Alternative back contacts for CZTS thin film solar cells

SVEN ENGLUND
In this thesis, alternative back contacts for Cu₂ZnSnS₄ (CZTS) thin film solar cells were investigated. Back contacts for two different configurations were studied, namely traditional single-junction cells with opaque back contacts and transparent back contacts for possible use in either tandem or bifacial solar cell configuration.

CZTS is processed under chemically challenging conditions, such as high temperature and high chalcogen partial pressure. This places great demands on the back contact. Mo is the standard choice as back contact, but reacts with chalcogens to form MoS(e)₂ while the CZTS decomposes, mainly into detrimental secondary phases. Thin MoS(e)₂ is assumed to be beneficial for the electrical contact, but excessive thickness is detrimental to solar cell performance. The back contact acts as diffusion medium for Na during annealing when soda-lime glass is used as substrate. Na influences both defect passivation and doping in CZTS and increases the efficiency of the solar cells. The ability of the back contact to facilitate Na diffusion is an important property that must be monitored.

Titanium nitride (TiN) as an interlayer between the opaque molybdenum (Mo) and CZTS as well as complete replacement of Mo with TiN back contacts were investigated. TiN was found to be chemically stable in typical anneal conditions. Formation of MoS(e)₂ was observed only in areas where the TiN interlayers did not fully cover the Mo, following from the surface roughness of Mo and insufficient step-coverage of the sputter-deposition of TiN. Thick TiN interlayers (200 nm) were found to increase the diffusion of Na to the absorber layer from the glass substrate. For precursors annealed in sulfur atmosphere, improved device efficiency was observed for increased TiN thickness.

Transparent back contacts can be used in either tandem configurations where two or more absorber materials are used to more efficiently use different parts of the solar spectra, or in bifacial solar cells to allow light to reach the absorber layer from two sides and thus increase the photocurrent. Thus far only a few studies have investigated transparent back contact materials in CZTS solar cell devices. Antimony-doped tin oxide (ATO) was studied as a transparent back contact for CZTS. Annealing of bare ATO resulted in complete reaction with S to form Sn–S compounds. When annealed below the CZTS, ATO was found to be stable at low temperature (<550 °C), and in some aspects even improved its properties. ATO back contacts resulted in significantly increased formation of Sn–S secondary phases on the CZTS absorber surface compared to the Mo reference. Sn–S secondary compounds on the absorber surface made it challenging to obtain good device performance. Adhesion and device behavior could be improved by pre-addition of NaF on the precursor prior to annealing.

Keywords: CZTS, thin film solar cells, back contacts, passivation, interface, titanium nitride, ATO, antimony-doped tin oxide, transparent back contact

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Till mitt älskade Sverige
To my beloved Sweden
致瑞典，我的挚爱
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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Personal contributions to the papers

I. Contributions mainly related to the back contact part; planning, literature review, writing, figures.

II. Definition of the research project, literature review, planning, sample preparation (deposition, annealing, STEM lamellae), characterization and analysis (SEM, XPS, XRD), discussion and writing with input from co-authors.

III. Literature review, part of planning, sample preparation (sputter deposition, annealing), some characterization (XPS), discussion and involved in writing process.

IV. Definition of the research project, literature review, planning, sample preparation (deposition of back contacts, annealing, STEM lamellae of interlayer sample), analysis (SEM, XPS, IV, QE, stress), discussion and writing with input from co-authors.

V. Part in definition of the research project, literature review, planning, sample preparation (deposition of back contacts, CZTS and NaF, annealing), analysis (resistivity, XRD, GDOES, IV, QE), discussion and writing with input from co-authors.
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Abbreviations

$\alpha$ Absorption coefficient (cm$^{-1}$)
$A_{\text{optical}}$ Optical absorption
ALD Atomic layer deposition
AM Air mass
AMX Air mass X (X e.g. 1, 1.5, 2-3)
AR Anti reflection
ASTM American Society for Testing and Materials
ATO Antimony-doped tin oxide
AZO Aluminum-doped zinc oxide
BIPV Building integrated photovoltaics
$c$ Speed of light in vacuum, (299792458 m s$^{-1}$)
CBD Chemical bath deposition
CIGS Cu(In,Ga)Se$_2$
$c$-Si crystalline silicon
CZTS Cu$_2$ZnSnS$_4$
CZTSe Cu$_2$ZnSnSe$_4$
CZTSSe Cu$_2$ZnSn(S,Se)$_4$
DC Direct current
DGIST Daegu Gyeongbuk Institute of Science and Technology
EDS/EDX Energy dispersive X-ray spectroscopy
EELS Electron energy-loss spectroscopy
$E_g$ Band gap energy (eV)
ERDA Elastic recoil detection analysis
$FF$ Fill factor (%)
GIXRD Grazing incidence X-ray diffraction
$I$ Current
IBM International Business Machine Corporation
IEA International Energy Agency
InGaAs Indium gallium arsenide
$IV/JV$ Current-voltage/current-density-voltage
$i$-ZnO Intrinsic zinc oxide
$J_0$ Dark saturation current (mA cm$^{-2}$)
$J_L$ Photocurrent density (mA cm$^{-2}$)
$J_{sc}$ Short circuit current density (mA cm$^{-2}$)
$k$ Boltzmann constant (8.617333… · 10$^{-5}$ eV K$^{-1}$)
$\lambda$ Wavelength (nm)
LCD  Liquid crystal display
LCOE  Levelized cost of energy
MEIS  Medium-energy ion scattering
MoO$_x$  Molybdenum oxide
$n$  Doping concentration (cm$^{-1}$)
PIXE  Particle-induced X-ray emission
ppb  Parts per billion
ppm  Parts per million
PV  Photovoltaic
$q$  Elementary charge, 1.602 176…·10$^{-19}$ C
QE  Quantum efficiency (%)
$\rho$  Resistivity (Ω m)
RBS  Rutherford backscattering spectrometry
RF  Radio frequency
$R_{\text{series}}$  Series resistance
$R_{\text{sheet}}$  Sheet resistance
$R_{\text{shunt}}$  Shunt resistance
S  Sulfur
Se  Selenium
SEM  Scanning electron microscopy
Si  Silicon
SILAR  Successive ionic layer adsorption and reaction
SIMS  Secondary ion mass spectrometry
SLG  Soda-lime glass
SRIM  Stopping and Range of Ions in Matter
STC  Standard test conditions
STEM  Scanning transmission electron microscopy
$T$  Temperature (K, °C)
$T_{\text{optical}}$  Optical transmission
TiN  Titanium nitride
ToF  Time-of-flight
TWh  Terawatt hour
UHV  Ultra high vacuum
$V$  Voltage (V)
$V_{\text{oc}}$  Open circuit voltage (V)
$x$  Depth (cm, nm…), multiplying factor
XPS  X-ray photoelectron spectroscopy
XRD  X-ray diffraction
XRF  X-ray fluorescence
Å  Ångström (10$^{-10}$ m)
Preface

This thesis is written to fulfil the requirements for a Doctor of Philosophy degree at Uppsala University. The project has been made possible thanks to financing from Stiftelsen för strategisk forskning (The Swedish Foundation for Strategic Research), grant numbers FFL12-0178 and RMA15-0030. The project has been run by me, under supervision of Prof. Charlotte Platzer-Björkman and co-supervision of Assoc. Prof. Jonathan J. S. Scragg. To my help, I have had fellow PhD students and senior colleagues at the Division of Solid State Electronics at Uppsala University. During the process, collaboration also evolved with the Ion Physics Group and the Tandem Laboratory at Uppsala University, and the Centre for Material Science and Nanotechnology at University of Oslo.

Nearly all the experiments have been made in cleanroom environment at the Ångström Laboratory (classification 10 000, temperature controlled within ±1 °C, humidity 45±3%), at Uppsala University, in order to make the experiments as controlled as possible.

In the ideal case, when making solar cell devices, I would have only varied the back contact in the experiments and let everything else be identical. However, the many steps in the procedure, in combination with the challenges to get e.g. the desired CZTS composition, makes it challenging to isolate reasons for changes in the solar cell behavior. Even with identical CZTS composition, e.g. device performance is not necessarily repeatable, due to reasons that sometimes are hard to isolate.

I have structured this thesis as follows. Introduction – I want to put this thesis into a context and describe why we put so much effort and time into this topic right now. Background – some basics of solar energy and the principles of solar cells devices. One chapter gives the background to the main material of this thesis – CZTS. The chapter is to some extent based on paper I. Since both knowledge about CZTS, and the components used in the CZTS device stack, to a large extent are inherited from the research on CIGS, along with the fact that all solar cells in some way are compared to c-Si, the reader may find random comparisons to both of them throughout the thesis. In the chapter Characterization methods, I describe the methods used to characterize and analyze the samples during the experiments for this work. In the chapter Results and discussion, the results from paper II-V are summarized and discussed, followed by Concluding remarks and outlook.
1. Introduction

We have probably seen nothing yet.

We are in a stage in the human history where development is happening at an unprecedented speed, where each generation grow up in a society unimaginable to the previous ones.[1] The fast development makes it hard to predict even the near future sometimes, as numbers and statistics valid today, may be outdated already tomorrow. Also an industrial field, or research field, may completely change over the time of a PhD project. From 2010 until today, early 2020, the price of solar photovoltaics (PV) has dropped by 90% and gone from being one of the most expensive electricity sources to become the cheapest source in many areas, as illustrated for the US market in Figure 1 (a).[2-4] The International Energy Agency (IEA) still forecasts that the price of solar PV will fall another 15-35% until 2024.[5] The future may be hard to predict, but many recent sources expect solar PV to clearly become the cheapest source of electricity over the coming decades.[2, 4] Ahead, we can expect a strong, market driven, increase of installed PV capacity over the coming decades.[6] The accumulated amount of installed solar PV has increased nearly exponentially since around 1992,[7, 8] and as that continues, the absolute numbers are now becoming substantial. As an example, more than 75% of the PV capacity worldwide has been installed after this PhD project started in 2014.[3] However, no single technology, and perhaps PV in particular, will ever be the whole solution, as electricity simply must be supplied also when the sun is not shining.

PV deployment is expected to grow in all possible applications, as illustrated in Figure 1 (b).[5] For some applications, however, like building-integrated PV (BIPV), or vehicle-integrated PV (VIPV), the otherwise dominating solar PV material, crystalline silicon (c-Si), is not very suitable due to inherent drawbacks. For example, it is inflexible and brittle for typical wafer thicknesses. Actually c-Si is not a very good solar cell material when it comes to some basic material properties either. The most common production method, the Czochralski method, is inevitably very energy intense,[9] and around 50% of the silicon is lost and non-reusable after wafer sawing.[10] Partly because of these reasons, but also as a result of some side effects of the combination of political decisions and immature markets in the 00’s, Si PV went through periods of crisis.[11] The situation catalyzed a lot of efforts, new inventions
that made it possible to reduce thickness of Si solar cells by 40% without losing efficiency.[11] But the situation also triggered interest and growth of the thin film PV technology, which is the technology used for the solar cells in this thesis. During the Si crisis in the 00’s, thin film PV rapidly increased its market share to around 17% forecasts suggested that thin film technology eventually would become the dominant PV technology.[11, 12] One problem that was identified already there was that the most successful thin film solar cells, namely CIGS and CdTe, both contain rare metals. With just a fraction of the anticipated PV market in the coming decades, the production of these elements would soon become a limitation - the needed production increase of some of the elements would be of an extent unprecedented for any metal in history.[13] Around the same time, increased efficiency of a new PV material was reported,[14] with the potential to overcome in principle all these problems, the material of this thesis – CZTS. It would combine the flexibility, low material consumption and low required production energy of thin film PV, but only consist of elements with high abundance and low toxicity. If it would reach close to the solar cell efficiencies reached by the existing thin film materials, it would simply take over the market without any bottlenecks in the production chain. Research on CZTS was initiated in many groups and companies around the world and new world records were frequently reported from 2009 to 2014, with IBM as the clear research leader.[15] The number of publications on CZTS (and its derivatives) during these years increased rapidly. Several key areas for further improvements were identified, with alternative back contact materials, the topic of this thesis, being one of them.[16-21] But also, much of the CZTS research has been focused towards understanding reasons for device limitations,[22] partly because of the long pause in world efficiency records after a time of fast development, despite extensive efforts. The last world record by IBM, and Wang et al.[23] before they discontinued their efforts was at 12.6%, a record that just recently was repeated by Son et al. at DGIST in South Korea.[24]
While economy and possible future bottlenecks may be some main drivers for technology development, the demand for fossil free and clean energy sources rises also for other reasons, including, but not limited to:

- To minimize (or preferably even mitigate) the temperature increase following the increase of the concentration of CO₂ in the atmosphere.

Temperature- and climate changes coincide with several examples of major disruptions of civilizations. The current situation is particularly critical as the speed of the ongoing temperature increase is unprecedented in human history.[25] Any increase in global average temperature is projected to affect human health, with primarily negative consequences.[26] Abrupt climate change may lead to the extinction of humans and other species.[27, 28]

- To improve air quality in urban and industrial areas from the often hazardous concentration of particular matter (PM) in the air.

Poor air quality has been linked to increased risk of mouth cancer,[29] lung cancer,[30] liver-, colorectal-, bladder-, kidney-, pancreas and larynx cancer,[31] asthma,[32] neonatal jaundice,[33] and brain cancer.[34] In Europe, the annual excess mortality rate from ambient air pollution is estimated to around 790 000 persons,[35] and in Sweden to around 8 000 persons.[35, 36]

- To avoid energy crises due to shortage of fossil resources.[37]

- To distribute energy production more evenly and reduce the dependence on concentrated fossil fuel resources, thereby reducing political risks and risk of conflicts due to exogenous dependence and unequal access and distribution of energy.[37-39]

Solving all these issues will need tremendous efforts and political will and decisions. What we as researchers can do is to explore all possible ways to facilitate the transition into a sustainable society. No technology can do it alone, but solar energy is anticipated to become our largest source of electricity within a few decades.[40] For this to take place we have to continue the struggle to improve efficiency, while minimizing energy- and material consumption for the solar cells we produce.[40, 41] For this purpose, CZTS has been the focus of this thesis.
1.1 Motivation and aim of the thesis

The aim of this thesis is to investigate and perform in-depth characterization of alternative back contact configurations and materials for CZTS thin film solar cells. In a traditional single-junction configuration, Mo is the standard material for back contacts in CZTS solar cells. It was inherited from another chalcopyrite thin film solar cell, the more mature, CIGS thin film solar cell, which has been developed for decades and commercialized. CZTS is chemically more challenging compared to CIGS and requires also more challenging processing (annealing) conditions, such as high temperature and high chalcogen (S, Se) partial pressure. This places great demands on the back contact, since it is the only part of the solar cell that is in contact with the CZTS during the mentioned annealing. Mo reacts with chalcogens to form MoS(e)2 at the interface while the CZTS decomposes, mainly into secondary phases. MoS(e)2 is assumed to be beneficial for the electrical contact between the layers, but excessive thickness is detrimental to solar cell performance, and much effort has been put in minimizing, but still not completely block the interface reaction. Na influences both defect passivation and doping in chalcopyrite thin film solar cells and increases the efficiency of the solar cells. For devices using soda-lime glass (SLG) as substrate, Na is supplied to the CZTS by diffusion from the SLG through the back contact when the temperature is increased during annealing. The ability of the back contact to facilitate Na diffusion, and monitor the effect of different back contact configurations on Na diffusion is important when analyzing device behavior of CZTS thin film solar cells.

In one part of this thesis, the aim is to study titanium nitride (TiN) with different thicknesses as chemically passivating layers on standard Mo back contacts. Particular attention is given to (1) the chemical stability of sputtered TiN in typical processing conditions, (2) the formation of MoS2 at the Mo/TiN interface and the ability of TiN interlayers to inhibit chalcogens from reaching the Mo, and (3) the effect of TiN interlayers on Na-diffusion, (4) the possible effect of thermal expansion of the SLG/Mo on TiN coverage on the Mo. Device performance of CZTS thin film solar cells using TiN interlayers is further investigated, and TiN back contacts (without Mo) is also tested for CZTS thin film devices. This work is described in paper II-IV.

Transparent back contacts can be used in either tandem configurations where two or more absorber materials are used to more efficiently absorb different parts of the solar spectra, or in bifacial solar cells to allow light to reach the absorber layer from two sides and thus increase the photocurrent. Thus far only a few studies have investigated transparent back contact materials in CZTS solar cell devices. In one part of this thesis, the aim is to study antimony-doped tin oxide (ATO) as a transparent back contact for CZTS in a single-junction configuration for straightforward comparison to the behavior of standard cells with Mo as back contact. ATO has not been investigated previ-
ously for this purpose, but has been suggested for devices used in high-temperature environments. Attention is given to (1) the chemical stability of ATO back contacts in typical processing conditions, (2) for reasons that will become apparent later in this thesis, attention is also given to optimizing the annealing process for CZTS with ATO back contacts along with (3) the formation of detrimental secondary compounds on the surface of the CZTS during annealing, (4) external supply of Na. Finally, (5) the impact of the Sn-content in the CZTS precursors is investigated. The work on ATO is described in paper V.
2. Background – solar energy and solar cells

2.1 Solar energy

The basis of solar energy is the *electromagnetic radiation* emitted by the sun. Different stars have different *spectral* characteristics, determined mainly by their temperature, giving rise to certain spectra of energies. Also our sun has a certain spectrum, similar to that of a 5778 K (5505 °C) blackbody. The solar spectrum basically determines how optimal solar cells should be designed on earth. The spectrum from the sun is visualized by the green area in Figure 2 in terms of the *irradiance*, i.e. the radiation which the earth is exposed to. However, since the earth has an atmosphere, which absorbs certain parts of the radiation, the radiation finally reaching the surface of the earth differs from the one radiated by the sun (even on a cloud free day). These different spectra are sometimes called *extraterrestrial* - outside atmosphere, and *terrestrial* - at sea level. The composition of the atmosphere changes over time, which recently has been getting attention due the unprecedented rapid increase of atmospheric concentration of CO₂.[42] However, as seen in Figure 2, water vapor is the main absorber/ reflector of solar radiation before the sun light reaches the ground.[43, 44]

![Figure 2. Spectra of solar radiation AM1.5 (ASTM G-173-03) and AM0 (ASTM E490) reference spectra, provided by NREL, atmospheric absorption is indicated.[44]](image-url)
The irradiance is also different depending on latitude and the specific location relative to the sun. One common way to quantify the distance the light travel through the atmosphere is \textit{air mass} (AM), defined by Equation 1,

\begin{equation}
AM = \frac{1}{\cos \Theta}
\end{equation}

where $\Theta$ is the \textit{zenith angle} as indicated in Figure 3. With the sun at its zenith, the radiation travels the shortest way from the top of the atmosphere to sea level, which defines the AM1. As soon as the sun is not in zenith seen from a certain point, its light must travel a longer distance through the atmosphere and undergoes \textit{attenuation}. However, when it comes to annual irradiation, also local effects have significant impact. Berlin and Stockholm have nearly the same annual solar irradiation, despite Stockholm’s latitude being 7° higher than Berlin, while London, located south of Berlin has significantly lower.[45]

When measuring solar cells, the standard spectra of AM1.5G is used to simulate as “\textit{common}” conditions as possible, the G stands for global and includes also some diffuse irradiation from the surrounding.

Integration of the incident solar photon flux over all wavelengths gives the maximum amount of photons. For an imagined ideal solar cell device which can convert all photons to electricity, the same number would give the maximum current of the cell, visualized by the red line in figure 4.[46] However, this is physically impossible in solar cells, because for a given semiconductor material, only photons possessing a certain minimum amount of energy can “create” free charge carriers. Photons below that energy cannot contribute to
the solar cell operation. The shadowed area in Figure 4 corresponds to the photon flux that theoretically could be absorbed and converted to current by a CZTS thin film solar cell. Apparently, the theoretical maximum current density to be converted by CZTS is therefore slightly above 30 mA cm$^{-2}$.[47] This energy is therefore probably the most defining parameter of a solar cell material and is called the band gap energy.

![Figure 4.](image)

Figure 4. Photon flux and for wavelengths $\sim$300-2700 nm (corresponding to energies $\sim$4.1-0.46 eV). The blue area corresponds to the part of the spectrum above the band gap energy of CZTS, at $\sim$1.45 eV, or wavelengths below $\sim$855 nm. Courtesy to Elsevier and Smestad et al.[46]

### 2.2 Semiconductors

Crystalline materials consist of atoms arranged in certain patterns, so called structures. The structure is defined by its lattice and its atoms placed at certain lattice positions. The energy band model describes how the electrons in the crystal are present in certain allowed states, or ranges of energies – so called energy bands. Of main interest here are two of these energy bands: those located just above and just below the previously mentioned band gap. The band gap refers to a range of energies where there are no allowed states, therefor also sometimes referred to as the forbidden gap. The bands below the band gap are called valence bands and the bands above it are called conduction bands. In the energy band model, however, mainly the energy of the highest valence band and the lowest conduction band are considered and therefore referred to as valence band maximum (VBM) and conduction band minimum.

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[1] In a device, this number will be lower, $\sim$24 mA cm$^{-2}$, due to losses from the layers above CZTS, see further in section 3.3.2.
(CBM), respectively. The electrons are present in the lowest possible energy states, and will therefore “fill up” the energy bands from the lowest energies. At 0 K, the valence bands will be entirely filled up to the VBM. The minimum energy required to excite electrons from the VBM, to become free electron in the conduction band, corresponds to the band gap energy. The added energy can be in form of e.g. thermal energy or – which is of main interest for solar cells – from incident photons, as illustrated in Figure 5. The creation of a free electron in the conduction band simultaneously creates a hole in the valence band, which through the movement of the surrounding electrons can move as a charge carrier itself. Since electrons and holes always are simultaneously created, they are often referred to as electron-hole pairs.

If the band gap is large, the material will be an insulator. What “large” means is not defined, different sources give different numbers, everything between >1.5 eV to >6 eV is commonly stated as band gaps for insulators.[48-51] On the other hand, if the energies of the VBM and CBM instead are overlapping, meaning that no energy is required to excite electrons above the band gap, and that the charge carriers can flow freely in the crystal, the material will be a conductor. In between insulators and conductors are the semiconducting materials, which are used for solar cells. But not only the location of the allowed states is of importance, also the occupancy of electrons is of utmost importance for the properties of a semiconductor. The electron occupancy is defined by the Fermi level, as illustrated in Figure 5. For a more comprehensive description of semiconductor physics, please refer to e.g. Pierret or Sze and Ng.[52, 53]

![Figure 5. Illustration of the valence band maximum and conduction band maximum of an insulator, semiconductor and conductor, respectively. The incoming photon has an energy that is large enough to excite an electron from the valence band to the conduction band in the semiconductor.](image-url)
2.3 Band gap of solar cell materials

On an ideal theoretical level, there is a certain band gap range for a certain solar spectrum that can give the best solar cells. This is related to the previously mentioned condition that only photons of energies higher than the band gap can be absorbed. At the same time, all photons with energy higher than the band gap, will release all their excess energy, i.e. the fraction of energy higher than the band gap, is lost as heat to the solar cell, also called **thermalization**. Consequently, there is a tradeoff between maximizing absorption and minimizing thermalization, which gives the theoretical limit for **power conversion efficiency** (PCE). This was first calculated by Shockley and Queisser in 1961.[54] As visualized in figure 6, this optimum occurs around 1.1-1.4 eV. This can also be understood if we again take a look at Figure 1 or Figure 4, 1.1-1.4 eV is located so that the main part (~60%) of the integrated photon flux can be absorbed. Solar cells with wider band gap “miss” part of this important range (~1.1-3 eV) of the spectrum, while solar cells with narrower band gap will simply lose more efficiency due to thermalization than they win from absorbing more photons.

![Figure 6](image)

*Figure 6. Visualization of losses due to thermalization (yellow area) and non-absorption (blue area), and the Shockley-Queisser limit (upper line of the black area).*[55]

The **Shockley-Queisser limit** is a very popular reference, and commonly seen as the most important contribution for understanding of PV energy conversion. However, it is based on idealized models and certain assumptions, and several materials outside the optimal range have reached higher efficiencies than materials within it.[56] This can of course change in the future as the research and technology development proceed, but in any case, we likely need to consider many more aspects than the band gap energy to find the limits of different solar cell materials.
The limits of a solar cell material should not be confused with the limits of a solar cell device. There are several strategies and inventions that can increase efficiency. At this point, a good example is tandem solar cells, or multijunction solar cells. The idea with this kind of solar cell is to stack materials with different band gaps, and in that way make a device with different layers, which each is optimized to absorb a certain part of the solar spectrum. Therefore, wider band gap materials are put on top to absorb the photons with the highest energy, and materials with lower band gap put below to absorb photons with lower energy. In this way, absorption can be increased and thermalization decreased. This is visualized in Figure 7 by a drawing of a 5 junction solar cell device, with five layers, each having different band gaps and therefore absorbing different parts of the spectrum. The current world record device, with a PCE record of 39.2% (47.1% with concentrator), consists of 6 different layers, all with different band gaps.[15]

![Figure 7. Illustration of a 5 junction solar cells device, absorbing different parts of the light spectrum. The different band gaps corresponds to those of the cell described by Chiu et al.[58] which QE is shown in Figure 8.](image-url)
Multi-junction solar cells can be produced *monolithically*, meaning that each absorber layer is grown directly on top of the other with a thin, so called *tunnel junction* in between. However, this requires rather strict optimization in current generation: due to *Kirchoff’s first law*, the current through all the stacked layers is constant, so each must produce the same amount of current, otherwise there will be losses. It is possible though: in Figure 8, the *EQE* (see section 2.4.4 for explanation) of a monolithical solar cell device with 5 absorber layers of different band gaps made by Chiu et al.[58] is shown. From top to bottom the band gap of the respective layer were 2.2 eV, 1.7 eV, 1.4 eV, 1.05 eV and 0.73 eV. One can notice here that each area has rather *sharp edges*, meaning that the respective layers have well-defined band gaps, which is not always the case for some solar cell materials. The cells in a tandem device can also be made as individual cells, the current can then be “extracted” from each of the cells, with fewer constraints on band gaps and thicknesses. For multi-junction solar cells, a requirement for the contact layers is that they are transparent to minimize optical *absorption losses*. Such a contact material is investigated for CZTS in paper V.

![Figure 8](image_url)

*Figure 8.* EQE of a 5 junction solar cell device by Chiu et al. From left (top) to right (bottom) the band gaps of the respective layers were 2.2 eV, 1.7 eV, 1.4 eV, 1.05 eV and 0.73 eV, in total giving an efficiency of 37.8%. [58] © 2014 IEEE

The band gap of a material can be further divided into either *direct* or *indirect*. If the band gap is indirect, the probability that absorption of a photon will result in generation of an electron-hole pair is much lower compared to direct band gap. Consequently, the absorption coefficient of indirect band gap materials is lower compared to direct band gap materials. The absorption of photons in (ideal) materials follows the Lambert-Beers law, equation 2,
\[ I(\lambda) = I_0(\lambda)e^{-x\alpha(\lambda)} \]  
(Eq. 2)

where \( I \) is the transmitted intensity (for a certain wavelength), \( I_0 \) is the incident light intensity, \( \alpha \) is the absorption coefficient of the material, and \( x \) is the depth below the surface.\[59-61\] CZTS has, just as all thin film solar cell material candidates, a direct band gap and therefore relatively high absorption coefficient. Over the range of wavelengths with most of the spectral irradiance of the sun, CZTS has roughly 100 times higher absorption coefficient than c-Si, as illustrated in in the spectrum in Figure 9.\[62\] Consequently c-Si solar cells must be at least a hundred times thicker than CZTS, and the thinnest commercial c-Si is around 150 µm.\[47\] A thickness study on the CZTS in our group indicated that the collection and efficiency increased with absorber thickness up to 1 µm, which therefore is chosen as our standard baseline absorber thickness.\[63\] It can be observed in Figure 9 that the absorption in CZTS does not end as expected at the band gap, this is because CZTS is one of those materials with less sharp band edges, which cause so called band tailing. The contribution from the band tail may look significant on logarithmic scale, so the reader may compare with the band tail near the band gap in the QE spectra in Figure 10 for a more fair impression.

![Figure 9. Absorption spectra of CZTS and c-Si. Schematic illustration of absorber standard thicknesses of CZTS vs. c-Si. Reference spectrum of c-Si absorption and AM1.5G provided by NREL.](image-url)
2.4 Solar cell devices

To make a solar cell device with some significant efficiency, one cannot simply put a semiconductor under sunlight. The different layers of a CZTS thin film solar cell device will be described more in detail in section 3.3, here I will very briefly describe some basic parts and principles of solid state semiconductor solar cell devices, and also give examples of how it works in CZTS, or thin films solar cells. On a basic level, the processes involved to get electron-hole pairs to perform work done in an external circuit involves two processes, *generation* and *collection*. Incident photons, which are not stopped by shadowing or get reflected on the surface, with energy higher than the band gap, can be absorbed and annihilated to excite electrons from the valence band to the conduction band, i.e generate electron-hole pairs. There are strategies to minimize reflection losses, e.g. by deposition of an *anti-reflecting coating*, such as MgF2, or by treatments to increase the surface roughness. *Transmission losses* are minimized simply by making the absorber layer thick enough, or using a reflective back contact. The average time (*lifetime*, $\tau$) and distance (*diffusion length*, $D$) that generated electron-hole pairs survive are both important figures of merit when comparing semiconductor materials. The longer diffusion length and lifetime, the higher probability that the electron-hole pairs will be collected. To describe the collection process, one has first to describe perhaps the most fundamental part of the solar cell device, the *pn-junction*.

2.4.2 Doping and formation of pn-junctions

The *pn-junction* has received its name from the configuration of two layers, of opposite *doping*, that are connected to form the junction. Doping refers to impurities, or *defects* in the crystal lattice of semiconductors that increase their concentration of either positive (“p”) or negative (“n”) free charge carriers. Some semiconductors, like CZTS can get substantial amount of doping from defects in the lattice, which is called *intrinsic doping*. It is also common to intentionally dope semiconductors by addition of other elements than the semiconductor itself consists of, which is called *extrinsic doping*. The most common doping defects in CZTS are (1) Cu atoms replaced by Zn atoms, labelled Cu_{Zn}^{+}, the plus-sign means that the defect is positively charged, because it has “donated” a free electron to the crystal, the defect is therefore called a *donor*. (2) Missing Cu atoms, labelled V_{Cu}^{-}, which analogously is an *acceptor* that donates a free hole to the crystal. CZTS is typically p-type, likely because defects contributing to p-type have lower formation energies than those contributing to n-type.[64, 65] The doping concentration is affected by the composition of the different elements, i.e. Cu, Zn, Sn and S(e), but can also be affected by adding other elements, e.g. Na.[66, 67]

For CZTS it is common to create the pn-junction through the p-type CZTS, and the n-type *window layer* stack containing *buffer layer* and aluminum-
doped zinc oxide (AZO). When two layers of opposite doping are connected to form the pn-junction, free charge carriers on both sides diffuse into the other side due to the concentration difference, i.e. high concentration of holes on the p-type side and high concentration of electrons on the n-type side. This diffusion results in depletion of free charge carriers, leaving behind the charged ions fixed in the lattice on the respective side of the junction, which gives rise to an electric field. The depleted region is called the space charge region or depletion region/layer/zone. The interesting result of this, is that if minority carriers are created, for example by shining light on the semiconductor, and they reach the junction, they will be swept over by the electric field. Minority carriers that are generated within a distance of the diffusion length, will statistically get swept over the junction. This how collection of electron-hole takes place in semiconductor solar cell devices. However, not all generated electron-hole pairs get collected, many of them recombine because of defect states in the band gap, especially those with an energy near the middle of the band gap. These defect states are present due to a number of reasons, such as poor crystal quality, grain boundaries and defects. Much of the work on solar cells is aiming at reducing the amount of recombination.

In CZTS devices, the pn-junction is a so called heterojunction, i.e. the n-type side consists of another material than CZTS. In case of heterojunctions, careful consideration is required in terms of energy band off-set. This means one has to take the energy levels of the VBM and the CBM of the materials on the respective side of the junction into account. These must be somewhat similar to promote and not inhibit the collection process described above. If they are misaligned, the electric transport through the junction may be blocked and result in severe efficiency loss and high resistance in the device. This is described more in detail in section 3.3.2.

2.4.4 Comparing properties of solar cell devices

When comparing the performance of solar cell devices, there are mainly two measurements that are used: the quantum efficiency (QE) and current(-density)-voltage (JV). QE, as given by Equation 3, is the ratio between the incident photon flux, $\Phi_{in}$ and the output current for a given wavelength.

$$QE(\lambda) = \frac{I_{out}(\lambda)}{q\Phi_{in}(\lambda)}$$  \hspace{1cm} (Eq. 3)

One distinguishes between internal QE (IQE), where only absorbed photons are taken into account, and external QE (EQE), where the whole structure, including reflection and shading losses are also taken into account. Reflection- and shadowing losses may often be less interesting for understanding of the device itself, and they can often be reduced significantly with an anti-reflection (AR) coating, hence application of AR is often stated when used in
research publications. It is common to QE to characterize the photocurrent and the losses that are responsible for reducing the short-circuit current ($J_{sc}$), as shown in Figure 10 and the corresponding explanations in Table 1. The figure shows a $QE$ measurement of the best CZTS device produced during the work of this thesis (same as 2Mo_S in Figure 11, paper IV) and a competitive CIGS device produced in the group. As previously described, incident photons of different wavelengths are absorbed at different depths, which makes it possible to some extent determine at which depth and which different parts of the solar cell that are responsible for a certain loss. The photocurrent is given by Equation 4,

$$J_L = q \int_0^\infty \Phi_{AM1.5G}(\lambda)EQE(\lambda)d\lambda$$

(Eq. 4)

which basically says that the $J_L$ is given by integrating the product of the photon flux of the AM1.5G spectrum with the EQE over all wavelengths. This number is often used to calibrate the intensity for the $JV$ measurement (described below), and to correct the $J_{sc}$ achieved from the $JV$. There are different

![Figure 10. QE spectra of a CZTS device (from paper IV) and a competitive CIGS device with AR coating. The areas within the dotted lines area approximate representations of the photocurrent losses, according to [69]. The band gaps for these samples were calculated to 1.44 eV (861 nm) for CZTS, and 1.17 eV (1060 nm) for CIGS. The numbers and arrows are explained in Table 1.](image)
ways to extract the band gap of the absorber material from the QE measurement, which is described in detail elsewhere.[68]

Table 1. List of photocurrent losses in a thin film solar cell for corresponding numbers in Figure 10. As described by Hegedus and Shafarman.[69]

<table>
<thead>
<tr>
<th>No.</th>
<th>Corresponding optical or electrical loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Optical shading from the collection grid. Equal over all wavelengths.</td>
</tr>
<tr>
<td>2.</td>
<td>Reflections from the interfaces, here minimized due to AR coating.</td>
</tr>
<tr>
<td>3.</td>
<td>Absorption in the TCO front contact layer.</td>
</tr>
<tr>
<td>4.</td>
<td>Absorption in the CdS buffer layer.</td>
</tr>
<tr>
<td>5.</td>
<td>Incomplete absorption in the absorber layer near the band gap.</td>
</tr>
<tr>
<td>6.</td>
<td>Incomplete collection of generated electron-hole pairs in the absorber.</td>
</tr>
</tbody>
</table>

JV measurements are conducted by contacting the front- (n-side) and back (p-side) contact and measuring the output current while sweeping the voltage, commonly called bias, applied to the cell, over the voltage range of interest, typically from a negative voltage (reverse bias) to a positive voltage (forward bias). The measurement is typically first done under dark conditions followed by a measurement under illuminated (light) conditions. Doing this makes it possible to identify e.g. light induced effects, however, the extraction of device performance parameters is done from the light measurement, and the procedure to extract parameters has been explained by e.g. Hegedus and Shafarman.[69] Ideal curves follow the diode equation from the one-diode model, which is an equivalent circuit of an ideal solar cell, given in Equation 5.[70]

\[
J = J_0 e^{\left(\frac{qV}{nkT}\right)} - J_L
\]  
(Eq. 5)

\(J_0\) is the dark saturation current density, and a measure of recombination in the device. \(n\) is the ideality factor, which is a measure of how well the diode follows the diode equation, \(k\) is the Boltzmann constant and \(T\) is the temperature. For low efficiency devices, or solar cells with non-ideal behavior, some caution should be taken as they deviate from the commonly used models.

Measured \(JV\) curves of a CZTS cell (again, same as 2Mo_S in Figure 10, paper IV) and a competitive CIGS cell, respectively, are shown in Figure 11. One can notice the \(J_L\), which ideally, according to the one-diode model, should be the difference (superposition) between the illuminated and the dark \(JV\)-curve. Short-circuit current density \((J_{sc})\) is current per unit area in the solar cell at 0 V. The \(J_{sc}\) is theoretically ultimately determined by the band gap as already mentioned, and further limited both by optical losses as well as recombination, simply everything that reduces the number of collection events. Open circuit voltage \((V_{oc})\) is the voltage in the cell at zero current, i.e at open circuit. The maximal theoretical \(V_{oc}\) that can be achieved in a single junction solar cell device is determined by its band gap, therefore, when comparing solar cell devices with different band gaps, it is common to refer to the \(V_{oc}\)
deficit, given by Equation 6. The $V_{oc}$ for a given band gap is mainly limited by recombination.

$$V_{oc, deficit} = V_{oc} - \frac{E_g}{q}$$  \hspace{1cm} (Eq. 6)

Table 2. Solar cell parameters extracted from the JV-curves in Figure 11.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZTS</td>
<td>19.5</td>
<td>640</td>
<td>55.4</td>
<td>6.9</td>
</tr>
<tr>
<td>CIGS</td>
<td>35.1</td>
<td>728</td>
<td>78.4</td>
<td>20.0</td>
</tr>
</tbody>
</table>

The fill factor (FF) is defined by Equation 7, the product of the voltage and current at the maximum power point ($V_{mp}$ and $J_{mp}$), i.e. the maximum power of the solar cell, divided by the product of $V_{oc}$ and $J_{sc}$. It gives a measure of the quality of a solar cell given certain values of $J_{sc}$ and $V_{oc}$.

$$FF = \frac{V_{mp} \cdot J_{mp}}{V_{oc} \cdot J_{sc}}$$  \hspace{1cm} (Eq. 7)

In Figure 11, one can graphically understand FF as the fraction that the smaller rectangle (of green dashed lines) makes up of the larger rectangle.

Finally, the king of measures, the efficiency, $\eta$ or PCE. It is the fraction of the maximum power output of the cell of the total incident irradiation power, as also given by Equation 8.
The efficiency is obviously important for a number of reasons, not least for commercial solar cell products, as higher efficiency also means reduced material and energy consumption, and less area required for the same amount of electrical production.

As further denoted in Figure 11, there are two kinds of parasitic resistances that are of interest. \( R_{\text{series}} \) refers to the total series resistance of the whole device, i.e. the sum of the resistances of the individual layers and contact resistances between the layers. In a \( JV \) curve, a higher \( R_{\text{series}} \) results in a less steep curve at, and above, the \( V_{\text{oc}} \). \( R_{\text{series}} \) should be as low as possible. The shunt resistance \( R_{\text{shunt}} \) is a measure of which paths the light-generated current takes in the device, through the diode as intended, or through parasitic shunts. Ideally, a diode only allows current in one direction, but shunts can make it flow in both directions and therefore result in current rather going through the shunts than running through the external circuit. \( R_{\text{shunt}} \) should be as high as possible, which results in a flat curve when negative voltage is applied. Lower \( R_{\text{shunt}} \) results in more slope when negative voltage is applied. \( R_{\text{shunt}} \) is often caused by incomplete coverage of the layers in the device, i.e. a manufacturing defect, so that layers that are not supposed to be connected, are connected. Both high \( R_{\text{series}} \) and low \( R_{\text{shunt}} \) reduces the \( FF \).
CZTS is the common abbreviation of Cu$_2$ZnSnS$_4$ and its derivatives. It was first observed as a mineral in 1958. The mineral was named kesterite, after the place it was found in, the Kester deposit in northeastern Russia. The mineral also gave name to its most common and stable structure, although it can also crystallize in stannite structure, both visualized in Figure 12.[47, 71, 72]

In its pure sulfide form, it is possible to produce a solar cell device only containing relatively abundant, inexpensive and non-toxic elements. Therefore, the work in this thesis was mainly focused on the sulfide form. There are however other reasons to depart from the pure sulfide CZTS, namely that the semiconductor properties of CZTS can be tuned. The band gap can for example be tuned by adding Se to replace S, resulting in band gaps of ~1 eV for CZTSe, to ~1.5 eV for CZTS. Both the world record cells CZTS contained both S and Se and state band gaps of 1.13 eV, i.e. more Se than S.[23, 24]
CZTS was first suggested as a potential thin film solar cell candidate in 1988 by Ito et al. [47, 73] Their group also reported the first attempts to produce CZTS solar cells, using reactive evaporation on a stainless steel substrate and different transparent conductive oxides (TCOs) as front and back contacts [47, 74], but their devices suffered mainly from “very small” $J_{sc}$. It took until 1997, when Katagiri et al. reported the fabrication of a CZTS solar cell using evaporation and achieving an efficiency of 0.66%. During the following 10 years, the research on CZTS was limited to a few Japanese groups and an isolated attempt in Stuttgart.[47, 65, 75] The interest surged after 2008, as mentioned in the introduction, catalyzed not least by the occurring Si crisis. For more details about the early development, please find further reading in e.g. Ito et al. [47] and Katagiri et al.[14]

3.2 Deposition techniques and processing

During this work, where the experimental work was focused on thin films, several deposition techniques were used. These are briefly described here. CZTS can also be deposited by other techniques, and different wet techniques based on dissolution of the constituents in a solvent are rather common in research. Here however, I describe mainly the techniques that were used for this thesis. An illustration of the CZTS stack with the corresponding process steps are shown in Figure 13.

![Figure 13: Illustration of the CZTS thin film solar cell stack and the corresponding processing steps.](image)

3.2.1 Sputtering

_Sputtering_ is the main deposition technique used in the sample preparations in this thesis. There are different kinds of sputtering, and they have in common that a target material with a predetermined composition is bombarded with accelerated ions so that atoms are ejected from the target surface and become
deposited on a substrate. The deposition is performed in a controlled atmosphere, which has first been pumped down to a base pressure typically of $10^{-5}$ Pa. During the deposition, which typically is performed at a pressure in order of 1 Pa, certain gases are introduced in the chamber, most commonly Ar. In the most common configuration, magnetron sputtering, the target is placed in front of a magnetron able to produce a strong magnetic field, and a negative voltage applied to the target. The configuration creates a plasma near the target, consisting of Ar atoms, electrons and Ar ions. The negative voltage accelerates the ions towards the target, and the collision at the target surface ejects target atoms. Usage of inert gases as Ar as sputtering gas ideally results in films composed only of the same atoms as the targets, which is why both gases and targets of high purity are preferred. Ar itself can be incorporated in the film and cause blister formation. This has been studied in our group and it was found that it could by tuning the sputter parameters.[76] Magnetron sputtering has been used for the deposition of CZTS, i-ZnO, AZO and Mo described later in this thesis. Another common configuration, reactive sputtering, reactive gases are used. In this configuration, the reactive gases react both with the target atoms as well as with the atoms at the growing film/substrate. In this case, the films ideally consist of atoms both from the target and the reactive gas. Reactive sputtering was used on several occasions in the sample preparation for this thesis. In paper II and III, TiN was deposited from a Ti-target with N$_2$ as the reactive gas, mixed with Ar. In paper V, ATO was deposited using reactive sputtering with O$_2$ mixed Ar. A photograph of the target and plasma taken during ATO deposition is shown in Figure 14.

For conductive target materials, the most energy efficient way to power the targets is usually DC magnetron sputtering. however, for less conductive ma-

![Figure 14. Sputtering chamber with target and plasma. Photograph taken through the chamber window during deposition of ATO for experiments in paper V.](image-url)
terials RF sputtering or pulsed DC magnetron sputtering is required. RF sputtering typically offers more stable power supply to the target, but also slower deposition rates while requiring higher sputter power, therefore DC is often preferred when possible.

The film composition can further be controlled in a number of ways, both, as mentioned, by the atmosphere composition and the target configuration. The targets may consist of a single element, or several elements, then often referred to as compound targets. Some work in our group has been done using quaternary CZTS compound targets,[77, 78] but in this work, co-sputtering with three binary metal-sulfide targets has been used. An alternative way used by many other groups is sequential sputtering of stacked metal layers.

There are several parameters that affect the final film properties and morphology. Some of them are more predetermined already from the design of the sputter system, like the size of the targets and magnetrons, or the distance between target and the substrate.[79] Other important parameters are substrate heating, substrate bias, sputter powers, and sputter pressure, as they affect the sputter rate, film density, residual stress etc.

3.2.2 Other deposition techniques
Evaporation is also a deposition technique performed in vacuum. Also in this case vacuum is needed both to increase the mean free path of the evaporated atoms, so that they can reach the substrate, and for purity. The source materials to be evaporated and deposited are typically put in a crucible and energy added in different ways. The simplest example is probably resistive evaporation, where the material is heated to its evaporation point using electrical energy. Another common configuration is the so-called electron beam (e-beam) evaporation, where the source material is heated by an electron beam created from a charged tungsten filament. The deposition rate is controlled by filament charge. In this work, e-beam evaporation was used to deposit the metal front contact grids. The samples were covered with a shadow mask with openings formed in the desired grid patterns. It was further used for deposition of NaF, in that case no mask was used since uniform films were desired.

Chemical bath deposition (CBD) is a wet chemical deposition technique where solid reactants are dissolved in a liquid solvent and mixed together. The samples to be deposited are submerged in the solution, which altogether often is heated to increase the reaction/deposition rate. As the sample is submerged, the CBD may also have an etching effect, or dissolve e.g. soluble surface compounds. CBD was used to deposit the CdS buffer layer on top of the CZTS absorber layer. It was further the only non-vacuum deposition technique used in this work.

In Atomic layer deposition (ALD), gases, often called precursors, are led into the process chamber in sequential pulses and reaction takes place at the surface, ideally one atomic layer is deposited per ALD cycle. Therefore, ALD
typically offers extraordinary step-coverage and thickness control. Compared to the other deposition techniques described here, ALD offers rather low deposition rates, which practically limits the film thickness. The deposition may be sensitive to contamination related to the deposition history of the chamber, as suspected after deposition of TiN in paper III.

3.2.3 Annealing

The as-sputtered CZTS precursor does not work as a solar cell, but a heat treatment is necessary in order to make it recrystallize. This is, in many aspects the most challenging process step during the solar cell production. It was found early on that the CZTS is not stable at the required annealing temperature, as mainly Sn and S is lost from the surface.[80] Therefore, additional S must be used during the annealing to keep up the S partial pressure in order to avoid decomposition of the CZTS at the surface, see further in section 3.3.3 about the CZTS absorber layer. Depending on substrate, one may need to add diffusion barriers between the substrate and the rest of the deposited films. When steel substrates are used, diffusion of Fe has been shown to be harmful for the solar cell.[81-83] In this work, only SLG was used as substrate, and in this case Na has been shown to diffuse into the absorber layer during the annealing. However, in opposite to Fe, Na has been shown to be beneficial, or even required for high-efficiency CZTS solar cells. Except for the substrate, the back contact film and the CZTS absorber typically are the only layers present during the anneal, thus the requirements of chemical and thermal stability are extra high on these layers, and the interface between them in particular. This will be described more in detail in the chapter about back contacts. Figure 15 is an illustration of the two-step sputtering+annealing process to obtain CZTS absorbers of device quality.

**Two step absorber fabrication process:**

1. Co-sputtering

   ![Co-sputtering Diagram](image)

   **Precursor film**

2. Annealing

   ![Annealing Diagram](image)

   **Load lock**  **Cooling zone**  **Annealing zone**

   **CZTS absorber**

   **Back contact**

   **Annealed film**

*Figure 15.* Schematic illustration of the two-step fabrication process of 1. absorber sputter deposition and 2. annealing heat treatment. Below SEM-cross-sections of the films after the corresponding step.
3.3 The CZTS solar cell stack

Here I will briefly describe the different layers of the CZTS thin film solar cell stack. As the thesis is mainly related to the back contact, the other layers will be described more briefly, and the back contact somewhat more in detail. I describe the layers of the stack from top to bottom, which is opposite to the order in which they are deposited.

3.3.1 Front metal contact grid

A front contact grid consisting of Ni/Al/Ni is used. This configuration is chosen for the high conductivity of Al, which is encapsulated by Ni to avoid the otherwise rapid oxidation. Sequential e-beam evaporation is used for deposition, and the contacts are shaped using a shadow mask which covers all area except the area to be deposited.

The front contact grid is not required but the benefits are that it reduces the distance charge carriers have to be conducted in the TCO layer before being collected to the circuit. This means that the larger the area of the device, the more need for front contacts and vice versa, or deposition of a thicker TCO, as described in the next section. Therefore, in this thesis, in cases where solar cells were made with areas of 0.5 cm$^2$, front metal contact grids were deposited, while for cells with area of 0.05 cm$^2$ it was not. The main reasons for reducing the cell size is time saving, both for saving time of the deposition itself, but also in terms of increasing the chance to find some working cells when there are problems with adhesion, pinholes/shunting etc. For official world records, a minimum area of 1 cm$^2$ is required.[84] Another important benefit with metal contacts is for mechanical protection: in devices where the layers are brittle or adhesion weak, electrical measurements where electrical probes need to be contacted to the cell mean a significant risk of accidental damage of the device. Punch-through is in these cases very hard to avoid, but means that the cell has been destroyed and cannot be re-measured or used for other characterization. The contact grid is shadowing the area that it is covering, and is therefore reducing the active area of the device, but again, for larger area solar cells, the win in conduction and charge collection is larger than the loss in current caused by shadowing, see further e.g.[85]

3.3.2 Window layer

The window layer, or maybe often more correct, the window layers, are the layers deposited on top the absorber layer. It normally consists of the front contact layer and a buffer layer that makes up the n-side of the pn heterojunction. For the front contact layer, there are two main requirements; it should consist of a material with a wide band gap to minimize optical losses and maximize photon transmission, and have high conductivity in order to maximize
conduction and minimize $R_{series}$. The conductivity of common TCOs is good, but still cannot match metals, thus the above described contact grid needs to be added for larger areas. The band gap of ZnO is $\sim3.3$ eV,[86] which means the layer may absorb the small fraction of the sunlight with higher energy, and this absorption normally does not create mobile electron-hole pairs that contribute to the $J_{sc}$.[87] It is common that the front contact layer has a two layer-structure, in our case it has first, from the bottom, an $\sim80$ nm resistive i-ZnO layer, deposited for prevention of shunting paths. Then a $\sim210$ nm AZO ($E_g \sim3.5$ eV), designed to have a low sheet resistance. The combined ZnO structure normally has a combined $R_{sheet}$ of $\sim40 \, \Omega/\square$. AZO is n-type.

The layer below is the buffer layer, which is also part of the n-side of the pn-junction. As “inherited” from the CIGS stack, CdS deposited by CBD is a common choice also for CZTS, partially due to logistic reasons and convenience, but also since it offers a uniform coverage also at rough surfaces.[88] The relatively narrow bandgap of $\sim2.4$ eV cause some absorption, for $\sim50$ nm used in the baseline, around 50% of the photons with band gap higher than 2.4 eV are absorbed, as indicated in Figure 10/Table 1. For CZTSSe the band alignment to CdS has been reported to be beneficial, i.e. a small difference between the conduction band minima or a slightly positive offset.[89] For sulfide CZTS on the other hand, the conduction band alignment with CdS has been reported to be slightly negative, resulting in a so called cliff configuration, causing higher interface recombination and a lower $V_{oc}$ compared to better aligned materials.[89, 90] Several alternative buffer materials, both with higher band gap and better alignment to CZTS, have been studied (not least in our own group), e.g. ZnO$_{1-x}$S$_x$ by Ericson et al. [91] and Zn$_{1-x}$Sn$_x$O$_y$ by Platzer-Björkman et al.[92] (also by Li et al. [93]) and SnO$_x$.[94] The alternative buffer layers are often reported to give improved device performance, e.g. our in-house record device had a ZnO$_{1-x}$S$_x$ buffer layer. [91]

One could principally combine buffer layer and front contact layer in one single window layer, which has been demonstrated with decent device efficiencies ($\sim18$%) for CIGS with Zn(O,S).[95, 96]

3.3.3 Absorber layer

The absorber layer defines the solar cell – we call our solar cells CZTS thin film solar cells because the absorber layer consists of a CZTS thin film. The layer is referred to as absorber since its main purpose is to absorb photons. As mentioned, a one step process and deposition by evaporation was initially used to fabricate the absorber layer, as it for a long time had been the most successful route for CIGS. Thus far, the record for a co-evaporation one-step process is 9.2% for a CZTSSe device,[97] and 8.4% for a CZTS device.[98] In a one step-process, however, achieving high-efficiency devices becomes challenging due to a combination of conditions. Namely that evaporation (also sput-
tering) in general requires low process pressures, and CZTS requires high substrate temperatures during deposition to recrystallize. But Sn-(S,Se) species are volatile which leads to decomposition of the CZTS surface according to Reaction 1 under these conditions, as opposite to CIGS, as illustrated in Figure 16 (for Se containing CZTS).[99, 100] To counteract the surface decomposition reaction, one needs a controlled and sufficiently high chalcogen partial pressure, but e.g. the cold chamber walls makes it hard to control the chalcogen partial pressure.[101]

$$Cu_2ZnSnS_4(s) \leftrightarrow Cu_2S(s) + ZnS(s) + SnS(s) + \frac{1}{2}S_2(g); SnS(s) \leftrightarrow SnS(g)$$ (1)

All higher efficiencies of CZTS thin film solar cells have been achieved by various two-step processes where the first step comprises the deposition of the thin film, followed by annealing. The deposition can then be executed at lower temperatures to avoid decomposition, and the annealing can ideally be performed at high temperature in a controlled atmosphere. The deposition can be executed by a number of different techniques, evaporation, sputtering or solution based deposition as mentioned, but also *successive ionic layer adsorption and reaction* (SILAR),[102] *pulsed laser deposition* (PLD),[103] etc. *Monograin powder embedment* in epoxy is principally a one step process for

*Figure 16. CIGSe film before (a) and after (b) annealing. CZTS film before (c) and after (d) annealing (at 550 °C for 8 h).[100]*
absorber formation, but differs in many aspects from the other techniques described here.[104] The world record CZTSSe device from 2013 was made by solution based deposition.[23] Despite the apparent success using this route, sputtering is a popular choice and has been used for deposition in several of the cases for reported efficiencies above ~8% for both CZTS and CZTSSe.[99] It was also the method used to produce the recent repetition of the world record.[24] But also when it comes to sputtering, distinctly different routes are used, mainly divided into either (i) sequential sputtering from metallic or binary metal-(S,Se) targets of precursors with stacked layers, or (ii) simultaneous co-sputtering of a homogenous precursor (if the inhomogeneity isn’t intentionally created). Initially in our group we investigated reactive sputtering with H2S as the reactive gas, and both metallic and binary targets.[105] However, the reactive process was rather challenging in terms of controlling composition, therefore we focused on co-sputtering from binary CuS, SnS and ZnS targets. Except for good compositional control, the main idea with this configuration is to achieve homogenous distribution of elements in the sputtered precursor, possibly minimizing the risk of formation of secondary phases within in the absorber bulk as well as the required annealing time in the later heat treatment.

Na plays a crucial role in CZTS. This understanding is partly based on the CIGS research. For CIGS, Hedström et al. [106] found that CIGS absorbers grown on Na containing SLG performed significantly better compared to Na free borosilicate glass. The reason was the in-diffusion of Na from SLG during the heated deposition process. Soon it was shown that improvement from addition of Na was independent of application method.[107] Today common ways to perform Na-doping includes (1) in-diffusion from SLG, (2) deposition of Na-containing Mo as back contact, so called MoNa, (3) predeposition of NaF prior to absorber deposition, (4) predeposition of NaF on the precursor surface prior to annealing, or (5) through a post-deposition treatment with substrate heating. Today alkali doping is considered as vital for high-efficiency devices.[97, 108, 109] Keeping track of how different treatments or changes of e.g. back contact configuration affect the supply of Na is important in order to understand possible reasons for changes in material properties or device performance. For the same reason, relying on Na-supply from the SLG may not be the best solution in the long-term. Gershon et al.[110] showed that compositional variations of the glass result in non-uniform distribution of Na, which could be related to lateral compositional variations also in the absorber layer. This has been called alkali-driven phase separation, and is one example of situations that create detrimental secondary phases.[111]

Research has been performed also on other extrinsic doping- or alloying elements, those that have shown some significant device performances include e.g. H,[112] Ag,[113] Mg,[114] Cd,[115] In,[116] Ge,[117] Sb,[118] Mn,[119] and Fe.[120] For a systematic review of the effects of the various extrinsic dopants, please refer to e.g. Romanyuk et al.[67]
However, perhaps most research has still been related to the intrinsic properties of CZTS. The composition is one aspect, as it is of utmost importance for phase formation and e.g. intrinsic doping density. CZTS has a rather narrow single phase region, i.e. the range of compositions where CZTS exists as one single phase, as shown in the phase diagram in Figure 17.[121] Outside this region, it is expected to find other phases, more or less harmful for the solar cell performance. Possible secondary phases are the binary compounds ZnS, SnS, SnS$_2$, Sn$_2$S$_3$, CuS, Cu$_2$S and the ternary compounds Cu$_2$SnS$_3$, Cu$_3$SnS$_4$. All these have different properties, and different impact on the device performance, some of them summarized in table 3, based on the review of secondary phases by Kumar et al.[17] Some of these phases are hard to distinguish from CZTS using common characterization methods as e.g. XRD or Raman, due to peak overlap, which have made the pursuit for single phase CZTS somewhat more complicated and required e.g. scanning transmission electron microscopy-electron-energy loss spectroscopy (STEM-EELS) or STEM-energy-dispersive X-ray spectroscopy (EDX).[122]

![Figure 17. Isothermal section of Cu2S-ZnS-SnS2 system at ~400 °C. Including a selection of CZTS compositions that were used in the papers. In paper IV: TiN interlayer series annealed in (a) S and (b) Se, and (c) TiN bulk back contact series. In paper V, ATO series with (d) “less Cu-poor” and (e) “more Cu-poor” CZTS compositions, and (f) CZTS composition of ATO sample with the best performing device.](image)
Table 3. Examples of secondary phases, their properties and impact on solar cell performance, according to [17].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Cu2ZnSnS4</th>
<th>ZnS</th>
<th>Cu2S</th>
<th>SnS2</th>
<th>Cu2SnS3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap</td>
<td>~1.5 eV</td>
<td>~3.6 eV</td>
<td>~1.2 eV</td>
<td>~2.2 eV</td>
<td>~1-1.3 eV</td>
</tr>
<tr>
<td>Structure</td>
<td>Kesterite</td>
<td>Sphalerite/ wurtzite</td>
<td>Chalcolite</td>
<td>Rhombohedral</td>
<td>Cubic/ tetragonal</td>
</tr>
<tr>
<td>Electrical properties</td>
<td>P-type semiconductor</td>
<td>Insulator</td>
<td>p-type, metal like, highly defective</td>
<td>n-type semiconductor</td>
<td>p-type semiconductor</td>
</tr>
<tr>
<td>Impact on device</td>
<td>Insulating, reduces active area</td>
<td>Shunts</td>
<td>Forms diodes and barriers for carrier collection</td>
<td>Affects carrier collection</td>
<td></td>
</tr>
</tbody>
</table>

How detrimental the impact of secondary phases is, may be dependent on where in the absorber they are formed. E.g. SnS on the top surface is expected to be detrimental, while it has been suggested to have a beneficial, passivating effect if present on the rear surface.[123] However, in general they are expected to have a negative impact on the solar cell performance, thus control of the composition is necessary throughout the process. This includes both the steps in the two-step process, which was introduced for the reason of having better control of the composition. For the deposition process; our group started using compound sputtering from binary targets by Ar instead of reactive sputtering for better process control.

In the second step, the annealing, reaction is mitigated by keeping the chalcogenide partial pressure sufficiently high. However, in the setup of the anneal furnace mainly used for the experiments in this thesis, where elemental S, Se or S+Se is added in the graphite box, keeping the chalcogenide sufficiently high has proved to be hard, which typically limits the length of annealing before decomposition of the absorber layer is observed.[124, 125] A consequence that is essential in this thesis is the reaction occurring at the back contact, which partly is even worsened due to the described setup, this will be explained more in detail in the next section. Many groups, including our own, suffer from fluctuating baseline efficiencies. For Se precursors, the fluctuation has been linked to presence of the secondary phase ZnSe.[126]

Since the very beginning, it was identified that higher efficiencies were often achieved when a Zn-rich and Cu-poor composition was used.[127] Similar composition has also been used in reported CZTS devices with efficiencies of 9% or above,[104, 128-131], as well as for all CZTSe/CZTSSe of 10% or above.[23, 97, 132-134] However, stoichiometric composition does not necessarily result in poor devices, as e.g. Scragg et al. [21] reported 7.9% for a CZTS device with a nearly stoichiometric, which even is one of the better efficiencies reported from our group for a sulfide device with a baseline CdS buffer layer.[22]
One issue related to the absorber layer that have gained much attention is Cu/Zn disorder, i.e. the defects related to the small formation energy of Cu/Zn antisites. This has been called the culprit of CZTS, and has been related to the often reported band-gap or electrostatic fluctuations commonly seen as the reason for the band-tailing. When saying that CZTS has a band gap of 1.45 eV, it should be understood that this is often a simplification, as clusters of varying band gaps are present.

3.3.4 Back contact

The primary function of the back contact is charge carrier collection and conduction during solar cell operation. But as the bottom layer in the stack, providing adhesion to the absorber layer is also a fundamental requirement. Depending on substrate, e.g. if Na doping is provided by in-diffusion from an SLG, it also has the function as medium in which the diffusion takes place. The absorber layer may be the defining layer of the solar cell stack, but it is to large extent the back contact that defines the configuration of the solar cell device. For e.g. bifacial solar cells, the back contact simply must be transparent to allow bifacial irradiation of the absorber. And for tandem solar cells, transparent contacts are necessary to minimize absorption losses. Therefore, this research area is on one hand related to the Mo/CZTS interface and the related chemistry, and on the other hand to investigations of potential transparent back contacts in CZTS. The title of this thesis, can only be understood in the context that there is a dominating standard material, which is Mo. Illustrations of alternative back contact configurations are shown in Figure 18.

Figure 18. Schematic illustration of thin film solar cell stacks with alternative back contact configurations
3.3.4.1 Opaque back contacts

Mo as back contact material was inherited from the CIGS stack where it has been the most successful material.[127] Therefore, Mo has been, and still is to a large extent, synonymous with the back contact both for CIGS and CZTS in the case of single junction devices. In this context, the back contact and its interface to CZTS have repeatedly been identified as a key area for research and improvement of the CZTS device performance.[17-19, 135, 136]

As described above, the two-step methodology for CZTS fabrication has to a large extent been developed to address and reduce decomposition of the absorber surface at elevated temperatures and has become the dominating methodology. But it was soon found that the surface decomposition could not alone account for the losses when CZTS is annealed in insufficient chalcogen pressure. Scragg et al. showed through thermodynamic calculations and experiments that CZTS(e)/Mo is unstable under typical anneal conditions and reaction 2 occurs.[21, 100]

\[2 \text{Cu}_2\text{ZnSnS}_4(e) + \text{Mo} \rightarrow 2\text{Cu}_2\text{S}(e) + 2\text{ZnS}(e) + 2\text{SnS}(e) + 2\text{MoS}(e)\_2\] (2)

The result is formation of MoS(e)\_2 and decomposition of the CZTS(e) to secondary phases, with calculated free energy change at 550°C of the reactions of around −100 kJ for CZTSe and −150 for CZTS. The corresponding reaction for CIGS was found to have a positive free energy, i.e. the interface is thermodynamically stable under the same conditions (see Figure 16). While reaction 1, taking place at the top surface, to large extent could be inhibited by supply of S(e), reaction 2 was found to occur in both cases, both with and without S(e) in the atmosphere, due to time window from the start of the anneal, until the S(e) has diffused through the absorber and become available to inhibit decomposition of CZTS. The decomposition into secondary phases is, as previously discussed, detrimental to the device, while the formation of MoS(e)\_2 is commonly considered as beneficial, as long as it does not grow too thick. A thin layer of MoS(e)\_2 is present also in CIGS after deposition in normal evaporation conditions, but it can grow (excessively) thick and cause high \(R_{\text{series}}\) under the similar sulfurization/selenization anneal conditions.[137] In this case, S(e) diffuses from the surface via grain boundaries so that S(e) is supplied and the MoS(e)\_2 continues to grow during the duration of the anneal without decomposition of the CIGS absorber, and one can conclude that in this case reaction 3 occurs.

\[\text{Mo} + S(e)\_2(g) \rightarrow \text{MoS}(e)\_2\] (3)

The diffusion of S(e) is rather fast, and investigated by both Scragg et al.[21] and by Shin et al.[138] Both could conclude that the diffusion, despite high partial S(e) pressure, and high temperature, takes long enough time to reach
the back contact interface for reaction 2 to still occur uninhibited. Consequently, the standard configuration with an absorber layer deposited directly on a Mo makes it difficult to avoid (i) decomposition of the absorber layer near the back contact, and (ii) risk of excessive growth of MoS(e)2.

Both Scragg et al.[20] and Shin et al.[139] suggested introduction of a thin, ~20 nm TiN layer for chemical passivation and suppression of reaction 2. In both cases, reaction 2 could be suppressed. For Scragg et al. [20], using reactive sputtering of the TiN layer, the thickness of MoS2 decreased to below the resolution limit for the SEM (the 20 nm TiN layer couldn’t be resolved either) but they found weak bands of MoS2 in Raman, when measured on the Mo after exfoliation of the absorber layer. TEM-EELS, limited to (only) a ~10 nm wide section, showed that the TiN layer was intact, and SIMS indicated no significant change in Na diffusion. Shin et al., [139] using reactive thermal co-evaporation, reported on the other hand a mixed TiN/MoSe2 layer. Shin et al.[139] re-optimized their anneal process as the TiN layer allowed higher temperatures to be used and could increase efficiency from 6.4% (540 °C, with AR) for the best Mo reference, to 8.9% with TiN interlayer (570 °C, with AR), still having a ~220 nm MoSe2 layer. In the re-optimized process, the efficiency for the Mo reference was reduced to 2.9%. Noticeable is also that with a TiN layer, annealing temperature could also be reduced from 570 °C to 480 °C and still achieve similar efficiency (6.3%, without AR) as for the best Mo. Scragg et al.[20] on the other hand only compared performance in the same process (560-570 °C), and in their case, the performance was not improved. One important conclusion here anyway, was that the parts of the required S(e) pressure during the anneal is needed to reduce formation of secondary phases at the back contact and not only on the top surface of the absorber. However, secondary phases were still (despite nearly stoichiometric composition) found at the back contact, covering ~10–20% of the back contact area in all samples, but consistently less for samples with TiN.

After these publications, many groups have studied a variety of alternative back contact configurations using interlayers between Mo and the CZTS(e) absorber layer, including e.g. ZnO,[140] Ag,[141-143], TiB2,[144] Au, W, Pd, Pt, Ni,[145] TiN, TiW, Cr, Ti, Al,[146] C,[147] Bi,[148] Al2O3,[149, 150] MoOx,[151-153] SnS,[154] MoN,[155] a-SiC,[156] Si3N4,[157] and TiN.[158] In some studies where TiN was used as an intermediate layer, the solar cell performance was reported to improve or even be the best out of a number of tested candidates, as in the cases of Shin et al.,[139] Oueslati et al.,[146] and Schnabel et al.,[158] Nevertheless, there are also publications reporting no improvement for solar cells when using TiN as interlayer, like Scragg et al.,[20] as discussed, and also e.g. [153]. However, TiN is an attractive candidate as interlayer material, and the scattered reports rather invite more detailed characterization and scrutiny. TiN has excellent thermal and electrical properties, which has made it one of the most studied, and state-of-the-art diffusion barrier materials in various applications of electronics.[159-161] In the context of interlayer barrier for CZTS, it is suitable since the work
function is close to that of Mo and could be considered as an ohmic contact to CZTSe, even more ohmic than Mo.[146] For these reasons, in Paper II, III and IV, in-depth characterization of TiN interlayers with varied thickness on Mo/SLG substrates was performed.

3.3.4.2 Transparent back contacts

Research on transparent back contacts is required to develop high-efficiency bifacial- or tandem solar cell devices. In contrast to the ‘opaque case’, there are few studies made on transparent back contacts for CZTS, and there is no established baseline option. However, due to their overall superior performance, SnO2-based TCOs have been the most common alternatives to study.

As can be understood from the introduction of bifacial- and tandem solar cells, the requirements are different for the two configurations. In case of bifacial solar cells it is about (i) increasing the amount of incident light to the absorber and, at the current stage of the research, (ii) making the absorber thin enough to enable electron-hole pairs generated at the back contact to reach the pn-junction at the top of the absorber. There are however no specific requirements on e.g. the absorber band gap; the solar cell itself should just perform as good as possible. Therefore, most of the research intended to make bifacial solar cells has been made mainly using CZTS since it historically and still today has shown superior performance compared to CZTS. For tandem solar cells on the other hand, the whole principle is about absorption and transmission of certain parts of the solar spectrum. Consequently, considering the band gap for each layer is essential. However, single-junction Si solar cells have reached about 90% of its SQ-limit and further progress will inevitably sooner or later require steps outside the single-junction configuration.[162-164] Addition of a wider band gap solar cell on top of a Si bottom cell is a hot candidate for this shift. In this context, CZTSe or CZTS does not make sense to use due to its narrow band gap. CZTS on the other hand, with a band gap ~1.5 eV makes more sense, and alloying with e.g. Ge would make it possible to tune the band gap, and achieve an optimal band gap between 1.6-2.0 eV.[165]

Mali et al.[166] were among the first to report some device efficiency (1.9%) after deposition of CZTS on fluorine-doped tin oxide (FTO) using SILAR. Mahajan et al. used a similar approach to deposit CZTS on both indium-doped tin oxide (ITO) and FTO, also reaching similar device results of 1.7% and 2.1% respectively. Ismael et al. were in the same range when they reached 2.2% by deposition of CZTSe on FTO using a solution-based route and spin-coating followed by a two-step sulfurization+selenization annealing. Ge et al. made some substantial contributions through a number of publications, first by deposition of CZTS by coelectroplating on ITO and found that In diffused into the absorber when using anneal temperatures above 500 °C.[167] Also they were initially in the same range by reaching an efficiency of 2.7%, with front illumination (and 3.1% with bifacial illumination) after annealing in H2S at 520 °C. However, in a following publication, they instead annealed at
540 °C in less reactive “S vapour atmosphere” and could reach a front illumination efficiency of 5.8%, partly attributed to a less deteriorated back contact compared to the previous study.[168] Kim et al.[169] sputtered Cu/Sn/Zn also on both ITO and FTO back contacts, followed by selenization. They reached the best efficiency on FTO, namely 6.1% (bifacial illumination), compared to 4.3% for ITO. The difference was partly explained by higher degree of voids when using ITO, however, in both cases interfacial reactions and secondary phases were found at the back contact interface. Recently a new strategy to improve performance has been used for transparent back contacts, namely the introduction of a thin Mo interlayer. Espindola-Rodriguez et al.[170] compared CZTSSe absorbers for both Mo- and MoNa interlayers on FTO substrates. The interlayers improved the bifacial device efficiency from 3.1 % to 7.7% with the Mo interlayer, and to 7.4% with MoNa interlayer. In both cases, the interlayers where found to improve adhesion and electrical contact between the layers. In another study they found that i-ZnO interlayer on ITO instead slightly degraded performance from 1.8% to 1.6%.[171]

In paper V, a previously not exploited alternative, namely antimony-doped tin oxide (ATO), and some of the above presented strategies are investigated for the production of CZTS solar cells devices with transparent back contacts. ATO is a well-known TCO and was initially commonly used in LCDs.[172] It was chosen, partly because it has been suggested for high-temperature applications and solar cells.[173-175]

3.3.5 Substrate

Thin film solar cells must have a substrate to be deposited on. There is a wide range of different substrates used, giving different properties to the solar cell. Polymers and textiles allow for particular light-weight and flexibility. Steel is ductile and bendable and also high-temperature tolerant and considered light-weight compared to the heavy frames required for Si solar cells. The possibility to use light-weight substrates makes thin film solar cell suitable for BIPV, a steadily increasing market.[176, 177] SLG is finally very common, and the substrate used in all experiments in papers II-V. Different substrates requires different solutions for various issues. Steel substrates for examples require a diffusion barrier for iron, as well as addition of Na, by e.g. using Na-containing Mo (Na2MoO4).[77]
4. Characterization methods

4.1 Ion Beam Analysis

Ion beam analysis (IBA), is a set of standard-less ion beam-based methods capable of providing elemental composition and depth-resolved information of the sample of interest.[178] In IBA, probing ions are accelerated to a well-defined energy and hit the “target” (i.e. the sample being analyzed). The result of the interaction between the ions/target materials is detected and analyzed, yielding different information about the sample. Different methods detect different kind of interactions, and they can be operated with different ion beams, and/or geometries.[179] IBA facilities usually require dedicated infrastructure with one or more particle accelerator, as well as different beam lines for different experimental approaches. In this thesis, we have used the IBA infrastructure of the Tandem Laboratory at Uppsala University,[180, 181] and employed four different techniques: Rutherford backscattering spectrometry (RBS), Particle-induced X-ray emission (PIXE), Elastic recoil detection analysis (ERDA) and Medium-energy ion scattering (MEIS) – as discussed in more details below.

Compared to many other techniques for elemental depth-profiling, IBA is considered “non-destructive” as the measurements commonly do not result in e.g. a sputtered crater.[178] However, due to the high energies being used, (typically several MeV per nucleon) there are observations of ion-induced modification of sample morphology and structure during the measurement. Therefore, one must monitor whether the detected IBA spectrum changes over time as the measurement proceeds, if e.g. elements with high vapor pressure are being analyzed. In this thesis, no IBA measurements were conducted on device structures, only at different thin film layers and substrates. However, the very same setup and beam lines are used for standardized tests to simulate accelerated space radiation. The radiation typically has a detrimental effect on solar cell performance which increases with dose of radiation/time. This phenomenon has been studied for CZTS in our group.[182, 183]

IBA is to a large extent based on the principles of classical mechanics, where ions and atoms are spheres with defined masses and velocities that collide and transfer energy and momentum. Matrix effects are limited, and the methods can therefore be used directly for quantitative elemental analysis, almost exclusively without need of standards. However, both probing ions and recoiled atoms will further lose their energy while they travel through matter
due to collisions with the electrons and nuclei of the target atoms, in a process referred to as stopping power.[184] Stopping power is a fundamental quantity in IBA as it gives depth the perception, hence it needs to be known with sufficient high accuracy.[185] At the same time, it can be complex and involves many kinds of interactions between the projectile ion, target nuclei and target electrons. These interactions have been intensively studied since the 20th century because of their significant importance in several fields of physics and technology,[178] and nowadays it still remains as a very active research field.[186-188] Experimental databases and the knowledge on stopping power are continuously expanding as much fundamental research is also going on, where e.g. RBS and ERDA have been more extensively studied and have a longer history than e.g. MEIS.[178, 189] The Stopping and Range of Ions in Matter (SRIM) code is the most used computational tool to import semi-empirical stopping power data and it was also used as default choice for the experiments in this thesis. For an extensive theoretical background of IBA, please refer to e.g.[178].

4.1.1 Rutherford backscattering spectrometry

RBS got its name from Ernest Rutherford, the physicist commonly known for his gold foil experiment after which he could formulate his new and rather accurate atomic model in 1911.[190] In RBS, the probing ions are preferably lighter than the atoms in the target. The ions are elastically backscattered after collisions with the atoms in the target, and their energies measured by a detector. Equation 9 is the key equation for RBS, where the parameters are also annotated in Figure 19.

\[
K_{\text{projectile}} = \frac{E_1}{E_0} = \left[ \frac{\pm \sqrt{M_2^2 - M_1^2 \sin^2 \theta + M_1 \cos \theta}}{M_1 + M_2} \right]^2
\]  
\text{(Eq. 9)}

The \textit{kinematic factor}, \( K \) is simply the ratio of the energy of the accelerated probing ion before \( (E_0) \) and after \( (E_1) \) collision with the target atom. \( M_1 \) and \( M_2 \) is the masses of the probing ion and target atom respectively, and \( \Theta \) is the scattering angle. From Equation 9 along with the semi-empirical stopping powers, it is possible to obtain a mass perception (i.e. composition), and distribution of target elements as a function of depth below the surface, as well as areal densities in atoms per unit area (which can be used to calculate film density if the film thickness is known). RBS is an absolute method that does not require standards, but it is often used to determine absolute compositions for references and calibration samples used for other methods. Common ions are \(^{3,4}\)He and up to C, and typical particle energies in the MeV range (hence it is possible to reach a depth up to \( \mu \text{m} \) scale, depending on the system). For an extensive discussion about RBS, see [191].
As can be further understood from Equation 7, RBS analysis alone can be challenging when elements with similar atomic masses are present in the matrix, as in paper V, when the composition of the ATO film was to be determined. In that case, PIXE was measured simultaneously and could lead to a correct ratio between Sn and Sb, as shown in Figure 20.

Figure 19. Illustration of Rutherford backscattering spectrometry.

Figure 20. RBS and PIXE spectra of ~850 nm thick ATO films on SLG, from paper V.
4.1.2 Time-of-Flight Medium-Energy Ion Scattering

MEIS is based on the same principle as RBS.[192] As the name reveals, it operates in a certain, “medium” energy domain, which is lower than standard RBS with MeV ions (sometimes RBS is even referred to as HEIS – High-Energy Ion Scattering). The underlying physics, however, are still simple when compared to Low-energy ion scattering (LEIS), which operates in a yet lower energy domain.[192] D⁺ and He⁺ are typically used as projectile ions, with energies typically around 50-200 keV. The lower energy regime, in combination with a ToF detection system (ToF-MEIS – as available at Uppsala University [193]) makes the method more sensitive to e.g. surface morphology, on the expense of possible probing depth, typically limited to few tens of nm. Within the probing depth on the other hand, it is possible to obtain depth profiles of sub-nm resolution.

For the experiments described in paper II and paper III, the samples with 20 nm TiN on Mo, ToF-MEIS with 80 keV He⁺ ions was chosen to study the surfaces in detail. ToF refers to the particular measurement setup being used, which actually has been used ever since MEIS was suggested as separate method.[189] Moreover, the ToF-MEIS from Uppsala University features a beam-chopper system that “cuts” the probing beam into beam packets, typically on ns time-scale, which makes it possible to measure the time-of-flight with sufficiently high resolution. The position-sensitive energy detector measures hence both the kinetic energy of the backscattered particles hitting the detector.

The main ToF-MEIS scattering chamber also features beside the detector itself more equipment to better imitate some in-situ processing conditions. In paper III and IV, the option of sample heating in the MEIS chamber was utilized to investigate the possible influence of thermal expansion on TiN coverage and surface morphology.

4.1.3 Time-of-Flight Elastic Recoil Detection Analysis

In ERDA, target atoms are knocked, to become recoils, by the probing beam, and travel onwards to the detectors. The kinematic factor in ERDA is given by Equation 10, with the corresponding parameters also annotated in Figure 21,

\[ K_{\text{recoil}} = \frac{E_2}{E_0} = \frac{4M_1M_2}{(M_1 + M_2)^2} \cos^2(\Phi) \]  
(Eq. 10)

where \( E_2 \) is the energy of the recoil atom, \( E_0 \) the energy of the probing ion, \( M_1 \) and \( M_2 \) the masses of the probing ion and the recoil atom, respectively, and \( \Phi \) is the recoil angle. The kinematics of elastic collisions only allows the recoils to occur in the forward hemisphere, why the angle between the incident probing beam and the exiting recoils always is >90° (i.e. \( \Phi \) in Figure 21 is <10°). Since it is easier to create recoils using heavier probing ions, ERDA make use
of the heaviest ions among the IBA methods described here. In paper II and III, $^{18+}$ was used as probing ion.

The yield of recoils of a certain element is directly proportional to the content of the element in the layer being investigated (the same principle as RBS). To accelerate the heavier ions, larger accelerators are generally required, which probably is the main drawback of heavy-ion ERDA in comparison to RBS. The main advantage on the other hand is that detection of recoils means particles of different size and charge, which can be independently determined in addition to their energy (in RBS, the detected particles are all of the same kind, and both mass and depth are mixed in one energy spectrum). In the setup used in this thesis, the separation is made through a ToF detector, e.g. as shown in the Figure 21.[194] Two timing detectors record the time of flight before reaching the final energy detector. The resulting coincidence ToF/Energy plot will give banana-like shapes of detected recoils for each present element when the time of flight vs. energy is plotted (see e.g. paper II and III). A fraction of the probing beam may also be scattered towards the ToF/E detector, depending on the combination of ion/target, which will increase the heavier elements that are being analyzed. It is therefore beneficial to use ions that are significantly heavier than the target material, otherwise they overlap, making the evaluation rather difficult. The setup will also result in implantation of the beam ions, which will increase the scattering events as the measurement goes on. Analogously, light elements are the easiest to separate and detect.[195] In conventional ERDA measurements, the energy domain is high enough to avoid “sputtering” of the sample materials, instead, incoming ions will be implanted in the sample, and only a fraction of the incident ions will result in a recoil event.

![Figure 21. Illustration of ERDA principle.](image-url)
4.1.4 Particle Induced X-ray Emission

PIXE is preferably measured simultaneously with RBS, if possible. The same beam generates both scatter events along with X-ray emission, however, most work thus far has been done with He ions (which usually is the first choice for conventional RBS), and heavier ions are less explored.[178] In PIXE, as illustrated in Figure 22, the impinging ions transfer their energy to the electrons surrounding the atom nuclei during their travel through the target material. Some events will result in electrons being excited to higher energy, and when they will relax back to their ground state, they release energy as X-rays which are detected. Each element has characteristic electron energies, and the intensity of the characteristic energies will be proportional to the amount of each element, i.e. PIXE is used as both quantitative and qualitative method, but can be used to determine ratios, as in Figure 20. Due to self-absorptions of the X-rays in the matrix of the sample, associated with depth-penetration by the incoming probing ion, a quantitative analysis requires an higher level of experience by the experimentalist (see for instance discussions in the Sec. 3.1 of [196]). Nevertheless, it can be used together with another IBA method as boundary conditions, when some limitations of some technique can be fulfilled with PIXE information. As many people are more familiar with EDX, PIXE is often described as “EDX with ions instead of electrons”.

![Figure 22. Schematic illustration of the PIXE principle.](image-url)
4.2 Electron microscopy and X-ray based analysis

4.2.1 Scanning electron microscopy

In SEM, a sample is scanned by a focused electron beam and the electrons that escape after interaction with the sample are detected. The electrons can either be backscattered beam electrons, or ejected from the material by the beam electrons, then commonly referred to as secondary electrons. For backscattered electrons, scattering on heavier atoms results in electrons with higher energy and vice versa, which produces an image with contrast between heavy and light elements. Backscattered electrons are mainly used to obtain images where compositional differences are visible. The probe volume depends on the acceleration voltage (which might be limited by (low) conductivity of the sample) and the atomic number of the elements (the heavier, the more shallow probing depth), but is typically a few µm for backscattered electrons. Secondary electrons have lower energy, which limits the depth from where they can escape to a few nm. The intensity depends on the number of secondary electrons that reach the detector while the beam scans over the probed area. It can be used to obtain images where shape and topography is to be analyzed.

For imaging, the main advantage of electrons compared to photons (in light microscopy), is the smaller wavelength, which allows electron microscopes to produce images of higher resolution as well as better depth of focus compared to light microscopes. In the microscopes used for the studies in this thesis, the focus, alignment of lenses, exposure as well as brightness and contrast are usually adjusted by an operator to achieve a sharp image of >100 000 magnification and close to nm resolution. Typical acceleration voltages are 0.5-30 kV. Some SEM are equipped with an EDX detector that can detect the characteristic X-ray emission from the sample induced by the incident electrons. SEM is non-destructive.

4.2.2 Scanning transmission electron microscopy

Electrons are detected also in STEM, but detection is made after electrons have transmitted through the sample. To obtain meaningful and clear results, rather extensive sample preparation using a Focused ion beam (FIB) is required along with acceleration voltages of a few hundred kV. The FIB is used to cut out a piece of the sample, and polish it down to a sufficiently thin, typically µm wide, cross-section of the sample, a STEM lamella. When the electrons in the beam transmit through the sample, they interact with the sample atoms, which can be detected by various kinds of detectors. In paper II, IV and V, bright field STEM was used along with either electron energy loss spectroscopy (EELS) or EDX. In STEM, the beam scans through the sample, pixel by pixel (spot size of ~0.1 nm) and an annular dark field detector detects the number of transmitted electrons for each pixel. Differences in atomic masses
(or sample thickness) give contrast and make it possible to distinguish different layers in e.g. a thin film solar cell stack. EDX, which is based on the same principles as for EDX in SEM, or EELS, which measures the amount of energy lost by electrons can both be used to obtain chemical maps of the samples. The loss is characteristic for different elements and the image can be interpreted as chemical maps.

4.2.3 X-ray photoelectron spectroscopy

For analysis of surface composition and chemistry, XPS is a powerful and non-destructive technique. XPS spectra are obtained by irradiating a sample with a monoenergetic X-ray beam, the one used in the experiments of paper II, III and IV comes from an Al K\textsubscript{α} source of 1486.7 eV. The X-ray interacts with atoms, causing them to be emitted by the photoelectric effect.[197] The kinetic energies of the emitted electrons are measured, and equation 11 is used to calculate the binding energy,

\[ E_{\text{kinetic}} = h\nu - E_{\text{binding}} - \Phi \]  

where \( h\nu \) is the energy of the photon and \( \Phi \) is the spectrometer work function. The binding energy will depend not only on the atoms of elements from which the electrons originate, but also on what other elements the atoms are bound to, giving rise to chemical shifts, which can be used to identify the chemical state of the materials being analyzed. When analyzing multi-element materials such as CZTS, peaks will likely overlap. Software can be used to fit the overlapping peaks, if one only has some knowledge about the element being present. Although the X-rays have probing depths of a few µm, the probing depth in XPS is limited by the limited path length of the photoelectrons, which only is few tenths of Å. Due to its high accuracy, XPS is commonly used for qualitative analysis, but furthermore, the intensity of the peaks is proportional to the amount of the related kinetic energies, XPS can therefore be used, with some caution, for relative quantification, as in paper II and IV, where the amount of Na on the surface was compared and used as a measure of Na-diffusion through the back contact during annealing.

4.2.4 X-ray fluorescence spectroscopy

In XRF, high-energy X-rays are used as probing beam. In a similar fashion as in the Ions Figure 22, the X-rays excite electrons from their orbitals, and when electrons from higher energy orbitals relax, they emit X-rays with energy corresponding to the difference between the higher-energy orbital and the lower-energy orbital involved in the transition. The energy of the emitted X-rays is detected. The intensity of peaks in the obtained spectra are proportional to the amount of the corresponding orbital transitions. However, elements with overlapping X-ray energies may be present in the sample, which is the case of
sulfur and molybdenum. Sulfur was therefore not included when the composition was measured for the as-deposited CZTS-precursors in paper IV and V. Compositional comparisons can be made, and with a reference calibrated by IBA, very accurate compositional ratios can be obtained in quick measurements. This approach is used in the group to obtain the cation ratios in the CZTS precursors and is described in detail elsewhere.[198]

4.2.5 X-ray diffraction

X-rays are used to irradiate a sample also in X-ray diffraction (XRD), but here, the diffraction caused by crystal structure are being detected. Different crystals have different spacing between their crystal planes, giving rise to reflections at certain angles, fulfilling Bragg’s law, Equation 12,

\[ 2d \sin \theta = n\lambda \]  

where \( d \) is the interplanar lattice distance, \( \theta \) is the angle between the incident beam and the sample plane, \( n \) is an integer and \( \lambda \) is the wavelength of the incident X-ray. When XRD was used in paper V, Cu K\( \alpha \) with wavelength of 1.54 Å was used.

There are a handful of different ways to utilize the XRD phenomenon. Two common configurations are the so-called \( \theta \)-\( 2\theta \) and grazing incidence. In the former one, the probe of irradiating X-rays is scanned by changing the angle \( \theta \), while the detector follows at the angle \( 2\theta \), as visualized in Figure 23, i.e. on the same height on the opposite side of the sample as measurement is conducted. In this configuration, only lattice planes parallel to the surface give rise to reflections. In grazing incidence, also shown in Figure 23, the X-ray probe is kept at a constant angle, and the detector scans over a desired range of angles. This configuration is popular for thin films, as a low incident angle make the beam path through the sample longer, and thus higher intensity can

\[ \text{Figure 23. Schematic illustrations of XRD, (a) } \theta \text{-}2\theta \text{ configuration, and (b) Grazing incidence configuration, where the X-ray source is fixed at an angle } \omega \text{ during the measurement.} \]
be achieved. It also gives information from grains with lattice planes not being parallel to the surface. In both configurations, the more lattice planes of a certain orientation, the higher intensity of the reflection. The acquired patterns can then be compared to patterns in databases where elements and compounds with known composition are to be found. For more complex samples, like CZTS, typically consisting of several phases, there may be reflections from different phases occurring at the same angle, making a complete interpretation challenging or even impossible.

4.3 Elemental depth-profiling

4.3.1 Secondary ion mass spectrometry
SIMS was conducted by, and in collaboration with, the Semiconductor physics group at the University of Oslo. It is used to analyze the composition and distribution of atoms in solids and thin films by sputtering the surface with a focused ion beam and detecting and analyzing the mass/charge ratio of the secondary ions, i.e. those being sputtered from the sample, by a mass spectrometer. The sputtered surface is destroyed and the method is therefore considered as destructive. It’s strength is a very low detection limit, between ppm and ppb, making it the most sensitive technique for compositional analysis.[199] However, factors, such as matrix effects and large variations in ionization probabilities mean it is not an absolute technique, making quantification difficult, unless standards with known composition are used. The depth resolution of 1-2 nm can be obtained depending on sputtering rate, roughness of the sample etc. For the samples used in paper IV, it was estimated to 10-50 nm. The spot size of the beam is typically between 0.5 to 5 µm. Normally, a depth profile for different ions are measured, but also lateral profiles can be measured by keeping the information of the beam position as it raster over an area.

4.3.2 Glow discharge optical emission spectroscopy
In GDOES the sample is being sputtered by argon ions by using the sample itself as a cathode (analogue to a target during sputter deposition). During the sputter process, photons are emitted with characteristic wavelengths for different elements. As the sputtering and recording is taking place continuously, compositional profiles are acquired. Metallic samples can be sputtered by a DC-plasma, but in the case of less conductive materials, as semiconductors like CZTS, RF can be utilized.
Table 4. Overview of chemical measurement- and imaging techniques.

<table>
<thead>
<tr>
<th>Method</th>
<th>Probing beam</th>
<th>Detection</th>
<th>Obtained information</th>
<th>Used in:</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBS</td>
<td>Ions (H-C) 2-36 MeV</td>
<td>back-scattered</td>
<td>Absolute concentrations</td>
<td>All papers²</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ions</td>
<td>of heavy elements</td>
<td></td>
</tr>
<tr>
<td>ToF-MEIS</td>
<td>Ions (H-He) 50-200 keV</td>
<td>back-scattered</td>
<td>Surface composition</td>
<td>II, III</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ions</td>
<td>and morphology</td>
<td></td>
</tr>
<tr>
<td>ToF-ERDA</td>
<td>Ions (Cl, I) 2-100 MeV</td>
<td>recoiled</td>
<td>Absolute concentrations</td>
<td>II, III</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ions</td>
<td>of light elements</td>
<td></td>
</tr>
<tr>
<td>PIXE</td>
<td>Ions (H-He) 2-4 MeV</td>
<td>X-ray emission</td>
<td>Qualitative and</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>quantitative information</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Electrons 0.1-30 keV</td>
<td>electrons</td>
<td>Morphology</td>
<td>All papers</td>
</tr>
<tr>
<td>SEM-EDX</td>
<td>Electrons 2-30 keV</td>
<td>X-ray emission</td>
<td>Chemical information</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>of objects in SEM</td>
<td></td>
</tr>
<tr>
<td>STEM</td>
<td>Electrons 2-30 keV</td>
<td>transmitted</td>
<td>High-resolution cross-</td>
<td>V</td>
</tr>
<tr>
<td>STEM-EDX</td>
<td>Electrons 300 keV</td>
<td>X-ray emission</td>
<td>sections</td>
<td>IV, V</td>
</tr>
<tr>
<td>STEM-EELS</td>
<td>Electrons 300 keV</td>
<td>transmitted</td>
<td>Chemical maps of STEM</td>
<td>II, III</td>
</tr>
<tr>
<td></td>
<td></td>
<td>electrons</td>
<td>micrographs</td>
<td></td>
</tr>
<tr>
<td>XRF</td>
<td>X-rays</td>
<td>X-ray emission</td>
<td>Quick composition</td>
<td>All papers</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>measurements³</td>
<td></td>
</tr>
<tr>
<td>XPS</td>
<td>X-rays</td>
<td>electrons</td>
<td>Chemical characterization</td>
<td>II, III, IV</td>
</tr>
<tr>
<td>SIMS</td>
<td>Ions</td>
<td>Mass/charge, sputtered ions</td>
<td>Elemental depth profiling</td>
<td>IV³</td>
</tr>
<tr>
<td>GDOES</td>
<td>Ions</td>
<td>optical emission</td>
<td>Elemental depth profiling</td>
<td>(IV³), V</td>
</tr>
</tbody>
</table>

¹In some cases, data processing may be required, and the methods are not limited to only obtain the mentioned information. ²At least indirect, since composition measurements by XRF were calibrated by RBS, ³If calibrated with some absolute method, e.g. RBS, ⁴Published in this thesis.

4.5 Electrical and optical characterization

4.5.2 Current(-density)-voltage measurements

The $JV$ measurements are to large extent described in section 2.4.4. The measurements here were performed under **Standard Test Conditions** (STC), i.e. 25 °C (the temperature is controlled by a water-flow system below the sample), AM1.5G spectrum and irradiation corresponding to 1000 W m⁻². There are different ways to adjust the light intensity, in some setups, the height of the lamp is adjustable: a reference with a known $J_{sc}$ can be used to find the height of the lamp where the intensity gives 1000 W m⁻² for a calibration cell with well-defined solar cell device parameters. In the setup used in paper IV and
V, the intensity was, however, calibrated by measuring, $J_{sc}$ in a $QE$ measurement and adjust the power of the lamp accordingly. In paper IV, both the current from the $JV$- and the $QE$ measurement were disclosed, and the $\eta$ both from the $JV$, and recalculated using $J_{sc}$ from the $QE$ (including correction for the expected shading from the metal contacts on top of the solar cells).

The measurements were performed in a one-sun solar simulator of model Sol2A of ABA class (according to ASTM classification, [200]) from Newport connected to a Keithley 2401 sourcemeter, in paper IV with a halogen lamp, and in paper V with an Xe lamp. To ensure stable intensity, the lamp was always turned on at least 30 minutes before the measurements were performed. Figure 24 shows a sample with cells area of 0.5 cm$^{-2}$ and a front grid, being measured in the $JV$ setup under light conditions.

4.5.3 Quantum Efficiency
The principles of $QE$ measurement are also described in section 2.4.4. The $QE$ measurements here were performed in a home-made setup calibrated by externally measured Si and InGaAs solar cells from Hamamatsu. The measurements were performed under dark- and short-circuit conditions, otherwise it is also possible to perform $QE$ measurements with both voltage bias and light bias conditions.

4.6 Comparing back contacts of CZTS thin film solar cells
The properties and effects of the different back contact configurations were to large extent compared by using many of the various methods previously described. The focus of this thesis is mainly on the chemical aspects, and also the effects on device performance when using different back contacts.
Here are some complementary methods described that also were used to characterize the back contact. Some certain properties of the back contact have great importance for the thin film solar cell. It must supply adhesion, but unfortunately there are few established methods to quantify adhesion of thin films. Rough methods as “scotch tape”-test is commonly used to give pass- or fail results, but for many thin film solar cell researchers, it is often a matter of finding out after each processing step if the device stack is sticking together. There may be various reasons for delamination when it occurs, if the thermal expansion coefficients of different layers differs significantly, “peeling” may occur during heat treatments. Contamination may also reduce the adhesion, which is partly why the rather careful cleaning procedure is used for the glass substrates. There may also be some phases in, particularly the CZTS absorber layer, which are soluble in water or KCN solution. The KCN etching is probably therefore the most common step where delamination of the CZTS absorber occurs. Delamination of any back contact layer from the SLG substrate was never experienced during the work of this thesis, despite sometimes so high residual stresses were present so that the 1 mm SLG substrate was bent in the direction of the residual stress during anneal. Manual mechanical scribing of the absorber layer may often give a good, although subjective, estimate of the adhesion. Adhesion of the samples used in this thesis has ranged from nearly unscribable, to delamination when touching the surface with fingers.

Optically and electronically, the properties of the back contacts are typically getting increasingly important the thinner the absorber layer is. This is both due to higher generation of electron hole-pairs close to the back contact if the device is thinner and to larger contribution to the dark recombination current if the back contact is within a diffusion length from the pn-junction. Back contacts are typically given less attention compared to other parts of solar cell devices in books about solar cells, but for a discussion of different back contact models, please refer to e.g. Ledinek,[201] or reviews that include discussion on back contacts, such as Platzer-Björkman et al.[83] or Karade et al.[16]

4.6.1 Four-point probe and sheet resistance

Four-point-probe measurements (also called four-terminal/4T sensing, or Kelvin sensing) are used to measure $R_{\text{sheet}}$, a measure of the resistance in a thin film. As the name reveals, it has four probes, which are placed with equal distance in a line. The two inner (see Figure 25) measuring voltage difference, the two outer measuring current. The use of separated voltage and current electrodes make it possible to eliminate the internal resistance from the components as well as the contact resistance from the probes during the measurement, which is necessary for precise measurements for low resistance values, given that the internal resistance of the voltage meter is high enough not to conduct any significant amount of current. During the measurement, a current
is passed through the outer probes and the resistance can be measured, and as the voltage drop is measured simultaneously across inner probes, Ohm's law (Equation 13), along with some geometrical correction factors can be used to get the resistance value. For derivation of the four-point probe measurement, see e.g. Smits.[202]

\[ R = \frac{V}{I} \]  
(Eq. 13)

For the baseline Mo, \( R_{\text{sheet}} \) is the typically the only figure of merit that is measured. If the thickness \( t \) of the measured thin film is known (it can be measured by e.g. SEM, or profilometry, see next section), one can simply multiply the \( R_{\text{sheet}} \) with the film thickness to get the resistivity of the material (Equation 14).

\[ \rho = R_{\text{sheet}} \cdot t \]  
(Eq. 14)

For back contacts, which are the main focus of this thesis, \( R_{\text{sheet}} \) is probably the most important electrical property of the layer itself, as it is the measure of its ability to conduct current. A four-point probe of model CMT-SR2000N from Advanced Instrument Technology was used to measure \( R_{\text{sheet}} \).

4.6.2 Profilometry

Profilometry is used to measure the profile of a surface by slowly scanning a needle over the surface and registering the change in height. This is commonly used to measure thickness of a thin film, often by attaching a piece of tape, or a dissolvable marking at the substrate before deposition, which can be removed together with the film deposited on it after deposition, leaving a step corresponding to the film thickness behind. Another way to measure film
thickness is to combine e.g. GDOES, where the measurement can be stopped at a desired interface and the step height be measured. For GDOES, profilometry can also be used to measure the profile of the crater, revealing e.g. uneven sputtering. Profilometry can also be used to measure curvature, which is useful for stress measurements of thin films. In this case, glass slips, thin enough to undergo bending by the residual stress typically present in thin films, can be used as substrates. The curvature radius before and after deposition is measured, and with the properties of the glass substrate and the thickness of the thin films known, Stoney’s formula (Equation 15) will give a measure of the stress.[203]

\[
\sigma = \frac{1}{6} \left( \frac{1}{r_{\text{post}}} - \frac{1}{r_{\text{pre}}} \right) E \frac{t_s^2}{1 - \nu t_f}
\]  
(Eq. 15)

Where \( r_{\text{post}} \) is the curvature radius of the substrate and film after deposition, \( r_{\text{pre}} \) the curvature radius before film deposition, \( E \) is Young’s modulus of the substrate, \( \nu \) is the Poisson ratio for the substrate, and \( t_s \) and \( t_f \) are the thickness of the substrate and the film respectively.

4.6.3 Absorption – UV-Vis-IR measurements

Absorption of matter, here thin films and SLG substrates, is obtained by measuring reflection (\( R_{\text{optical}} \)) and transmission (\( T_{\text{optical}} \)) and using Equation 16.

\[
A_{\text{optical}}(\lambda) = 1 - R_{\text{optical}}(\lambda) - T_{\text{optical}}(\lambda)
\]  
(Eq. 16)

Reflection and transmission were measured using a Perkin Elmer Lambda 900 spectrometer with an integrating sphere. The measurements are conducted by simply measuring the intensity of the reflected, or the transmitted light through the sample over the desired wavelengths.
5. Results and discussion

5.1 TiN interlayers back contacts

TiN interlayers with three different thicknesses on standard Mo back contacts were annealed along with Mo references in typical anneal processes for sulfurization- and selenization respectively. The model experiment, described in paper II and further characterized in both paper III and IV, allows to test the chemical stability of the TiN interlayers in the challenging anneal conditions without any possible protective effects from the CZTS layer, which, as seen in Figure 26, leads to complete selenization of the bare Mo layer. It also makes it possible to directly measure any possible change of coverage of the TiN interlayers on the Mo substrate. The same configuration of varied TiN thickness was also tested in baseline device configuration and this work is presented in paper IV.

![Figure 26. SEM images of cross-sections.](image)

5.1.1 Chemical stability of TiN and inhibition of MoS(e)₂

The chemical stability of the TiN interlayers themselves were investigated by XPS and STEM-EELS. In Figure 27, the XPS peaks of Ti 2p show that the as-sputtered TiN surface consists of a mix of TiN and TiOₓ. This is expected, as discussed in e.g.[204]. After annealing, Ti 2p peaks are still present. Overlap of the Ti 2p peaks for TiO/TiN/TiS₂/TiSe₂ makes it hard to draw further conclusions from them, but presence of TiS₂ and TiSe₂ could be ruled out by the
absence of the corresponding S 2p and Se 3d peaks for the sample with 200 nm TiN (the other samples have MoS(e)₂ present, which overlaps). The N 1s-, and O 1s peaks (not shown here) also fit better than the S peaks, along with the apparent shift towards the more O rich side of the Ti 2p peaks after sulfurization.[205-207] STEM-EELS, shown in Figure 28 also confirmed that TiN was fully intact after selenization. The reduced peak intensity of Ti 2p can therefore likely be explained by the presence of e.g. Na-compounds and MoS(e)₂ on the surface after annealing, as further discussed below.

Table 5. XPS energies (eV).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ti 2p₃/₂</th>
<th>Ti 2p₁/₃</th>
<th>S 2p₃/₂</th>
<th>S 2p₁/₂</th>
<th>Se 3d₅/₂</th>
<th>Se 3d₃/₂</th>
<th>Mo 3d₅/₂</th>
<th>Mo 3d₃/₂</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>455.8</td>
<td>461.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[207]</td>
</tr>
<tr>
<td>TiO</td>
<td>455.1</td>
<td>460.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[207]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>458.7</td>
<td>464.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[207]</td>
</tr>
<tr>
<td>TiS₂</td>
<td>456.1</td>
<td>462.2</td>
<td>160.7</td>
<td>161.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[205]</td>
</tr>
<tr>
<td>TiSe₂</td>
<td>455.8</td>
<td>461.7</td>
<td>54.8</td>
<td>55.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[206]</td>
</tr>
<tr>
<td>Mo</td>
<td></td>
<td></td>
<td>228.0</td>
<td>231.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[207]</td>
</tr>
<tr>
<td>MoO₂</td>
<td></td>
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<td>229.3</td>
<td>232.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[207]</td>
</tr>
<tr>
<td>MoO₃</td>
<td></td>
<td></td>
<td>232.6</td>
<td>235.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[207]</td>
</tr>
<tr>
<td>MoS₂</td>
<td>162.5</td>
<td>163.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[207]</td>
</tr>
<tr>
<td>MoSe₂</td>
<td>54.5</td>
<td>55.4</td>
<td>228.3</td>
<td>231.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[208, 209]</td>
</tr>
</tbody>
</table>

Figure 27. XPS spectra of Ti, around the tabulated values of Ti 2p peaks. Annotated energies are also listed in table 3.

XPS was used also to investigate the ability of TiN layers to inhibit reactions between Mo and Se. As already mentioned, a non-complete coverage of the 20 nm TiN sample was found before annealing. After annealing S 2p/Se 3d, seen in Figure 28, and Mo 3d, in Figure 29 appeared in a way that clearly indicates a direct relation between reduced amount of MoS(e)₂ with increased TiN thickness, and no detection of MoS(e)₂ for the 200 nm TiN samples. It could be concluded that the thin TiN layers could not inhibit the reaction.
ERDA was measured to obtain depth profiles and to investigate how deep into the structure that S(e) reached during annealing. In Figure 30, showing ERDA profiles of the 20-200 nm before and after sulfurization, it is apparent that S is present below the TiN, independent of thickness. The same was seen also for selenized samples. It could therefore be concluded that TiN in this configuration does not fully block S(e) from reaching the Mo.

Figure 28. XPS Spectra of S 2p and Se 3d peaks.

Figure 29. XPS Spectra of Mo 3d peaks.

Figure 30. ERDA depth profiles and corresponding ToF-E energy diagrams.
MEIS and STEM-EELS was used to characterize the interface of the thin TiN layer in detail. The findings are shown in Figure 31 and Figure 32, and they both clearly revealed the characteristics of the interface. Before annealing, Mo is exposed to the surface due to non-complete coverage caused by the surface roughness of Mo. The somewhat poor step coverage of the TiN sputtering leaves the valleys between the Mo grains exposed. After annealing, MoS(e)2 is present, but only in the very vicinity of the discontinuities in the TiN layer.

A similar study was repeated for the identical set of samples deposited with CZTS in paper IV. With CZTS on top, it is expected that the local chalcogen partial pressure is lower at the back contact interface. The result was similar, however, as seen in Figure 33: S was found to be present below the 20 nm TiN interlayer, and was seen to follow the grain boundaries of TiN in the 200

![Figure 31](image1.png)

*Figure 31. ToF-MEIS Spectra and simulation of 90% and 99% TiN coverages.*

![Figure 32](image2.png)

*Figure 32. STEM images and STEM-EELS maps of samples with 20 nm TiN before and after selenization. Notice that the N map marked with yellow has a different magnification.*
nm sample. Also in this case, Mo was found above the TiN layer, but in significantly lower amounts than in the previous case without CZTS on top. The findings confirmed that formation of MoS(e)₂ occurs due to the discontinuities in the TiN interlayer that are present as a result of surface roughness of Mo and insufficient step coverage of the sputter deposition of TiN.

5.1.2 ALD-deposited TiN layers

In order to investigate if a higher initial coverage of the TiN layer on Mo could completely inhibit formation of MoS(e)₂, ALD was used to deposit TiN with varied thicknesses. The results are partly described in paper I-II, but limited and made with caution, since the layers were visually rather inhomogeneous - possibly a consequence of the deposition history of the chamber (used mainly for deposition of oxides). Deposition was done at 350 °C using TiCl₄ and NH₃ as precursors. Rather strong peaks of Cl were also found in XPS, a residual from the ALD-precursors, which further made the chemistry deviate from the intention. Improved coverage was indeed found this time as no Mo 3d peaks were detected in XPS for a thickness of 20 nm, as seen in Figure 34. However, as also seen, Mo 3d signals were detected for both sulfurized and selenized samples. Thicknesses of 5 and 50 nm were also used, and they followed the same trend, improved coverage compared to sputtered TiN, but still incomplete inhibition of MoS(e)₂ formation.

![Figure 33. STEM-EELS maps of TiN/Mo back contact interfaces.](image-url)
5.1.3 Coverage of TiN layers during thermal expansion

One hypothesis that arose, was that the coverage, and thereby the passivating capacity of the TiN interlayers, can be reduced temporarily during annealing as a consequence of thermal expansion of SLG and the thin films. If this took place, it would further explain why higher coverage in the case of ALD-TiN could not inhibit formation of MoS\(^2\).

To investigate this, ToF-MEIS was measured in-situ with heating applied to the target (sample). A significant difference compared to the measurement shown in Figure 35 (a) was absence of S(e) in the atmosphere, as the measurement was conducted in UHV (10\(^{-8}\) bar). In a first experiment, described in paper II, the temperature was increased to over 700 °C and led to melting of the SLG. The results that far clearly indicated increased exposure of Mo at the surface. However, it also clearly showed that Mo gets accumulated on the surface and not inside the TiN layer, i.e. the phenomenon of Mo reaching the surface during annealing as previously seen is not limited to conditions where S(e) is present in the atmosphere during annealing. The experiment was repeated in paper IV, and the temperature was increased to only 600 °C to avoid the melting, and then reduced to room temperature again. The shape of the ToF-MEIS spectra did not change upon cooling. STEM-EDX gave complementary understanding, as shown in Figure 35 (b): a thin layer of Mo could be observed at the surface of the TiN layer. So, the observed increase in Mo content at the surface could be concluded not to be related with thermal expansion. The mechanism behind this diffusion was not investigated in depth, but could possibly be related to the diffusion of Na, as discussed below.

![Figure 34. XPS spectra of samples with 20 nm TiN on Mo.](image-url)
5.1.4 Effect of TiN thickness on Na diffusion

The influence of the TiN interlayers on Na diffusion was investigated by comparing XPS-signals from the Na 1s peaks as well as the ERDA ToF-E diagrams. The Na 1s-signals are shown in Figure 36, and indicate in both cases increase of Na content when a TiN layer is present. In both cases, the strongest signal was achieved for the 200 nm TiN-samples. The ERDA measurement, shown previously in Figure 30, shows accumulation of Na in the TiN layer. The results are initially perhaps a bit counter-intuitive, since it is often assumed that interlayers would have an inhibiting effect on Na diffusion in the literature. The same trend was found also for ALD-deposited TiN layers.

Figure 35. (a) ToF-MEIS spectra and (b) STEM-EDX Mo+20 nm TiN annealed in the MEIS chamber.

Figure 36. XPS spectra of Na 1s, for references, sulfurized and selenized samples, respectively.

In paper IV, the Na-diffusion was investigated further with SIMS, after annealing with CZTS on top. The results resembled the XPS results, as seen in Figure 37, with a significant increase of Na signal in the absorber for the selenized sample and 200 nm TiN. An increased Na signal was seen also for the corresponding sulfurized sample, but this could still be within the error of the method.
After paper IV was published, the samples were re-measured in GDOES, and this time the same trend was found again for the same set of samples. As seen in Figure 38, the 200 nm TiN sample resulted in significantly higher Na signal, both for the sulfurized and the selenized samples. GDOES has a larger spot size, i.e. the area being measured, 2.5 mm compared to a few µm for SIMS, which gives a statistically more reliable result, in this case it could confirm the higher Na-signal measured by SIMS.

The Na diffusion was measured by XPS also for TiN bulk back contacts, as shown in Figure 40. In that case, however, all the TiN contacts had significantly lower Na-signal compared to the Mo reference after annealing. So the effect of increased Na diffusion for thick TiN layers may be a result from a combination of TiN and Mo, which is not achievable by only using TiN on its own.

Figure 37. SIMS Na depth profiles of annealed CZTS absorbers with varied thickness of TiN interlayers.

Figure 38. GDOES depth profiles of Na in CZTS absorbers on samples with Mo and TiN of varied thickness annealed in (a) S anneal, and (b) Se anneal.
5.1.5 Device performance of CZTS thin film solar cells with TiN back contacts

Finally, the device performance was measured for both the sulfurized and the selenized samples with varied TiN thickness. It should be noted that the samples did not have the desired “Cu-poor, Zn-rich” precursor composition, but a somewhat Zn-poor composition, as seen in table 6.

Table 6.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[Cu]/[Sn]</th>
<th>[Zn]/[Cu+Sn]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfurised series</td>
<td>1.91</td>
<td>0.30</td>
</tr>
<tr>
<td>Selenized series</td>
<td>1.86</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Box plots of $V_{oc}$, $J_{sc}$, FF and efficiency can be seen in Figure 39. The Mo reference is in the lower range of typical performance for baseline references, but the most significant result here was the clear improvement of performance for samples with TiN interlayers, and improved efficiency with increased TiN thickness for the sulfurized samples. This differed from previous results in the group.[20] But perhaps most interesting is that the sulfurized sample with 200 nm TiN was the best performing cell, as the previous results had shown that there was no MoS$_2$ present in this sample, which commonly has been assumed to be necessary for good electrical contact at the back contact. If MoS$_2$ would have been necessary for good electrical contact, one would expect a significant decrease of $FF$, but instead the 200 nm sample had the highest $FF$ in this series, and was even high when comparing to a good baseline reference (62.2%, compared to e.g. 60.0%, as reported by Scragg et al.[20]). Also the selenized samples had improved performance with TiN interlayers, but in this case, the performance decreased with TiN thickness. A possible reason for that was the

![Figure 39](image_url)
morphology, i.e. shunt paths created as a result of rapid grain growth (see Figures 2-3, paper IV). The higher Na content could have enhanced grain growth, and would have required a re-optimized, i.e. shorter, annealing process to avoid this issue.

The trend of improved device performance with TiN thickness obviously led to speculation that back contacts consisting only of TiN could be an alternative to Mo back contacts, which previously had been tested with very thick, 1 µm TiN, without success.[20] Three different configuration of TiN back contacts, with same thickness as the baseline Mo, was tested. As seen in Figure 40, this time the device performance of the Mo reference was in the better range for baseline reference. Na diffusion was compared by measuring the Na 1s signal on the surface on annealed samples in XPS, in this case all TiN samples had significantly lower Na signal compared to the Mo reference. No external addition of Na was investigated. Lower Na content could be one contributing reason why the device performance was lower for the TiN samples compared to the Mo reference. The residual stress of the layers was measured, and one speculation was that this could play a role, since the sample with strongest stress (with opposite sign compared to the Mo reference, for which the CZTS precursor deposition was optimized) also performed worse, despite having the lowest $R_{sheet}$. More research would be required to draw any conclusions. As a proof of concept, this showed that it is possible to make devices on TiN back contacts, but for fair comparisons, re-optimization of absorber composition and stress would be necessary.

Figure 40. (a) Device performance of samples with different TiN bulk back contacts. (b) Na 1s signals of samples with different back contacts annealed in S.
5.2 Transparent ATO back contacts

5.2.1 Optimization of ATO sputter deposition

As the group had no previous experience of deposition of ATO, optimization of deposition parameters was required before further experiments could be performed. ATO targets were ordered from a manufacturer with a specified composition based on the optimal Sb-content found in literature.[210] Both transparency and resistivity could then be further optimized by adding O₂ to the atmosphere during deposition. As seen in Figure 41, an optimum for both transparency and resistivity was found around 0.4-0.6 sccm O₂, with a fixed Ar flow of 60 sccm. Significant improvement of the resistivity was achieved by annealing of the samples at 500 °C in vacuum after the deposition. Tests were also made with heating during the deposition, but the resistivity, and the residual stress, was higher for these samples. The best resistivity obtained was 3.6 mΩ⋅cm, which was in the range commonly reported for ATO in literature.[210, 211] ATO layers of ~850 nm thickness was used for experiments. RBS and PIXE was used to determine the composition, presented previously in Figure 20, to ~66.5/31.3/2.2 at% of O/Sn/Sb.

5.2.2 Chemical stability of ATO back contacts

The chemical stability of the ATO back contacts was investigated first in a model experiment where ATO thin films on SLG substrates were annealed at three different temperatures, namely 580 °C, 547 °C, and 534 °C, in S atmosphere. Visually, it was apparent that the films did not withstand the conditions, as they lost transparency after annealing, and the resistivity also increased.

![Figure 41. $R_{\text{sheet}}$ and resistivity values for different O₂ flows.](image-url)
XRD, shown in Figure 42 showed that the ATO films had reacted with S to form Sn$_2$S$_3$ for the highest temperature, and SnS$_2$ for the lower temperature. This result can be understood when considering the properties of the anneal setup that has been discussed previously by both Ren et al.[124] and Ross et al.[212] The S partial pressure will initially increase rapidly as the elemental S in the box is vaporized, but then decay since the box is not completely sealed and the S vapor will be spread in the tube furnace. This process expectedly happens faster at higher temperatures, and consequently, as the rapidly formed AT(O,S) film is not stable, at the highest temperature the formed films have a lower S content compared to the films annealed at lower temperature. As seen in Table 7, however, reducing the temperature also reduced the deterioration of the resistivity.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$R_{\text{sheet}}$ (vacuum anneal)</th>
<th>$R_{\text{sheet}}$ (annealed ATO)</th>
<th>$R_{\text{sheet}}$ (ATO annealed below CZTS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>580 °C</td>
<td>~80</td>
<td>~70 $\cdot 10^3$</td>
<td>~130</td>
</tr>
<tr>
<td>547 °C</td>
<td>~80</td>
<td>~9 $\cdot 10^3$</td>
<td>~60</td>
</tr>
<tr>
<td>534 °C</td>
<td>~80</td>
<td>~240</td>
<td>~50</td>
</tr>
</tbody>
</table>

The experiment was repeated with baseline CZTS layers on top. After annealing, the CZTS was removed and the ATO characterized. The XRD patterns are shown in Figure 43. The XRD showed that no large structural changes had taken place, as the patterns were more or less identical to the unsulfurized reference, only some minor peak appeared after annealing at the highest temperature, 580 °C. A STEM-EDX image was obtained for this sample to further investigate if some chemical reaction had taken place. As seen in figure 44,
small amounts (<5at.%) of S were found to be incorporated in the ATO after annealing.

![XRD patterns for ATO films annealed at different temperatures](image1)

*Figure 43. XRD patterns for ATO films annealed at different temperatures below 1 µm of CZTS.*

It was visually apparent that the ATO films were much less affected by the annealing when being covered by CZTS, as they were still transparent after removal of the CZTS. The absorption, shown in Figure 45, showed that optically there was no drastic change after annealing. The absorption did increase in the longer wavelengths, which could be an indication that the charge carrier concentration increased during annealing. This would explain the decreased $R_{sheet}$ for some of the samples, as listed in right column in Table 7, but the incorporation of S, shown by STEM-EDX for the higher temperature, might have an opposite, degrading effect.

![STEM image of the CZTS and ATO annealed in 580 °C](image2)

*Figure 44. STEM image of the CZTS and ATO annealed in 580 °C with overlay from STEM-EDS showing S-content below 5 at%.*
5.2.3 Effect of ATO back contacts on absorber growth

SEM and SEM-EDX were used to study the recrystallization of the absorbers during the annealing for the same samples, the main findings shown in Figure 46. The starting point of 580 °C was chosen simply because it’s the temperature for the baseline, used for Mo standard devices. The ATO annealed in this temperature was found to have “cracks” on the surface, which in higher magnification turned out to be areas with pinhole trenches. It was also apparent that phase segregation had occurred on the surface of this sample. As seen in the SEM-EDX map in Figure 46, the segregating phase was ZnS, this could be somewhat expected due to the Zn-rich composition. However, the corresponding Mo reference did neither have cracks, nor close to the same density of ZnS at the surface. When the temperature was reduced, the “cracks” disappeared, but instead, a rather high density of SnS secondary phases was found on the surface, as seen in Figure 46 (d). Reducing the temperature also reduced the CZTS grain size more for samples on ATO compared to the Mo reference, as seen when comparing (e) and (f), in the figure. A possible explanation for this may be reduced diffusion of Na through the ATO, as discussed in section 5.2.5.

Figure 45. Absorption calculated from reflectance and transmission measurement, for an as-deposited+vacuum annealed ATO on SLG, and ATO films on SLG annealed below CZTS.
To investigate the formation of Sn–S secondary phases at the CZTS TS surface for samples on ATO, a series of anneals at the lower temperature, 534 °C was performed with different duration, namely 13 min, 30 min, 2 h and 10 h. The surfaces were again analyzed in SEM, and the corresponding surfaces are shown in Figure 47. After 13 min, the surface was covered by Sn–S-rich sticks, Figure 47 (a). After 30 min, the sticks had turned into flakes, and at some locations, trench-shaped pinholes were observed, as marked by the red rings, in Figure 47. Further annealing increased the size of the present Sn–S secondary phases, and the density of pinhole-trenches. Finally, after 10 hours (Figure 47 (d)), the surface resembled the surface of the sample annealed for 13 min at 580 °C, with the similar phase segregation. The results of the experiment could possibly give insights and a time-resolved explanation of the result for the observation after annealing at 580 °C. CZTS absorbers on ATO back contacts have a tendency to form large amounts of Sn–S secondary phases. These evaporate as the S partial pressure decays and result in the observed pinholes.

Figure 47. SEM images of CZTS absorber surfaces, with the respective back contact and anneal temperature annotated. In (b) and (d), SEM-EDX maps are disclosed, showing the presents ZnS and Sn–S, respectively.

Figure 46. SEM images of CZTS absorber surfaces on ATO back contacts annealed for different anneal times.

Formation of Sn–S(e) secondary phases have been previously been observed in studies on Mo back contacts, also in our group by Ren et al. [123]. Gang et al. found a relation to the precursor composition, and more Sn-rich precursors.
increased the amount of SnS$_2$ at the surface and resulted in worse device performance. Bolke studied the formation of SnS$_2$ in Sn-rich CZTS and found different anneal conditions that could reduce the amount of SnS$_2$ in their setup.\[213\] E.g. annealing without additional S or Sn led to “overwhelming” amounts of SnS$_2$. He suggested selective etching as a solution, but none of the most common etchants could etch SnS$_2$ efficiently enough. He further suggested “thermal etching”, similar to described in the previous section, as a possible route. In his case, this “thermal etching” of SnS$_2$ seems not to cause pinholes in the way that was observed when using ATO. In his case, however, it was found to be insufficient as etching method. For CZT(S,Se), Xie et al.\[214\] suggested that the presence of Sn–S(e) may originate from condensation during cooling and/or the composition of the absorber and found (NH$_4$)$_2$S to be an effective etchant. Wang et al.\[215\] wrote that “the inhibition and removal of the SnS$_2$ impurity phase in the kesterite Cu$_2$ZnSnS$_4$ (CZTS) layer is a major challenge for the improvement of CZTS solar cells; this impurity phase can critically damage device performance by forming a diode and a barrier for carrier collection.” They suggested that the formation of SnS$_2$ takes place during cooling, and they managed to improve device efficiency by exfoliate the SnS$_2$ by using sticky tape and mechanically pull them off from the absorber. Figure 48 shows surfaces of CZTS absorbers annealed on ATO for 13 min at 534 °C (a) and on Mo (b) respectively. The samples were annealed next to each other, and the ATO sample shows a large amount of Sn–S, clearly indicating that it cannot be related solely to either the initial precursor composition, or condensation, but must be related to the back contact. In this case, however, the sample with ATO back contact behaves as it had a much higher Sn-content then the Mo reference, as described above. We also speculate that the higher Sn-content that may be released from the ATO sample, actually stabilizes the absorber on the Mo sample. This speculation is suggested by the observation that the devices made from the Mo reference annealed for 10 hours were func-

![Figure 48. SEM images of CZTS absorber surfaces, (a) annealed on ATO with Sn–S secondary phases visible as black spots, (b) annealed on Mo.](image)

- For standard CZTS stacks in our anneal setup have previously resulted in poor devices due to loss of Sn.\[124\]
5.2.4 Varied CZTS precursor composition

To investigate also the effect of precursor composition on formation of Sn–S secondary phases, a second time-resolved series of anneals was performed. As mentioned in section 2.5.4, the best CZTS devices are typically obtained by Cu-poor and Zn-rich compositions. In this case however, also the Sn-content may play a significant role. Two different compositions were deposited. The Zn/(Cu+Sn) ratio was kept fixed, while the Cu/Sn-ratio was 1.85 for one set of samples, and 1.96 for the other set. Samples annealed for 2 min on ATO and Mo for the respective composition are shown in Figure 49. The CZTS precursor composition was found to influence the amount of Sn–S compounds on the surface of the samples annealed on ATO.

![Figure 49. SEM images of CZTS annealed on ATO (upper) and Mo (lower) with the lower Cu/Sn ratio (left) and higher Cu/Sn ratio (right).](image)

The samples followed the same trend as in the previous time series, the amount of Sn–S secondary phases was initially high, and decayed when the anneal time was increased. This is very clearly illustrated in Figure 50. The samples have very thick ATO, since they were intended to have low $R_{\text{sheet}}$, but (likely) the very high residual stress resulted in a crackled absorber surface, where the Sn–S secondary phases had a very strong preference to form along the cracks. While large flakes can be seen for the more Sn-rich composition, they were completely absent for the less Sn-rich composition.
5.2.5 Supply of Na and adhesion of absorber layers on ATO back contacts

The diffusion of Na from the SLG substrate was investigated by comparing by GDOES depth-profiles. When annealed in 580 °C, the levels of Na in the absorber layers were comparable, when the temperature was reduced to 534 °C on the other hand, the samples on ATO had lower levels of Na compared to the corresponding sample on Mo. Therefore, alternative ways to supply Na were investigated. Pre-deposition of NaF on the back contact before precursor deposition was tested repeatedly in the TiN interlayer project with very poor outcome and delamination or poor quality of the precursor layer. This time, Na addition was tested through (1) pre-deposition of Na on the precursor prior to the annealing, and (2) addition of Na through an application of a piece of SLG on top of the precursor during the annealing, as suggested by Yang et al.[216] It was indeed found to be possible to increase the amount of Na in the stacks by both the suggested methods, as seen in Figure 51. However, while

Figure 50. SEM images of CZTS annealed on thick (23 µm) ATO back contacts. Formation of Sn–S initiates in cracks of the absorber. Lower Cu/Sn ratio clearly results in more Sn–S secondary phases.
pre-addition of NaF resulted in significantly higher levels of Na in the absorber, the sample with SLG on top only showed significantly increased levels of Na in the ATO.

Pre-deposition of NaF further proved to give significantly improved adhesion, which otherwise had been an issue for samples annealed on ATO. Initially it was meant that annealing at 505 °C also should be included, as it had resulted in the best devices for other TCO’s elsewhere.[217] In this study, however, after annealing at 505 °C, the adhesion was extremely weak and the CZTS films delaminated by almost any mechanical contact, thus this temperature was not used further. In other studies of CZTS(e) on TCO’s, e.g. Kim et al.[217] and Espindola-Rodriguez et al.[170] a successful strategy has been to use Mo interlayers between the TCO and the absorber. This was investigated rather thoroughly also in this work, and it indeed improved the adhesion, but devices produced with this method was very poor, even compared to those only on ATO. Neither of the alternative ways to supply Na, nor Mo interlayers had a significant effect on formation of Sn–S secondary phases.

5.2.6 Device performance of CZTS devices on ATO back contacts

Device performance was tested for all the samples discussed above, some selected results are shown in Table 8 (the full table of device samples, see Table S2 of paper V). Device efficiencies above 2% were only achieved for samples with additional supply of Na, as described in section 5.2.5. This could follow both from the improved adhesion when using NaF, as well as the increased level of Na. The sample annealed with SLG on top resulted in the highest

![Figure 51. GDOES depth profiles of Na in ATO samples annealed at 534 °C.](image-url)
efficiency of all tested ATO samples. It had one of the best $V_{oc}$ values in the whole study and is even fairly good for CZTS in general. This observation, however, may not only be a result from the additional Na. It has been shown previously for Mo samples, that this configuration can also affect the surface dynamics and e.g. reduce the loss of S from the precursor in a S poor environment.[20] Also the $J_{sc}$ is close to Mo reference, but the fill factor ($FF$) is worse. The corresponding $JV$-curves are shown in Figure 52. Despite giving the best device performance using the top-SLG-route, it was not chosen in the later experiments because it did not improve adhesion in the way pre-deposition of NaF did. As only one thickness of NaF was used in this study, it is also likely that the NaF thickness could be optimized. As mentioned, also Mo interlayers improved adhesion, but low $J_{sc}$ resulted in very poor devices and was therefore not taken into consideration for further use.

In the different anneal-time series, the best devices were those annealed in the intermediate, 13 min, anneal time. This observation could possibly be related to the formation, and later evaporation of Sn–S secondary phases, leading to high amount of dead area and poor integrity of the later deposited top layers for samples with short anneal times, or high amount of shunt paths caused by the pinholes left after evaporated Sn–S surface compounds.

Reducing the amount of Sn–S secondary phases by deposition of more Sn-poor (higher Cu/Sn-ratio) precursors, as described in section 4.2.4, also resulted in better performance. In Figure 50 it can be seen that the $J_{sc}$ is higher for the sample with the higher Cu/Sn ratio, consistent with the lower coverage of Sn–S secondary phases. The $V_{oc}$ is still only slightly higher and the $FF$, despite the lower series resistance, is even smaller for this sample.

The best ATO samples still had a high amount of the secondary Sn-S phases, which is believed to contribute to the overall low performance. All ATO samples exhibited a rather low fill factor ($FF$), dominated by the high $R_{series}$ (and to a more various extent with contribution from low $R_{shunt}$). This could partly be explained by high $R_{sheet}$ of the ATO, e.g. it was observed that $JV$-characteristics of the cells on ATO were affected by the distance between probe contact and the cell. Thick ATO was deposited to address this issue and reduce $R_{sheet}$, but the absorbers cracked due to the high stress in the thick ATO.

Figure 52. $JV$-curves of ATO samples, details about the sample is disclosed in table 8.
Therefore deposition of thicker ATO would require further optimization. A promising finding though was that deposition temperature could be used to control stress in the film. As suggested by studies on SnS$_2$, selective etching or mechanical exfoliation of SnS$_2$ would also be a strategy to improve device performance of CZTS on ATO back contacts.

For the devices with Mo back contacts in this study, long anneal times (at 580 °C) typically result in deteriorated devices due to loss of S and Sn according to literature.[218] In this study, however, it was repeatedly found that long anneal times resulted in not only working devices, but also better devices compared to those processed with shorter anneal times. One hypothesis is that the formation of the Sn–S surface compounds and continuous degradation of the ATO results in a sufficient high $P_s$ and $P_{Sn}$ to stabilize the CZTS surface of the Mo samples.

Table 8.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>ATO_13/534_2</td>
<td>1.97, 0.37</td>
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<td>534</td>
<td>13</td>
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<td>4.7</td>
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<td>0.4</td>
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<td>11.6</td>
<td>34.2</td>
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<td>0.51</td>
<td>10.3</td>
<td>39.5</td>
<td>2.1</td>
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<td>16.5</td>
<td>47.1</td>
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<td>1.85, 0.35</td>
<td>0.05</td>
<td>580</td>
<td>13</td>
<td>0.25</td>
<td>13.0</td>
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<td>1.2</td>
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<td>Mo_30/580L</td>
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<td>580</td>
<td>30</td>
<td>0.60</td>
<td>15.2</td>
<td>48.1</td>
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</tbody>
</table>
6. Concluding remarks and outlook

6.1 Conclusions

The aim of this thesis was to investigate and perform in-depth characterization of alternative back contact configuration and materials for CZTS thin film solar cells. Back contacts for two different configurations were studied, namely traditional single-junction cells with opaque back contacts and transparent back contacts for possible use in either tandem or bifacial solar cell configuration.

Titanium nitride (TiN) as an interlayer between the opaque molybdenum (Mo) and CZTS as well as complete replacement of Mo with TiN back contacts were investigated. The studies showed (1) that TiN was chemically stable in typical anneal conditions, except for some minor oxidation; (2) Sputtered TiN reduced the formation of MoS(e)₂. However, it did not completely inhibit MoS(e)₂ formation, which could be correlated to areas where TiN interlayers did not fully cover the Mo, following from the surface roughness of Mo and insufficient step-coverage of the sputter-deposition of TiN. TiN interlayers could not block chalcogens from reaching the Mo, as it was found below the TiN interlayers also when thickness of 200 nm was used; (3) Thick TiN interlayers (200 nm) were found to increase the diffusion of Na to the absorber layer, while complete replacement of Mo to TiN decreased the Na diffusion; (4) the possible effect of thermal expansion of the SLG/Mo on TiN coverage on the Mo, but the only conclusion was that Mo diffused to the surface of the TiN layer; (5) Device performance of pure sulfide CZTS was found to improve with increased TiN interlayer thickness. Devices on TiN back contacts (without Mo) could be produced, but solar cell performance was worse than the Mo reference.

Important conclusions are that the total back contact stacking configuration is important, having Mo below the TiN gives, different properties compared to only having TiN in the back contact. Contrary to the intuitive and common notion that interlayers, and in particular thick interlayers may inhibit diffusion of Na, it was concluded that Na diffusion increased significantly when applying thick TiN interlayers. The successful implementation of TiN as back contact, widens the processing window of CZTS in terms of e.g. annealing temperature and chalcogen partial pressure as back contact interface reactions is inhibited.
ATO was studied as a transparent back contact material for CZTS. The study showed (1) that ATO was stable when annealed below CZTS at low enough temperature, and in some aspects even obtained improved layer properties. Annealing of bare ATO resulted in complete reaction with S to form Sn–S-compounds; (2) ATO back contacts resulted in significantly increased formation of Sn–S secondary compounds on the CZTS absorber surface compared to the Mo reference; (3) Increased annealing time could reduce the amount of Sn–S secondary compounds on the surface through evaporation, but the evaporation resulted in trench-shaped pinholes on sites where the compounds had been located. Reduced Sn content in the CZTS precursor could also reduce the amount of Sn–S compounds; (4) External supply of Na could facilitate recrystallization of the CZTS layer during annealing and improve adhesion between the ATO and the CZTS; (5) Improved device performance could be achieved by optimized anneal conditions, external supply of Na and decreased Sn-content in the CZTS precursor. The Sn–S secondary compounds on the surface still made it challenging to obtain good device performance when using ATO as back contact.

6.2 Future work

TiN offers a chemically inert back contact material that allows for a larger anneal process window compared to the traditional Mo. A larger processing window allows exploration of new pathways in improving the device efficiency of CZTS. The use of TiN as a back contact opens up a possibility to decouple effects from the back contact reaction in several aspects, in particular for CZTS researchers to study the effect of back contact reactions on the formation of secondary compounds in the absorber layer. The effects of different properties of TiN layers could be further investigated, such as varied composition, stress and density through varied deposition parameters.

To explore the possibility to improve device performance of devices with TiN back contacts, the other device processing steps need to be re-optimized, including (1) re-optimized deposition temperature of CZTS precursors, which now to a large extent is optimized to match the residual stress of the baseline Mo back contact; (2) Re-optimized CZTS precursor composition, which today to some extent may be optimized for effects that are only present with Mo/MoS₂; (3) When Mo is completely exchanged to TiN in the back contact, an external supply of Na should be investigated, as it was found that diffusion of Na through TiN without Mo was significantly lower; (4) Exchanging the CdS window layer to alternatives with more suitable band structure.

CZTS is a candidate for the top cell in tandem configurations to push the efficiency of e.g. Si solar cell devices as they start to reach their theoretical limits. All the advantageous properties of single junction CZTS will still be there when choosing the material for alternative device configurations in the
future. However, the processing of CZTS creates a challenge for other parts in a multi-junction stack. Therefore, individual processing and contacting is an attractive route, and that will require transparent back contacts. Thus far, only a few studies have been performed on transparent back contacts, and the field needs more attention in general. For ATO, the formation of Sn-S needs more attention, and re-optimization of the CZTS precursor deposition and processing, as well as optimization of NaF-thickness, are yet to be conducted. The possibility to remove Sn–S surface compounds through more efficient etchants should be investigated. The possibility to use ATO as a source for slow release of Sn-S in the anneal process, in order to stabilize the CZTS surface (of other samples) should also be investigated.

Since the electronic interface of the back contact/CZTS absorber interface is not well-studied and thus poorly understood, more measurements are required to increase knowledge of the electronic properties of the back contact interface.

In whichever way the world will be powered in the future, and whatever solar cell devices that the future will bring, we may have seen nothing yet.
Efterfrågan på solceller har ökat exponentiellt sedan 90-talet, och Internationella energiorganet IEA spår att användningen av solceller kommer växa till att bli en av största produktionskällorna för elektricitet år 2050. Tunnfilmssolceller, med en tjocklek på ungefär en tusendels millimeter, kan deponeras på lätta och flexibla material, vilket möjliggör att de kan integreras på ställen där solceller gjorda av det marknadsdominerade solcellsmaterialet kisel inte passar. Solceller i husfasader, på fordon och båtar, och placeringar som enbart tillåter solceller med låg vikt är exempel på områden där användningen av tunnfilmssolceller spås öka de kommande årtiondena. De tunnfilmssolceller som finns på marknaden idag innehåller grundämnen som både är toxiska, förekommer i låga koncentrationer i jordskorpan, eller produceras i relativt små mängder i dagsläget, vilket sammantaget förutspås bli hinder i framtiden när tillverkningen ökar.

Materialet Cu2ZnSnS4, förkortat CZTS, består av koppar, zink, tenn och svavel, alltså enbart icke-toxiska och relativt billiga grundämnen med hög förekomst i jordskorpan, är ett attraktivt alternativ till de etablerade materialen som används i tunnfilmssolceller. Traditionellt består CZTS tunnfilmssolceller av ett glassubstrat, en bakkontakt av molybden (Mo), själva CZTS absorbtionskiktet, och ett fönster- och framkontaktslager av kadmiumsulfid och zinkoxid. Flera av dessa komponenter har egentligen valts ut för att passar de mer etablerade tunnfilmssolcellsmaterialen, så samtidigt som det pågår forskning på att förbättra själv CZTS absorbtionskiktet, så pågår också forskning för att kunna byta ut eller förbättra alla övriga delar i CZTS tunnfilmssolcellen.

Den här avhandlingen syftar till att undersöka alternativa bakkontaktskonfigurationer, vilket görs i två olika aspekter. Den ena är för den traditionella konfigurationen, nämligen för tunnfilmssolceller som består av ett enkelt CZTS absorbtionskikt och med en icke-genomskinlig bakkontakt. Den andra är transparenta bakkontaktskonfigurationer för antingen (1) dubbel- eller flerskiktsskonfigurationer, som används för att mer effektivt kunna ta tillvara på olika våglängdsområden av solspektrat, eller (2) för dubbelsidiga solceller, där tanken är att kunna få in solljus både på framsida och baksida av solcellen, och på så sätt öka den ljusgenererade strömmen.

Ett problem med CZTS är att det är relativt kemiskt instabilt jämfört med andra, mer vältablerade solcellsmaterial. Framförallt svavel och tennsulfid har relativt höga ångtryck, vilket gör att de förångas vid de höga temperaturer,

Antimon dopad tennoxid (ATO) studeras som transparent bakkontaktsmaterial i artikel V. Studien visade (1) att ATO var kemiskt stabilt när det värmebehandlades under CZTS absorbatorskiktet vid tillräckligt låg temperatur, och då kunde det även erhålla förbättrade egenskaper. Samma värmebehandling utan CZTS ovanpå resulterade i att ATO:n helt reagerade med svavel och bildade tennsulfider. (2) Att användning av ATO bakkontakter kraftigt ökade mängden tennsulfid på ytan av absorbatorskiktet jämfört med Mo bakkontakter. (3) Förlängd värmebehandlingstid kunde minska mängden tennsulfid på CZTS absorbatorskiktets yta genom förångning, men detta ledde samtidigt till avlänga hål på ytor där tennsulfiden förångats ifrån. Minskad tennandel i CZTS-skiktet minskade mängden tunnsulfid på CZTS-ytan. (4) Extern tillförsel av Na (genom förångningsdeponering av natriumflorid, NaF) förbättrade omkrystalliseringen av CZTS under värmebehandling och förbättrade även vidhäftningen mellan bakkontakt och absorbatorskikt. (5) Solcellsprestandan kunde förbättras genom omoptimering av värmebehandlingen, extern tillförsel av Na och minska andel tenn i CZTS-skiktet. Tennsulfiden på ytan gjorde det fortfarande svårt att erhålla bra solcellsprestanda när ATO användes som bakkontakt.
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μακρὺς ὁ δρόμος, γεμάτος περιπέτειες, γεμάτος γνώσεις, νυν τέλος στο λιμάνι.
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