with ZnO:In than with ZnO:Al. The highest open circuit voltage of 0.405 V was, however, measured for a device with an electrodeposited ZnO:Al film. The ALD-ZnO films resulted in higher photocurrents, up to 5.47 mA cm\textsuperscript{-2}, than the electrodeposited ZnO films. The best photoresponses, with a maximum conversion efficiency of 1.3\%, were measured for the devices with sputtered ZnO films.
Preface

This thesis is based on experimental work carried out during the years 1998 - 2002 in the Laboratory of Inorganic Chemistry at the Department of Inorganic Chemistry at the University of Helsinki. I owe my deepest gratitude to my supervisors Prof. Markku Leskelä and Doc. Mikko Ritala for the excellent guidance that I have received during this work. I am also thankful to Ms. Ada Chan for revising the English language of this thesis.

I am indebted to Dr. Heini Ritala for her valuable advice, support, and great company during the years. Also my other coworkers Dr. Timo Sajavaara, Dr. Eero Rauhala, Mr. Frédéric Dartigues, as well as Mr. Antti Niskanen, Mr. Pierre Cowache and Dr. Steffen Schuler are gratefully acknowledged for their contributions to this work. It has been a pleasure to work with you. I also wish to thank Dr. Seppo Lindroos who shared the office with me until recently, and Mr. Mikko Heikkilä who has worked in the electrochemistry lab during the recent years, for good company.

I wish to thank the staff in the Laboratory of Inorganic Chemistry, especially the members of the thin film group, for the wonderful and inspiring working atmosphere, as well as for great time also outside the laboratory. Above all, I am grateful to my dear Viljami, and to my dear friends Marko, Antti R., and Petri, for their encouragement, help and friendship.

Special thanks to my long-time friends, especially Kaisa, Janne, Esko, Pirjo and Ismo, for many great moments during the years.

I also want to express my gratitude to my parents Leena and Markku and to my brothers Harri-Heikki and Jari-Matti. Words cannot describe how important your continuous love and support have been to me.

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Helsinki, April 2003

Marianna Kemell
List of original publications

This work is based on the following original publications which are referred to in the text by their Roman numerals. Moreover, unpublished data, including results of capacitance-voltage measurements and of photovoltaic characterization, are presented and discussed.


The author has written all the papers and done most of the experimental work, including thin film growth experiments and cyclic voltammetry, cyclic photovoltammetry and EQCM measurements as well as photoelectrochemical, XRD, SEM, and EDX studies. The author has also prepared most of the solar cells and done most of the electrical characterization.

Ion beam analyses were done in the Accelerator Laboratory at the Department of Physics at the University of Helsinki. Most of the ZnO growth experiments and cyclic voltammetry measurements reported in Paper V were done by Frédéric Dartigues under supervision of the author. Some of the solar cells were completed and characterized in Ecole Nationale Supérieure de Chimie de Paris or in Hahn-Meitner-Institut in Berlin.
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<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of vacuum</td>
</tr>
<tr>
<td>$\varepsilon_\infty$</td>
<td>Dielectric constant</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Efficiency</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Shear modulus</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$A$</td>
<td>Surface area</td>
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<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance</td>
</tr>
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<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<tr>
<td>DMZ</td>
<td>Dimethylzinc</td>
</tr>
<tr>
<td>$e$</td>
<td>Elemental charge ($1.602 \times 10^{-19} \text{ C}$)</td>
</tr>
<tr>
<td>$E$</td>
<td>Potential</td>
</tr>
<tr>
<td>EE</td>
<td>Standard potential</td>
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<tr>
<td>$E_F$</td>
<td>Fermi level</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band gap</td>
</tr>
<tr>
<td>$E_V$</td>
<td>Valence band</td>
</tr>
<tr>
<td>ECALE</td>
<td>Electrochemical atomic layer epitaxy</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediamine tetraacetic acid</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray analysis</td>
</tr>
<tr>
<td>EQCM</td>
<td>Electrochemical quartz crystal microbalance</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$f_0$</td>
<td>Fundamental resonant frequency</td>
</tr>
<tr>
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<td>Faraday constant ($96485.31 \text{ C mol}^{-1}$)</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>$h\nu$</td>
<td>Photon energy</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
</tr>
<tr>
<td>$I_{\text{dark}}$</td>
<td>Dark current</td>
</tr>
<tr>
<td>$I_{\text{mp}}$</td>
<td>Photocurrent at the maximum power point</td>
</tr>
<tr>
<td>$I_{\text{ph}}$</td>
<td>Photocurrent</td>
</tr>
<tr>
<td>$I_{\text{sc}}$</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>ILGAR</td>
<td>Ion layer gas reaction</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium doped tin oxide, SnO$_2$:In</td>
</tr>
</tbody>
</table>
\( j \)  
Current density

\( J_{\text{dark}} \)  
Dark current density

\( j_{\text{mp}} \)  
Photocurrent density at the maximum power point

\( J_{\text{ph}} \)  
Photocurrent density

\( j_{\text{sc}} \)  
Short-circuit current density

\( K_{\text{s}} \)  
Solubility product

\( m \)  
Mass

\( M \)  
Molar mass

MBE  
Molecular beam epitaxy

MLE  
Molecular layer electrodeposition

MOCVD  
Metal organic chemical vapor deposition

\( n \)  
Number of moles

\( N_{\text{A}} \)  
Acceptor concentration

ODC  
Ordered defect compound

OVC  
Ordered vacancy compound

\( P_{\text{max}} \)  
Maximum power point

PEC  
Photoelectrochemical

PLD  
Pulsed laser deposition

PVD  
Physical vapor deposition

\( Q \)  
Charge (quantity of electricity)

QCM  
Quartz crystal microbalance

RBS  
Rutherford backscattering spectrometry

RT  
Room temperature

SEM  
Scanning electron microscopy

SCE  
Saturated calomel electrode

TCO  
Transparent conducting oxide

TOF-ERDA  
Time-of-flight elastic recoil detection analysis

UPD  
Underpotential deposition

\( V_{f} \)  
Forward bias

\( V_{\text{oc}} \)  
Open circuit voltage

\( V_{r} \)  
Reverse bias

XRD  
X-ray diffraction

\( z \)  
Number of electrons in an electrochemical reaction
1. Introduction

Most of the present global energy production is accomplished by burning fossil fuels. However, the inherent problems associated with the use of fossil fuels such as their limited availability and the environmental issues force the mankind to look for new, more sustainable long-term energy solutions to provide the future energy supply.

One of the most powerful alternatives for future large scale electricity production is photovoltaics, i.e., the conversion of sunlight directly into electricity. Sunlight is available in most locations, and it provides such an enormous supply of renewable energy that if the whole global electricity demand would be covered exclusively by photovoltaics, the total land area needed for light collection would be only a few percent of the world’s desert area. [1, 2] Solar cells are easy to install and use, and their operational lifetimes are long, which eliminates the need for continuous maintenance. Since photovoltaic systems are modular, they are equally well suited for both centralized and non-centralized electricity production. Therefore their potential uses range from consumer electronics (pocket calculators, wristwatches etc.) to large power plants.

Due to its reliability and stability, solar energy is a good choice in applications where power outages or shortages cannot be tolerated, for example in hospitals and certain production plants. Photovoltaic systems can be installed on rooftops and facades of buildings, and they can be combined with solar water heating systems. The power generated by rooftop solar cells can be used locally, and the surplus can be exported to the commercial grid if there is one in the region. [2, 3] The possibility for local electricity production offers consumers more freedom by reducing their dependence on the availability and price of commercial electricity. This is a crucial feature especially in remote areas that lack the infrastructure of electrification. It is actually more cost-effective to install a photovoltaic system than to extend the grid if the power requirement lies more than about half a kilometer away from the electrical line [4]. Rooftop photovoltaic installations, both by public institutions and by individual citizens, are becoming more and more common worldwide. [3]

One of the main obstacles for photovoltaics to become more popular in the short term is the fact that the price of the electricity (cost per watt) produced by photovoltaics is in most cases not yet competitive with that produced by the conventional methods. Cost reduction can be achieved by either improving the efficiencies or reducing the production costs of photovoltaic modules.

Among the most promising absorber materials for solar cells are CuInSe$_2$-based chalcopyrite materials (copper indium selenide, CIS). The material properties can be varied by replacing part of the indium by gallium and/or part of the selenium by sulfur to form Cu(In,Ga)(S,Se)$_2$. High conversion efficiencies of almost 19% [5] have been achieved using these materials. Moreover,
CIS-based solar cells are very stable, and thus their operational lifetimes are long. The favorable optical properties of these materials (direct energy band gap and high absorption coefficient) allow the use of thin films (few micrometers) of material instead of thick slices of bulk silicon, reducing the consumption of materials. CIS-based thin films can be prepared both from gas and liquid phases by a variety of methods.

Electrodeposition is a liquid phase deposition method that can be used for the preparation of metal, semiconductor and conducting oxide thin films. Its advantages include the feasibility of upscaling to large substrate areas and production volumes. Moreover, the deposition equipment is relatively simple and the deposition temperatures are considerably lower than in many other methods. These features make electrodeposition a low-cost deposition method. Thus the fact that the solar cell efficiencies achieved with electrodeposited films are generally somewhat lower than those achieved by the more expensive gas-phase methods is not necessarily a major drawback, since it is compensated by the lower process costs.

The purpose of this study was to develop and study electrodeposition processes for the preparation of thin films for CuInSe₂ solar cells. Cu₂₋ₓSe, CuInSe₂ and doped ZnO films were deposited from aqueous solutions. Cu₂₋ₓSe and CIS films were deposited by the induced co-deposition method [6] where the compound formation occurs underpotentially, that is, at less negative potentials than where at least one of its component ions would reduce into its elemental state. This positive potential shift is caused by the energy released in compound formation. Reproducible film growth is achieved since the film composition is not sensitive to small variations in growth conditions such as precursor concentrations and deposition potential but is automatically directed toward being stoichiometric. The most well-known example of the utilization of the induced co-deposition mechanism is CdTe [7]. The mechanism had not been utilized for the deposition of ternary compounds prior to [1] where suitable conditions for induced co-deposition were achieved by complexing Cu⁺ ions with thiocyanate ions to form strong complexes, thereby shifting the deposition potential of metallic Cu to negative direction which enables the deposition of Se first.

The formation mechanisms of Cu₂₋ₓSe and CIS thin films were studied in detail by cyclic voltammetry and electrochemical quartz crystal microbalance measurements. The properties of the CIS films and the effects of post-deposition treatments were studied by cyclic photovoltammetry, photoelectrochemical measurements and capacitance-voltage measurements.

ZnO films doped with In and Al were prepared electrochemically for the first time. Finally, solar cell structures were prepared using the electrodeposited CIS and ZnO thin films. For comparison, for some devices the ZnO films were deposited by atomic layer deposition and sputtering.
The present thesis introduces first the concept and operation principle of thin film solar cells as well as the most important thin film solar cell materials. Next, the methods used for the preparation of thin films used in CuInSe₂ solar cells are reviewed, with particular attention to electrodeposition of CuInSe₂-based absorber materials. Last part of the literature survey deals with cyclic voltammetry and related methods used for the characterization of thin films and growth processes in this study. After the experimental details, the main results of this study will be presented and discussed.
2. Thin film solar cells

Solar cells, or photovoltaic devices, are devices that convert sunlight directly into electricity. The power generating part of a solid-state solar cell consists of a semiconductor that forms a rectifying junction either with another semiconductor or with a metal. Thus, the structure is basically a pn-diode or a Schottky diode. In some junctions, a thin insulator film is placed between the two semiconductors or the semiconductor and the metal, thereby forming a semiconductor-insulator-semiconductor or a metal-insulator-semiconductor junction. Moreover, pn-junctions may be classified into homojunctions and heterojunctions according to whether the semiconductor material on one side of the junction is the same as or different from that on the other side. Also liquid-junction solar cells exist where the junction is formed between a semiconductor and a liquid electrolyte. Thin film solar cells are usually pn- or pin-diodes, and therefore only these types of devices are discussed here in more detail.

When the junction is illuminated, the semiconductor material absorbs the incoming photons if their energy $h \nu$ is larger than that of the band gap of the semiconductor material. The absorbed photons are converted into electron-hole pairs. These photogenerated electron-hole pairs are separated by the internal electric field of the junction: holes drift to one electrode and electrons to the other one. [4, 8]. The electricity produced by a photovoltaic device is direct current and can be used as such, converted into alternating current, or stored for later use.

Figure 1 presents a schematic energy band diagram of a pn-heterojunction solar cell (a) at thermal equilibrium in dark, (b) under a forward bias, (c) under a reverse bias, and (d) under illumination, open circuit conditions. Numbers 1 and 2 in Figure 1 refer to an n-type and a p-type semiconductor, respectively, and $E_{C1}$ and $E_{V1}$ to their conduction and valence bands, respectively. $E_g$ and $E_F$ are the band gaps and Fermi levels, respectively. In the absence of an applied potential (Fig. 1a), the Fermi levels of the semiconductors coincide, and there is no current flow. A forward bias $V_f$ (Fig. 1b) shifts the Fermi level of the n-type semiconductor upwards and that of the p-type semiconductor downwards, thus lowering the potential energy barrier of the junction, and facilitating the current flow across it. The effect of a reverse bias $V_r$ (Fig. 1c) is opposite: it increases the potential barrier and thus impedes the current flow. Illumination of the junction (Fig. 1d) creates electron-hole pairs, causing an increase in the minority carrier concentration. The potential energy barrier decreases, allowing the current to flow, and a photovoltage $V_{OC}$ (photovoltage under open circuit conditions, or open circuit voltage) is generated across the junction. [4, 9]
Solar cells are characterized by current-voltage (I-V) measurements in the dark and under standardized illumination that simulates the sunlight [10, 11]. Figure 2 shows an example of diode characteristics of a solar cell in the dark and under illumination. The most important parameters that describe the performance of a solar cell (open circuit voltage $V_{OC}$, short circuit current density $J_{SC}$ and fill factor $FF$) can be derived from the I-V curve measured under illumination.

The open circuit voltage is limited by the band gap energy $E_g$ of the absorber material, and its maximum value is calculated by dividing the band gap energy by the charge of an electron ($E_g/e$). Because of electron-hole pair recombination, the open circuit voltages of real solar cells are considerably below their maximum limits. The maximum value of short circuit current
density, in turn, is the photogenerated current density $j_{ph}$ [8] that depends on the amount of absorbed light. Fill factor, which describes the shape of the illuminated I-V curve, is expressed according to the following equation:

$$FF = \frac{V_{mp}j_{mp}}{V_{OC}j_{SC}}$$  \[1\]

where $V_{mp}$ represents the photovoltage and $j_{mp}$ the photocurrent at the maximum power point $P_{max}$. The conversion efficiency $\eta$ of a solar cell is simply the ratio of the incoming power to the maximum power output $P_{max} = V_{mp}j_{mp}$ that can be extracted from the device:

$$\eta = \frac{V_{mp}j_{mp}}{P_{in}}$$  \[2\]

Based on the above considerations, the band gap value is one of the most important properties of the absorber material of a solar cell. The optimum band gap value for the absorber material of a single-junction solar cell is about 1.5 eV which results in a theoretical maximum efficiency of 30% [8]. This is because $V_{OC}$ and FF increase, and $j_{SC}$ decreases with increasing band gap. [4] Even higher efficiencies can be achieved with tandem solar cell structures or by using solar irradiation concentrators, but these are not included here.

Most commercial solar cells of today are made of mono- or polycrystalline silicon. Silicon is a very abundant and well-known material of which a lot of experience has been gained over the decades - the first pn-junction solar cell based on crystalline silicon was made already in the 1950’s [12]. Silicon photovoltaics owes a lot to the microelectronics industry that has gained the knowledge of the material properties as well as developed the manufacturing techniques. Additionally, rejects from microelectronics industry have served as a supply for high quality source material that has thus been available at a relatively low price. [8, 13]

However, owing to its indirect band gap, silicon is not an ideal absorber material for solar cells. Semiconductor materials with indirect band gaps do not absorb light as efficiently as those with direct band gaps, and therefore a thick layer of material is needed to achieve sufficient light absorption. For example, 100 μm of crystalline silicon is needed for 90% light absorption in comparison with 1 μm of GaAs that is a direct band gap semiconductor. [13] An inevitable result of such a large thickness is that the silicon used in solar cells must be of very high quality in order to allow for minority carrier lifetimes and diffusion lengths long enough so that recombination of the photogenerated charge carriers is minimized, and they are able to contribute
to the photocurrent. These strict material requirements increase the production costs. Moreover, due to the current production technologies, material losses during the fabrication of silicon solar cells are high.

The high production costs of crystalline silicon solar cells are compensated by their high efficiencies. Moreover since the 1950's, an important application of silicon solar cells has been as power sources in space vehicles where reliability and high efficiency are far more important issues than the cost. Also other expensive high-efficiency materials, such as GaAs and InP have been used in space applications. [2]

Due to the limitations of crystalline silicon, other absorber materials have been studied extensively. These are semiconductors with direct band gaps and high absorption coefficients, and consequently they can be used in thin film form. Thin film solar cells have several advantages over crystalline silicon cells [13]. The consumption of materials is less because the thicknesses of the active layers are only a few micrometers. Therefore, impurities and crystalline imperfections can be tolerated to a much higher extent as compared to crystalline silicon. Thin films can be deposited by a variety of vacuum and non-vacuum methods on inexpensive substrates such as glass. Also curved and/or flexible substrates such as polymeric sheets can be used, leading to lighter modules. Furthermore, composition gradients can be obtained in a more easily controllable manner.

The main candidates for low-cost thin film solar cell materials are amorphous hydrogenated silicon (a-Si:H), CdTe (cadmium telluride) and CuInSe₂ and its alloys with Ga and/or S. [14, 15] Of these, amorphous silicon solar cells have currently the largest market share. [3] The absorption coefficient of amorphous silicon is higher than that of crystalline silicon which enables its use in thin film form, and its band gap is closer to the ideal value of about 1.5 eV. A serious disadvantage is the light-induced degradation of solar cells made of this material which leads to a drop of conversion efficiency from the initial value. [8] This Staebler-Wronski effect results from defects (dangling bonds) created by illumination that act as recombination centers. The stabilized efficiencies of amorphous silicon solar cells are quite low, about 13 % [15].

The polycrystalline compound semiconductor materials (CdTe and Cu(In,Ga)(S,Se)₂) do not suffer from light-induced degradation. In fact, the performances of CIS-based solar cells have even shown some improvement after illumination under normal operating conditions [16, 17]. Another advantage is that they are direct band gap materials that have high absorption coefficients. The band gap of CdTe (1.4 eV) is very close to the ideal value. Despite that, the record efficiency for CdTe solar cells is only 16.5 % [18].
2.1. CuInSe2 solar cells

2.1.1. Properties of the absorber material

The band gap of CuInSe2 is relatively low, 1.04 eV, but it can be adjusted to better match the solar spectrum by substituting part of In by Ga or part of Se by S. The flexibility of the material system allows in principle the band gap variation from 1.04 eV of CuInSe2 via 1.53 eV of CuInS2 and 1.7 eV of CuGaSe2 (CGS) to 2.5 eV of CuGaS2 [14]. The ternary Cu-chalcogenides crystallize in the tetragonal chalcopyrite structure [19]. Sometimes, however, the cubic sphalerite phase [20], a disordered form of the chalcopyrite, is observed. The Cu-chalcopyrites exhibit the highest efficiencies among thin film solar cells – the present record efficiency is 18.8% for a device with a Cu(In,Ga)Se2 (CIGS) absorber [5]. The Ga/(Ga+In) ratio in the absorber is about 25-30%, and the resulting band gap is between 1.1 and 1.2 eV [5]. An additional advantage of the Cu-based absorber materials is that they do not have the acceptability problems associated with CdTe since these materials are less toxic [21]. Nevertheless, the Cd issue is somewhat shared also by the Cu(In,Ga)(Se,S)2 technology because a CdS buffer layer is commonly used. The amount of Cd is, however, much less in the Cu(In,Ga)(Se,S)2 cells than in the CdTe cells since the CdS layer is very thin.

One would expect that the higher band gap absorbers of the Cu(In,Ga)(S,Se)2 system would result in devices with higher conversion efficiencies, but this is not the case – conversion efficiencies achieved by CuInS2 or CuGaSe2 absorbers lag far behind those achieved by Cu(In,Ga)Se2 or even CuInSe2. This is partly due to the longer research history of CuInSe2 and Cu(In,Ga)Se2 solar cells, but also due to some fundamental differences between the low band gap (CuInSe2 and Cu(In,Ga)Se2 with a low Ga content) and wide band gap (CuInS2 and CuGaSe2) materials. [22] Of these, issues related to doping and recombination are described briefly in the following.

The overall composition of the photovoltaic-quality Cu(In,Ga)Se2 absorber film is slightly Cu-deficient, with a thin, even more Cu-deficient surface layer, the composition of which corresponds to the stable ordered vacancy or ordered defect compound (OVC/ODC) Cu(In,Ga)3Se5. [16, 23, 24]. The formation of this OVC layer occurs automatically on the top surfaces of Cu-In-Ga-Se thin films at high deposition temperatures [23], thus resulting in significant differences between the bulk and surface compositions of photovoltaic-quality Cu(In,Ga)Se2 films. The OVC surface layer is weakly n-type [23], and since the bulk of the absorber is p-type, they form a buried pn-junction [16, 23, 25]. The inverted surface minimizes the recombination at the CIGS/CdS interface [24]. The thickness of the OVC layer is about 10 nm [23]. Thicker, deliberately prepared OVC layers have been reported to result in deteriorated device performances [26] which was attributed to increased series resistance because of the low conductivity of the OVC and light absorption in the OVC instead of the
junction region. The band gap of the surface layer is direct and wider than that of the bulk, values between 1.23 [27] and 1.3 eV [23] have been observed, in agreement with the predicted value of 1.21 eV [28]. The wide band gap of the surface layer increases further the barrier for recombination at the CIGS/CdS interface. [29].

In agreement with the doping pinning rule of Zhang et al. [30], CuInSe₂ and CuInS₂ can be either p-type or n-type, depending on the composition. CuGaSe₂, in contrast, is always p-type which prevents the formation of the inverted surface. A factor that limits the use of CuInS₂ is that attempts to prepare Cu-poor CuInS₂ lead often to the formation of n-type CuIn₅S₈. [22]

Recombination in the bulk of the absorber is the main loss mechanism in CuInSe₂, Cu(In,Ga)Se₂ and CuGaSe₂ solar cells [31, 32]. Increased recombination losses observed in CuGaSe₂ cells as compared to CuInSe₂ or Cu(In,Ga)Se₂ cells are due to increased contribution of tunneling to the recombination in the bulk of the absorber. [32] Recombination mechanisms of CuInS₂ cells, in turn, differ in the dark and under illumination: bulk recombination dominates in the dark and interface recombination dominates under illumination [22]. This is probably due to the difficulty of preparing CuInS₂ absorbers with Cu-poor composition since according to Turcu et al. [33] interface recombination dominates in all devices where the final absorber composition is Cu-rich. In all cases, the open circuit voltages of the cells correlate inversely with the defect densities of the absorbers, measured by admittance spectroscopy. [22, 32] This is particularly manifested by the fact that the open circuit voltages of CuInSe₂ solar cells increase linearly with the addition of Ga to the absorber, until a Ga/(Ga+In) ratio of about 30 % and a band gap of about 1.2 eV is reached. The increase of the open circuit voltages is faster than that of the band gap, and is accompanied by a decreasing defect density. Beyond the Ga/(Ga+In) ratio of about 30 %, the increase of \( V_{oc} \) slows down [32, 34], accompanied by an increase of the defect density [32, 35]. Thus the optimum composition of a CIS-based absorber film seems to be Cu(In,Ga)Se₂ with a Ga/(Ga+In) ratio of about 25-30 %. The Ga content and therefore the band gap of the absorber is usually graded in such a way that the regions near the Mo back contact contain more Ga than those closer to the film surface [24]. This grading enhances the separation of the photogenerated charge carriers and reduces recombination at the back contact [36, 37]. Moreover, as explained above, since the open circuit voltage increases and the short circuit current decreases as a function of the band gap, careful design of the grading profile allows a separate optimization of the open circuit voltage and short circuit current density: the higher band gap value of the graded material determines the open circuit voltage and the lower value the short circuit current density [36, 38].
2.1.2. Device structure

Figure 3 shows a schematic representation of a CIGS solar cell. Cell preparation starts by the deposition of the Mo back contact on glass, followed by the p-type CIGS absorber, CdS or other weakly n-type buffer layer, undoped ZnO, n-type transparent conductor (usually doped ZnO or In$_2$O$_3$), metal grids and antireflection coating. Finally, the device is encapsulated to protect it against its surroundings.

![Figure 3. A schematic view of the CIS solar cell structure](image)

The structure of a CIGS cell is quite complex since it contains several compounds as stacked films that may react with each other. Fortunately, all detrimental interface reactions are either thermodynamically or kinetically inhibited at ambient temperatures. The formation of a thin p-type MoSe$_2$ layer between the Mo and the absorber that occurs during the absorber preparation at sufficiently high temperatures under (In,Ga)$_x$Sey-rich growth conditions [39, 40] is beneficial for the cell performance for several reasons: first, it forms a proper ohmic back contact. The Mo/CIGS contact without the MoSe$_2$ layer is not an ohmic but a Schottky type contact which causes resistive losses. [39, 41] Another advantage is the improved adhesion of the absorber to the Mo back contact. Further, since the band gap of MoSe$_2$ is wider (about 1.4 eV [39]) than that of a typical CIGS absorber, it forms a back surface field for the photogenerated electrons [29, 39, 42], providing simultaneously a low-resistivity contact for holes [29]. The back surface field reduces recombination at the back contact since the insertion of a wider band gap layer (of the same conductivity type as the absorber) between the back contact and the absorber creates a potential barrier that confines minority carriers in the absorber [43]. Finally, the MoSe$_2$ layer prevents further reactions between CIGS and Mo [40].
A moderate interdiffusion of CdS and CIGS, that occurs to some extent in photovoltaic-quality material too [44, 45], is potentially beneficial to the cell performance. [40] Further, the reaction of CdS with CIGS to form detrimental Cu$_2$S is inhibited as long as photovoltaic-quality (Cu-deficient) material is used. Similar stability is not present at a CIGS/ZnO interface since Cu-poor CIGS may react with ZnO to form ZnSe and In$_2$O$_3$ or Ga$_2$O$_3$ [40]. This, in addition to the sputter-induced damage during ZnO deposition (see Chapter 3.3), may contribute to the lower efficiencies of buffer-free devices. [40]

Figure 4 shows the structure of an alternative, inverted configuration. The preparation of this so-called superstrate cell starts with the deposition of the transparent conductor, followed by the absorber deposition. The CdS layer is usually omitted in modern superstrate cells because the high absorber deposition temperatures would cause its intermixing with the CIGS layer. [46, 47] The advantages of the inverted configuration include lower cost, easier encapsulation and the possible integration as the top cell in future tandem cells. [47] The conversion efficiencies achieved by superstrate cells are, at least so far, several percentage units lower than those of the substrate cells. This may be due to the fact that the substrate cells have been studied to a much greater extent than the superstrate cells. Because of these reasons, superstrate cells are not considered here in more detail.

![Figure 4. A schematic view of a CIS superstrate solar cell structure](image)

### 2.1.3. Stability and defect chemistry of CIGS

In addition to the conversion efficiency, another crucial issue of a solar cell is its stability since it affects directly the cost of the electricity produced, and thus the energy payback time. Despite the complex solid state chemistry of the CIGS solar cell structure, they have shown exceptionally stable performances both under normal operating conditions [16, 17] as well as under harsh conditions such as irradiation by X-rays [48], electrons [49-51], or protons [50, 52, 53]. Radiation hardness demonstrates the suitability of CIGS cells to space applications.

Besides the interfacial stability discussed above, the most important factors that contribute to the
electrical and chemical stability of the CIS-based solar cells are the unique properties of the absorber material, especially the wide single-phase domain and the fact that the doping level remains non-degenerate (below $10^{18}$ cm$^{-3}$) over a wide composition range. Both of these effects result from the strong self-compensation of the chalcopyrite compounds: defects that are caused by deviations from the stoichiometry are compensated by new defects that neutralize them, i.e., formation energies of the compensating ionic defects are low. As a result, most of the defects or defect complexes are electrically inactive with respect to the carrier recombination. [40]

According to Zhang et al. [28], the formation energies of defects and defect complexes in CuInSe$_2$ are low. The energetically most favored isolated point defect is the shallow copper vacancy $V_{Cu}$ that contributes to the very efficient p-type doping ability of CIS. The most favorable defect complex is $(2V_{Cu} + In_{Cu})$ that prevents degenerate doping in In-rich material. Because of the high concentration of $(2V_{Cu} + In_{Cu})$ complexes, they interact with each other which lowers the formation energies further. The existence of the ordered defect compounds (ODC) CuIn$_3$Se$_5$, CuIn$_5$Se$_8$ etc. may be explained as periodically repeating $(2V_{Cu} + In_{Cu})$ units. Other defects may be present too but their formation energies are higher. [28]

CIGS solar cells exhibit electrical metastabilities that are manifested as the increase of the open circuit voltage and improvement of fill factor upon illumination, and the effect of reverse biasing the junction. Illumination-induced metastabilities may occur both in the absorber or at the CIGS/CdS interface, depending on the wavelength of illumination. [40, 54] Effects caused by long-wavelength (red) illumination are related to the CIGS absorber since red light (low energies) is mostly absorbed in CIGS. Red illumination causes a metastable increase of net carrier concentration, which decreases the width of the space charge layer. The open circuit voltage increases due to the reduced recombination in the narrower space charge layer. [54] Thus the increase of the open circuit voltage upon illumination is related to the CIGS absorber. [40, 54]

Short-wavelength illumination (blue light), in turn, affects mostly the regions at or near the CdS/CIGS interface. Blue light is to a great extent absorbed into the buffer layer, and the photogenerated holes are injected into the near-surface region of the CIGS absorber [54]. Illumination by blue light has been reported to improve the fill factor which probably results from the ionization of deep donors in CdS. The positively charged fixed donors cause downward band bending in the CdS and reduce the barrier height to electrons. [40, 55] The photogenerated holes have also been suggested to neutralize the negative defect states that are present on the CIGS surface [54]. The improvement of the FF upon illumination is therefore related to the CIGS/CdS interface.

Reverse bias has the opposite effect, and since it can be counterbalanced by blue illumination, it is reasonable to attribute also the effect of reverse bias to the interface region. Reverse bias
generates negative charge states to the buffer layer and to the surface defect layer of CIGS. [54] These negative charges may be neutralized by blue illumination. [54]

Thus the illumination-induced defect reactions are beneficial to the device performance, and moreover reversible. Self-annealing of the metastable states prevents accumulative long-term damage since it occurs at ambient temperatures and with an adequate time scale. [40]

Radiation hardness has also been suggested to be due to the self-repair of the radiation-induced damages rather than due to the resistance of the material to damage. The self-healing mechanism is a result of the mobility of Cu and reactions involving Cu-related defects or defect complexes. [56] Thus the electrical stability of the CIGS material system seems to be of dynamic nature rather than static. The material is not resistant to changes but it is flexible because of inherent self-healing mechanisms. Particularly, the mobility of Cu, as well as the high defect density of CIGS, are actually advantages in CIGS since they help in repairing damages, thus contributing to the unusual impurity tolerance and to the radiation hardness. Also the Cu-poor surface composition of photovoltaic-quality CIGS films has been proposed to result from the migration of Cu in the electric field of the space charge region. [40] The wide range of possible preparation techniques and preparation conditions for Cu-chalcopyrites has been suggested to be an indication of a stable energetic minimum that can be reached via different routes [56].

2.1.4. Effects of sodium and oxygen

Yet another interesting feature is the beneficial effect of sodium on the structural and electrical properties of Cu-chalcopyrite thin films. The phenomenon was discovered in 1993 [57, 58] when solar cells prepared on soda lime glass substrates showed considerably higher efficiencies than those prepared on borosilicate glass. X-ray photoelectron spectroscopy and secondary ion mass spectrometry studies revealed the presence of Na at relatively high concentrations both on the surface and in the bulk of the CIGS films deposited on Mo/soda lime glass. [57] Sodium is normally detrimental to semiconductors but its presence during the growth of CIS-based films has been reported to increase the grain size [57-60], smoothen the surface morphology [59, 60], enhance the crystallinity and (112) orientation [57-62], and increase the p-type conductivity (carrier concentration) [61-65]. Sodium has been suggested to aid the formation of the beneficial MoSe₂ layer between Mo and CIGS [39]. As a result, improved solar cell efficiencies have been obtained in the presence of Na [59-64].

Sodium thus affects both the growth and the doping of Cu-chalcopyrite films. Na⁺ ions migrate from the substrate to the CIGS film along grain boundaries [66], and their incorporation into a CIGS film occurs via interaction with Se [66, 67]. The Na contents in the CIGS films are quite high, typically about 0.1 at.% or higher [61, 65, 66, 68, 69]. According to Granata et al. [65], the
ideal Na content in CIS and CIGS films is between 0.05 and 0.5 at.% Most of the sodium is located at the film surface, near the Mo back contact, or at the grain boundaries [60, 62, 64-67, 70].

In an attempt to explain the influence of Na on the structural properties of CIGS films prepared by co-evaporation, Braunger et al. [66] proposed a model according to which Na\(^+\) ions diffuse to the CIGS surface along grain boundaries and react subsequently with the elemental selenium to form sodium polyselenides (Na\(_2\)Se\(_x\), \(x = 1-6\)). When the Se partial pressure is low, mainly Na\(_2\)Se is formed. Na\(_2\)Se is a very stable compound which renders the release of Se from it highly unlikely. Thus, no Se is available for the growth of the CIGS film. At higher Se pressures, the formation of polyselenides dominates. Because of the easier release of Se from them, polyselenides act as a Se source during the growth.

The increased p-type conductivity of Na-containing Cu-chalcopyrite films is generally attributed to the suppression of donor-type defects such as In\(_{\text{Cu}}\) [62, 63, 71, 72] that act as majority carrier traps. On the other hand, the removal of a minority-carrier trap state has also been reported [63].

As explained in Chapter 2.1.3, the concentration of In\(_{\text{Cu}}\) in photovoltaic-quality films is high. Sodium eliminates the In\(_{\text{Cu}}\)-related donor states or inhibits their formation by incorporating at the Cu site which results in an increased hole concentration [62, 69]. The calculations of Wei et al. [72] support the conclusion that the main effect of sodium on the electronic properties of CIS is to reduce the amount of intrinsic donor defects. When present at low concentrations, Na eliminates first the In\(_{\text{Cu}}\) defects which results in a higher p-type conductivity. [72] This removal of In\(_{\text{Cu}}\) antisites may lead to a more ordered structure which may explain also the enhanced (112) orientation. [62] Wei et al. [72] even propose the formation of layered NaInSe\(_2\) that directs the CIS film to the (112) orientation.

Overly high Na doses are detrimental to the electronic properties since they result in the elimination of V\(_{\text{Cu}}\) acceptor states and thereby reduce the carrier concentration. [72] On the other hand, Na contents of higher than 1 at.% were reported to increase the carrier densities to excessively high values (above 10\(^{18}\) cm\(^{-3}\)) which reduced the cell performances. This may be due to the formation of Na-containing compounds [65]. The formation of additional phases at too high Na concentrations has in fact been observed [62], and it may result from the limited mutual solubility of NaInSe\(_2\) and CuInSe\(_2\) [72].

In most cases, the diffusion of Na into the absorber film from the soda lime glass through the Mo back contact at high deposition temperatures is considered to provide a sufficiently high Na concentration, but deliberate incorporation of Na by introducing Na-containing precursors such as NaF [59, 60, 63], Na\(_2\)S [70, 71], Na\(_2\)Se [64, 73], Na\(_x\)O [74], NaHCO\(_3\) [73] or elemental Na [61], has also been studied. The advantage of this approach is the possibility of a better control
over the sodium content and thus a better reproducibility since the Na supply from the glass depends on the absorber deposition process as well as on the properties of the Mo back contact [59, 73] and the glass itself [59]. Thus, the amount of Na diffusing from the substrate is difficult to estimate accurately. Moreover, since the diffusion of Na from the substrate slows down at low temperatures, the deliberate addition of Na allows one to use lower deposition temperatures without so much degradation of the cell efficiency [60, 61]. For instance, Bodegård et al. [60] were able to decrease the CIGS deposition temperature from 510 to 425°C with essentially no degradation of the conversion efficiency. In another study [61], the conversion efficiency decreased only 1.3 percentage units upon decreasing the deposition temperature from 550°C to 400°C in the presence of additional sodium. In both cases, the efficiencies achieved under insufficient supply of sodium were several percentage units lower. [60, 61] Furthermore, preparation of efficient superstrate cells may require the deliberate addition of Na since its diffusion from the glass is blocked by the transparent conductor [47] or the thin Al₂O₃ layer that is often present under commercial conducting oxide thin films.

Effects of other alkali metal fluorides (LiF [60], KF [62] and CsF [62]) have also been studied. The addition of LiF was reported to cause an increased grain size and enhanced (112) orientation but to a smaller extent than NaF. The grain sizes were comparable to those of the Na-containing films but the film surfaces were rougher. [60] The addition of KF increased the conductivity somewhat, but CsF had in some cases the opposite effect since it decreased the photoconductivity. [62] Thus, NaF had the highest influence on the film properties. In the case of LiF, this may result from its higher chemical stability as compared to NaF which results in a different decomposition behavior [60]. The smaller influence of KF and CsF was explained by the differences in the ionic radii: the smaller ionic radius of Na helps its substitutional incorporation into the chalcopyrite lattice [62].

In addition to the effects discussed above, Na also enhances the influence of oxygen in the CIS-based films [74-77]. The main role of oxygen is the passivation of positively charged Se vacancies (V₇ₓ) that are present on the surfaces and grain boundaries of the Cu-chalcopyrite thin films. [72, 76, 77]. The presence of Se vacancies at grain boundaries is especially detrimental since they decrease the effective p-type doping of the film. Additionally, they act as recombination centers for the photogenerated electrons [75-78]. The passivation of Se vacancies is therefore of significant importance to the performance of the solar cell. [75-77] Air-annealing has in fact been used routinely to improve the photovoltaic properties of the CIGS solar cells [68]. Physisorbed oxygen that is present on the surfaces and grain boundaries of oxygen-exposed CIGS films, chemisorbs as O²⁻ which occupies the positively charged vacant Se sites, and thus obviates their disadvantageous effects. Sodium has been suggested to promote the formation of chemisorbed O²⁻ ions by weakening the O-O bond [72, 74, 75]. The correlated concentration distributions of these two elements in air-exposed CIGS films [62, 64, 66, 70, 74] support this idea.
3. Thin film deposition methods for CuInSe₂-based solar cells

A wide range of preparation methods exist for the thin film materials used in the CIS-based solar cells. The deposition method has generally a large impact on the resulting film properties as well as on the production cost. In this section, the most important deposition methods are reviewed, with the main focus on those used for the absorber deposition. Moreover, since CuInSe₂ and Cu(In,Ga)Se₂ are the most important Cu-chalcopyrite absorber materials, they are emphasized in this presentation. To some extent the deposition methods apply to CuGaSe₂ and CuInS₂ films as well.

The preparation of a standard CIS-based solar cell involves several steps every one of which is important. The preparation of a normal substrate configuration Cu-chalcopyrite solar cell starts from the deposition of the 1-2 µm thick Mo back contact that is most often sputtered. The quality of the back contact and its adhesion to the underlying glass substrate are very important issues. After the deposition of absorber, buffer, and transparent conductor, metal grids (most often Al or Ni/Al) are deposited on the transparent conductor in order to enhance its conductivity. Finally, an antireflection coating (MgF₂) is added in order to minimize reflection losses and thus increase the efficiency.

3.1. Absorber layer

Although various techniques can be used to obtain stoichiometric CIS and CIGS films, only a few of them have resulted in high efficiency (over 15%) solar cells so far. The absorber films for the high efficiency solar cells are usually prepared either by co-evaporation from elemental sources or by reactive annealing of precursor films (elemental or compound layers) under selenium-containing atmospheres. [24]

Regardless of the deposition method, the absorber films of CIS-based high-efficiency devices have smooth surface morphologies and consist of large, densely packed grains. The films are crystalline with the chalcopyrite structure [19], and their overall compositions are slightly Cu-deficient, in order to enable the formation of the Cu-poor ordered vacancy compound (OVC) on the surface [23, 29]. Also, no additional phases are allowed in the films, copper selenide phases especially are detrimental to the solar cell performance since, being a degenerate semiconductor, Cu₂-xSe is very conductive which results in high dark currents.

The formation of a photovoltaic-quality film requires generally a high temperature (400 °C or above) during film growth or post-deposition annealing. The formation of Ga-containing phases (CGS and CIGS) requires generally higher temperatures or longer reaction times than for CIS [24, 79-82]. Higher temperatures also facilitate the formation of the MoSe₂ interlayer [39]. The
formation of a Cu-rich phase during the earlier stages of the growth enhances the formation of smooth, dense, and large-grained films. The presence of Na during the growth has a similar effect as well as other beneficial consequences, as reviewed in Chapter 2.1.4. As the high process temperatures may cause the loss of Se, that must be compensated for, for instance by maintaining a Se-containing atmosphere.

3.1.1. Co-evaporation from elemental sources

The most successful absorber deposition method for high-efficiency small-area devices seems to be the three-stage co-evaporation of CIGS from elemental sources in the presence of excess Se vapor [36, 83]. Deposition is often performed under ultra high vacuum conditions using a molecular beam epitaxy (MBE) system. The three-stage process, developed at the US National Renewable Energy Laboratory (NREL), is based on the bilayer process of Boeing [82] that involves the co-evaporation of Cu-rich CIGS layer at a lower substrate temperature (450°C), followed by In-rich layer at a higher temperature (550°C). The layers intermix, forming a homogeneous film with a slightly Cu-deficient overall composition. The three-stage process involves first the deposition of (In,Ga)2Se3 at a lower substrate temperature (about 300-350°C) and then the evaporation of Cu and Se at a higher temperature (500-560°C) to yield Cu-rich CIGS. After adding some more (In,Ga)2Se3, a slightly Cu-deficient final film composition is achieved. A Se vapor treatment is carried out during the cooling step. [36] The Ga/(Ga+In) ratio is usually varied as a function of depth. Since the band gap of CGS is higher than that of CIS, the graded Ga content results in a graded band gap of about 1.1 to 1.2 eV which in turn improves the separation of the photogenerated charge carriers and reduces recombination at the back contact [36]. For example, in the NREL world record cell the Ga/(Ga+In) ratio is about 30 % near the Mo back contact and about 25 % on the top surface [5].

CIGS films prepared by the three-stage co-evaporation process have resulted in solar cell efficiencies of around 18 % by many groups: world record 18.8 % of NREL [5], 18.5 % of Matsushita [84], 18.0 % of Aoyama Gakuin University of Tokyo [85], 17.6 % of Tokyo Institute of Technology [86], as well as the best Cd-free device with a CBD-ZnS buffer of 18.1 % [87].

A remarkable feature in [5] is that the CIGS films were (220/204) oriented – the typical orientation of chalcopyrite CIGS films is either random or (112). The orientations of CuInSe2 and CIGS thin films were shown to depend on the orientation of the underlying (In,Ga)2Se3 precursor layer which in turn was a function of the properties of the Mo layer such as morphology, grain size and stress. The (220/204) oriented CuInSe2 thin films were achieved only on dense, almost pinhole-free, large-grained Mo films with low tensile stress and a low Na content on the surface. [88] Under Na-free conditions [89], the film orientation was found to depend on the substrate orientation, i.e., (100) oriented Mo resulted in (112) oriented CIGS and
(110) oriented Mo in (220/204) oriented CIGS. The orientation of the (In,Ga)$_2$Se$_3$ precursor was also dependent on the Se/(In+Ga) flux ratio and substrate temperature during the evaporation. High flux ratios increased the (220/204) orientation of CIGS by increasing the (300) orientation of the (In,Ga)$_2$Se$_3$ precursor. Increasing substrate temperature was reported to have the opposite effect. [86]

The (220/204) oriented films were found to be more resistive than the (112) oriented films, and their apparent band gaps were lower than those of the (112) oriented films. The higher conversion efficiencies achieved with the (220/204) oriented absorbers were mainly due to increased fill factors and lower series resistances, whereas the $j_{sc}$ and $V_{oc}$ were in most cases only moderately higher. [89] The increase of the efficiency from 15.5 % with the (112) oriented absorber to 17.6 % with the (220/204) oriented one may be explained by an easier diffusion of Cd atoms during the deposition of CdS into the (220/204) oriented films. Possible reasons are a higher dissolution rate of Cu into an NH$_3$ solution from the (220) surfaces and/or the fact that there are less atoms on the (220) surface as compared to the (112) surface. [86]

Co-evaporation can also be performed with a constant Cu/(In+Ga) flux ratio through the entire process. It was shown [90] that the flux ratio profile did not have a large impact on the device efficiency (best 16.4 %) when the co-evaporation was done at 550 $^\circ$C. At 400 $^\circ$C, in contrast, the presence of a Cu-rich growth stage improved the device efficiencies (best 14.1 %), whether in the beginning or in the middle of deposition [90].

In order to gain information about the material properties such as defects, high-quality CIS and CGS films have been deposited on GaAs and InGaAs [91] and on Si [92] by MBE. The use of epitaxial films in these studies eliminates the effects of grain boundaries and other non-idealities, and allows thus to get reliable and reproducible information of the intrinsic properties of the materials. [91, 92]

Despite its unquestionable power in preparing high-quality material on small areas, co-evaporation exhibits some problems related to upscaling. This is due to the fact that co-evaporation requires a strict control of the evaporation fluxes to achieve the desired film properties such as composition, texture, and electrical properties. This is particularly difficult with large substrate areas. As an inevitable consequence, the conversion efficiencies of large area cells and modules are considerably lower than those of the smaller-area devices [93], for example the efficiency reported by Matsushita laboratories was 12.6 % for a 81.54 cm$^2$ submodule [94] as compared to 18 % for a small-area cell [84]. Moreover, in addition to the sophisticated and expensive equipment, the high deposition temperatures and incomplete utilization of source materials add to the complexity and cost of the co-evaporation method. [93]

According to ZSW/Würth Solar [95], the production of CIGS modules by co-evaporation should,
however, be possible well below the common market price of the crystalline Si solar cell technology. Their in-line co-evaporation process [95, 96] is based on one-step co-evaporation of Cu, In, Ga, and Se from elemental sources onto moving substrates at high temperatures. Efficiencies of 30 cm x 30 cm CIGS modules average 11.3 %, with a maximum value of 12.7 %. The maximum efficiency for a Cd-free module of the same size was 9.7 % [95].

3.1.2. Selenization of metallic precursor layers

Although the difficulties in upscaling are somewhat shared by all the deposition methods, the alternative multistep approach where the absorber is prepared by combination of simple, well-established deposition techniques for the more simple precursor layers offers certain advantages: compositional uniformity over large areas may be easier to achieve, and in many cases the throughput is increased as compared to the co-evaporation. Moreover, the processes are often very cost-effective because of the low deposition temperatures. This is important because apart from its efficiency and implementation, the energy payback time of a photovoltaic module depends on its production cost. For example, the energy payback time for CIS modules of Siemens Solar Industries (SSI), manufactured by selenization of metals, has been calculated to be 9 to 12 years at a pilot production rate and about 2 years in full production. Empirical calculations show that during its lifetime (estimated to be 30 years), a CIS panel generates up to 14 times the energy required to produce it. [97]

The most common multistep method is the selenization of stacked metal or alloy layers. The metals or alloys can be deposited by a variety of methods, the most common of which are sputtering [80, 93, 98-102], evaporation [79, 101, 103-114], and electrodeposition [98, 102, 108, 113, 115-122].

Selenization is most often carried out under a selenium-containing atmosphere at high temperatures, typically above 400 °C. Selenium may be present either as H₂Se [80, 101, 103, 108, 109, 114, 116, 119, 122], most often diluted by Ar, or elemental Se [79, 98-100, 102, 105-107, 109, 113, 115, 120]. Selenization time depends on thickness, structure, and composition of the film, as well as on the reaction temperature and selenium source. Generally, the formation of CIS by selenization is faster and occurs at lower temperatures than for CGS [79, 81]. As a result, CIGS films may contain CIS and CGS as separate phases if the reaction temperature is too low or the time is too short [80]. High reaction temperatures also facilitate the formation of MoSe₂. [39, 99, 109]. The chalcogenization method offers also a possibility of forming CuIn(S,Se)₂ thin films by introducing both Se and S precursors into an annealing atmosphere [105].

Influence of the chalcogenide source in selenization of evaporated Cu-In alloys at different
temperatures (between 250 and 600 °C) has been studied in detail in [109]. Three selenization methods were compared: (i) H2Se/Ar at atmospheric pressure, (ii) solid Se source under Ar flow at atmospheric pressure, (iii) elemental Se vapor in vacuum. In all cases the samples were heated for 10 min to the reaction temperature, and the reaction time was 40 min. At temperatures below 500 °C, the H2Se method was found to be most efficient, resulting in films with about 50 at.% Se already at 400 °C. The Se vapor approach was the most inefficient. Above 500 °C, a Se content of about 46-52 % was achieved by all methods. Single-phase CuInSe2 films were obtained only by the H2Se method at 400 °C. Additional phases, Cu and In selenides and/or Cu-In alloys, were detected in all other samples. The H2Se method also resulted in the best compositional uniformity and the largest grain sizes. The formation of MoSe2 was detected only after selenization by H2Se at 600 °C. [109] Thus, H2Se is the most efficient selenization source but its toxicity is a serious drawback. Recently, diethylselenide was introduced as an alternative, less toxic selenium source. Promising results were obtained from the selenization experiments with Cu-In and Cu-In-O precursors [110].

Chalcogenization can also be done by depositing the chalcogen film on or between the metallic layers, again either by evaporation [93, 104, 105, 114, 117, 123] or electrodeposition [111, 112, 118, 121] and annealing the stack under an inert atmosphere [104, 112, 114, 117, 118], thus forming the desired compound and avoiding the use of toxic vapors such as Se and especially H2Se. Sometimes, however, a chalcogen-containing annealing atmosphere [105, 114, 121, 123] is required in order to compensate for the chalcogen loss at high temperatures. Alberts et al. [114] observed significant Se losses upon annealing of stacked In/Se/Cu/In/Se layers above 200 °C, irrespective of whether the annealing was performed in vacuum with elemental Se vapor or under an Ar flow at atmospheric pressure in the absence of Se. No In loss was detected until above 650 °C. [114]

The metal precursors are most often deposited at or near room temperature, but higher temperatures have been used as well. In order to facilitate the interdiffusion of the metal precursors and alloy formation between them, the metal precursors can be pre-annealed at a lower temperature [79, 101, 103, 107, 112, 118] prior to selenization. Another approach is the deposition of Cu/In/Cu/In/Cu/In... multilayers instead of a bilayer [99, 105, 106]. The multilayer approach has been reported to result in smoother surfaces and better crystallinity [106].

The process of Showa Shell [124, 125] involves sputtering of stacked precursor layers (Cu-Ga alloy and In) followed by selenization with dilute H2Se and surface sulfurization with dilute H2S at high temperatures. The thin (about 50 nm) Cu(In,Ga)(S,Se)2 surface layer is thought to improve the surface quality and thus the fill factor via the passivation of shallow defects such as selenium vacancies and SeCu antisites [125]. Module efficiency of 12.5 % was achieved for an area of 859.5 cm² [124]. A remarkable feature is that the device was Cd-free, with Zn(O,S,OH)₆ as the buffer layer [124, 125].
The process of Siemens AG [126], in turn, eliminates the use of toxic H$_2$Se gas since the absorber is prepared by depositing the constituent elements at room temperature, followed by rapid annealing under a sulfur-containing atmosphere at 550°C or lower temperatures to yield Cu(In,Ga)(S,Se)$_2$. CuGa and In layers were sputtered, and Se was evaporated thermally. The amount of Se exceeded the stoichiometric one by about 40% in order to compensate for the Se loss that occurs during annealing. [123, 126] Moreover, the process involves a controlled Na incorporation as a Na compound deposited on Mo before the absorber deposition. [123] Module efficiency of 14.7% (average 13.2%) for 18.9 cm$^2$ aperture area was achieved by this process, as compared to 11.8% (average 11%) when the annealing was performed without sulfur [126]. This increase in efficiency was due to an increase of band gap and open circuit voltage of the absorber material [126]. The depth distributions of sulfur and gallium were nonuniform – their amounts were highest close to the Mo back contact where the absorber consisted of smaller grains than closer to the top surface. Thus, sulfur was thought to incorporate preferentially at grain boundaries [123].

Surface sulfurization is used also for co-evaporated absorbers, for example in [84] the CIGS films were soaked in a solution containing InCl$_3$ and thioacetamide (CH$_3$CSNH$_2$) to sulfurize the surface. The thin CuInS$_2$ layer on the absorber surface increases the stability and conversion efficiency of the cell since it improves the quality of the pn-junction by passivating the surface. [127]

The incorporation of sulfur in CIS and CIGS thin films prepared by selenization of evaporated metal precursors [128] or by co-evaporation [129] has been studied. The sulfur distribution in the chalcopyrite films was found to depend strongly on the composition and microstructure of the original film. The distribution was nearly uniform in copper-rich films, whereas in near-stoichiometric and indium-rich films most of the sulfur was on the surface. In indium-rich films, sulfur was found also close to the Mo/absorber interface. The Ga content of the film affected the distribution as well: more S was found close to the Mo/absorber interface when the Ga/(Ga+In) ratio in the near-stoichiometric film was increased. In that study, the H$_2$S annealing time was long, 20 min, and the temperature was 575°C [128]. Surface sulfurization (10-50 min by H$_2$S at 350-550°C) of co-evaporated CIS and CIGS films was reported to result in surface roughening, i.e., nonuniform and porous surface layers. The sulfurization of CIS films resulted in the formation of sulfoselenides below the CuInS$_2$ surface layer, and improved cell performance. In CIGS films, a phase separation to Cu(In,Ga)Se$_2$ and Cu(In,Ga)S$_2$ occurred, and the resulting cell performance was poor [129].

The in-line process of Lockheed Martin Astronautics involves sequential sputtering of Cu, Ga, and In from elemental targets at room temperature, followed by selenization in a Se vapor at higher temperatures [130, 131]. Compound formation occurs via reactions of binary selenides. [130, 131] Homogeneous CIS [130] and CIGS [131] films with uniform compositions are formed
over 900 cm$^2$ substrates. Small-area efficiencies of over 10% have been achieved on soda lime glass by using optimized post-annealing conditions [132].

3.1.3. Evaporation from compound sources

Binary [133-135], ternary [81, 107, 136-140], and even quaternary [137] compounds can be used as evaporation sources too. This approach is potentially simpler and easier to control than the co-evaporation from elemental sources, provided that the compound does not decompose during heating, thus resulting in a film composition that differs from the source material. Very often at least Se is lost, in which case a Se atmosphere is required during deposition and/or post-deposition annealing. Decomposition may be avoided by a very fast heating to sufficiently high temperatures so that the material evaporates before it decomposes [140]. This approach is utilized for example in flash evaporation [136-140] and related methods [135] as well as in pulsed laser deposition [141, 142].

Park et al. [133] evaporated In$_x$Se (x~1) / Cu$_2$Se double layers from In$_2$Se$_3$ and Cu$_2$Se sources at room temperature and annealed them in a Se atmosphere at 550°C to yield crystalline single-phase Cu- and Se-rich CuInSe$_2$ films. After annealing, small amounts of In$_2$Se$_3$ and Se were deposited on the film surface at the same temperature in order to form a thin CuIn$_3$Se$_5$ layer. A solar cell efficiency of 5.4% was achieved with the Ag/n-ZnO/i-ZnO/CdS/CuIn$_3$Se$_5$/CuInSe$_2$/Mo structure. [133] The efficiency increased to 9.6% when the process was slightly modified: Se was co-evaporated with In$_2$Se$_3$ during the initial stage at substrate temperature of 150°C, and in the Cu$_2$Se evaporation stage, the substrate temperature was increased to 440°C which was also used for the subsequent Se annealing (10 min). The Cu-poor surface layer was formed again by evaporating small amounts of In$_2$Se$_3$ and Se. An efficiency of 9.3% was achieved with no OVC layer but a slightly Cu-poor surface. [134]

The sequential "quasi-flash evaporation" of In$_2$Se$_3$ and Cu$_2$Se onto unheated substrates and a subsequent anneal at 500°C under Ar for 1 h resulted in single-phase chalcopyrite CIS films with random orientation and p-type conductivity. The evaporation of In$_2$Se$_3$-Cu$_2$Se mixtures by the same method led to the formation of (112) oriented single-phase CIS after annealing at 400°C. The control of the film composition in the latter method was difficult, however, because In$_2$Se$_3$ melted earlier than Cu$_2$Se, and the evaporating In$_2$Se$_3$ vapor caused some loss of the unmelted Cu$_2$Se powder. That is why the films evaporated from mixture of In$_2$Se$_3$ and Cu$_2$Se were very Cu-deficient and thus n-type. [135]

Thermal evaporation of p-type CuInSe$_2$ thin films from a single CIS source at substrate temperatures ranging from 200 to 600°C was reported by Sadigov et al. [107]. Because of difficulties in achieving stoichiometric, crystalline and binary phase free films with good surface
morphology, additional Cu and In were evaporated on the films at room temperature, and the films were subsequently selenized in a Se containing atmosphere. [107]

Klenk et al. prepared CIS, CGS and CIGS films from CIS and CGS powders and their mixtures at substrate temperatures between room temperature and 350 °C both by thermal [81] and flash [136] evaporation. In both cases, the resulting films were Se-deficient unless the evaporation was done in the presence of additional Se vapor [81, 136]. The films were annealed in the presence of Se vapor at high temperatures of up to 550 °C [81, 136]. Thermal evaporation resulted in uniform and dense films when the substrate temperature was between 200 and 300 °C; film thickness (1.5 µm) and composition were nearly constant over an area of 10 cm x 10 cm. Film formation was found to proceed via the formation of binary selenides—probably because the relatively slow heating rate of the precursor powders caused their decomposition. A significant difference between the formation kinetics of CIS and CGS was observed: the formation of single-phase CuGaSe₂ required reaction temperatures above 500 °C, whereas single-phase chalcopyrite CuInSe₂ was obtained already at temperatures as low as 350 °C, with no significant improvement of crystallinity at higher temperatures. Moreover, single-phase CIGS was obtained only when the Ga content of the film was below 6 at.%. [81] Solar cell efficiencies above 10 % were achieved with CIGS absorbers [81], whereas the efficiencies with the ternary absorbers were lower, between 3-4 % for CGS [81, 136] and 6 % for CIS [81]. Substrate temperature did not affect the composition of flash evaporated films significantly [136].

Often, however, the compositions of flash evaporated films have been found to depend on substrate temperature. Merino et al. [137] studied the flash evaporation of CIS and CIGS from two types of crucibles and at different substrate temperatures. About 10 wt.% of Se powder was added to the crucible with the compound source, in order to prevent the formation of Se-poor films. The deviations of the film stoichiometry from the source material were minimized by carefully choosing the temperatures of crucible and substrate and keeping the deposition rate low enough. Most films were n-type but became p-type after annealing in Se vapor. Solar cells with standard CdS and ZnO were made by co-evaporating a thin CuIn₂Se₃.₅ layer on the absorber. The best efficiencies were 5.1 % for CIS and 6 % for CIGS. [137]

Amorphous CIS films have been deposited by flash evaporation onto unheated substrates [138, 139]. XRD peaks of CIS and Cu₃In₄ together with some unidentified peaks appeared when the substrate temperature was 200 °C or above. Also post-annealing at 350 °C resulted in the formation of CIS, Cu₃In₄ and In₂Se₃. The optimum conditions for the formation of CIS were determined to be substrate temperature 250 °C and post-annealing at 350 °C for 3-4 h. [139] On the other hand, Joseph and Menon [140] prepared crystalline p-type CIS films by flash evaporation from a single CIS source onto unheated substrates. Single-phase chalcopyrite films were obtained after annealing in vacuum at 50 °C for 1 h. [140]
In pulsed laser deposition (PLD), a rotating target that consists of the source material is heated by a pulsed laser beam. Victor et al. [141] prepared (112) oriented CIS thin films by PLD at a substrate temperature of 150 $^\circ$C. The chalcopyrite phase was present already in the as-deposited films, and the crystallinity was further increased by annealing in Ar at 500 $^\circ$C for 10 or 20 s. Kuranouchi et al. [142] deposited CIS films on unheated substrates and at a substrate temperature of 500 $^\circ$C. The films were post-annealed at 500 $^\circ$C in vacuum. The films deposited at room temperature exhibited (112) orientation after annealing. [142]

### 3.1.4. Chemical vapor deposition

Chemical gas phase deposition techniques such as metal organic chemical vapor deposition (MOCVD) [143-146] and close-spaced vapor transport [147, 148] have also been used for the preparation of CIS and CIGS thin films. A possible advantage is lower deposition temperatures than in evaporation processes.

McAleese et al. [143] deposited CIS thin films at 400-450 $^\circ$C by thermal MOCVD at low pressures from methyl-$n$-hexylselenocarbamate complexes of Cu(II) and In(III) (Cu(Se$_2$CNCH$_3$C$_6$H$_{13}$)$_2$ and In(Se$_2$CNCH$_3$C$_6$H$_{13}$)$_3$). The resulting films were close to stoichiometric, and their band gaps were estimated to be about 1.08 eV. XRD patterns of the films showed the main reflections of the chalcopyrite phase.

A plasma-enhanced CVD process was also reported [144] where hexafluoroacetylacetonate complexes Cu(hfac)$_2$ and In(hfac)$_3$ were used as the metal precursors and 4-methyl-1,2,3-selenadiazole as the Se source. H$_2$ was used as the carrier gas for the metal precursors. Deposition temperatures ranged from 150 to 400 $^\circ$C. The resulting films were Se deficient probably due to a Se loss during post-deposition cool-down in vacuum. [144]

Cu(hfac)$_2$ complexed with trimethylamine N(CH$_3$)$_3$ [145] or diethylamine NH(C$_2$H$_5$)$_2$ [146] have been used as the Cu precursors in atmospheric pressure MOCVD of CIS films. Trimethylindium In(CH$_3$)$_3$ and triethylindium In(C$_2$H$_5$)$_3$ were used as the In precursors and H$_2$Se as the Se precursor. H$_2$ was used as the carrier gas. The depositions were carried out at 400 $^\circ$C, and the resulting films exhibited strong (112) orientation regardless of the metal ratio. [145, 146] Solar cells fabricated from the CVD-grown films were not very efficient; the maximum open circuit voltage was 0.26 V [146]. For comparison, the open circuit voltages of high-efficiency devices are generally above 0.6 V [5, 84-87].
3.1.5. Close-spaced vapor transport

CIS [148], CGS [148], and CIGS [147, 148] thin films have been deposited by close-spaced vapor transport using iodine as a transport agent [147, 148]. The reactor is a vertical vacuum tube that contains the desired compound as a powder, a substrate, and solid iodine. The tube is heated, and the reaction starts when iodine vaporizes and reacts with the source powder to form gaseous metal iodides and Se₂. The gaseous species then react on the substrate surface, forming the desired compound and liberating iodine. Advantages of the method include low cost and the possibility to deposit films on large substrate areas. CuIn₁₋ₓGaₓSe₂ films with compositions identical to those of the source materials were obtained within the whole composition range (x from 0 to 1). Moreover, the films exhibited chalcopyrite structure, good surface morphology and p-type conductivity. [148] The morphology of the deposit was found to depend on the grain size of the source powder: large-grained source powder resulted in a bilayer structure where the initial (lower) layer consisted of considerably smaller grains than the upper one. The formation of the small-grained initial layer could be prevented using smaller-grained source powder which resulted in the formation of large-grained, smooth films. [147]

3.1.6. Low-temperature liquid phase methods

Non-vacuum deposition methods, including electrodeposition, electroless deposition, chemical bath deposition as well as spray pyrolysis and "particle-based methods" etc., have also been used for the preparation of CIS-based absorber films. These methods are inherently low-cost, since the deposition temperatures are generally low and the equipments are simple. Absorbers prepared by these methods need often at least a post-deposition treatment at high temperatures under selenium-containing atmospheres to obtain high-efficiency devices.

Bhattacharya et al. have studied extensively the preparation of CIGS solar cells from precursors prepared by electrodeposition [149], electroless deposition [150] and chemical bath deposition [151, 152]. A feature common to all their non-vacuum processes is that the film stoichiometry has to be adjusted after deposition by adding In, Ga and Se by physical vapor deposition at high temperatures. Although this may be considered as a drawback, these are nevertheless promising methods for the preparation of precursor films.

The electrodeposited precursors were deposited at room temperature from aqueous solutions containing CuCl₂, InCl₃, H₂SeO₄, GaCl₃ and LiCl. The resulting films were very Cu-rich but resulted in solar cell efficiencies of 15.4 % after the stoichiometry correction [149]. It must be noted that electrodeposition of CIS-based materials has been studied extensively, and the process described here uses the electrodeposited film only as a precursor layer. The numerous other electrodeposition processes will be described in more detail in Chapter 4.
Electroless deposition is based on redox reactions without an external current source. Cu-rich Cu-In-Ga-Se films were prepared from aqueous solutions containing CuCl₂, InCl₃, H₂SeO₃, GaCl₃, and LiCl, using a Fe electrode as the reductant. After stoichiometry correction, the films were used for the preparation of solar cells and a conversion efficiency of 13.4 % was achieved [150].

CIS [151, 153] and CIGS [152] thin films have been prepared by chemical bath deposition using sodium selenosulfate (Na₂SeSO₃) as the selenium precursor. In [153], the films were deposited at 40 °C using Cu(NH₃)₄²⁺ and In³⁺ complexed by citrate as the metal precursors. After post-annealing at 520 °C in air, VOC about 0.3 V was measured for a n-Si/p-CIS heterojunction [153]. Bhattacharya [151] used triethanolamine complexes of Cu⁺ and In³⁺ as the metal precursors. Cu-rich CIGS precursor films were deposited from solutions containing Cu(NO₃)₂, In(SO₃NH₂)₃, Ga(NO₃)₃, Na₂SeSO₃, triethanolamine, NH₄OH, and/or NaOH. After stoichiometry correction, the films were used as absorbers of solar cells that exhibited an efficiency of 7.3 % [152].

3.1.7. Spray pyrolysis

Single-phase chalcopyrite CIS and CIGS thin films with strong (112) orientation and p-type conductivity have been prepared by spray pyrolysis from acidic aqueous [154] and aqueous-ethanolic [155] solutions of CuCl₂, InCl₃, GaCl₃, and N,N-dimethylselenourea. The [Cu²⁺]/([In³⁺] + [Ga³⁺]) concentration ratios in the solutions were kept at 1, but an excess of selenium precursor was needed in order to compensate for the Se loss during deposition [154, 155]. Films deposited from aqueous solutions at 400 °C [154] were reported to be uniform and adherent to the substrate, with compositions close to those of the deposition solutions, whereas films deposited from aqueous-ethanolic solutions [155] at the same temperature were slightly (In+Ga)-rich, with a higher Ga/(In+Ga) ratio than in the deposition solution. At slightly lower substrate temperatures (360 °C) the films were either Cu- or (In,Ga)-rich, depending on the In/Ga ratio in the deposition solution, and their Ga/(In+Ga) ratios were closer to those in the deposition solutions. [155] Despite these promising results, the solar cell efficiencies reached with spray-pyrolysed absorbers were low.

3.1.8. Particle deposition techniques

The "particle deposition techniques" involve the deposition of particulate precursor materials onto substrates at low temperatures, and subsequent sintering under a chalcogen overpressure. The precursors are typically sub-micron powders of metals, alloys, oxides or chalcogenides, and they are deposited as inks, suspensions, or pastes by simple techniques such as printing, casting,
spraying, doctor-blading, spin-coating or dip-coating. The porous precursor layer then converts into a dense, large-grained film at the high (400 °C or above) sintering temperature. An important advantage of these methods is that since the metal ratio is fixed already in the precursor material, the stoichiometry of the final film is independent of thickness. Consequently, compositionally uniform films can be prepared over large areas and relatively large thickness variations can be tolerated. \[156, 157\] Cell efficiencies between 10 and 13 % \[156-158\], submodule efficiencies between 7 and 8 % (area 50-150 cm\(^2\)) \[156\] and module efficiency of 5 % \[157\] have been achieved by these techniques. An example of an ink-coating process was presented in \[158\]. Metallic powder containing Cu-In alloys was spread over a substrate as an ink and selenized under 5 % H\(_2\)Se/N\(_2\) at 440 °C for 30 min to form CIS. Solar cells prepared using the ink-coated absorber exhibited efficiencies of 10-11 %. \[158\]

### 3.2. Buffer layer

As was seen in Fig. 3, most high-efficiency CIGS solar cells of today have a thin (50 nm or less) CdS buffer layer and an undoped ZnO layer between the absorber and the transparent conducting oxide. The roles of CdS and undoped ZnO are related to some extent \[159\]. Although the open circuit voltages of high-efficiency CIGS devices are mostly determined by the electronic quality of the bulk absorber material \[31, 32\], the cell performances are nevertheless heavily influenced by the formation of the ZnO/CdS/CIGS heterojunction. \[159\] The role of the buffer layer is twofold: it both affects the electrical properties of the junction and protects it against chemical reactions and mechanical damage. From the electronic point of view, the CdS layer optimizes the band alignment of the device \[41, 160\] and builds a sufficiently wide depletion width that minimizes tunneling and establishes a higher contact potential that allows higher open circuit voltage values \[160\]. The buffer layer plays also a very important role as a "mechanical buffer" since it protects the junction electronically and mechanically against the damage that may otherwise be induced by the oxide deposition (especially sputtering, see next chapter). Moreover, in large-area devices the electronic quality of the CIGS film is not necessarily the same over the entire area, and recombination may be enhanced at grain boundaries or by local shunts. Together with the undoped ZnO layer, CdS enables self-limitation of electrical losses by preventing electrical inhomogeneities (defective parts of the CIGS film) from dominating the open circuit voltage of the entire device. \[159\]

The thickness as well as the deposition method of the CdS layer have a large impact on device properties. During the early days, the device structure consisted of a CuInSe\(_2\)/CdS junction with a thick (about 1-3 μm) CdS layer \[161-163\]. The CdS layers of these devices were most often prepared by evaporation at substrate temperatures between RT and about 200 °C, or in some cases by sputtering \[162\], and the CdS film was often doped either with In \[162\] or Ga \[58\]. In some cases, a CdS bilayer was used \[119, 164\], consisting of a thinner high-resistivity layer,
prepared either by evaporation [119] or chemical bath deposition [57, 119, 164] and a thicker low-resistivity layer, doped with 2 % In [164] or Ga [57]. Evaporated CdS has been used also in combination with the transparent conducting oxide layer [23, 165, 166].

Nowadays chemical bath deposition (CBD) is used almost exclusively [16, 24], and therefore this thesis focuses mainly on the effects caused by CBD-CdS. CBD is a liquid phase deposition method that is based on a spontaneous precipitation reaction between the constituent ions. The deposition is most often done in an aqueous solution. Precipitation occurs if the concentrations of the ions in solution are high enough so that their ionic product exceeds the solubility product (K_s) of the compound to be deposited [167]. The solubility product of CdS is about 10^{-28} [167], and thus its formation in a 1 mM Cd^{2+} solution starts when free the sulfide ion concentration exceeds 10^{-28} M^2 / 10^{-3} M = 10^{-25} M.

Commonly used Cd-precursors include simple compounds as CdSO_4 [86, 160], CdI_2 [45, 168], Cd(CH_3COO)_2 [59, 159], and CdCl_2 [169]. In order to slow down the reaction and to avoid the formation of Cd(OH)_2, the metal ion is usually heavily complexed by a ligand [168], most often NH_3 [45, 59, 86, 159, 160, 168, 169].

The most common sulfur precursor is thiourea NH_2CSNH_2 [45, 59, 86, 159, 160, 168, 169], the amount of which in the deposition solution is usually much higher than that of the metal precursor. The deposition is usually performed at an elevated temperature, and the solution is often stirred during the deposition. After immersing the substrates in the deposition solution at room temperature, the bath is heated to the desired temperature that is usually between 55 and 90 \textdegree C [45, 86, 160, 168, 169]. Deposition temperature influences strongly the film morphology and impurity content [160]. The formation of CdS occurs according to the following net reaction:

\[
[Cd(NH_3)_4]^{2+} + NH_2CSNH_2 + 2 OH^- \rightarrow 6 \text{CdS} + 4 NH_3 + CH_2N_2 + 2 H_2O \quad [3]
\]

Intermediate steps of the reaction involve the release of Cd^{2+} ions from the ammonia complex and the decomposition of thiourea by OH^- ions which releases S^{2-} ions. The mechanisms of CBD reactions have been studied extensively, and will not be discussed here.

In contrast to evaporated films [170], CBD films contain high amounts of oxygen-related impurities that originate from the deposition solution; the amount of oxygen in the films can be as high as 10-15 at.\% [45, 170]. Most of the oxygen is present as OH^- and H_2O. [45, 170] Thus, the composition of CBD-CdS films is more accurately stated as Cd(S,O,OH) [45]. Additional impurities such as C and N containing compounds result from side reactions of the chalcogen precursor [170]. The amount and identity of the impurities, and consequently the performance of the solar cell depend strongly on the CdS deposition conditions [160, 168, 171, 172]. For instance in [84], the conversion efficiency increased from 17.6 % to 18.5 % when the CBD-CdS
process was improved.

In addition to the CdS film deposition, the chemical bath modifies the absorber surface. The bath has been suggested to re-establish positively charged surface states and the surface type inversion by removal of O$_{Se}$ acceptors and creation of Cd$_{Cu}$ donors at the surface region [16, 77]. Thus the interface between CIGS and CBD-CdS is not abrupt but the layers are intermixed to some extent [44, 45]. Both Cu-and Cd-diffusion play a role, and the intermixing is further enhanced during the post-deposition air-annealing [159]. According to Nakada and Kunioka [45], Cu is substituted by Cd at the surface region of CIGS (depth about 10 nm). The diffusion depth of Cd atoms may be related to the thickness of the Cu-deficient surface layer (CuIn$_3$Se$_5$) of CIGS [45]. On the other hand, Heske et al. [44] have observed diffusion of Se and In from CIGS into CdS and the diffusion of S from CdS into CIGS. The extent of interdiffusion depends on the structure of the absorber: (220/204) oriented CIGS films have been found to allow more Cd atoms to diffuse into the CIGS film [86].

One advantage of CBD as compared to evaporation is that a complete, conformal coverage of the CIGS surface can be obtained at very low thicknesses: already 10 nm has been reported to be sufficient [173]. The coverage depends on deposition conditions, particularly on the metal/chalcogen precursor ratio, being better with higher metal/chalcogen precursor ratios [171].

Absorption of light in the CdS layer, the band gap of which is 2.4 eV [174], decreases the short circuit current density. The absorption of light in the ZnO, in turn, is a less severe problem since its band gap is higher, 3.2 eV [174]. Thus the reduced absorption in the thinner CdS layer results in a better device performance [57, 58]. The CdS layer must, however, be thick enough in order to obtain high open circuit voltage and fill factor [160]. If the CdS layer is too thin or does not exist at all, recombination in the space-charge region of CIGS increases, causing losses in $V_{OC}$, FF and spectral response [160]. Although the collection at short wavelengths (<550 nm) is enhanced in buffer-free devices, the collection at the longer wavelengths is poor [5], and consequently the conversion efficiencies are lower than those of standard devices. For instance, a conversion efficiency of 15 % was achieved without CdS, while the world record efficiency of 18.8 % with CdS was announced in the same publication [5]. Thus the optimum thickness of the CdS layer is a result of a compromise between increase in $V_{OC}$ and FF, and loss in $j_{SC}$ [160].

Performances of buffer-free devices have been found to improve upon dipping the absorbers in solutions containing only CdSO$_4$ and ammonia but no thiourea at 60-80 $^\circ$C before the deposition of the transparent conductor [160, 175, 176]. Further improvement of cell performances were observed upon applying a cathodic potential during the dip: Lincot et al. [175] achieved efficiencies of 11.3 % and 9.4 % with and without an applied potential during the dip, respectively. For comparison, an efficiency of 14.9 % was measured for a device with the standard CdS and 5.9 % for a buffer-free device without the CdSO$_4$-ammonia treatment [175].
These results support the idea of Cd incorporation and doping of CIGS [160]. According to Contreras et al. [5], their buffer-free device may, instead of being a buried junction, actually be a true heterojunction device. CdSO4-ammonia treatments in combination with a very thin CdS film provided enhanced spectral response in the blue part of the spectrum (short wavelengths) [160] as compared to the world record device. Since the jSC values of the modified devices were slightly higher and the Voc and FF similar to the high-efficiency devices with standard CdS, this approach may result in improved cell performances [160].

In order to decrease the optical absorption losses and to enhance the response in the short-wavelength region, alternative, more transparent buffer materials have been looked for. For instance, part of the Cd can be replaced by Zn to form (Cd,Zn)S, the band gap of which is higher [82, 174, 177]. Devaney et al [82] deposited conformal, uniform (Cd,Zn)S buffer layers by CBD from ZnCl2, CdCl2, NH4Cl, NH4OH and thiourea at 85°C. The Zn content was varied, and the Zn / (Zn+Cd) ratio in the best films was 15-20 %, resulting in a conversion efficiency of 12.5 % with absorbers prepared by co-evaporation [82]. Başol et al. [177], in turn, prepared (Cd,Zn)S buffers with about 10 % Zn by CBD from Zn-acetate, Cd-acetate, triethanolamine, NH4OH and thiourea at 55°C, and achieved conversion efficiencies between 10 and 13 % with absorber films prepared by particle deposition and subsequent selenization [156, 158].

Due to the environmental concerns associated with Cd-containing materials, serious efforts have been directed towards completely Cd-free buffer materials. The materials studied include Zn- and In-based materials such as sulfides, selenides, hydroxysulfides and -selenides that can be prepared by CBD [87, 125, 178-180], ion layer gas reaction (ILGAR) [181], MOCVD [182], atomic layer deposition (ALD) [183, 184], evaporation [26, 185-189] and sputtering [33]. Analogously to the Cd-pretreatments described above, Zn- and In-pretreatments have led to improved device performances as well, either with or without an additional buffer layer [150, 175, 181, 183, 190].

The conversion efficiencies of Cd-free devices are approaching those of the standard devices. Recently, a conversion efficiency of 18.1 %, close to those of the best CdS containing devices, was achieved using a CBD-ZnS buffer layer in combination with a CIGS absorber prepared by three-stage co-evaporation in a MBE system [87]. ZnS layer was deposited by CBD from ZnSO4, NH3 and thiourea at 80°C [87]. It contained a significant amount of Zn(OH)2 and ZnO phases and C and S impurities [191]. The band gap of the layer was, however, close to that of ZnS, 3.8 eV. When the structure was annealed in air at 200°C for 10 min [87], the O-related impurities studied by XPS were not affected but the cell performance improved markedly [191]. The improvement was probably due to diffusion of Zn into CIGS and the formation of a buried pn-homojunction on the absorber surface. This intermixing explains why the conversion efficiency is surprisingly high in spite of the large conduction band offset between CIGS and ZnS [87, 126, 191].
The diffusion of evaporated Zn into CIGS has also been observed [190]. Junction electron beam-induced current measurements revealed that the pn-junction of the Zn-diffused device is located in CIGS, in contrast to the devices with CdS and ZnO buffers where it is at the interface. The Zn-diffused buffer-free junction resulted in a conversion efficiency of 11.5 %. [190]

One of the Cd-free approaches of NREL [150] involved a Zn-diffused homojunction as well. The absorber was dipped in a ZnCl₂ solution and annealed at 200°C in air. Then the ZnCl₂ residue was removed from the absorber surface by washing in water and etching in concentrated HCl, followed by deposition of the ZnO bilayer by sputtering. The conversion efficiency of this device was 14.2 %. [150]

The CBD-ZnS was found to be sensitive to oxygen-induced damage during sputter deposition of undoped ZnO, and thus the device was prepared without the undoped ZnO layer [87]. The optimum thickness of the ZnS layer was 130 nm, indicating the need for reduction of shunt paths between CIGS and ZnO:Al [87]. As expected on basis of the higher band gap of the buffer, the cell exhibited higher quantum efficiency at short wavelengths than a CdS-containing cell [87, 191]. This resulted in a higher J_{sc} but the V_{oc} was lower, resulting in a similar conversion efficiency as the standard cell with CdS [87].

Showa Shell [124, 125] likewise uses a ZnS-based CBD-buffer for their absorbers prepared by selenization of sputtered metal layers. A Zn(OH,S)₃ film is deposited from a solution containing Zn-sulfate or acetate, NH₃, and thiourea at a temperature above 80°C, followed by annealing of the CIGS/buffer structure at 200°C for 15 min, resulting in a buffer layer with a composition of Zn(O,S,OH)₉ (oxyhydroxysulfide). [178] The efficiency of 12.5 % for a 30 cm x 30 cm module [124] demonstrates the suitability of this buffer deposition process to large substrate areas.

Kushiya et al. [178] studied also CBD-Zn(O,OH)₉ as buffer layers. The films were prepared by depositing Zn(OH)₂ at 60-80°C from similar solutions as Zn(OH,S)₃ but without thiourea, and annealed to yield Zn(O,OH)₉. The improved performance after annealing was attributed to conversion of hydroxide to oxide [178], and not to Zn diffusion as was done by Nakada and Mizutani [191]. The Zn(O,S,OH)₉ buffer of Kushiya et al. [178] suffered from sputter-induced damage during the ZnO deposition too, indicating the need for optimization of buffer thickness (currently 50 nm) and the ZnO deposition method. Again, gain at shorter wavelengths and loss at longer wavelengths was observed as compared to CdS. [178] Light soaking, especially in combination with annealing, caused a remarkable improvement of the cell performance [125] which was attributed to the release of H₂O molecules from the hydroxide during light soaking [192].

Ennaoui et al. [179] deposited Zn(S,OH) and Zn(Se,OH) buffer layers on CIGSS absorbers of
Siemens by CBD at 50 and 70 °C, respectively. The deposition solutions contained ZnSO₄, hydrazine hydrate, NH₃ and thiourea or selenourea. The buffer deposition process was somewhat different from those mentioned above since it involved a Zn pretreatment: the absorbers were first dipped for a few minutes into the heated solution that contained the metal precursor and the ligands, and the chalcogenide precursor solution was added only thereafter. The growth mechanism was self-limiting, allowing the deposition of very thin buffer layers with homogeneous surface coverages. [179] This approach led to total area efficiencies of 14.2 % both for Zn(S,OH) and for Zn(Se,OH) buffer layers. [179] Minimodule efficiencies (aperture area 20 cm²) achieved by Zn(Se,OH) were between 10.7 and 11.7 %, comparable to those achieved by the standard CdS buffer (11.7-12.7 %) [179].

Indium-based materials have resulted in high conversion efficiencies too. Hariskos et al. [180], for instance, deposited Inₓ(OH,S)ᵧ films on co-evaporated CIGS absorbers by CBD from InCl₃ and CH₃CSNH₂ (thioacetamide) at 70 °C. Post-anneal at 200 °C and light soaking resulted in an active area efficiency of 15.7 %. Compared to the standard CdS buffer, the Inₓ(OH,S)ᵧ buffer resulted in improved Vₐₒₚ, comparable FF and slightly reduced jₛₑ values. Again, gain in short-wavelength region and loss in long-wavelength region was observed. The former was due to the improved transparency of the buffer layer, and the latter due to the modification of the electrical properties of the absorber such as a reduced space-charge width [180].

Despite its above mentioned benefits, the CBD method has two disadvantages: first, the materials yield is low which causes large volumes of Cd-containing waste. This problem can be partially solved by recycling the deposition solution: the CdS-containing colloidal material is filtered off after deposition, the concentrations of NH₃ and thiourea are adjusted again to the initial level, and Cd-precursor is added. The properties of the CdS layers deposited from the recycled solution do not differ significantly from those deposited from fresh solutions. [193] The second problem is the difficulty of combining the CBD step as a part of an in-line vacuum process: if both the absorber and the ZnO bilayers are prepared by PVD methods in vacuum, the CBD step causes an undesirable interruption of the vacuum process.

Recently, a new deposition method called ion layer gas reaction (ILGAR) was developed for the deposition of buffer layers. It is a cyclic method that consists of application of a metal precursor on a substrate by dipping or spraying, drying the substrate, and the reaction of the metal precursor layer with gaseous hydrogen chalcogenide or water to form the corresponding metal chalcogenide or oxide. Thus, an evident advantage of ILGAR is that it produces less waste than CBD does. The resulting films are conformal, and the film thickness is easily controlled by the number of deposition cycles. [176, 181] The application of a ILGAR-ZnS buffer to Siemens absorbers resulted in total area conversion efficiency of 14.2 % when a Zn-pretreatment in a ZnCl₂-NH₃ solution was performed before the deposition of the ILGAR-ZnS [181].
To avoid the second problem of CBD, i.e., its incompatibility with PVD processes, "dry", potentially more easily integrated, gas phase methods for buffer deposition have been studied. Siebentritt et al. [182], for instance, deposited ZnSe buffer layers on Siemens CIGSS absorbers by photoassisted MOCVD using ditertiarybutylselenide as the selenium source and dimethylzinc or its adduct with triethylamine as the zinc sources. Hydrogen was used as the carrier gas, and UV illumination was used in order to enhance the decomposition of the Zn-precursor at low deposition temperatures. The highest total area efficiency, 11 %, was achieved with a 10 nm thick buffer layer deposited at 280 °C. This efficiency is the highest ever achieved with a MOCVD buffer. [182]

Lincot et al. [183, 184] deposited Zn(O,S), In₂Se₃ and Al₂O₃ buffer layers by ALD. Diethylzinc, indium acetylacetonate, and trimethylaluminum were used as the metal precursors, water as the oxygen precursor and H₂S as the sulfur precursor. Efficiencies of 10.4 % for ZnO₀.₈₅S₀.₁₅, 13.5 % for In₂Se₃, and 9 % for Al₂O₃ were achieved.

Konagai et al. used co-evaporation to prepare ZnSe [185] and ZnInₓSeᵧ [186] buffer layers. The best conversion efficiencies achieved by these buffers were 9.1 % [185] and 15.1 % [186], respectively, whereas the standard CdS resulted in 15.9 % [186]. ZnSe buffers prepared by pulsed MBE resulted in conversion efficiency of 11.6 % after light soaking [185]. In₂Se₃ (or InₓSeᵧ) buffer layers prepared by co-evaporation, have resulted in conversion efficiencies of 8.5 % on CIS [26] and 13 % on CIGS [187], whereas (In,Ga)ₓSe buffer layers prepared by the same method led to a conversion efficiency of almost 11 %. [188]

Delahoy et al. [189] prepared ZnIn₂Se₄ (ZIS) and ZnGaₓSeᵧ (ZGS) by evaporation of bulk material. The best efficiency achieved by ZIS was 11.6 %, and no light soaking effect was observed. For comparison, the standard CdS buffer resulted in efficiency of 16.3 %, whereas 10.3 % was measured for a buffer-free device. [189]

### 3.3. Oxide layer

The requirements for the electrical top contact of a CIGS device are: sufficient transparency in order to let enough light through to the underlying parts of the device, i.e., its band gap must be high enough, and sufficient conductivity to be able to transport the photogenerated current to the circuit without too much resistance losses. Nowadays, transparent conducting metal oxides (TCO) are used almost exclusively as the top contacts. Narrow lined metal grids (Ni-Al) are usually deposited on top of the TCO in order to reduce the series resistance. The quality of the front contact is thus a function of the thickness, sheet resistance, absorption and reflection of the TCO as well as the spacing of the metal grids [82].
Referring to Fig. 3, most devices utilize nowadays an oxide bilayer that consists usually of a thin (50-100 nm) high-resistivity layer, and a thicker (100-1500 nm) low-resistivity layer. The high-resistivity layer is most often undoped ZnO. Its benefit to the device performance is the increase of the $V_{oc}$ of the device by 20-40 mV [159]. Its role is not completely understood yet, however. As was discussed in Chapter 3.2., the resistive oxide layer provides together with the buffer a local series resistance that protects the device from electrical losses that may result from electronic inhomogeneities of the absorber. [159] Admittance spectroscopy and capacitance-voltage measurements [159] indicated that the presence of this resistive layer affects the electronic properties of the heterojunction only to the extent that is expected on the basis of band diagrams. The conducting part of the oxide bilayer is most often ZnO doped with either Al [5, 36, 57, 59, 81, 85, 95, 126, 157, 182], B [85, 86, 123, 177, 190, 194], or Ga [125, 179, 195]. Also tin doped In$_2$O$_3$ (In$_2$O$_3$:Sn, ITO) [26, 84, 94] is used commonly.

The oxide bilayer is most often deposited by sputtering [5, 26, 36, 57, 59, 81, 84, 85, 95, 97, 125, 126, 157, 179, 182, 195] with no intentional heating of the substrate [36, 57, 85, 195]. The resistive layer is sputtered in Ar/O$_2$ (about 0.1-2 %) ambient [34, 36, 57, 82]. Besides sputtering intrinsic ZnO, the resistive layer may also be made from a doped target (ZnO:2 wt.% Al$_2$O$_3$) [34, 57, 82], provided that the sputtering ambient contains enough oxygen. Oxygen is needed to prevent the formation of oxygen vacancies that might render even the undoped ZnO too conductive.

The conductive layer (most often ZnO:Al) is usually deposited from a ZnO:2 wt.% Al$_2$O$_3$ target in a pure Ar ambient. [36, 57, 82, 85] In some cases the sputtering ambient may contain a small amount of O$_2$ [34]. The ZnO:Ga layers of HMI [179] and Showa [195] are sputtered in Ar from ZnO:Ga$_2$O$_3$ targets with Ga$_2$O$_3$ contents of 3.4 wt.% [195] or 5.7 wt.% [179]. Doping of the oxide layer can be accomplished also by reactive sputtering as was done for instance by Hagiwara et al. [85] who sputtered their ZnO:B electrodes from an undoped ZnO target in B$_2$H$_6$-Ar mixture.

Although sputtering is a fast and well-known deposition method for oxide thin films, its disadvantage is that it may damage the underlying layers [87, 178]. Damage occurs especially during the deposition of the resistive layer that is done in an Ar/O$_2$ ambient. Nakada et al. [87], for instance, had to leave the resistive ZnO layer out and deposit a thicker ZnS buffer instead.

In order to reduce the damage caused by oxide deposition, softer, less damaging deposition methods have been studied. The most important of these are MOCVD [98, 123, 177, 190, 194, 196] and ALD [175, 183, 184, 197] since they can be used for the deposition of the whole bilayer. In some cases only the resistive part of the oxide bilayer is deposited by a softer method, for instance MOCVD [198], ALD [196], ILGAR [176], CBD [178] or electrodeposition [199] and the conductive part by sputtering.
The less damaging oxide deposition methods are especially useful for the preparation of buffer-free devices where the protecting interlayer is absent. These buffer-free approaches have shown promising results: a conversion efficiency of 12.7 % was measured for a device where the resistive ZnO layer was prepared by MOCVD and the conductive layer by sputtering [198]. For comparison, a device with MOCVD-ZnO bilayer showed efficiency of 11.5 % [190]. ALD-ZnO bilayers have resulted in even higher efficiencies, up to 14.9 % with Cd pretreatment [175]. The combination of the two methods has also proven to be successful: a conversion efficiency of 12.1 % was measured for a device with ALD-grown resistive ZnO layer and MOCVD-grown conductive layer [196].

Bär et al. [176] measured a total area efficiency of 14.6 % for a device where part of the ZnO layer was deposited by ILGAR and the rest was sputtered. Cell preparation involved pretreatment in an aqueous CdSO₄-NH₃ solution. The success of the ILGAR method was demonstrated by the somewhat higher efficiency than for the standard device, 14.1 %. [176] Gal et al. [199] measured a conversion efficiency of 11.4 % for a device with electrodeposited resistive ZnO layer and sputtered conductive ZnO layer. For comparison, the efficiency of a standard device with CdS and sputtered ZnO bilayer was 13.3 % [199].
4. Cathodic one-step electrodeposition of CuInSe₂ and Cu(In,Ga)Se₂ thin films

Electrochemical techniques for the preparation of CIS-based films include one-step deposition, sequential deposition of binary compounds, and deposition of elemental layers followed by annealing either under an inert or a reactive atmosphere. The sequential electrodeposition techniques were discussed in Chapter 3.1. This chapter focuses on one-step electrodeposition of CuInSe₂ and Cu(In,Ga)Se₂ thin films.

Electrodeposition is a liquid phase thin film deposition method that is based on electrochemical reactions (reductions or oxidations) carried out using an external power supply. In addition to the power supply, at least two electrodes are needed, between which the current flows in the deposition solution. One of the electrodes is a working electrode, or substrate on which the film grows, and the other one is a counter electrode. The film growth occurs most often via reduction reactions, i.e., the working electrode is a cathode. Usually a three-electrode setup is used where the third electrode is a reference electrode with respect to which the electrochemical potential of the working electrode is controlled or measured. If the potential of the working electrode is controlled, the resulting current may be measured, and vice versa. Deposition is often carried out at a constant potential (potentiostatically) or at a constant current (galvanostatically), but voltage and current waveforms or pulses can be used too.

In cathodic one-step electrodeposition of compound semiconductor thin films, simultaneous reduction of all the constituent ions at the same potential in suitable proportions is necessary in order to achieve the desired film composition. This can be achieved by two ways: balancing the diffusion fluxes of the constituent ions to the cathode, or employing the induced co-deposition mechanism. The balancing of fluxes can be done by careful optimization of the deposition conditions, that is, adjusting the concentrations in the solution as well as the deposition potential. If the reduction potentials are far apart, they can be shifted closer to each other by complexing the more noble ions with a ligand that forms strong complexes with them and thereby shifts their reduction potentials towards more negative (less noble) values. The disadvantage of the flux balance approach is that the concentration and potential ranges for the formation of stoichiometric product are often narrow, and thus small, unavoidable variations in concentrations and potential may result in large changes in the film compositions. This deteriorates the reproducibility and may render upscaling to larger substrate areas problematic.

When induced co-deposition mechanism is exploited, the film composition is determined by thermodynamics [6, 7]. Using the most well-known system, CdTe, as an example, the more noble ion (H₃TeO₅⁺ in the case of CdTe) that reduces at a less negative potential, deposits first on the electrode surface (Eq. 4) and induces the reduction of the less noble ion (Cd²⁺) and the formation of CdTe (Eq. 5) at less negative potentials than where the reduction of Cd²⁺ to metallic
Cd (Eq. 6) would take place.

$$\text{HTeO}_2^+(aq) + 3\text{H}^-(aq) + 4 \text{e}^- \rightarrow \text{Te(s)} + 2\text{H}_2\text{O}$$ \[4\]

$$\text{Te(s)} + \text{Cd}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{CdTe(s)}$$ \[5\]

$$\text{Cd}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Cd(s)}$$ \[6\]

The reason for the underpotential reduction of the less noble ion (Cd$^{2+}$) is the energy released in the compound formation. When the concentrations in the deposition solution are chosen so that the solution contains a large, 10-100 fold, excess of the less noble ion (Cd$^{2+}$), the reaction (4) is almost exclusively followed by the reaction (5) rather than by the reaction (4) itself. When the potential is adjusted less negative than that required for the reaction (6), the deposition of stoichiometric CdTe is ensured over a range of electrolyte compositions and electrode potentials. This kind of induced co-deposition process, employed most widely for CdTe but also for many other binary compound semiconductors [200-202] is much less sensitive to the unavoidable variations in the electrolyte compositions than processes which rely on balancing the diffusion fluxes. In addition, small potential drops across large substrates will have minimal effects. [6, 7]

Electrodeposition of CIS-based thin films has been studied a lot by several groups since 1983. The majority of the existing electrodeposition processes for CIS thin films are based on the flux balance approach. Although the reaction mechanisms in the Cu-In-Se system have been studied thoroughly [203-209], and the underpotential assimilation of In into the films has been frequently noticed and mentioned in the literature, the induced co-deposition approach had not been utilized in the preparation of CIS thin films prior to [I]. This is illustrated by the fact that one-step electrodeposition of CIS has usually been carried out from solutions where the Cu and Se precursor concentrations are of the same order of magnitude, and only In precursor is present in excess. Under such conditions, film stoichiometry is determined by the deposition potential and the ratio of diffusion fluxes of Se and Cu to the substrate surface. Electrodeposition processes based on balancing the diffusion fluxes will be described in this chapter, and the only process that utilizes induced co-deposition will be described in Chapter 7.

One reason for the lack of electrodeposition processes utilizing the induced co-deposition is that the electrodeposition of CIS occurs via the formation of copper selenide which does not follow the induced co-deposition mechanism [203, 204]. The complicated behavior of the Cu-Se system may be attributed to the following facts. First, the reduction of Se$^{4+}$ to Se requires a large overpotential, i.e. its actual reduction potential is much more negative than the corresponding standard reduction potential ($E_E = +0.556 \text{ V vs. Ag/AgCl}$ [210]), and this potential is also dependent on the electrode surface. Second, the standard reduction potentials of Cu$^+$ and Cu$^{2+}$...
(E = +0.298 V and +0.115 V vs. Ag/AgCl [210], respectively) are close to the observed reduction potential of Se$^{4+}$ and, depending on the required Se overpotential, may be either more positive or more negative than that of the Se$^{4+}$ ions. As a consequence, independent co-deposition rather than induced co-deposition is observed in the Cu-Se system [203, 204]. Further complications may arise from the passivating nature of Se deposited at room temperature [204]. These issues can, however, be overcome [I] as will be described in Chapter 7.

One-step electrodeposition of CIS is usually carried out from an aqueous acidic solution containing simple compounds of Cu$^{2+}$ or Cu$^{+}$ and In$^{3+}$, most often sulfates [104, 203, 206-208, 211-218] or chlorides [149, 150, 161, 163, 166, 209, 211, 216, 217, 219-224]. Because of the limited solubility of Cu$^+$ compounds and the instability of the free Cu$^+$ ions in aqueous solutions, Cu$^{2+}$ compounds are used considerably more frequently than Cu$^+$ compounds. The most popular Se precursor is SeO$_2$ which dissolves into mildly acidic solutions in the form of HSeO$_3^-$ [210], but Na-selenosulfate [161] has been used too. Acidic solutions are used because the reduction of HSeO$_3^-$ is facilitated in acidic solutions [210].

The deposition solution contains often a complexing agent in order to shift the reduction potentials of Cu and In closer together and/or to improve the film quality. The most popular complexing agent is citric acid [161, 203, 206-209, 212, 213, 215, 225] that acts also as a pH buffer, but other ligands such as ammonia [151, 161], triethanolamine [151], ethylenediamine [226], ethylenediaminetetraacetic acid (EDTA) [222], and thiocyanate [211, 216, I-IV] can be used too. Sometimes a supporting electrolyte such as sulfate (K$_2$SO$_4$) [203, 206, 218] or chloride (LiCl [149, 150] or NaCl [222]) is added.

Electrodeposited CIS and CIGS films are usually amorphous or poorly crystalline and consist of small grains. They tend to be Cu-rich and contain frequently degenerate Cu$_{2-x}$Se phases that are detrimental to the device performance. Cu-rich films have generally larger grain sizes than stoichiometric or In-rich films. The films may also contain impurities that originate from the aqueous deposition solution or from the complexing agents. For the above reasons, the films require at least annealing under an inert atmosphere prior to completing the device preparation. Very often the film stoichiometry needs to be corrected too, for instance by annealing under a Se-containing atmosphere and/or by selective etching in cyanide-containing solutions.

Bhattacharya [151] was the first one to electrodeposit CuInSe$_2$ thin films. The deposition solution contained 0.018 M In$^{3+}$, 0.018 M Cu$^+$ and 0.025 M SeO$_2$ as well as 0.006 vol.% triethanolamine and 0.007 vol.% NH$_3$ at pH of about 1. The films were deposited on SnO$_2$-F coated glass substrates at -0.7 V vs. SCE at room temperature, and the solution was stirred during the deposition. Film compositions were not analyzed, but X-ray diffractograms of the post-annealed films (1 h at 600 $^\circ$C under Ar) showed many of the reflections of the chalcopyrite phase. [151]
Vedel et al. [203-205] have studied systematically the reaction mechanisms involved in the electrodeposition of CuInSe$_2$ thin films. The film formation reactions were studied on SnO$_2$ electrodes, both by cyclic voltammetry and deposition experiments. Similar results were obtained in sulfate and citrate solutions [203]. Since the deposition of CIS proceeds via the formation of copper selenide, the binary Cu-Se system was studied first [204]. The reduction potential of Se$_4^+$ was found to shift to the positive direction in the presence of Cu$^{2+}$ in the solution. In fact, the deposition of Se in reasonable quantities was observed only in the presence of Cu$^{2+}$ in which case the formation of copper selenide enables the deposition of Se. Thus the Cu-Se system does not follow the induced co-deposition mechanism in the same way as the Cd-Te system does [6, 7].

In contrast, the behavior of the Cu-Se system in the presence of In$^{3+}$ is analogous to that of Te in the presence of Cd$^{2+}$, that is, copper selenide induces the formation of CIS. In the presence of an excess of In$^{3+}$ in the solution, the film composition is controlled by the Se$_4^+$/Cu$^{2+}$ flux ratio ($\alpha$) arriving at the electrode. [203] At low values of $\alpha$, two co-deposition processes were observed, and the resulting films consisted of either CIS + Cu$_2$Se or CIS + Cu. If the Se$_4^+$ flux is in excess (at high $\alpha$), the two processes merge and only CIS + In$_2$Se$_3$ are obtained. [203] When In$^{3+}$ concentration is not high enough, the electrodeposition process is limited by diffusion of all the three ions. Consequently, the film composition is determined by both flux ratios $\alpha$ and $\beta$, where $\beta$ is the In$^{3+}$/Cu$^{2+}$ flux ratio. [205]

Pottier and Maurin [206] studied the electrodeposition of Cu-In, Cu-Se and CIS thin films on Ti and Ni rotating disc electrodes from acidic sulphate and citrate solutions containing 5-10 mM CuSO$_4$, 10-20 mM In$_2$(SO$_4$)$_3$, 10-20 mM SeO$_2$, 60-80 mM K$_2$SO$_4$, and 0-80 mM Na-citrate. The presence of citrate was found to decrease the plateau current of copper by modifying the diffusion coefficient of Cu$^{2+}$ ions and slowing down its reduction rate. Small amounts of citrate in the deposition solution resulted in the formation of smooth films, whereas large amounts caused powdery deposits. The formation of smooth layers of crystalline compounds (Cu$_9$In$_4$, Cu$_2$Se or CIS) was correlated with a plateau on the polarization curves. The current in the plateau region was found to be limited both by mass transport via convective diffusion and by a slow surface process. The slow surface process was thought to suppress non-compact morphologies and allow crystallization of a material with the desired composition. Films deposited outside the potential range corresponding to the plateau had poor crystallinity, morphology, and composition. Thus the main function of the complexing agent was to promote the formation of well-defined crystallized compounds. [206]

Molin et al. [207, 208] studied the reactions in the citrate system on Ti electrodes. The deposition solution consisted of 3 mM CuSO$_4$, 6 mM In$_2$(SO$_4$)$_3$, 5 mM SeO$_2$, and 0.4 M citric acid at pH 1.7. By shifting the deposition potential to the negative direction, it was possible to obtain CuSe,
Cu$_3$Se$_2$, CuInSe$_2$, and In-enriched CuInSe$_2$ from the same deposition solution [207, 208]. The formation of CIS was proposed to occur by the reaction of In$^{3+}$ with Cu$_3$Se$_2$ [208]. The potential range of CIS formation widened when the solution was stirred during the deposition. Moreover, the deposition rate as well as the current efficiency were found to increase but the film morphology did not change. The potential ranges for the formation of the various compounds depend on the total conductivity of the solution, cathode surface area (ohmic drops) and electrolyte temperature [207]. Therefore the addition of Na$_2$SO$_4$ as a supporting electrolyte was found to narrow the potential range of CIS formation due to increase of the solution conductivity [208]. The kinetic study [208] revealed that in the citrate system, the rate of electrodeposition is determined by ion mass transfer and a chemical reaction at all potentials. The chemical reaction determining the rate of electrodeposition was proposed to be the reduction of SeO$_3^{2-}$ by metallic Cu [208], analogously to the mechanism proposed by Massaccesi et al. [204]. The addition of Se$^{4+}$ to Cu$^{2+}$ solution was also found to shift the reduction potential of Cu$^{2+}$ to more positive values and increase the limiting current [208] which is in agreement with [204]. Similar behavior was observed also in solutions where thiocyanate ions were used as the complexing agents [211].

Oliveira et al. [209] studied the formation of CIS on Mo and on itself by cyclic voltammetry and growth experiments. Their electrolyte contained 0.4 M citric acid, 3 mM Cu(NO$_3$)$_2$, 3 mM InCl$_3$, and 5 mM SeO$_2$ at pH 2.0. In agreement with the other authors [203, 208], the formation of Cu$_x$Se and its reaction with In$^{3+}$ in the solution was observed which leads to assimilation of In into the film. In contrast to most of the other studies on CIS electrodeposition from citrate solutions, however, they observed the reduction of Se$^{4+}$ at a more positive potential than that of Cu$^{2+}$ and suggested therefore the formation of copper selenide via induced co-deposition, analogously to [I]. [209] When the cyclic voltammograms were measured on a previously deposited CIS film, the currents corresponding to the reductions of Cu$^{2+}$ and In$^{3+}$ began to flow earlier and were stronger than on a Mo film. This suggests a surface-induced deposition mechanism. The current corresponding to the reduction of Se$^{4+}$ to Se on CIS, in contrast, was smaller than on Mo which was attributed to the formation of an insulating film. [209] Parallel to Vedel et al. [203], similar results were obtained in sulfate and citrate solutions [209]. On the other hand, other authors [225] have observed cathodic shifts in the reduction potentials of both Cu$^{2+}$ and HSeO$_2^{+}$ on Ti substrates upon addition of citrate ions, whereas the reduction potential of In$^{3+}$ was unaffected. These differing results are an indication of the effect of the substrate on the electrochemical reactions.

Herrero et al. [212] deposited CIS films on Mo substrates from solutions containing 3 mM CuSO$_4$, 3 mM In$_2$(SO$_4$)$_3$ and 5 mM SeO$_2$ at pH 1.7 with 0.4 M citric acid as the complexing agent. Cu$_x$Se was found to be present also in the In-rich samples. They also studied the effects of post-deposition treatments such as annealing for 15 min under Ar (at 200 to 600 °C) and etching in 0.5 M KCN at 40 °C for 2 min. The film characteristics were found to depend on the
sequence of post-deposition treatments. Etching of the as-deposited films resulted always in In-rich films, whereas etching after annealing resulted in more stoichiometric films since it removed smaller amounts of Cu and Se. This is in agreement with other published data [226, IV]. The as-deposited films consisted of different components and the formation of CIS was observed only after annealing. Only Cu-rich films could be identified as chalcopyrite, XRD patterns of In-rich films did not show the characteristic chalcopyrite reflections but only those common to chalcopyrite and sphalerite. No evidence of secondary phases was seen when the deposition potential was between -0.5 and -0.8 V vs. SCE, whereas films deposited at -0.4 V showed the peaks of Cu2Se after annealing. [212] In a later publication [227], annealing was studied in more detail. Annealing under a Se atmosphere was reported to result in a higher degree of crystallization than annealing in vacuum. Improved adhesion and film crystallinity were observed when a thin Cu layer was electrodeposited on Mo prior to the CIS deposition. The improved crystallinity was attributed to a small copper selenide excess that originated from the underlying Cu layer when the structure was annealed in a Se atmosphere. The surfaces of the CIS films were found to be In-rich [227].

An In-rich surface layer was detected also on CIS films deposited from uncomplexed chloride solutions [219, 220]. The films were deposited at -0.5 V vs. SCE, and the typical deposition solution contained 0.004 M CuCl2, 0.008 M InCl3, and 0.008 M H2SeO3 at pH 1.5. The as-deposited semicrystalline films became polycrystalline after annealing at 500 °C under Ar for 30 min. Also the grain size increased upon annealing. The bulk of the film was found to be Cu-rich which was attributed to the growth mechanism: Cu and Se deposit during the first seconds, forming a Cu2Se layer which enables the assimilation of In3+ ions. At the beginning, more Cu is deposited than In, but the amount of In increases as the deposition proceeds. That is why the film surface is poor in Cu. [219] This explains why photoelectrochemical (PEC) measurements showed p-type conductivity and C-V measurements n-type conductivity [220]. PEC measurements characterize mostly the bulk of the film where the light is mainly absorbed, whereas C-V measurements give information about the surface since the depletion region is on the film surface [220].

On the other hand, C-V measurements performed by Xu et al. [213] on electrodeposited and vacuum-annealed CIS thin films showed p-type conductivity for films with In-rich bulk compositions. Their CIS films were deposited from solutions containing 1 mM CuSO4, 10 mM In2(SO4)3, 5 mM H2SeO3 and 25 mM Na-citrate at pH 3. [213]

Ueno et al. [214] deposited CIS films on Ti substrates from 10 mM CuSO4, 25 mM In2(SO4)3, and 30 mM SeO2 at pH 1 at 50-55 °C. They observed that In can be co-deposited with Cu and Se at 0.6 V more positive potentials than its equilibrium reduction potential. The as-deposited films deposited between 0 and -0.6 V vs. SCE showed XRD reflections of CIS and Cu2Se whereas only those of CIS were found for films deposited at -0.8 V. After annealing, the reflections
became stronger and the chalcopyrite phase could be identified. Films deposited at -1.0 V showed the reflections of metallic In in addition to those of CIS. The films were metal-rich, as evidenced by high dark currents observed during photoelectrochemical measurements. The films were compositionally nonuniform and exhibited poor surface morphologies. Moreover, the deposition process was not very reproducible and was very sensitive to small changes in conditions since photoelectrochemical measurements showed different conductivity types for films deposited under nominally identical conditions. [214]

CIS thin films electrodeposited on SnO₂ substrates from uncomplexed chloride solutions containing 5 mM of both CuCl₂ and InCl₃ and 10 mM SeO₂ at pH 1.5 were reported to be In-rich and Se-deficient in the beginning of the deposition. Cu/In ratio of 1 was obtained at -0.5 V vs. SCE. Poorly adherent films were deposited at -0.7 V or more negative potentials due to H₂ evolution. The as-deposited films had XRD peaks of CIS and In₂Se₃, but only the characteristic chalcopyrite peaks were detected after annealing under N₂ at 350°C. The amount of Se decreased during annealing, as did the Cu/In ratios of both Cu-rich and In-rich films. The Cu/In ratio for the stoichiometric films did not change. A low conversion efficiency of 1.5 % (active area 0.01 cm²) was obtained for a film with Cu/In ratio of 0.95. [166]

CIS films deposited on rotating Ti electrodes at -0.8 V vs. SCE from 3.7 mM CuCl₂, 22 mM InCl₃ and 3.6 mM SeO₂ at pH 1.5 were reported to contain small amounts of binary phases, possibly In₆Se₇ that is formed together with CIS. The broad and weak XRD peaks of the as-deposited films became sharper and more intense after annealing. The films were n-type and had rough surface morphologies and were thus potentially suitable for photoelectrochemical (liquid-junction) solar cells. [221]

Raffaello et al. [215] prepared all-electrodeposited CIS/CdS pn-junctions that showed good I-V characteristics in the dark. The p-type CIS films of these structures were deposited from solutions containing 1 mM CuSO₄, 10 mM In₂(SO₄)₃, 5 mM SeO₂, and 25 mM Na-citrate. [215] They prepared also CIGS films by electrodepositing CIS films on previously electrodeposited CuGa₂ layers [228].

Se-rich CIS films were deposited on Mo from ethylenediamine solutions containing Cu²⁺, In³⁺ and H₂SeO₃ at pH 1.7. The as-deposited films consisted of CIS, Cu₅Se, In₅Se and Se. Annealing decreased the Se amount to 50 at.% but did not affect much the metal ratio. Cu-rich films were conductive and showed the chalcopyrite reflections with preferred (112) orientation after annealing at 350°C or above whereas In-rich films were resistive and showed only the reflections of the sphalerite phase. Thus, the transition from chalcopyrite to sphalerite with composition was observed for the first time for electrodeposited CIS thin films. Chemical treatments in Br₂ (0.05-0.1 vol.%) / MeOH and 0.1-0.5 M KCN solutions were studied too. The Br₂ treatment caused surface leveling but did not change the film composition whereas KCN was
found to dissolve selectively Cu and Se. The sequence of the post-deposition treatments was again found to be of importance and the results obtained were similar to those in [212], [226].

Ugarte et al. [222] used EDTA as the complexing agent. Their deposition solutions contained 10 mM of both CuCl₂ and SeO₂, 15 mM InCl₃, 10-20 mM EDTA, and 50 mM of glycine, NaCl and HCl each. The pH was 2. The films were deposited on SnO₂ films and on Ti sheets potentiostatically at -0.45 to -0.75 V vs. SCE. The as-deposited films showed some XRD peaks of CIS, and the crystallinity improved upon annealing. The films were etched in a cyanide solution prior to the photoelectrochemical measurements that were performed in 0.5 M K₂SO₄ at pH 4.5. Despite the high dark currents (caused by the metal-rich film composition as stated earlier by Ueno et al. [214]), the measurements revealed that the films were p-type. The best photoresponses were achieved when the deposition solution contained EDTA. [222]

KSCN has been used as the complexing agent too [211, 216]. Due to its selectivity towards Cu⁺ ions it is a very promising ligand. The acidic deposition solution in [211] contained 2.75 mM CuCl, 2.55 mM In₂(SO₄)₃, 3 mM SeO₂ and 4 M KSCN. The deposition solution was modified later by increasing the pH to 5, decreasing the KSCN concentration to 2 M and adding 0.4 M acetate buffer [216]. The effect of electrolyte composition was studied by varying the concentrations of the metal and selenium precursors. The In:Se ratio in the films was reported to change with the deposition potential, while the Cu percentage in the films was approximately equal to its concentration percentage in the electrolyte. Annealing under a Se atmosphere increased the crystal size more than annealing under Ar. In addition to the chalcopyrite phase, also binary Cu-Se and In-Se phases were detected in the annealed films. [216].

In addition to potentiostatic electrodeposition, CIS thin films have been prepared galvanostatically. [104, 161, 163] Chowles et al. [104] electrodeposited near stoichiometric CIS films at 7 mA on graphite from uncomplexed solutions containing CuSO₄, In₂(SO₄)₃ and SeO₂ at pH 1. Annealing under Ar at or above 400 °C for 15 min caused the loss of excess Se and improved the surface morphology.

The deposition solution of Sahu et al. [163] contained 0.73 mM CuCl, 5.27 mM InCl₃ and 0.9 mM SeO₂ at pH 1.0. Upon scanning the potential to the negative direction during the cyclic voltammetry measurement, Se was observed to deposit first, followed by copper and later indium. Stoichiometric CIS films were reproducibly deposited on Mo sheets at 6 mA cm⁻² from stirred solutions at room temperature. The as-deposited films were amorphous, and XRD peaks of CIS as well as those of In₂Se₃ and CuSe were detected after annealing. Annealing resulted in a loss of excess Se already at 150 °C, and at 350 °C also In was lost. The as-deposited and the annealed films were p-type, with high carrier concentrations of 3.63x10²⁰ cm⁻³, and resulted in low open circuit voltages and short circuit current densities of 0.188 V and 0.056 mA cm⁻², respectively. [163] For comparison, other devices with electrodeposited absorbers have shown...
open circuit voltages of about 0.36 V, short circuit current densities between 25 and 35 mA cm\(^{-2}\), and conversion efficiencies between 4.8 and 7 % [164, 218].

The process of Garg et al. [161] was somewhat different since they used sodium selenosulfate (Na\(_2\)SeSO\(_3\)) as the Se source. Moreover, the deposition was carried out from basic solution (pH > 9). CuCl and InCl\(_3\), complexed with ammonia and citric acid, were used as the metal precursors. The Cu/In ratio in the films was found to decrease with increasing deposition current. Stoichiometric, Cu-rich, or In-rich films were obtained by controlling two variables: deposition current density and the solution composition. The as-deposited films showed the chalcopyrite XRD reflections which became more intense after annealing for 5 min at 400 °C. All films were p-type, but resulted in poor photoresponses (\(V_{oc} 0.165 \text{ V}, j_{sc} < 1 \text{ mA cm}^{-2}\)). [161]

CIS thin films have been prepared by pulse plating too. [217, 223, 224]. The advantages of pulse plating over normal dc electrodeposition include high momentary current densities as well as improved stoichiometry and smoother surface morphology, caused by rearrangement and partial dissolution of the film during the off-time. The duty cycle, or the ratio of the on-time to the total time (\(t_{on}/(t_{on} + t_{off})\)) is thus an important variable. Improved deposit distribution and adhesion and a lower impurity content have been reported for the pulse-plated films as compared to the dc electrodeposited ones. [217, 223, 224]

Lokhande [223] deposited CIS thin films by pulse plating on various substrates (Ti, oxidized Ti, Mo, MoSe\(_2\), stainless steel and SnO\(_2\) film) from 0.1 M InCl\(_3\), 0.02 M CuCl and 0.05 M SeO\(_2\) at pH between 1 and 2. The depositions were carried out at room temperature with a duty cycle of 33 % (5 ms on, 10 ms off). Stoichiometric CIS films were deposited when the pulse height was between -0.8 and -0.9 V vs. SCE. The deposition process was poorly controlled since the first few films from a fresh solution were reported to be always Se-rich, and the Cu:In ratio increased when the deposition time was longer than 30 min. Cu-rich films consisted of larger grains than In-rich films. The as-deposited films were poorly crystalline but the crystallinity improved upon annealing at 300 °C under Ar. On the other hand, Se loss was observed at temperatures higher than 200 °C. [223]

Edamura and Muto [217] deposited CIS on ITO/glass from 2 mM CuSO\(_4\), 20 mM InCl\(_3\), 2 mM SeO\(_2\) at pH 1.5. The depositions were carried out at room temperature, and the optimum deposition parameters were found to be: a duty cycle 33 % and a pulse height -0.8 V vs. SCE. The on- and off-times were 2 and 4 ms, respectively. Longer on-times resulted in nonuniform films, and shorter in scarce deposition. The as-deposited films had poor crystallinity, but chalcopyrite reflections with (112) preferred orientation were identified after annealing in air at 300 °C for 1 h. The films had compact columnar structure and good adhesion. Hall measurements showed them to be n-type with a carrier concentration of 1.0x10\(^{17}\) cm\(^{-3}\). The band gap was 0.99 eV, and the absorption coefficient was high, between 10\(^4\) and 10\(^5\) cm\(^{-1}\) at energies
Nomura et al. [224] deposited CIS thin films on Mo/glass from 1 mM CuCl₂, 12 mM InCl₃, and 2 mM SeO₂ at pH 1.8 and 40 °C. Nonpulse potential of 0.0 V vs. SCE, and pulse potentials between -0.2 V and -0.9 V were used. The optimum pulse potential was found to be -0.7 V. Pulse duration was 1 ms, and the duty cycle was varied between 10 and 100 %. Se/metal ratio of about 1 was maintained for a wide range of pulse potentials for duty cycles between 20-50 %. Smoothest surface was obtained for a duty cycle of 33 %. The as-deposited films were again poorly crystalline, but annealing under N₂ for 30 min improved the crystallinity, and preferred (112) orientation was observed with duty cycles of 33 % and higher. Composition of the almost stoichiometric films did not change upon annealing unless the temperature was very high. Annealing above 500 °C resulted in Se deficiency and decomposition into binary compounds. [224]

Recently, an interesting new electrochemical technique, molecular layer electrodeposition (MLE) [229], was introduced for the preparation of CuInSe₂ thin films. The deposition solution that contains all the constituent ions flows over a horizontal cathode in a thin layer flow cell. The cathode potential is controlled by a potentiostat. In addition to the advantages of normal or pulsed electrodeposition, this technique offers an additional controllable parameter, i.e., the volume of the flowing solution. At low solution volumes, the amount of ions available for reactions is limited. Consequently, the film composition may differ from that obtained from a larger volume of solution that contains a relatively unlimited supply of ions. [229] Moreover, since the deposition is carried out from a single electrolyte that contains all the constituent ions, the method is simpler than electrochemical atomic layer epitaxy (ECALE) [230] that is based on alternating underpotential electrodeposition of the elements from separate solutions. Although the formation of stoichiometric CIS films by MLE has not been reported yet, the technique certainly shows promise. [229]

Generally, the CIS-based absorbers prepared by one-step electrodeposition have not resulted in high-efficiency devices. Electrodeposited CIGS films can anyhow be used as precursors for the preparation of high-efficiency devices (15.4 %) [149, 150], if the film composition is adjusted by evaporation of In, Ga and Se afterwards. The CIGS precursor films of [149, 150] were deposited at room temperature from unstirred acidic solutions (pH about 2) containing 0.02-0.05 M CuCl₂, 0.04-0.06 M InCl₃, 0.01-0.03 M H₂SeO₃, 0.08-0.1 M GaCl₃ and 0.7-1 M LiCl. The deposition potential was -1.0 V vs. Pt, and the resulting film composition was CuIn₀.₃₂Ga₀.₀₁Se₀.₉₃ before and CuIn₀.₇₂Ga₀.₄₇Se₂.₀₅ after the PVD step [149, 150].

The highest conversion efficiencies achieved by one-step electrodeposited CuInSe₂ absorber films without subsequent annealing under Se-containing atmospheres are those of Qiu and Shih [164, 169]. Their CIS films were deposited from a single solution that contained "ions and
complexes of Cu, In, and Se". [162] The films were post-deposition annealed at temperatures between 300 and 420 °C for 20 min under Ar or in vacuum, and resulted in conversion efficiencies of 7% [164] with a Mo/CIS/CdS structure and in 6.3% with a Mo/CIS/CdS/ZnO structure [169].

Kampmann et al. [218] electrodeposited CuInSe₂ films on large substrate areas (80 cm²) from solutions containing 1.0 mM CuSO₄, 3.0 mM In₂(SO₄)₃ and 1.7 mM SeO₂ at pH 2.4. 0.3 M K₂SO₄ was used as the supporting electrolyte. The as-deposited films were selenized at 500 °C under elemental selenium atmosphere, and resulted in conversion efficiency of 4.8%.

Guillemoles et al. [42] obtained a conversion efficiency of 6.5% using electrodeposited CIS films. The films were deposited according to [203] and post-deposition annealed under elemental Se atmosphere for 20-30 min at 400-450 °C. The Cu/In ratio did not change upon annealing but the Se content increased, partly due to the formation of MoSe₂ between Mo and CIS. After annealing, the characteristic chalcopyrite reflections were observed also for the In-rich films, and they were also strongly (112) oriented. Cu-rich films had larger grain sizes and less preferential orientation. [42]
5. Characterization of thin films and their growth processes by methods based on cyclic voltammetry

Cyclic voltammetry is one of the most widely used electroanalytical methods for semiquantitative studies in redox systems. It is based on varying the potential applied to the working electrode of an electrochemical cell at a constant rate, and monitoring the current caused by electrochemical reactions taking place during the scan. The scan is typically chosen to start at such a potential value where no electrochemical reactions occur in the system. At a predetermined switching potential, the direction of the scan is reversed and the potential is scanned back to the initial value. The shape, location, sign, and magnitude of the current peaks or waves provide information about the electrochemical reactions.

5.1. Cyclic voltammetry combined with electrochemical quartz crystal microbalance

More detailed information about the reactions taking place in an electrochemical system can be gained when cyclic voltammetry is used in combination with other methods, for instance electrochemical quartz crystal microbalance (EQCM).

The operation of the quartz crystal microbalance (QCM) is based on the converse piezoelectric effect: an electric field applied across a piezoelectric material induces a mechanical strain in that material. The magnitude of the strain is proportional to the applied potential and its direction depends on the polarity of the potential. Therefore, when an oscillating electric field is induced perpendicular to the crystal surface, it produces a mechanical oscillation in the quartz crystal. The resonant frequency of the oscillation depends on the mass and thickness of the crystal which allows the use of the quartz crystal in the determination of very small mass changes. The quartz crystal microbalance consists of a thin quartz crystal which has thin metal film electrodes on both sides. The electrodes are used to induce the oscillation in the quartz crystal, and in the electrochemical application (EQCM), one of the electrodes serves also as the working electrode in the electrochemical cell. [231, 232]

During the measurement, the potential of the EQCM electrode is changed and both the current at the electrode and the frequency change of the quartz crystal are recorded simultaneously. As a primary data, an EQCM measurement gives the electrode potential dependence of current and frequency change ($\Delta f$) of the QCM crystal. Integration of the current gives the charge consumed ($\Delta Q$) that is related to the mass change of the deposit according to Faraday’s law (Eq.7)

$$\Delta Q = Fz\Delta m/M$$

[7]
where \( F \) is the Faraday constant (96485.31 C mol\(^{-1}\)), \( z \) the number of electrons consumed in the reaction, \( \Delta m \) the mass change of the deposit during the reaction, and \( M \) the molar mass of the corresponding chemical species.

The frequency change (\( \Delta f \)) may be converted to a deposit mass change \( \Delta m \) by the Sauerbrey [233] equation:

\[
\Delta f = -2 \Delta m f_0^2/A(\mu \rho)^2 = -K\Delta m \tag{8}
\]

where \( f_0 \) is the fundamental frequency of the crystal, \( A \) the area of the electrode, and \( \mu \) the shear modulus (\( \mu = 2.947 \times 10^{11} \) g cm\(^{-1}\) s\(^{-2}\)) and \( \rho \) the density \( \rho = 2.648 \) g cm\(^{-3}\) of quartz. All the constants in the equation can be included into a single constant (\( K \)) which can be determined experimentally, using a deposition reaction that has a Faradaic efficiency of 100 %. As seen from the Equation (8), a mass increase causes a decrease in the resonant frequency and a mass decrease results in a higher frequency. The mass sensitivity of the EQCM can be calculated from the \( K \) value if the electrode area is known. The theoretical mass sensitivity for a 5 MHz quartz crystal is 17.7 ng Hz\(^{-1}\) cm\(^2\), or, expressed differently, 56.6 Hz cm\(^2\) \( \mu \)g\(^{-1}\) which means that a mass change of 1 \( \mu \)g per square centimeter causes a frequency change of 56.6 Hz. The mass sensitivity for a 10 MHz crystal is 4-fold (4.4 ng Hz\(^{-1}\) cm\(^2\) or 226.4 Hz cm\(^2\) \( \mu \)g\(^{-1}\)) since the sensitivity depends on the square of the resonance frequency. Depending on the resolution of the frequency counter, mass changes as low as 10 ng cm\(^{-2}\) can be detected [231].

The high sensitivity of the EQCM makes it suitable for in situ mass measurements on a monolayer level or below. On the other hand, it can be used for studies on bulk processes too since the Sauerbrey equation is valid as long as the resonant frequency change caused by mass loading is less than 2 \% of the fundamental frequency, that is, 0.1 MHz for a 5 MHz crystal. [234]. EQCM has been used for various applications, including studies on underpotential deposition of metals, formation of surface oxides and self-assembled monolayers, adsorption and desorption as well as monitoring of ion transport phenomena and electropolymerization. Bulk electrodeposition and electroless deposition as well as corrosion of metals have been studied too. [231, 232, 234]

Due to the complex electrochemistry of chalcogens and their compounds, EQCM studies in these systems are of particular interest. Deposition and dissolution reactions occurring during cyclic voltammetry measurements and/or growth experiments have been studied in several semiconductor and oxide systems including Te [235], Cd-Te [236, 237], Pb-Te [238], Cd-Se [239, 240], Pb-Se [241], Ag-Se [242] Cu-Se [243, III], Cu-In-Se [III], Cu-S [244], In-S [245], Fe-S [246], Pb-S [247] and Zn-O [248]. EQCM measurements allow to distinguish between electrochemical reactions leading to deposition or stripping and those occurring in the solution.
phase [235]. The depositing and stripping species can be identified, thus yielding information about the deposition and stripping mechanisms, even to the extent that enables in situ compositional analysis of compound semiconductor thin films either during growth [242, 243] or stripping [237, 239, 240]. Further, Faradaic efficiencies of reactions can be evaluated by comparing $\Delta Q$ and $\Delta f$ data [236], and naturally the $\Delta f$ data alone can be used for monitoring growth rates.

For characterizing the electrochemical and other processes at the electrode surface, the primary EQCM data may be treated by different ways. A simple and straightforward way is to combine the Sauerbrey equation (Eq. 8) with the Faraday’s law (Eq.7). By defining the signs of $z$, $\Delta m$, and $M$ appropriately [II, III], one obtains

$$\Delta f = K\Delta Q M/F z = (K/F)(M/z)\Delta Q$$  \hspace{1cm} [9]

If the frequency change ($\Delta f$) is plotted as a function of the charge consumed ($\Delta Q$), then the slope of such a plot ($d\Delta f/d\Delta Q$) may be used for the calculation of $M/z$ values:

$$M/z = (d\Delta f/d\Delta Q)(F/K)$$  \hspace{1cm} [10]

The theoretical $M/z$ is simply the change of the molar mass of the deposit divided by the number of electrons involved in the reaction. The experimental $M/z$ values obtained by this way do not involve any hypothesis about the reaction mechanisms but still represent directly the primary data. On the other hand, a theoretical $M/z$ value is easily calculated for any suggested reaction. An agreement between the observed and theoretical $M/z$ values gives thus a quite solid proof for the dominance of the suggested reaction while differences call attention for other mechanisms. [II, III]

Figure 5 [II] presents examples of $\Delta f$ vs. $\Delta Q$ plots for the deposition of Cu$_{2-x}$Se at different potentials, as well as the corresponding $M/z$ values calculated from the slopes of the plots. The different slopes obtained for different deposition potentials may indicate changing film compositions, morphologies, or growth mechanisms at the different potentials.
5.2 Cyclic photovoltammetry and photoelectrochemical characterization under chopped illumination

Similar to cyclic voltammetry, cyclic photovoltammetry and photoelectrochemical characterization are semiquantitative techniques that give information of photoactivity and conductivity type of semiconducting films. In both techniques, the working electrode is illuminated during the measurement. Often chopped illumination is used but it is also possible to make the measurements separately in the dark and under illumination and compare the difference afterwards. Usually polychromatic illumination (white light) is used but monochromatic illumination can be used too as long as the energy of light is higher than that of the band gap of the semiconductor. If the film is photoactive, a photocurrent is detected, i.e., the current is higher under illumination than in the dark. The direction of the photocurrent gives information of the conductivity type of the film. Cyclic photovoltammetry can be used for in situ detection of formation of a photoactive deposit, and photoelectrochemical measurements for evaluating photoactivity as a function of, for instance, different post-deposition treatments.

When a semiconductor is immersed in a solution, an electric field develops at the solid/liquid interface via charge transfer reactions between the two phases. The electric field enables the separation of charge carriers, analogously to a pn-junction of a Schottky junction. Illumination of the semiconductor causes a dramatic increase of the concentration of minority carriers, e.g., electrons in a p-type semiconductor. The electric field drives the photogenerated minority carriers towards the semiconductor/liquid interface, where they may participate electrochemical reactions in the solution with a suitable redox species. Thus a p-type semiconductor is capable of reducing more species under illumination than in the dark, causing an increase of cathodic current while...
the anodic current remains unaffected. An n-type semiconductor acts the other way: anodic current is enhanced under illumination as compared to dark, whereas cathodic current is not affected. Semiconductor/liquid junctions are the basis of photoelectrochemical solar cells that are used for production of electricity or fuels. The photoelectrochemistry on semiconductor electrodes has been studied a lot [249, 250].

In cyclic photovoltammetry, a cyclic voltammogram is measured in the deposition solution under illumination. Formation of a photoactive deposit during the measurement can easily be detected by comparing the currents in the dark and under illumination. Thus the potential range corresponding to the formation of a semiconducting compound as well as the conductivity type of the compound can be identified. [251] Cyclic photovoltammetry has been used for the reaction mechanism studies in a variety of semiconductor systems [251], also in the Cu-In-Se system [207, 252, 253, IV].

Photoelectrochemical (PEC) measurements, in turn, give information about the film properties after deposition. The measurements are performed in an electrolyte solution that contains a redox species the potential of which is in a suitable position with respect to the band edges of the semiconductor so that charge-transfer reactions between the semiconductor and the solution are possible. [249, 250] Photoelectrochemical measurements allow a simple and fast characterization of the semiconducting properties of the film, and they have been used especially for comparative studies between different post-deposition treatments.

PEC measurements on p-type CIS films are often performed in sulfate solutions, either sulfuric acid [106, 220, 254] or mildly acidic K₂SO₄ [222, IV] but other solutions such as the polysulfide (NaOH/Na₂S/S) can be used too [116, 214]. In addition to conductivity type and the magnitude of photocurrent, PEC measurements can be used for the determination of flat-band potential. The band edge positions of CIS are strongly dependent on the electrolyte and on the surface chemistry of the film which may complicate the interpretation of the data, however [254, 255].
6. Experimental

6.1. Deposition of films

The films were electrodeposited potentiostatically, i.e., at constant potential, using either an Autolab PGSTAT20 or a Metrohm 626 potentiostat with a three-electrode setup. A Ag/AgCl/3 M KCl electrode was used as the reference electrode to which all the potentials in this work are referred to, and a Pt plate or a graphite rod was used as the counter electrode. Substrates were 100 nm Mo or ITO films sputtered on glass, and they were washed ultrasonically in water and ethanol before the depositions. The ZnO films were deposited using a standard three-electrode setup, and the Cu$_{2-x}$Se and CIS films using a two-compartment three-electrode arrangement where the anodic and cathodic compartments were separated with a salt bridge in order to prevent side reactions at the anode. The salt bridge was filled with saturated KCl solution, and 0.1 M KCl solution served as the counter electrolyte in the anodic compartment. All films were deposited from unstirred solutions.

The Cu$_{2-x}$Se and CIS depositions were carried out at room temperature from acidic (pH between 2.4 and 3.1) solutions containing CuCl, SeO$_2$, and in the case of CIS also InCl$_3$. In order to enable film growth by the induced co-deposition mechanism, thiocyanate ions (SCN$^-$) were used as complexing agents for the Cu$^+$ ions to shift their reduction potentials to the negative direction so that selenium deposits first and induces the formation of Cu$_{2-x}$Se and CIS. The thiocyanate ion concentration had to be very high (2-4 M) in order to prevent precipitation of the sparingly soluble CuSCN. At such high SCN$^-$ concentrations the Cu$^+$ ions were mainly present as [Cu(SCN)$_4$]$^{3-}$ complexes [256]. The concentrations of the Cu and In precursors were chosen to be considerably higher than that of the Se precursor, in order to prevent the deposition of elemental selenium.

The doped ZnO thin films were electrodeposited at 80°C from aqueous 0.05 M zinc nitrate baths containing additionally either InCl$_3$ or Al(NO$_3$)$_3$. The InCl$_3$ concentration was varied between 0.0005 M and 0.005 M and the Al(NO$_3$)$_3$ concentration between 0.001 and 0.01 M.

All solutions were prepared using ion-exchanged water and chemicals of minimum 98 % purity.

6.2. Characterization of films

Film morphology was studied by a Zeiss DSM 926 scanning electron microscope (SEM) at the Electron Microscopy Unit at the University of Helsinki. Approximate cation ratios and film thicknesses were determined by a Link ISIS energy dispersive X-ray spectrometer (EDX) using...
20 kV accelerating voltage. The results were calculated using a GMR Electron Probe Thin Film Microanalysis program [257]. Density values of 5.99 g/cm³ for Cu₂Se, 5.77 g/cm³ for CuInSe₂, 5.6 g/cm³ for ZnO and 10.2 g/cm³ for Mo [174] were used in the thickness calculations.

More accurate film compositions as well as the impurity contents were determined by ion beam measurements that involved Rutherford backscattering spectrometry (RBS) and time-of-flight elastic recoil detection analysis (TOF-ERDA), performed at the Accelerator Laboratory of the University of Helsinki. Ion beams of ⁴He⁺ at 6.5 MeV were used for RBS and ¹⁹⁷Au⁹⁺ at 48 MeV TOF-ERDA measurements. The ion beams were generated by a tandem EGP-II accelerator.

The crystallinity of the films was examined by Philips MPD 1880 and Bruker AXS D8 powder X-ray diffractometers, using Cu Kα radiation. The step width was 0.02° and the time per step was 1, 2, or 10 s.

The thicknesses of the ALD-grown ZnO films were determined by fitting their transmission spectra according to [258]. The transmission spectra were measured with a Hitachi U-2000 UV-vis spectrophotometer at a wavelength range of 370-1100 nm.

### 6.3. Characterization of film growth processes

Preliminary studies on film growth processes included cyclic voltammetry and cyclic photovoltammetry that were performed using the Autolab PGSTAT20 potentiostat and the three-electrode setup described previously. In addition to Mo and ITO films, also previously deposited Cu₂Se and CIS films were used as the substrates. The cyclic photovoltammograms were measured under chopped polychromatic illumination provided by a 50 W halogen lamp. More detailed characterization was done by using the above mentioned techniques in combination with the electrochemical quartz crystal microbalance (EQCM). The potential scan rate was 10 mV/s in all measurements, whether performed with or without the EQCM.

For the combined cyclic voltammetry and EQCM studies, the Autolab PGSTAT20 potentiostat was equipped with EQCM (Institute of Physical Chemistry, Polish Academy of Sciences in Warsaw, Poland) [259]. A standard three electrode configuration was employed where one of the electrodes of the quartz crystal served as the working electrode. A Fluke timer/counter PM6680B was used for recording the frequency change of the quartz crystal. The quartz crystals were unpolished 5 MHz AT-cut plano-convex crystals with evaporated Au film electrodes on both sides, and they were operated at the fundamental mode. The crystals were mounted vertically at a PTFE holder [259] where the projected area of the Au electrode was 0.236 cm².

The electrolytes used in the EQCM studies of Cu and In depositions contained 4 M KSCN and
0.05 M CuCl or 0.05 M InCl₃, respectively. The solutions used for the studies on the binary selenides contained additionally 0.001 M SeO₂. The solution used in the studies on the ternary Cu-In-Se system contained 0.05 M CuCl, 0.05 M InCl₃ and 0.001 M SeO₂ in 4 M KSCN. In all solutions that contained Cu or In precursors, 4 M KSCN was used as the complexing agent. The electrolyte for the Se deposition study contained 0.001 M SeO₂ and 0.1 M KCl as the supporting electrolyte. pH was 3 in all solutions except in the In and In-Se solutions where it was 2.

6.4. Post-deposition treatments

In order to make their properties to match better to those required for photovoltaic quality material, the CIS films were subjected to post-deposition treatments that included crystallinity improvement by annealing as well as stoichiometry correction either by etching or by depositing an In₂Se₃ layer on the CIS film.

The annealing was done in a tube furnace under a N₂ atmosphere either at 400 °C for 15 min or at 500 °C for 2.5 h. In either case, the films were allowed to cool down to room temperature slowly under N₂. Some of the CIS films were dipped in a saturated NaCl solution before or after annealing, to study the effect of Na⁺ ions because they should have beneficial effects on film morphology, conductivity and defect distribution (see Chapter 2.1.1).

To improve the film stoichiometry, the excess Cu and Se were removed by etching the films in 0.5 M KCN aqueous solution for different time periods (30 s-30 min). KCN etch is the traditional way to remove the excess copper and chalcogen from chalcopyrite thin films [205, 212, 222].

An alternative attempt to correct the film stoichiometry without etching was made by depositing an In₂Se₃ film on the CIS film before annealing at 500 °C. In some cases, the CIS film was previously annealed at 400 °C. The In₂Se₃ films were electrodепosited according to Massaccesi et al. [260] at 80 °C except that InCl₃ was used instead of In₂(SO₄)₃. The deposition solution contained 0.1 M K₂SO₄, 0.01 M H₂SO₄, 0.002 M InCl₃ and 0.001 M SeO₂. The deposition potential was -0.6 V and the deposition time ranged from 5 to 30 min, resulting in film thicknesses between about 22 and 134 nm.

The effects of the post-deposition treatments on the photoactivity of the films were studied by measuring photoelectrochemical (PEC) scans in 0.5 M K₂SO₄ at pH 4.0-4.5. The PEC characterization was carried out using the Autolab PGSTAT20 potentiostat and polychromatic illumination provided by a 50 W halogen lamp. The light was modulated with a timer relay and the distance between the lamp and the working electrode was held constant, about 25 cm. A light chopping sequence of 0.5 s on, 0.5 s off was used. The CIS films in the PEC studies were about 400-500 nm thick and they were deposited at -0.5 V vs. Ag/AgCl.
6.5. Preparation of solar cells

Both substrate and superstrate solar cell structures were prepared (see Figures 3 and 4 in Chapter 2.1). Most of the solar cells were prepared using 400-500 nm thick CIS films that were deposited at -0.5 V. The films were annealed and etched as described in the previous chapter. Some of the devices were prepared using the annealed CIS+In$_2$Se$_3$ films that were not etched. In some experiments, thicker CIS films of about 1 µm were used.

The CdS films were prepared by chemical bath deposition (CBD). The pretreated CIS films were immersed in solutions containing in most cases 1 M NH$_3$, 0.001 M Cd(CH$_3$COO)$_2$ and 0.06 M thiourea ((NH$_2$)$_2$CS) at 60 or 80 °C. [261] Some of the CdS films were deposited at 65 or 90 °C using cadmium sulfate as the metal precursor according to [160]. The thicknesses of the CdS films were either 50 or 150 nm. Some devices were prepared without the CdS film.

The ZnO layers were prepared either by electrodeposition, ALD, or sputtering. The electrodeposited as well as the ALD-grown ZnO films were prepared in our laboratory and the sputtered films were prepared either in Laboratoire d’Electrochimie et de Chimie Analytique, Ecole Nationale Supérieure de Chimie de Paris or in Hahn-Meitner-Institut (HMI) in Berlin.

All electrodeposited ZnO:In films used in the solar cells were deposited from solutions where the InCl$_3$ concentration was 0.005 M, and the ZnO:Al films from solutions where the Al(NO$_3$)$_3$ concentration was 0.001 M. The deposition potential for the ZnO:In films was -1.2 V unless told otherwise, and that for the ZnO:Al films -1.1 V. The undoped ZnO films used in some devices were deposited at -0.8 V from 0.05 M Zn(NO$_3$)$_2$ solutions at 80 °C [262]. The thicknesses of the undoped and doped electrodeposited ZnO films were about 100 and 400 nm, respectively.

The ALD-ZnO films were prepared in a flow-type F120 ALD reactor (ASM-Microchemistry Ltd.) at 250 °C using dimethylzinc (DMZ), trimethylaluminum (TMA) and water as the precursors. The temperature of the DMZ source was -20 °C, and TMA and water were used at RT. For the Al doped ZnO films, 3% of the metal precursor pulses were TMA pulses. The pulse and purge lengths were 0.2 and 0.5 s for DMZ, 2 and 10 s for TMA and 1 and 3 s for water, respectively. The resistivities of the undoped and doped ALD-ZnO films were 2-4x10$^{-2}$ and 5-10x10$^{-3}$ Ω cm, respectively, and their thicknesses were 50 and 350 nm, respectively.

The superstrate structures were prepared by depositing first a CdS film on ITO and then a CIS film on the CdS. The structure was annealed under N$_2$ at 400 °C for 15 min. Au films (70 nm) were evaporated on the CIS for back contacts.
6.6. Electrical characterization

Information about the conductivity type of the CIS films was obtained by three methods: cyclic photovoltammetry, photoelectrochemical measurements and thermoelectric probe measurements. The descriptions of the first two methods were given in Chapter 5.2. The thermoelectric probe method allows the determination of conductivity type by the sign of thermal voltage generated by a temperature gradient [263]. The measurements were made using a CEM DT-3900 digital multimeter with one of the two tips at room temperature and the other cooled to the temperature of liquid nitrogen.

Sheet resistances of the ALD-grown ZnO films were measured by the four point probe method using a Keithley 2400 Source Meter and Alessi C4S Four Point Probe head.

Current-voltage (I-V) characteristics of the devices were measured in dark and under illumination of a 50 W halogen lamp, using the Keithley 2400 source meter. Source delay of 0.1 s and step widths of either 0.01 or 0.05 V were used.

For the devices prepared with the electrodeposited ZnO films, it was necessary to evaporate thin (10 to 100 nm) Al films for the front contacts. This was because of the low conductivity of the electrodeposited ZnO films. The ZnO films prepared by the gas phase methods were conductive enough so that no additional contacts were needed.

A Hewlett-Packard 4284A Precision LCR meter was used for the capacitance-voltage measurements. The LCR meter measures the complex impedance (the magnitude and phase angle of impedance) that is the total opposition of the device or the circuit to the alternating current flow at the measurement frequency. The capacitance is then calculated using equivalent circuit modes that contain a capacitor and a resistor, either in parallel or in series with each other. The most appropriate of the two possible modes is chosen according to whether the parallel or the series resistance of the circuit is more significant. For polycrystalline thin film solar cells, the parallel resistance seems to be more significant [264], and thus the parallel circuit mode was used here. The measurement frequencies were between 100 kHz and 1 MHz, and the amplitude of the alternating current was 5 mV. Measuring direction was usually from reverse to forward, and the voltage step was between 0.01 and 0.1 V, in most cases 0.05 V. In order to ensure that the junctions were rectifying, I-V curves were measured from the same contact dots.

The electrical front contacts for the measurements (when needed) were done by evaporating thin (about 10 to 100 nm) Al dots on the samples by electron beam evaporator IM9912 (Instrumentti Mattila Oy) with a Telemark 241 electron beam source. Contact area was either 0.052, 0.204, or 3.14 mm². The back contacts for the capacitance measurements were made by contacting a thin Cu wire to the Mo substrate using In as a solder.
7. Results and discussion

This chapter summarizes the main results of this thesis. The results that are not included in the publications, i.e., the capacitance results and most of the solar cell results, are discussed in more detail here.

7.1. Cu$_{2-x}$Se films

7.1.1. Film growth [I]

In order to achieve suitable conditions for induced co-deposition, the Cu$^+$ ions were complexed with SCN$^-$ ions to form strong complexes [270]. The concentration of the SCN$^-$ ions had to be much higher than that of Cu$^+$ ions in order to avoid the precipitation of insoluble CuSCN. The complex formation equilibria depend also on the pH of the solution. For instance, a SCN$^-$ concentration of 4 M was required for Cu$^+$ concentration of 0.05 M at the pH range used in this study. Under these conditions, the Cu$^+$ ions were mainly present as [Cu(SCN)$_4$]$^{3-}$ [256]. The complexing shifted the reduction potentials of the Cu$^+$ ions to the negative direction, so that the reduction of HSeO$_3^-$ occurred at less negative potentials than that of [Cu(SCN)$_4$]$^{3-}$. The deposition of Se thus induced the reduction of [Cu(SCN)$_4$]$^{3-}$ ions at potentials less negative than where the deposition of metallic Cu started.

The induced co-deposition mechanism allowed a wide potential range where the film composition was nearly constant. The films deposited between -0.3 and -0.6 V contained about 60-65 % Cu, corresponding to Cu$_{2-x}$Se with x = 0.15-0.5. At potentials less negative than -0.3 V, the current density was very low, corresponding probably to the deposition of Se. At potentials more negative than -0.6 V, the current density increased due to the deposition of Cu-rich material, and at even more negative potentials metallic Cu was deposited. The growth rate of the Cu$_{2-x}$Se films was about 0.07-0.1 $\mu$m h$^{-1}$.

The as-deposited films were amorphous but showed reflections of the cubic Cu$_{2-x}$Se phase [265] after annealing at 400 $^\circ$C under N$_2$ for 15 min. SEM studies revealed that the surface morphology of most of the Cu$_{2-x}$Se films was rough, containing rather large pores. Similar structures have been presented in the literature for Cu$_3$Se$_2$ [207] and CuSe [111] films.
7.1.2. Growth processes studied by cyclic voltammetry and EQCM [I, II]

The electrochemical behavior of the Cu-Se system was studied first in a preliminary manner by measuring cyclic voltammograms on Mo films and on previously deposited Cu$_{2-x}$Se films. More detailed characterization of the deposition processes was performed by using cyclic voltammetry in combination with EQCM. The reaction mechanisms were ascertained by growth experiments performed with the EQCM at constant potentials.

The reduction of HSeO$_3^-$ to Se on the Au electrode was found to proceed via a 4e$^-$ net reaction (Eq. 11) at the potential range between +0.12 and -0.38 V. At low overpotentials, i.e., in the positive end of this potential range, the deposition of Se was found to proceed via a surface-induced process that resembles the underpotential deposition (UPD) of metals.

\[
\text{HSeO}_3^{\text{aq}} + 5 \text{H}^+ + 4 \text{e}^- \rightarrow \text{Se} + 3\text{H}_2\text{O} \quad [11]
\]

Theoretical $M/z = 19.74 \text{ g mol}^{-1}$

The formation of H$_2$Se via the reduction of the deposited Se film (Eq. 12) was found to begin at -0.41 V which was verified also by measuring the scans on a previously deposited Se film in 0.1 M KCl. The reduction potentials of the Se species were found to be strongly dependent on the electrode surface.

\[
\text{Se} + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{Se} \quad [12]
\]

Theoretical $M/z = -39.48 \text{ g mol}^{-1}$

The reduction of [Cu(SCN)$_4$]$^{3-}$ to metallic Cu according to the reaction (13) started at -0.65 V, which is considerably more negative than the equilibrium reduction potential of Cu$^+$ (+0.298 V) [210], thus verifying the strong complexing ability of the SCN$^-$ ions towards Cu$^+$. Thus the reduction potential of the [Cu(SCN)$_4$]$^{3-}$ complex was prominently more negative than those observed for either HSeO$_3^-$(+0.12 V) or Se (-0.41 V).

\[
\text{[Cu(SCN)$_4$]}^{3-} + \text{e}^- \rightarrow \text{Cu} + 4 \text{SCN}^- \quad [13]
\]

Theoretical $M/z = 63.55 \text{ g mol}^{-1}$

The reduction of [Cu(SCN)$_4$]$^{3-}$ on a previously deposited Se film was found to begin at -0.25 V, i.e., at considerably more anodic potential than on the Au electrode. This is apparently due to the formation of Cu$_{2-x}$Se according to the reaction (14).
Se(s) + 2 [Cu(SCN)₄]³⁻(aq) + 2 e⁻ Ĵ Cu₂Se(s) + 8 SCN⁻(aq) \[14\]

Theoretical $M/z = 63.55 \text{ g mol}^{-1}$

The current flow ceased at about -0.4 V, indicating that the initial Se surface was now completely covered with Cu₂₋₃Se. The current began to flow again at about -0.63 V where the deposition of metallic Cu started. Figure 6 shows the cyclic voltammograms for [Cu(SCN)₄]³⁻ on Au and on Se.

![Cyclic voltammograms measured in a [Cu(SCN)₄]³⁻ solution on Au (solid line) and on Se (dotted line) surfaces](image)

This result verifies that Se induces the reduction of [Cu(SCN)₄]³⁻ and thus the formation of Cu₂₋₃Se before the deposition of metallic Cu begins, and it was further supported by the fact that the formation of Cu₂₋₃Se from a solution containing both [Cu(SCN)₄]³⁻ and HSeO₅⁻ was observed to occur between -0.23 and -0.65 V.

Thus, during the cyclic voltammogram measurement, Se deposited first according to reaction (11), followed by the formation of copper selenide. The formation mechanism of copper selenide changed gradually from reaction (14) to reaction (15) as the previously formed Se film became covered with Cu₂₋₃Se. The deposition of metallic copper began only at the more negative potentials.

$2 [Cu(SCN)₄]³⁻(aq) + HSeO₅⁻(aq) + 5 H⁺(aq) + 6 e⁻ Ĵ Cu₂Se(s) + 8 SCN⁻(aq) + 3H₂O \[15\]

Theoretical $M/z = 34.34 \text{ g mol}^{-1}$

The observed M/z values were in excellent agreement with the theoretical ones, thereby
illustrating good Faradaic efficiencies and thus the absence of side reactions, and most importantly the validity of these reaction mechanisms.

In contrast to the case with cyclic voltammetry measurements, the \( M/z \) values obtained during the growth experiments at constant potentials were not equal: at \(-0.3\) V the \( M/z \) value was \(33.40\) g mol\(^{-1}\) corresponding to reaction (15) whereas at \(-0.5\) V a larger value, \(50.04\) g mol\(^{-1}\), was obtained, i.e. the apparent mass of the deposit increased faster at \(-0.5\) V than at \(-0.3\) V although the current densities were equal. Since the film compositions (measured by EDX) were similar at both potentials, the difference has to be attributed to the roughening of the film surface during the film growth at \(-0.5\) V. A similar explanation was given by Marlot and Vedel [243] too. Surface roughness is known to cause liquid trapping in surface cavities which in turn results in additional mass increases [266].

The idea of morphology being responsible for the above difference was further supported by the observation that when the deposition was started at \(-0.3\) V and continued at \(-0.5\) V, the \( M/z \) value remained between \(30\) and \(35\) g mol\(^{-1}\) during the whole deposition [I]. This implies that when the deposition starts at \(-0.3\) V with a smooth morphology, the film surface remains smooth even if the potential is shifted to a more negative value that normally produces a rougher surface. At the same time, the \( M/z \) value remains unchanged. This finding quite convincingly rules out also the possibility that the \( M/z \) difference would be due to differing impurity amounts, like water or thiocyanate, at the different deposition potentials.

### 7.2. \textbf{CuInSe}\textsubscript{2} films

#### 7.2.1. Film growth [I, IV]

A typical example of the relative composition (measured by EDX) of the CIS films as a function of the deposition potential is presented in Figure 7a. The film composition was constant and close to the stoichiometric Cu:In:Se ratio of 1:1:2 over a wide potential range. All systems studied behaved similarly: neither the film composition, growth rate nor the potential range for the compound formation was affected significantly by the solution composition, as long as two requirements were met: the concentrations of the metal precursors in the solutions were much higher than that of the selenium precursor, and the concentration of the SCN\(^-\) ions was high enough to keep all the Cu\(^+\) ions as [Cu(SCN)\(_4\)]\(^{3-}\) so that there were no free Cu\(^+\) ions in the solution.

The film compositions remained essentially constant also when the concentration ratio of the metal precursors in the solution was changed between 0.1 and 2.5, as illustrated in figure 7b. This provides further evidence that the induced co-deposition mechanism is operating in the system.
Figure 7. Relative amounts of Cu, In and Se in the CIS films by EDX a) as a function of the deposition potential (Deposition solution: 0.05 M CuCl, 0.07 M InCl, 0.001 M SeO₂ and 4 M KSCN,) and b) as a function of the Cu/In ratio in the deposition solution (Deposition potential -0.5 V vs. Ag/AgCl.)

The constant composition was Cu₁.₃₀In₁.₀₀Se₂.₂₀ according to RBS and Cu₁.₃₀In₁.₀₀Se₂.₁₈ according to TOF-ERDA, i.e, the films contained an excess of Cu₂⁻⁻⁻⁻Se. According to TOF-ERDA, the films contained also a large amount of impurities, the main ones being oxygen, hydrogen, sulfur, carbon, and nitrogen. The oxygen and hydrogen impurities (both about 8 at.%) originate from water and hydroxyl residues from the deposition solution. Since the amounts of S, C, and N were equal, about 6 at.% each, the films were deduced to contain thiocyanate ions. Similar to the Cu₂⁻⁻⁻⁻Se films, also the CIS films were amorphous as deposited. This may partly be due to the high amount of impurities hindering the crystallization.

Annealing at 400 °C under N₂ for 15 min was enough to make the films crystalline with the characteristic chalcopyrite XRD reflections [19]. Despite the large Cu₂⁻⁻⁻⁻Se excess in the films, no reflections corresponding to Cu-Se phases were detected, possibly because the diffraction peaks of the cubic Cu₂⁻⁻⁻⁻Se phase [265] may overlap with the some peaks of the CIS chalcopyrite phase [19].

The relative amounts of Cu, In, and Se in the films remained essentially the same after annealing, but the impurity contents decreased. The thiocyanate ions probably decomposed during annealing since the carbon and nitrogen contents in the films decreased to about 1 at.% while the sulfur content remained higher, about 4 at.%. 

Etching in 0.5 M KCN decreased the amounts of Cu and Se in all the films. In an agreement with literature [212, 226], the order of the post-deposition treatments was found important. If the films were annealed before etching, their compositions approached the stoichiometric but film morphology or crystallinity were not affected. On the other hand, etching of the as-deposited
films resulted in partial removal of the film, and the remaining part showed larger decrease of the Cu and Se contents. After annealing these samples showed several broad XRD peaks that could not be identified unambiguously. The only peaks possibly corresponding to the chalcopyrite phase were the (112) and (204/220) reflections, and the remaining peaks were attributed to In$_y$Se or In$_y$Se-rich CIS phases.

7.2.2. Growth processes studied by cyclic voltammetry and EQCM [III, IV]

The combined cyclic voltammetry and EQCM studies confirmed the formation of CIS by the induced co-deposition mechanism at potentials more positive than where Cu$^+$ or In$^{3+}$ alone are reduced. Although the reduction of In$^{3+}$ began earlier on a Se surface than on a Au surface, implying formation of In-Se compounds at more positive potentials than where the deposition of metallic In occurs, no binary In$_y$Se compounds could be deposited at the potential range where CuInSe$_2$ formation was observed. Thus the formation of CIS is concluded to proceed via the formation of Cu$_{2-x}$Se, and may be described as follows: Se deposits first (reaction 11) and induces then the formation of Cu$_{2-x}$Se (reaction 14) at more positive potentials than where Cu$^+$ or In$^{3+}$ alone are reduced. The formation of Cu$_{2-x}$Se then induces, at the same potential range, the underpotential assimilation of In$^{3+}$ and the formation of CIS (reaction 16).

\[
\begin{align*}
\text{Cu}_2\text{Se}(s) + 2 \text{In}^{3+}(aq) + 3 \text{HSeO}_3^-(aq) + 15 \text{H}^+(aq) + 18 \text{e}^- & \rightarrow 2 \text{CuInSe}_2(s) + 9 \text{H}_2\text{O} \quad [16] \\
2 \text{HSeO}_3^-(aq) + [\text{Cu(SCN)}_4]^{3-}(aq) + \text{In}^{3+}(aq) + 10 \text{H}^+(aq) + 12 \text{e}^- & \rightarrow \text{CuInSe}_2(s) + 4 \text{SCN}^-(aq) + 6 \text{H}_2\text{O} \quad [17]
\end{align*}
\]

Theoretical $M/z = 28.02$ g mol$^{-1}$

Figure 8 shows a cyclic voltammogram (solid line) and the simultaneous frequency change (dotted line), measured in the CIS deposition solution. The slope of the $\Delta f$ vs. $\Delta Q$ plot (Fig. 5c in III) corresponding to the CuInSe$_2$ formation decreased during the cyclic voltammogram until it settled to a constant value. This suggests that the CIS formation begins on the previously formed Se film and that the deposition mechanism changes during the cyclic voltammogram when the Se film becomes covered with CIS, analogous to the behavior observed in the Cu-Se system [II]. An $M/z$ value of 23.19 g mol$^{-1}$ was observed between -0.28 and -0.64 V. In contrast to the Cu-Se system, film depositions at constant potentials (-0.3 V and -0.5 V) yielded also essentially equal slopes. This may be due to smoother surface morphology of CIS as compared to that of Cu$_{2-x}$Se.
The formation of p-type semiconducting films was confirmed by cyclic photovoltammetry measurements in the deposition solution on Mo and Au surfaces, in the latter case in combination with EQCM measurements. The current densities on the Au electrode were always higher than on the Mo electrode which may result from the different work functions of the two metals. Ideally, the formation of a low-resistance, or ohmic, contact between a metal and a p-type semiconductor requires the work function of the metal to be higher than that of the semiconductor [9]. Therefore, as the work function of Au is higher than that of Mo [174], the current flow across the Au/CIS junction may be facilitated because of lower contact resistance as compared to the Mo/CIS junction.

When measured on previously deposited CIS films, the photoactivities started at more positive potentials and were stronger than on bare electrodes. This is due to the improved light absorption in a thicker semiconductor film than in a thinner one. Fig. 9 presents the cyclic voltammogram and the simultaneous frequency (mass) change, measured on a Au surface. The reason for the photoactivity starting in this case already in the very beginning of the scan is that the scan in the figure is a third successive scan. A weak photoeffect can be seen also in the frequency plot although it is much weaker than that observed in the cyclic voltammogram. Thus the film growth rate under illumination does not differ significantly from that in the dark. The maximum value of $I_{\text{dark}} - I_{\text{ph}}$ is about 7.4 $\mu$A which corresponds to a photocurrent density of about 30 $\mu$A/cm$^2$. The measurements yielded similar $M/\lambda$ values as those obtained in [III].
7.2.3. Photoelectrochemical characterization [IV]

Photoelectrochemical characterization of the CIS films was performed in order to study the effects of post-deposition treatments on their photoactivities. The as-deposited films were very weakly p-type. Photoactivity was lost completely after annealing, regardless of the annealing temperature. This may be due to the segregation of the detrimental Cu$_{2-x}$Se phase to the surface or at the grain boundaries. On the other hand, it is possible that the as-deposited films contain CuSCN as an impurity. CuSCN is a p-type semiconductor, and thus the lowering of photoactivity may result from its decomposition upon annealing.

The photoactivities of the as-deposited and the annealed films improved markedly after etching in 0.5 M KCN. The films were p-type regardless of the post-deposition sequence. The best photoactivity was achieved when the annealing treatment was performed before the etching, and the optimum etch time was determined to be 1 min, resulting in a photocurrent density of 50 µA/cm$^2$. All the PEC scans showed high dark currents which is probably due to the metal-rich composition [214, 222] or the presence of Cu$_{2-x}$Se in the films.

The PEC experiments enabled also the modification of the deposition process to consume less metals (by a factor of five) and KSCN (by a factor of two) since the films deposited from the modified solution exhibited similar photoactivities to those deposited from the original one. When the CuCl concentration was lowered from 0.05 M to 0.01 M, the KSCN concentration could be lowered from 4 M to 2 M. Because of the lower KSCN concentration, the amounts of sulfur and nitrogen impurities in the films decreased to about 2-3 at-%. The growth rate was not affected since it was determined by the HSeO$_3^-$ concentration that was not changed.
The highest photocurrent densities, about 100 \( \mu A/cm^2 \), were measured for the films prepared by depositing an In\(_2\)Se\(_3\) film on the CIS film and annealing the bilayer at 500 \( ^\circ C \). Despite their Cu-poor compositions, these films were p-type too. Fig 10 shows an example of the PEC response of such a film in 0.5 M \( K_2SO_4 \) solution.

![Graph showing PEC response](image)

**Figure 10.** Photoelectrochemical response of a CIS + In\(_2\)Se\(_3\) bilayer film in 0.5 M \( K_2SO_4 \). The bilayer film was prepared by depositing In\(_2\)Se\(_3\) for 20 min on as-deposited CIS before annealing at 500 \( ^\circ C \).

### 7.2.4. Capacitance-voltage measurements

One of the important properties of a semiconductor material is its charge carrier density. For a semiconductor to be useful as an absorber material in a solar cell, its carrier concentration has to be, on one hand, high enough in order for the material to be conductive enough. On the other hand, a too high carrier concentration causes unwanted recombination of the photogenerated charge carriers and thus deteriorates the conversion efficiency of the solar cell.

Capacitance-voltage (C-V) measurement is the most commonly used method for the determination of carrier densities in semiconductor materials. When the capacitance of a reverse-biased semiconductor junction is measured as a function of the applied reverse bias \( V \), the apparent carrier density can be calculated from the slope of the \((A/C)^2\) vs. \( V \) plot according to the equation

\[
N_A = \frac{2}{e \varepsilon_0 \varepsilon_r d (A / C)^2 / dV}
\]

where \( N_A \) is the acceptor concentration in a p-type material, \( e \) is the elemental charge, \( \varepsilon_0 \) is the
permittivity of vacuum and \( \varepsilon \), the dielectric constant of the semiconductor material. [263]

Successful employment of the method requires the depletion layer approximation, i.e., that there are no mobile charge carriers in the depletion region. Further assumptions are that all dopants are ionized and that there are no minority-type dopants. [263] Deviations of real systems such as polycrystalline diodes [264] from these assumptions may complicate the situation, and therefore interpretation of C-V data is not always straightforward, and the results presented here should be considered just indicative.

Both Schottky junctions (glass/Mo/CIS/Al) and pn-junctions (glass/Mo/CIS/CdS/Al) were studied, and similar results were obtained, in agreement with literature [267]. The apparent capacitance values were smaller at higher frequencies which may indicate the presence of traps or interface states [267, 268].

The carrier concentrations of annealed, unetched films were very high; values between 3x10\(^{19}\) and 6x10\(^{19}\) cm\(^{-3}\) were obtained that are several orders of magnitude higher than those measured for high-efficiency CIS absorbers. These high carrier concentrations were probably due to the presence of Cu\(_{2-x}\)Se that is known to be a degenerate p-type semiconductor and has therefore a high carrier concentration. [269] High carrier concentrations are in fact very common to electrodeposited CIS films; see, for example [163, 215]. On the other hand, carrier concentrations in those electrodeposited CIS films that have resulted in relatively high conversion efficiencies are lower, about 1-2x10\(^{16}\) cm\(^{-3}\) [42, 164].

The KCN etching reduced the carrier concentrations by approximately a decade, to 1.3-10x10\(^{18}\) cm\(^{-3}\), but these values were still very high. This may be due to incomplete removal of copper selenide from the material. Another possible reason is that the etching treatment caused pinholes.

The carrier concentrations of the CIS + In\(_2\)Se\(_3\) bilayer films were closer to those measured from good CIS samples, between 4x10\(^{16}\) and 5x10\(^{17}\) cm\(^{-3}\). This is in an agreement with the results of PEC measurements that showed the highest photoactivities for the CIS+In\(_2\)Se\(_3\) bilayer films.

7.3. Doped ZnO films [V]

The cathodic electrodeposition of oxides from nitrate solutions is thought to proceed via the reduction of nitrate ions according to reaction 19. The electrochemically generated hydroxide ions then react with the metal ions in the solution to form a metal hydroxide deposit at the cathode (reaction 20). [262]

\[
\text{NO}_3^- + \text{H}_2\text{O} + 2 \, \text{e}^- \rightarrow 6 \, \text{NO}_2^- + 2 \, \text{OH}^- \tag{19}
\]
\[ M^{n+} + n \text{OH}^- \rightarrow M(\text{OH})_n \]  \[ (M = \text{metal}) \]  \[ [20] \]

Under suitable conditions, either already during the deposition or during post-deposition annealing, the hydroxide decomposes to the corresponding oxide:

\[ M(\text{OH})_n \rightarrow M\text{O}_{n/2} + n/2 \text{H}_2\text{O} \]  \[ [21] \]

In the present experiments, the current flow started at less negative potentials when the \( \text{Zn(NO}_3\text{)}_2 \) solution contained also \( \text{Al(NO}_3\text{)}_3 \) or \( \text{InCl}_3 \) as compared with the solution containing only \( \text{Zn(NO}_3\text{)}_2 \). This suggests that the electrochemically generated hydroxide ions react more easily with the \( \text{Al}^{3+} \) or \( \text{In}^{3+} \) ions than with the \( \text{Zn}^{2+} \) ions. This idea was supported by film compositions (Fig. 11). In the Zn-Al-O films, aluminum is the main metal in the deposit formed at low cathodic potentials (more positive than -0.9 V). At more negative potentials, the amount of Zn in the deposit increases and that of Al decreases. Between -1.0 and -1.6 V the Al/(Zn+Al) ratio in the films was 0.042 to 0.17 corresponding to 2-8 at.% Al concentration in ZnO which has generally been found suitable doping level. The Zn-In-O films behaved similarly: the films deposited at low cathodic potentials consisted mainly of indium oxide or hydroxide, and In doped ZnO was formed at more negative potentials. The In/(Zn+In) ratio in the films was 0.02 to 0.1 between -1.0 and -1.2 V, corresponding to doping concentration of 1 to 5 at.%. These results are in an agreement with the fact that aluminum hydroxide and indium hydroxide are thermodynamically more stable than zinc hydroxide [270].

![Figure 11. Relative metal ratios of Al doped ZnO films as a function of the deposition potential. Deposition solution contained 0.05 M Zn(NO_3)_2 and 0.001 M Al(NO_3)_3.](image)

The situation for the ZnO:In films was somewhat more complicated since the amount of In in the deposit started to increase again at even more negative potentials. This may be attributed to the
formation of $\text{Zn}_m\text{In}_2\text{O}_{3+m}$ ($m = 1, 2, 3, ...$) compounds that are known to exist in the ZnO-In$_2$O$_3$ system [271, 272]. All the XRD reflections measured from these films could, however, be identified with those of the wurtzite ZnO [273]. It is of course possible that part of the deposit is in amorphous form. The increasing amount of In at the negative potentials was not observed with lower InCl$_3$ concentrations which suggests that the formation of $\text{Zn}_m\text{In}_2\text{O}_{3+m}$ compounds is feasible only when the amount of the In precursor in the solution is high enough.

The films where the main cation was Zn were crystalline as deposited, showing the characteristic ZnO (wurtzite) XRD reflections [273] with a preferred (002) orientation (Fig. 12), as observed often with electrodeposited ZnO films [248, 262]. The orientation was not affected by doping. Most of the films where the main cation was In, i.e. those deposited at potentials more positive than -0.8 V, showed the reflection of In(OH)$_3$ [274]. No reflections were detected from the films where the main cation was Al.

![XRD patterns of In doped ZnO films deposited on Mo at -0.9 V vs. Ag/AgCl with different InCl$_3$ concentrations.](image)

Figure 12. XRD patterns of In doped ZnO films deposited on Mo at -0.9 V vs. Ag/AgCl with different InCl$_3$ concentrations.

### 7.4. Solar cells

The electrodeposited CIS films were used for the preparation of solar cells. The CIS films were annealed and etched prior to the solar cell preparation as described in Chapter 6.5. Some devices were prepared using the CIS+In$_2$Se$_3$ bilayer films that were not etched. The CdS films were prepared by chemical bath deposition. Three different preparation methods for the ZnO films were compared: electrodeposition, ALD, and sputtering. Superstrate structures were prepared too but no photoresponses could be measured for them. This was probably due to the too high carrier concentrations of the unetched CIS films (see Chapter 7.2.4).
7.4.1. Solar cells with electrodeposited ZnO

The rectification ratios of the solar cells with electrodeposited ZnO films were quite good, that is, the devices clearly behaved as pn-junction diodes. The best rectification ratios were obtained with structures containing a thin (100 nm) undoped ZnO film between CIS and the doped ZnO film. In spite of the good diode behavior in the dark, the photoresponses measured for these devices were very weak. This is at least partly due to that the illumination had to be done through a thin Al film which was required for the front contacts because of the very low conductivity of the electrodeposited ZnO films.

Indium doped ZnO films resulted generally in higher forward currents and photoresponses than the aluminum doped films. This is in agreement with results obtained with spray pyrolysed films [275] where the properties of the In doped ZnO films were found to be better than those of the Al doped films. This may be due to a more optimal doping concentration and thus better conductivity of the In doped films, or to small differences in the structure or crystallinity of the In and Al doped films.

Figure 13 shows current-voltage characteristics of two solar cell structures with electrochemically prepared In or Al doped ZnO films, both measured in the dark. No photoresponses at all could be detected from structures that were prepared without CdS.

![Figure 13. Dark I-V curves for two solar cell structures with electrodeposited ZnO films. Solid line: Mo/CIS/CdS/i-ZnO/ZnO:Al, dotted line: Mo/CIS/CdS/i-ZnO/ZnO:In.](image)

The best open circuit voltage value, measured under 50 W halogen lamp illumination, was 0.405 V, obtained for a Mo/CIS/CdS/ZnO:Al structure, where the ZnO:Al film was deposited at -1.1
V from 0.05 M Zn(NO$_3$)$_2$ and 0.001 M Al(NO$_3$)$_3$. Typical $V_{oc}$ values varied between 0.1 V and 0.25 V. The short circuit current densities and the $P_{max}$ values were generally very low. The values measured for the device with the best $V_{oc}$ value were 0.13 mA cm$^{-2}$ and 0.015 mW cm$^{-2}$, respectively, but the FF was 0.34 which is the best value obtained for the structures with electrodeposited ZnO films. FF was typically about 0.25.

The highest short circuit current density was 8.65 mA cm$^{-2}$, measured from a Mo/CIS/CdS/i-ZnO/ZnO:In structure where the ZnO:In film was deposited at -1.2 V from 0.05 M Zn(NO$_3$)$_2$ and 0.005 M InCl$_3$. The same device also yielded the highest $P_{max}$ value, 0.12 mW cm$^{-2}$.

### 7.4.2. Solar cells with ALD-ZnO

The short circuit current densities for the devices with ALD-ZnO films were higher than for those with electrodeposited ZnO films. Typical values were between 2 and 4 mA cm$^{-2}$. This is probably due to the higher transparency and better conductivity of the ALD-ZnO films. Consequently, the $P_{max}$ values were also higher than with the electrodeposited ZnO films. The open circuit voltages and fill factors were similar to those obtained with electrodeposited ZnO films. Figure 14 shows a typical example of current-voltage characteristics for a device with ALD-ZnO, measured in the dark and under illumination.

![Figure 14](image.png)

Figure 14. Dark (solid line) and illuminated (dotted line) I-V curves of a device with ALD-ZnO film

The best photoresponse was measured from a Mo/CIS/CdS/i-ZnO/ZnO:Al structure with a thick (about 150 nm) CdS. The $V_{oc}$, $j_{sc}$, $P_{max}$ and FF for this device were 0.21 V, 5.47 mA cm$^{-2}$, 0.34 mW cm$^{-2}$ and 0.30, respectively. The fact that the best response was obtained from a device with
a thick CdS film is probably a result of the low resistivity of the undoped ZnO layer (2-4x10^-2 Ωcm). Because of this low resistivity, a thick CdS film was needed to prevent shunting between CIS and ZnO. This conclusion is further supported by the poor (short circuited) current-voltage characteristics obtained with devices without CdS.

7.4.3. Solar cells with sputtered ZnO

The solar cells with the sputtered ZnO films were prepared in cooperation either with Ecole Nationale Supérieure de Chimie de Paris, or with the Hahn-Meitner-Institut (HMI) in Berlin. In both cases, the electrodeposited CIS films were prepared in Helsinki, and the ZnO bilayers were prepared and the I-V measurements were made in Paris or in Berlin using light sources calibrated to give light intensity of 100 mW cm^-2.

The results obtained from Paris were not markedly better than those obtained in our laboratory with ALD-ZnO films. This may be due to the prolonged air-exposure of the Mo/CIS/CdS structures before the cell completion. On the other hand, similar results were obtained also for Mo/CIS samples that were annealed, etched and covered with CdS in Paris, just before the ZnO sputtering. The best open circuit voltage was 0.195 V, and the values were in general a bit lower than those measured from devices with ALD-ZnO. The short circuit current densities, in contrast, were similar to those measured from the devices with ALD-ZnO. The best value was 5 mA cm^-2. Often a sample with high VOC yielded a low jSC and vice versa, for example, 0.195 V and 0.5 mA cm^-2, and 0.035 V and 5 mA cm^-2.

The best results were obtained from the glass/Mo/CIS samples completed in Berlin. The annealed CIS samples were CN-etched prior to the deposition of the CdS buffer and the ZnO bilayer by the standard processes of HMI. The photoresponses were measured under standard AM1.5 illumination and the best solar cell efficiency was 1.3 %. The VOC, jSC, FF, and Pmax of this sample were 0.32 V, 10 mA cm^-2, 0.39, and 1.3 mW cm^-2, respectively. Even though the conversion efficiency is low compared to the highest values measured for electrodeposited CIS absorbers, about 5-7 % [42, 164, 169, 218], it demonstrates that the electrodeposited CIS films can in principle be used in solar cells. Figure 15 shows I-V curves of two different devices with sputtered ZnO bilayers, measured under AM 1.5 illumination in Berlin. The difference between the results obtained from Paris and from Berlin might be due to the two different CdS deposition processes.
Figure 15. I-V curves of two different devices with sputtered ZnO films, measured under AM 1.5 illumination at HMI in Berlin. The solid line corresponds to a device where the CIS thickness was about 0.5 µm whereas the dotted line corresponds to one with a thickness of about 1 µm.

Devices with electrodeposited CIS absorbers have generally shown V_{oc} values between 0.33 and 0.39 V, j_{sc} values between 25 and 42 mA cm\(^{-2}\), and FF values of about 0.52-0.59, respectively [42, 164, 169, 218]. On the other hand, the 1.5 % efficient device of Sudo et al. [166] showed a high short circuit current density of 31.5 mA cm\(^{-2}\) in combination with a very low open circuit voltage of 0.188 V. Low short circuit current densities in combination with low open circuit voltages are not uncommon either for devices with electrodeposited CIS absorbers. For instance, the preliminary devices of Garg et al. [161] and Sahu et al. [163] showed j_{sc} and V_{oc} values of less than 1 mA cm\(^{-2}\) and 0.188 V, respectively, and 0.056 mA cm\(^{-2}\) and 0.165 V, respectively [163].

Thus the V_{oc} values measured in this study were comparable to or higher than those measured for other electrodeposited devices [42, 161, 163, 164, 166, 169, 218]. The main difference between the devices prepared in this study and the most efficient devices with electrodeposited CIS absorbers was that the short circuit current densities measured in this study were considerably lower.

The results indicated that the main reason for the poor solar cell performance was undoubtedly the insufficient quality of the CIS films, resulting partly from the too high carrier concentrations even after etching. In addition, the CIS films were probably porous which may result from the escape of impurities during the annealing. Also the CN\(^{-}\) etching may have caused pinholes. The CIS films (thickness about 500 nm) used in these studies might also have been too thin for efficient light absorption. However, the results from thicker films were in general even worse – possibly because of incomplete removal of copper selenide from the thicker film.
Yet another problem might be the interface between Mo and CIS. The presence of a MoSe$_2$ interlayer improves the adhesion between Mo and CIS [39]. This layer has even been suggested to be the prerequisite for the formation of a proper ohmic contact [39, 41]. The formation of MoSe$_2$ occurs under In- and Se-rich conditions at high temperatures [39, 40] and thus it is very unlikely to be present in the samples studied in this work. In any case, the quality of the Mo back contact is known to have a strong effect on the quality of electrodeposited CIS films [276]. Further, the thickness of the Mo films may also have an effect: the Mo films used in these studies were only 100 nm thick whereas usually about 1 µm thick films are used.
8. Conclusions

CuInSe\textsubscript{2} and related chalcopyrite compounds are the most promising absorber materials for polycrystalline thin film solar cells. CuInSe\textsubscript{2} solar cells have shown the highest conversion efficiencies of all thin film solar cells. The record efficiency is 18.8 \%, and several groups have achieved efficiencies over 18 \%. Further, the operational lifetimes of this type of solar cells are long due to their extraordinary stability. CuInSe\textsubscript{2} thin films can be prepared both from gas and liquid phases by a variety of methods, but the highest efficiencies have so far been obtained by absorbers prepared by co-evaporation. In order to lower the production costs of photovoltaic modules, alternative, low-cost deposition methods need to be developed. Electrodeposition is one alternative since it is a low-temperature liquid phase deposition method. The deposition equipment is relatively simple, and the advantages of the method include the potential for upscaling to large substrate areas and production volumes.

Electrodeposited CIS-based absorber films require generally annealing either under a Se-containing or an inert atmosphere prior to the cell preparation. Such approaches have resulted in conversion efficiencies between about 5 and 7 \%. Even higher efficiencies, over 15.4 \%, can be achieved if the stoichiometry of the electrodeposited precursor film is adjusted by adding In, Ga and Se by PVD prior to the cell preparation.

CIS-based films have been prepared by a variety of electrochemical techniques such as one-step deposition, sequential deposition of binary compounds, and deposition of elemental layers followed by annealing either under an inert or a reactive atmosphere. One-step electrodeposition is the most widely studied option. There are basically two alternative ways to control the film composition: either by balancing the diffusion fluxes of the constituent ions to the cathode, or by relying on thermodynamics. In the former case, the film composition is heavily dependent on the deposition potential and on the concentrations in the deposition solution. Small, unavoidable variations in concentrations and deposition potentials may therefore result in large changes in the film compositions which deteriorates reproducibility and may render upscaling to larger substrate areas problematic.

The latter option, in turn, utilizes induced co-deposition that has been used widely for binary compounds, especially CdTe. In a binary system, the deposition of the more noble ion induces the underpotential reduction of the less noble ion and the formation of the compound at less negative potentials than where the less noble ion would reduce on its own. The reason for the underpotential reduction of the less noble ion is the energy released in the compound formation. When the deposition solution contains a large excess of the less noble ion, induced co-deposition ensures the formation of stoichiometric compound over wide concentration and potential ranges. These kind of processes are thus much less sensitive to electrolyte composition and deposition potential than those based on the flux balance approach.
Despite its success in deposition of binary compounds, induced co-deposition had not been utilized for the deposition of ternary compound semiconductors prior to this work. In the case of CIS, this is partly because the formation of CIS occurs via Cu$_{2-x}$Se, and the latter does not follow the induced mechanism. In the present work, suitable conditions for the induced co-deposition of Cu$_{2-x}$Se and CuInSe$_2$ were achieved by complexing the Cu$^+$ ions by thiocyanate ions in order to shift the reduction potential of metallic Cu to the negative direction. Under these conditions, Se reduced first, i.e., at more positive potentials than Cu. The reduction of Se induced the formation of Cu$_{2-x}$Se at more positive potentials than where the bulk deposition of metallic Cu began. Cu$_{2-x}$Se, in turn, induced the formation of CuInSe$_2$ at the same potential range, i.e., at more positive potentials than where the deposition of metallic Cu or In began. The electrochemistry of the Cu-Se and Cu-In-Se systems was studied by cyclic voltammetry and electrochemical quartz crystal microbalance measurements that verified the deposition mechanisms. Induced co-deposition allowed wide potential and concentration ranges for the formation of almost stoichiometric CuInSe$_2$ films (Cu$_{1.34}$In$_{1.00}$Se$_{2.20}$ according to RBS) as long as the concentrations of the metal precursors were much higher than that of the selenium precursor, and the concentration of the SCN$^-$ ions was high enough to keep all the Cu$^+$ ions as [Cu(SCN)$_4$]$^{3-}$ so that there were no free Cu$^+$ ions in the solution.

The films were studied by a number of techniques: XRD, SEM, EDX, RBS, TOF-ERDA, photoelectrochemical and capacitance-voltage measurements. The as-deposited films were amorphous and contained hydrogen, oxygen, sulfur, carbon, and nitrogen as impurities. Hydrogen and oxygen originated apparently from the aqueous deposition solution and the other impurities from the thiocyanate ligands. The films became crystalline upon annealing that also reduced the impurity contents drastically. The relative amounts of Cu, In, and Se in the films remained essentially the same after annealing.

Since photovoltaic-quality CIS films should be Cu-deficient rather than Cu-rich like the films deposited in this study, two approaches were made to adjust the film compositions after deposition: etching in KCN solutions and addition of In$_2$Se$_3$. The effects of the post-deposition treatments on the film properties were studied by EDX, photoelectrochemical and capacitance measurements that verified more stoichiometric composition and more suitable carrier concentrations after the post-deposition treatments. However, the carrier concentration was still much higher than those measured for high-efficiency absorbers.

Solar cells were prepared from films deposited and treated under the conditions bound to give the highest photoactivities and lowest carrier concentrations. Doped ZnO films for the devices were prepared either electrochemically, by ALD, or by sputtering. For the first time, Al and In doped ZnO films were prepared by electrodeposition. The electrodeposited ZnO films were prepared from solutions containing Zn(NO$_3$)$_2$ and Al(NO$_3$)$_3$ or InCl$_3$. The films were crystalline as deposited but did not result in good photoresponses due to their high resistivity. The current-
voltage characteristics measured in the dark showed, however, good rectifying behavior. This was also the first time when electrodeposited ZnO:Al and ZnO:In films were used as front electrodes in solar cells.

The photoresponses with the ALD-ZnO films were better than with the electrodeposited ZnO films. Yet, the best photoresponses were obtained from the devices with sputtered ZnO bilayers, prepared at HMI Berlin. The highest conversion efficiency, measured under AM 1.5 illumination, was 1.3 %. Although the efficiency was low, the open circuit voltages of these devices were comparable to those of higher efficiency devices with electrodeposited CIS absorbers.
References


