Reactive sputtering and composition measurements of precursors for Cu$_2$ZnSnS$_4$ thin film solar cells

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Abstract

Cu$_2$ZnSnS$_4$ (CZTS) is a thin film solar cell material that only contains abundant elements and for which promising conversion efficiencies of 9.2 % [1] have been shown. In this thesis composition measurements and reactive sputtering of precursors for CZTS films have been studied. These precursors can be annealed to create high quality CZTS films.

Accurate control and measurement of composition are important for the synthesis process. The composition of a reference sample was determined using Rutherford backscattering spectroscopy. This sample was thereafter used to find the composition of unknown samples with x-ray fluorescence measurements. Pros and cons with this approach were discussed.

The reactive sputtering process, and the resulting thin films, from a CuSn- and a Zn-target sputtered in H$_2$S-atmosphere were investigated and described. A process curve of the system was presented and the influence of sputtering pressure and substrate temperature were examined. The pressures tested had little influence on the film properties but the substrate temperature affected both composition and morphology, giving less Zn, Sn and S and a more oriented film with increasingly facetted surface for higher temperatures.

The precursors produced with this method are suggested to have a disordered phase with randomized cations, giving a CZTS-like response from Raman spectroscopy but a ZnS-pattern from x-ray diffraction measurements. The films have an excellent homogeneity and it is possible to achieve stoichiometric sulfur content.

The complete steps from precursors, to annealed films, to finished solar cells were investigated for three controlled compositions and three substrate temperatures. The films sputtered at room temperature cracked when annealed and thus gave shunted solar cells. For the samples sputtered at higher temperatures the trend was an increased grain size for higher copper content and increased temperature. However, no connection between this and the electrical properties of the solar cells could be found.
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1 Aim and background

1.1 Aim of work

The need for sustainable energy sources is always current and solar cells can be one of the main solutions. Especially thin film solar cells have a high potential since only a small amount of active material is needed for every solar cell. Cu(In,Ga)Se₂ (CIGS) is one of the most high-performing, commercial alternatives, but due to the high price and limited availability of the metal indium, it has been increasingly interesting to search for replacements for this material. One of the most promising alternatives is Cu₂ZnSnS₄ (CZTS), which is the topic of this licentiate thesis.

A two-stage fabrication approach was chosen to produce the CZTS films. This is because the CZTS material has shown a tendency to decompose when low pressures are combined with high temperatures. The first stage is therefore comprised of a reactive sputtering at moderate temperature, to produce a precursor film that contains all the necessary elements in the correct amounts. The second stage is a short, high temperature annealing where the film is allowed to recrystallize to form large-grained CZTS. The focus of this licentiate is the first stage, and the reactive sputtering process and the properties of the resulting precursors are investigated.

Due to the complexity of the material it is necessary to have a very good control of the sample composition. A large part of this licentiate thesis has therefore been dedicated to refinement of the measurement of the Cu, Zn and Sn amount in the films. The selected compositional measurement is x-ray fluorescence (XRF) calibrated with Rutherford backscattering spectroscopy (RBS), since this gives an absolute value of areal density from a large (∼cm²) part of the sample.

1.2 Basic solar cell theory and solar cell types

The purpose of a solar cell is to convert sunlight into electricity. The first step in this process is the energy transfer from the light into the material. On an atomic scale this is accomplished by incoming photons exciting electrons from their ground state to higher energy levels. There are several ways of extracting these electrons. The most common and, so far, most efficient, is to use a semiconductor solid state junction. In the semiconductor the absorption of photons with sufficient energy will enable electrons to be transferred from the valence band to the conduction band, where they can move. By forming a pn-junction between semiconductors with p- or n-
doping, a built-in electric field can be created. The most common semiconductor used is doped silicon but also semiconductors comprised of two (GaAs, CdTe) or more (CIGS, CZTS) elements are used. In a solar cell these materials are called absorbers, due to their function of absorbing photons.

For the solar cells to work as efficiently as possible, the energy difference between the conduction band and the valence band, the band gap, has to be just below the energy of the incoming photons. Sunlight consist of a spectrum of photon energies, where the exact distribution depends on the temperature of the sun, the composition of the atmosphere and the distance the photons have to travel through the atmosphere. The standard spectrum used for characterizing solar cells is called AM1.5 which means that the photons travel through 1.5 times the thickness of the atmosphere, see Figure 1.

![Figure 1 Solar light spectrum AM1.5, meaning the photon wavelength distribution after the sunlight has passed 1.5 times the thickness of the atmosphere.](image)

To fully utilize the complete spectrum several different materials with a range of band gaps would have to be used. This is applied in multi-junction solar cells, which consist of several semiconductor junctions stacked on top of each other. These kinds of solar cells give the highest efficiencies but are complex and expensive to produce. The more widely used solar cells therefore contain only one band gap. It has been calculated that, when using only one material, the optimal band gap is in the range of 1.3-1.6 eV [2], an energy which corresponds to a photon wavelength of 950-780 nm.

The band gap of a material can be either direct or indirect. This affects how efficiently photons can be absorbed in the material. Crystalline silicon has an indirect band gap and therefore requires hundreds of micrometers to absorb the sunlight. For materials with direct band gaps,
such as CZTS, a much thinner film, in the order of one micrometer, can be used to achieve the same absorption. This means that less raw material is needed and that a larger variety of substrate materials can be used, which allows for cheaper and lighter solar cell modules.

Another advantage of thin film materials is that it can be grown over large areas, opposite to crystalline silicon where individual solar cells are first made and then connected into modules. The thin film modules therefore have the possibility of a more facile production process.

A thin film semiconductor solar cell stack, see Figure 2 (in which also the materials used in this thesis are indicated), is usually built up of a substrate, a back contact, the absorber, a buffer layer, a transparent front contact and finally a metallic grid contact (not seen in Figure 2, usually Ni:Al:Ni).

![Figure 2 Structure of a thin film solar cell. Here exemplified with cross section image, from a secondary electron microscope (SEM), of a CZTS cell. The materials used in this thesis are given at the right side.](image)

There are also other types of solar cells, such as dye-sensitized solar cells and organic solar cells, which have shown promising efficiencies in recent years and could be an alternative to solid state junction semiconductor solar cells for certain applications. However, the long term stability is still an uncertainty for many of these solar cells [3].

### 1.3 Properties of Cu$_2$ZnSnS$_4$

The CZTS compound has several beneficial properties which make it suitable as an absorber material in solar cells. All its constituents are abundant and cheap and its direct band gap ensures efficient absorption of photons, which means that only a thin layer of active material is needed.
By exchanging some of the S for Se it is possible to tune the band gap between 1.0 eV (pure selenide) to 1.5 eV (pure sulfide) [4] which is in the optimal range for a single junction solar cell. The atomic and electronic structure is similar to the commercially used CIGS-absorber, which could allow for an easy exchange of absorber material in already established production processes, if CZTS proves to be the better alternative.

CZTS has been measured to be a p-type semiconductor, for example in [5], and calculations indicate that the defect Cu\textsubscript{2}Zn is an acceptor and mainly responsible for the doping [6].

The structure of CZTS can be either stannite or kesterite (see Figure 3), the difference being the ordering of Cu and Zn. Calculations show that kesterite has a slightly lower formation energy and therefore should be the most stable form [4]. The difference is however small and it is likely that stannite and kesterite structures coexist in the solar cell material produced. Due to the similarity of Cu and Zn, both in weight and electronic properties, it is hard to distinguish between the structures, but measurements with neutron diffraction have confirmed that kesterite is the dominating structure [7].

![Figure 3 CZTS crystal structures. The difference is the ordering of Cu and Zn.](image)

The CZTS material has some possible disadvantages compared to CIGS. In CIGS a variation in In/Ga-ratio will not cause secondary phases. Changing the Zn/Sn ratio in CZTS will however quickly move the composition away from the single phase region, which can be seen in the ternary phase diagram shown in Figure 4. Composition control in the CZTS case is therefore even more crucial. Just considering the sulfur compounds there are several secondary phases, both binary (ZnS, SnS, Sn\textsubscript{2}S\textsubscript{3}, Sn\textsubscript{2}S\textsubscript{9}, CuS and Cu\textsubscript{2}S) and ternary (Cu\textsubscript{2}SnS\textsubscript{3}, Cu\textsubscript{3}SnS\textsubscript{4}). Many of these phases are also hard to detect due to overlap with CZTS in common characterization methods such as XRD and Raman.
Figure 4 The central part of the ternary phase diagram for CZTS at 400°C, courtesy of J.J. Scragg, based on [8]. The imaginary axis for sulfur content is perpendicular to the plane of the paper and a cut has been made at the stoichiometric amount for CZTS. Note that the Cu-axis is for Cu$_2$S, meaning that the single phase region is in the middle of the triangle even though it contains twice as much Cu as Zn and Sn.

There have been many indications that the CZTS surface is sensitive to decomposition in low pressures and high temperatures. A possible explanation to this was presented in [9] and is summarized here. Sn can have several oxidation states and is in its IV-state in CZTS. At low $S_2$ pressures, however, the lower oxidation state, Sn$^{II}$, is the stable form. A reduction, according to Reaction (1), of CZTS is therefore possible.

$$\text{Cu}_2\text{ZnSn}^{IV}\text{S}_4 (s) \leftrightarrow \text{Cu}_2\text{S} (s) + \text{ZnS} (s) + \text{Sn}^{II}\text{S} (s) + \frac{1}{2}\text{S}_2 (g) (1)$$

Additionally one of the products of this reaction, SnS, has a high vapor pressure and will leave the CZTS surface quickly at low pressures and high temperatures according to Reaction (2).

$$\text{SnS} (s) \leftrightarrow \text{SnS} (g) \quad (2)$$

Comparing to the CIGS case, the stability of In$^{III}$ is higher and the volatility of In$_2$S lower which makes the problem negligible for CIGS processing. Calculations show that a certain $S_2$ and SnS pressure is needed to keep the CZTS surface stable during high temperature processing. For example at 550 °C, which is a normal annealing temperature, the sulfur partial pressure should be greater than $2.3 \times 10^{-4}$ mbar and the product of the partial pressure of SnS and the square root of the partial pressure of $S_2$ should be greater than $3.8 \times 10^{-5}$. 
In [10] an instability of CZTS together with the usual back contact material, Mo, is shown. This is due to Reaction (3) which was calculated to have a large negative change in free energy.

\[
2\text{Cu}_2\text{ZnSnS}_4 + \text{Mo} \rightarrow 2\text{Cu}_2\text{S} + 2\text{ZnS} + 2\text{SnS} + \text{MoS}_2
\]  
(3)

For the CIGS case the corresponding reaction has a positive change in free energy indicating that the CIGS and Mo interface is thermodynamically stable. These calculations suggest that Mo is not optimal as a back contact for CZTS and more development is needed in this area.

The properties and challenges of CZTS have also been described in several review articles, for example [11,12].

Despite these obstacles, the increase in record CZTS solar cell efficiency has been rapid, starting at 0.7 % in 1997 [13] and continuously increasing up to 6.7 % in 2008 [14] from the efforts of only a few research groups. In recent years many more, both universities and companies, have initiated research on this material and the record is now 9.2 % [1]. For the selenium containing compound, the record is currently 11.1 % [15].

### 1.4 Deposition techniques for Cu\textsubscript{2}ZnSnS\textsubscript{4}

Several deposition techniques have been used for production of CZTS. Most of them contain two or more steps but there are also a few where the material is grown directly into solar cell quality. The most common one step technique is evaporation, where the elements are evaporated together in a chamber and then condense on the substrate to create a film. A problem with applying this technique has been the instability of CZTS phase at low pressures in combination with high temperatures (described in Chapter 1.3) which means that Sn is easily lost by pumping out SnS from the chamber. However, lately several groups have presented good results, see for example [16], since this behavior has been taken into account and compensated for. Evaporation has also been used for depositing just the metal layers which have then been sulfurized.

Metal layers can also be deposited by sputtering. But also here, sulfur can be included already in the deposition step. One way is to sputter from targets containing sulfur, such as the binaries or even a target containing all the elements. Another way is to add sulfur in the sputtering atmosphere and do reactive sputtering. Some attempts have been done with single-step processes including sputtering but they have so far yielded low solar cell efficiencies, for example 1.4 % in reference [17].

A non-vacuum method for creating metal layers is electrodeposition, where metal ions are drawn to a substrate by a voltage difference. The plated layers can then be sulfurized in a similar way as the evaporated or sputtered films, which was done for example in [18] giving solar cells with an efficiency of 7.3 %.

Most successful so far are the solution based deposition techniques. Here all the constituents of the material are dissolved in a liquid which is then distributed on a substrate. The sample is then heated to remove the solvent. Several different solvents have been tried with good results [15,19]. The non-vacuum based techniques are usually cheaper due to lower cost of machines,
but generally create material with more impurities, which could mean lower top-efficiencies. That the techniques work well for CZTS could have to do with the high vapor pressures of SnS, Zn and S, which require that processing of CZTS is carried out at lower temperatures and higher pressures than are normally used with the vacuum based processes.

For all methods where the film is deposited at lower temperatures, annealing is necessary to ensure a good film quality. The annealing step can be performed in a furnace or on a hot plate, with or without addition of sulfur and tin sulfide in different forms. The temperatures are usually between 500-600°C but the time varies widely between groups, for example 580°C for 3 h [14] or 550-590°C for 5-15 min [18].
2 Composition -
calibration and measurements

2.1 Introduction

Due to the complexity of the CZTS material and the small single phase region it is preferable to
know the metal composition within a couple of atomic percent. A good knowledge of the
composition also makes interpretation of experimental results more reliable. Composition can
either be measured in absolute numbers (for example atoms/cm$^2$) or in relative quantities, e.g.
at%. In a relative measurement, the values must either be calibrated with reference to a known
sample (which has been characterized with an absolute method) or derived by modeling of the
expected signal.

To create an easy and reliable composition measurement for the precursor films and CZTS
samples, it was decided use metallic thickness series, characterized with Rutherford
backscattering spectroscopy (RBS), to calibrate the x-ray fluorescence spectroscopy system
(XRF). With RBS it is possible to determine an absolute areal density for thin films of heavy
elements, while XRF is a quick technique giving a signal from a large part of the sample. RBS
measurements are time consuming and therefore appropriate for determining reference
samples or measuring limited sample series. The latter was done in Paper III where RBS was
used to determine the Sn/(Sn+Zn) ratio for three of the five samples in the Zn-Sn-O-buffer series
investigated.

2.2 Methods

2.2.1 EDS

The most commonly available method for composition measurements is energy dispersive
spectroscopy (EDS). An electron beam (usually in an electron microscope) is directed towards
the sample surface and interacts with the material, creating secondary electrons, backscattered
electrons and x-rays. The electrons can be used for imaging by a secondary or backscattered
electron detector. The EDS-detector, on the other hand, analyzes the energy of the x-rays. Some
of the x-rays come from electrons that have been slowed down by the material, called
bremsstrahlung. The energy distribution of these x-rays creates a background that increases towards lower energies. But x-rays can also be created when the incoming electron excites an inner shell electron in the atom and an outer shell electron takes its place. These x-rays have a specific energy depending on the element and between which electron shells it transfers. It is therefore possible to decide in which element the x-ray was created and thus which elements the material consist of. The amount of a certain element is to a certain degree proportional to the amount of characteristic x-rays coming from the sample, but it also depends on how easy it is to excite electrons in that specific atom, how likely it is that an x-ray will be formed and also the other elements that are included in the material, since these will shield the electrons going in and the x-rays coming back to the detector. The composition data from EDS is therefore always relative and based on software calculations. To refine this, one can add a known standard which has a similar composition to the unknown sample, therefore accounting for the aforementioned shielding effects. In some softwares, one can also insert models of how the elements are distributed in the sample, for example that some of the materials are in a thin film on top of others. If this is not done, the software will assume the sample is homogenous, potentially giving misleading results.

A problem can be that the characteristic energy peaks of difference elements overlap. This is the case for Mo and S, where the energy distance between the innermost shell and the next in sulfur, is almost the same as between the second innermost and the next in molybdenum. Using a detector which measures the wavelength instead of the energy improves the resolution, but these detectors are generally slower and therefore less commonly used. If the overlapping elements are at different depths it can be possible to distinguish between them by reducing the incoming electron energy, meaning the electrons will not go as far into the material and the signal will only come from a layer close to the surface.

2.2.2 RBS

In RBS the material of interest is bombarded with ions with high and well-defined energy. The ions get backscattered on the atoms of the material and their energy will differ depending on the mass of the atom it interacts with and the distance through the material it had to travel before it reached this atom. The intensity of backscattered ions as a function of their energy is recorded, see example in Figure 5. An ion that has been backscattered on a heavy atom has a higher energy than if it would have been backscattered on a light one. Additionally, an ion that has travelled through some material and been scattered from an atom deeper in the film has lower energy than an ion that has been backscattered from an atom on the surface. The relationship between the intensities from different elements gives the composition, and the widths of peaks give the thickness of the film. The interactions can be simulated in a program and compared to the measured data. If a good fit can be found, the measurement gives an absolute areal density of the atoms in the thin film.
Figure 5 Example of a result from a RBS measurement. The sample is a thin CuSn-film on top of a Si-wafer. The red dots are measurement data and the solid blue line is the simulated curve. Sn is the heaviest atom of these three and therefore has the edge at the highest energy. Since the CuSn-layer is thin, its peaks are well defined. The Si-wafer is thicker than the thickness ions get backscattered from and the signal goes all the way down to the measurement limit. The relationship between the Cu and the Sn peak heights gives the composition of the CuSn-alloy. The widths of the peaks give the thickness of the film.

To be able to simulate the spectrum the backscattering angle (where the detector is placed) and the type, charge and amount of the incoming ions have to be known. The total number of ions can either be externally measured or retrieved from comparison with the substrate edge in the simulation.

The RBS method works best for thin films of heavy atoms on top of substrates containing only light atoms, since overlap then can be avoided and it is easier to fit the simulated spectrum to the data.

If measuring on highly crystalline samples there is a risk for channeling effects. The crystal is well-ordered and between the rows of atoms there are channels in certain directions. If the sample is oriented in a way so that these channels are directed towards the incoming ions, the ions can be steered into the channels and fewer ions than expected will be backscattered. This can sometimes be remedied by tilting the sample holder so that the channels are no longer easily accessible for the ions. Channeling can be seen in the measurement in several ways. An indication can be that the signal increases towards the high energy side of the substrate edge.
Another sign of channeling can be that, when using the substrate edge as a calibration for the number of ions, it is not possible to simulate a high enough curve for the film peaks. This is because the ion count in reality was higher than shown from the crystalline substrate edge.

As for most measurement techniques, a certain amount of energy is added to the sample by the incoming species, in this case ions. It is therefore important to make sure that the sample is not affected by this energy addition during the measurement. The risk for this to occur is higher for samples that have a non-equilibrium form or are easily evaporated. A way of noticing this is to monitor the measurement and make sure that the peak profile does not change during the measurement.

Due to the very similar atomic mass of Cu and Zn, their peaks overlap almost completely in RBS when a 2 MeV He⁺ ion beam is used. For our composition calibration of CZTS we therefore chose to make two different thickness series, one with a CuSn-alloy and one with pure Zn. Another benefit with this is that pure Sn thin films have a tendency to be uneven, as seen for example in [20] and the presence of Cu makes the film smoother. A roughness would be seen in RBS as a slightly smeared out profile at the low energy side of the peaks and a less sharp substrate edge.

Another way to separate the Cu and Zn signals could be to go to higher ion energies. This was tried in reference [21] and they concluded that 4.5 MeV was not enough to resolve Cu and Zn but at 10 MeV the signals were reasonably separated. However, with this high energy, nuclear forces come into play when the ion interacts with the atoms and the cross-section is no longer correct according to the Rutherford model.

A complementary ion technique used for composition measurements is PIXE (Particle Induced X-ray Emission). A similar ion beam as in RBS is used, usually 3 MeV H⁺, and when the ions interact with the sample they excite some of the inner shell electrons. When outer shell electrons take their place characteristic x-ray photons are emitted. The energy of these is measured and a relative composition can be determined. Cu and Zn are possible to resolve with this technique.

### 2.2.3 XRF

In the x-ray fluorescence (XRF) technique, characteristic x-rays are analyzed, as in EDS and PIXE, but instead of generating the characteristic x-rays with an electron beam or ion beam, they are generated with other x-rays. The fluorescence effect is largest when the incoming x-rays have an energy just over the characteristic absorption edge of the element. This means that, to get as large a signal as possible, different incoming x-ray energies, for the different elements to be detected, should be used. This is usually achieved by having one x-ray source but several secondary targets in the XRF-system. These can then be changed depending on the element to-be-measured. X-rays can penetrate much deeper than electrons which means that information depth generally is larger for XRF compared to EDS.

The intensity of the XRF signal at a certain x-ray energy directly gives an indication of the amount of material if two similar samples are compared, but to be able to get the composition in atomic percent (at%), a calibration has to be made.
For films that are thinner than a few micrometers, it can be assumed that the fluorescence counts are proportional to the thickness. The equations that describe the system can then be written as in Equation system (4), where $S_i$ is the fluorescence count for the specific element $i$, $k_i$ is the coefficient of proportionality, $C_i$ is the atomic percentage and $d_{tot}$ is the total thickness of the layer.

\[
S_{Cu} = k_{Cu}C_{Cu}d_{tot}
\]
\[
S_{Zn} = k_{Zn}C_{Zn}d_{tot}
\]
\[
S_{Sn} = k_{Sn}C_{Sn}d_{tot}
\]
\[
S_S = k_{S}C_{S}d_{tot}
\]
\[
\Sigma C_i = 100
\]

When measuring a sample of known thickness and composition, the coefficients of proportionality can be found from Equation system (4). These are then inserted in Equation system (5) to get the composition of an unknown sample.

\[
\left( \begin{array}{c} C_{Cu} \\ C_{Zn} \\ C_{Sn} \\ C_S \end{array} \right) = \frac{100}{G} \left( \begin{array}{c} S_{Cu}k_{Zn}k_{Sn}k_S \\ S_{Zn}k_{Cu}k_{Sn}k_S \\ S_{Sn}k_{Cu}k_{Zn}k_S \\ S_Sk_{Cu}k_{Zn}k_{Sn} \end{array} \right)
\]

\[
d_{tot} = \frac{G \times 1}{k_{Cu}k_{Zn}k_{Sn}k_S}
\]

where

\[
G = S_{Cu}k_{Zn}k_{Sn}k_S + S_{Zn}k_{Cu}k_{Sn}k_S + S_{Sn}k_{Cu}k_{Zn}k_S + S_Sk_{Cu}k_{Zn}k_{Sn}
\]

To get a more exact result, especially for thicker films, also the attenuation of the x-rays can be taken into account. The attenuation follows Equation (6), where $A$ is the attenuation, $I$ is the intensity coming from the sample, $I_0$ is the unattenuated intensity, $x$ is the sample density multiplied by the thickness, and $c$ is the mass attenuation coefficient.

\[
A = 1 - I/I_0 = 1 - e^{(-cx)}
\]

The density multiplied with the thickness is the same as areal density, which is the result that is received from RBS. The RBS values can therefore directly be inserted in this equation without knowing the physical thickness of the film. The mass attenuation coefficients are taken from [22] and are defined for a certain element but can be calculated for a compound by using the weight percent (wt%) of the constituents.

Assuming that characteristic x-rays are created evenly throughout the film thickness, the attenuation should be integrated, from the deepest emission point of x-rays, to the surface. This integral and its solution are shown in Equation (7), where $A_{tot}$ is the total attenuation that the signal will suffer and $u$ is the fraction of film between the emission point and the surface.
An even more exact calculation would include what happens to the attenuated x-rays since these can for example be re-emitted as characteristic x-rays from the atom that absorbed it. However, in our case the characteristic x-ray energy from Zn is not high enough to ionize electrons from the Cu K-shell and that from Sn is so much higher in energy that the fluorescence it creates in Cu and Zn is negligible.

\[ A_{tot} = \int_0^1 (1 - e^{-\gamma u}) \, du = 1 + \frac{1}{c_x} (e^{-c_x} - 1) \quad (7) \]

2.3 Metal composition calibration procedure

For a certain range, the intensity of XRF signal increases linearly with the amount of material, which means that when measuring a series of samples with varying thicknesses in this range, a linear equation connecting XRF intensity with the number of atoms from RBS can be formulated. This can be done for all the elements of interest. When measuring an unknown reference sample at the same occasion, the composition of the sample can be calculated by the equations. This reference sample can then be measured every time a new unknown sample is measured and the composition of the new unknown sample can be found.

2.3.1 Measurement of thickness series with RBS

Signals from Cu and Zn overlap in RBS and thus two different metallic thickness series, four Zn samples and four CuSn samples, were sputtered in the same system later used for precursor sputtering, described in detail in Chapter 3.2.2. Si-wafers were chosen as substrates since Si is lighter than the elements of interest. The thicknesses of the films ranged from 100 to 350 nm for the CuSn samples, calculated by assuming bulk density and confirmed by a profilometer, and from 70 to 250 nm for the Zn samples, assuming bulk density.

The two thickness series were measured with RBS at the Uppsala Tandem Laboratory (Ion Technology Center) with a 2 MeV He\(^+\) beam and a backscattering angle of 170\(^\circ\), on two different occasions (one for the CuSn-films and one for the Zn-films). To analyze the results, the simulation program SIMNRA [23] was used. Care was taken to fit the peaks both by matching the integral of the measured data, and to get the correct shape of the peaks. The Zn films were relatively rough, which made the fitting more complicated.

Channeling effects were seen in some of the measurements due to the high crystallinity of the Si-wafers (the sample holder was not tilted). The height of the Si-edge could therefore not be used for the calibration of the number of incoming ions and instead the plateaus of film peaks were used to fit the height of the simulated curve. This approach could overestimate the amount of metal atoms if there were small amounts of light element impurities in the film, which lower the film peak but cannot be distinguished due to overlap with the substrate edge. For the thinnest of the Zn-samples, no plateau existed and the parameters used were therefore kept similar to the other samples since the level of impurities in the films is not expected to change with thickness. The Zn-films were simulated containing 4-5\% O impurities. This is further discussed in Chapter 2.3.6.1.
Some of the simulation details are shown in Table 1 and Table 2 and the resulting areal densities are shown in Table 4, Table 5 and Table 6.

### Table 1 Details for SIMNRA simulation of the CuSn films.

The sputtering time for the samples is given in brackets under the sample name. The "Offset" and "Energy/ch" is used to set the correct scale of the x-axis. The "Particles*sr" is used to set the correct height of the curve and reflects the amount of incoming ions multiplied with the solid angle of the detector. The integrals are the areas under the measured and the simulated curves respectively.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>7224a2</td>
<td>55</td>
<td>3.635</td>
<td>2.25E+10</td>
<td>59</td>
<td>41</td>
<td>8562</td>
<td>8534</td>
<td>17643</td>
<td>17644</td>
</tr>
<tr>
<td>7224c2</td>
<td>55</td>
<td>3.635</td>
<td>1.65E+10</td>
<td>59</td>
<td>41</td>
<td>10966</td>
<td>10921</td>
<td>22467</td>
<td>22566</td>
</tr>
<tr>
<td>7224a1</td>
<td>55</td>
<td>3.635</td>
<td>2.16E+10</td>
<td>59</td>
<td>41</td>
<td>32993</td>
<td>32906</td>
<td>48326</td>
<td>48473</td>
</tr>
<tr>
<td>7224b2</td>
<td>55</td>
<td>3.635</td>
<td>1.81E+10</td>
<td>60</td>
<td>40</td>
<td>55029</td>
<td>54954</td>
<td>67202</td>
<td>67500</td>
</tr>
</tbody>
</table>

### Table 2 Details for SIMNRA simulation of the Zn films.

The sputtering time for the samples is given in brackets under the sample name. The "Offset" and "Energy/ch" is used to set the correct scale of the x-axis. The "Particles*sr" is used to set the correct height of the curve and reflects the amount of incoming ions multiplied with the solid angle of the detector. The integrals are the areas under the measured and the simulated curves respectively.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>7976a21</td>
<td>44</td>
<td>3.700</td>
<td>4.67E+10</td>
<td>95</td>
<td>5</td>
<td>24514</td>
<td>24529</td>
<td></td>
</tr>
<tr>
<td>7976b11</td>
<td>44</td>
<td>3.700</td>
<td>4.66E+10</td>
<td>95</td>
<td>5</td>
<td>41870</td>
<td>41683</td>
<td></td>
</tr>
<tr>
<td>7976b12</td>
<td>44</td>
<td>3.700</td>
<td>4.56E+10</td>
<td>96</td>
<td>4</td>
<td>61664</td>
<td>61554</td>
<td></td>
</tr>
<tr>
<td>7976c21</td>
<td>44</td>
<td>3.700</td>
<td>4.67E+10</td>
<td>96</td>
<td>4</td>
<td>80081</td>
<td>80225</td>
<td></td>
</tr>
</tbody>
</table>

#### 2.3.2 Measurement of thickness series with XRF

The same thickness series were measured in XRF. The system used was a PANalytical Epsilon 5. The noise and background were low, see Table 3. Measuring on Si or Mo-coated soda lime glass (SLG) makes therefore little difference, as long as the interesting peaks do not overlap with any of the substrate peaks. A Ge secondary target was chosen for the measurement of Cu and Zn and BaF₂ for Sn. The measurement live time was set to 60 s in each case. For deciding the counts for each element, certain energy regions (indicated in the top row of Table 3) were chosen. Cu and Zn are close in energy and thus, if the count is high, the tails of their peaks could overlap slightly. The chosen range was therefore kept closer to the middle of the peak for these elements.
Table 3 Counts within the regions indicated in the top row, from XRF measurements on bare substrates and examples from typical precursors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu-counts [cps/mA] (7.93-8.15 keV)</th>
<th>Zn-counts [cps/mA] (8.51-8.74 keV)</th>
<th>Sn-counts [cps/mA] (24.89-25.43 keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean SLG</td>
<td>3.77</td>
<td>2.89</td>
<td>13.84</td>
</tr>
<tr>
<td>Clean Si</td>
<td>2.95</td>
<td>1.65</td>
<td>8.86</td>
</tr>
<tr>
<td>Mo on SLG</td>
<td>3.80</td>
<td>3.21</td>
<td>15.22</td>
</tr>
<tr>
<td>Only mask</td>
<td>3.75</td>
<td>2.53</td>
<td>40.23</td>
</tr>
<tr>
<td>Mask + Si</td>
<td>4.25</td>
<td>2.97</td>
<td>44.16</td>
</tr>
<tr>
<td>Mask + Mo on SLG</td>
<td>4.53</td>
<td>3.83</td>
<td>52.04</td>
</tr>
<tr>
<td>Typical precursor</td>
<td>1935.33</td>
<td>1681.19</td>
<td>810.91</td>
</tr>
<tr>
<td>Typical precursor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>measured with mask</td>
<td>1216.24</td>
<td>1011.84</td>
<td>505.51</td>
</tr>
</tbody>
</table>

The sample size of the thickness series was smaller than the opening of the XRF system and a mask was therefore needed. The mask is made of a 130 µm thick Mo-foil which should block all characteristic x-rays from Cu and Zn and let through maximum 0.4 % of the characteristic Sn-radiation. Unfortunately, the Mo-foil also contained traces of Sn complicating the analysis. The measurement of the mask together with different substrates is shown in Table 3. To compensate for the extra Sn-signal from the mask, these values are subtracted from the sample results (“Mask+Si”-signal for the thickness series and “Mask+Mo on SLG” for normal samples). This procedure introduces an uncertainty in the composition value, especially since the Sn-signal from the mask is in the same order as the Sn-signal from the thickness series. This is further discussed in Chapter 2.3.6.1.

The XRF values, both for the thickness series and the measured samples, are corrected for attenuation of the outgoing characteristic x-rays. The attenuation correction is small, but affects the Cu/Sn and Zn/Sn ratios most, because the Sn-signal is much less attenuated than the signal from Cu and Zn. The attenuation correction in the thickness series uses the composition found by RBS for calculating the mass attenuation coefficient for the CuSn-alloy.

The XRF detector sits at an angle of roughly 45 degrees to the sample surface. The attenuation is therefore calculated for the thickness of the film that the detector sees.

The resulting XRF-counts; as-measured, corrected for the mask and then corrected for attenuation are shown in Table 4, Table 5 and Table 6 for Cu, Zn and Sn respectively.

2.3.3 Combination of RBS and XRF results

By combining the RBS and XRF results (corrected for mask and attenuation), linear expressions for the number of metal atoms per area versus XRF counts could be retrieved for the three different elements, see Table 7. The best linear fit does not give an equation that goes through zero, this is further discussed in Chapter 2.3.6.1.
Table 4 Resulting areal densities from RBS measurement, and XRF counts, for Cu from the CuSn thickness series. The sputtering time for the samples is given in brackets after the sample name.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atoms/cm²</th>
<th>XRF-counts [cps/mA] (7.93-8.15 keV)</th>
<th>XRF-counts minus signal from mask</th>
<th>XRF-counts including attenuation corr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7224a2 (100s)</td>
<td>3.39E+17</td>
<td>217</td>
<td>213</td>
<td>215</td>
</tr>
<tr>
<td>7224c2 (170s)</td>
<td>5.81E+17</td>
<td>353</td>
<td>349</td>
<td>355</td>
</tr>
<tr>
<td>7224a1 (250s)</td>
<td>8.20E+17</td>
<td>499</td>
<td>495</td>
<td>506</td>
</tr>
<tr>
<td>7224b2 (375s)</td>
<td>1.24E+18</td>
<td>736</td>
<td>732</td>
<td>757</td>
</tr>
</tbody>
</table>

Table 5 Resulting areal densities from RBS measurement, and XRF-counts, for Zn from the Zn thickness series. The sputtering time for the samples is given in brackets after the sample name.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atoms/cm²</th>
<th>XRF-counts [cps/mA] (8.51-8.74 keV)</th>
<th>XRF-counts minus signal from mask</th>
<th>XRF-counts including attenuation corr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7976a21 (180s)</td>
<td>4.42E+17</td>
<td>359</td>
<td>356</td>
<td>356</td>
</tr>
<tr>
<td>7976b11 (350s)</td>
<td>7.45E+17</td>
<td>603</td>
<td>600</td>
<td>601</td>
</tr>
<tr>
<td>7976b12 (500s)</td>
<td>1.11E+18</td>
<td>863</td>
<td>860</td>
<td>863</td>
</tr>
<tr>
<td>7976c21 (650s)</td>
<td>1.40E+18</td>
<td>1072</td>
<td>1069</td>
<td>1074</td>
</tr>
</tbody>
</table>

Table 6 Resulting areal densities from RBS measurement, and XRF-counts, for Sn from the CuSn thickness series. The sputtering time for the samples is given in brackets after the sample name.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atoms/cm²</th>
<th>XRF-counts [cps/mA] (24.89-25.43 keV)</th>
<th>XRF-counts minus signal from mask</th>
<th>XRF-counts including attenuation corr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7224a2 (100s)</td>
<td>2.36E+17</td>
<td>142</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>7224c2 (170s)</td>
<td>4.04E+17</td>
<td>204</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>7224a1 (250s)</td>
<td>5.70E+17</td>
<td>274</td>
<td>230</td>
<td>231</td>
</tr>
<tr>
<td>7224b2 (375s)</td>
<td>8.24E+17</td>
<td>389</td>
<td>345</td>
<td>346</td>
</tr>
</tbody>
</table>

Table 7 The resulting linear expressions (y=kx+m) fitted to the RBS and mask and attenuation corrected XRF data.

<table>
<thead>
<tr>
<th></th>
<th>k-value</th>
<th>m-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu – equation</td>
<td>1.65E+15</td>
<td>-1.07E+16</td>
</tr>
<tr>
<td>Zn – equation</td>
<td>1.34E+15</td>
<td>-4.44E+16</td>
</tr>
<tr>
<td>Sn – equation</td>
<td>2.35E+15</td>
<td>1.78E+16</td>
</tr>
</tbody>
</table>

2.3.4 Reference sample

On the same occasion as the thickness series were measured with XRF, a reference sample containing all three metals was measured. The number of atoms of each element in the reference piece could then be calculated via the linear equations in Table 7, and the composition in atomic percent for the sample was retrieved, see Table 8. The areal densities received in the calculation agree well with an in-house RBS measurement on a sample on Si from the same sputtering run.
The sum of the Cu and Zn signals match very well and the Sn areal density is 2% higher from RBS compared to the values received by the thickness series calibration.

The reference piece should preferably have a composition which is close to that of the samples which will be measured. In our case, we chose a precursor with close to the CZTS metal composition, and containing some sulfur, since we have seen that the pure metal samples tend to be more inhomogeneous over the thickness. The amount of sulfur in the sample has only a minor influence on the result, since it does not overlap with any of the interesting metals and the attenuation correction is barely affected by sulfur content, see example in Table 9.

Table 8 Values for the reference piece.

<table>
<thead>
<tr>
<th>Ref sample: 7950a21</th>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRF counts [cps/mA]</td>
<td>533</td>
<td>340</td>
<td>277</td>
</tr>
<tr>
<td>With mask corr.</td>
<td>529</td>
<td>336</td>
<td>225</td>
</tr>
<tr>
<td>With attenuation corr.</td>
<td>541</td>
<td>343</td>
<td>226</td>
</tr>
<tr>
<td>No of atoms/cm²</td>
<td>8.81E+17</td>
<td>4.14E+17</td>
<td>5.48E+17</td>
</tr>
<tr>
<td>Atomic percent</td>
<td>47.80</td>
<td>22.45</td>
<td>29.75</td>
</tr>
</tbody>
</table>

Table 9 Comparing how different amount of sulfur affects the attenuation calculation and thus the composition value, exemplified for the measurement with mask of B2 precursor.

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Cu [at%]</th>
<th>Zn [at%]</th>
<th>Sn [at%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No sulfur</td>
<td>47.12</td>
<td>28.83</td>
<td>24.06</td>
</tr>
<tr>
<td>20 % S</td>
<td>47.10</td>
<td>28.83</td>
<td>24.07</td>
</tr>
<tr>
<td>Matching oxidation state (roughly 50 % S)</td>
<td>47.07</td>
<td>28.83</td>
<td>24.11</td>
</tr>
</tbody>
</table>

At all subsequent XRF measurements, the reference piece was remeasured and coefficients of proportionality were based on this measurement combined with the assumption that the composition of the reference piece remains constant over time. The XRF system used has been very stable, giving almost the same counts for the reference piece during the last two years, see Table 10.

Table 10 Measurement of reference piece (sample name 7950a21) over time.

<table>
<thead>
<tr>
<th>Date</th>
<th>Cu-counts [cps/mA] (7.93-8.15 eV)</th>
<th>Zn-counts [cps/mA] (8.51-8.74 eV)</th>
<th>Sn-counts [cps/mA] (24.89-25.43 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011-04-29</td>
<td>857</td>
<td>543</td>
<td>417</td>
</tr>
<tr>
<td>2011-07-04</td>
<td>854</td>
<td>544</td>
<td>421</td>
</tr>
<tr>
<td>2011-10-13</td>
<td>855</td>
<td>546</td>
<td>419</td>
</tr>
<tr>
<td>2012-03-14</td>
<td>860</td>
<td>547</td>
<td>423</td>
</tr>
<tr>
<td>2012-07-02</td>
<td>855</td>
<td>543</td>
<td>421</td>
</tr>
</tbody>
</table>
When a new, unknown piece is measured, the calculation routine is as follows. Both the XRF signal from the unknown sample and the reference sample are corrected for mask and background counts. Then a preliminary composition is calculated by Equation system (5) and the non-attenuation corrected value for the reference piece, these can be seen in Figure 7b as the pale colored markers. To calculate the attenuation in the measured piece, it is assumed that its sulfur content matches the oxidation states of the metals. The sulfur content is thus based on the preliminary composition, as is the rest of the mass attenuation coefficient, which is retrieved by converting the at%, now including also the sulfur content, of the preliminary composition, to wt%. To get the areal density for the attenuation correction it is assumed that the measurement system has not changed since the thickness series calibration and that the linear equation in Table 7 is still valid to use for converting XRF counts to areal density. The attenuation is now calculated for the three metals and new, compensated, XRF counts are retrieved. These are then used together with Equation system (5) and the attenuation corrected value for the reference piece to get to a final composition value for the unknown piece.

### 2.3.5 Measurement of sulfur content

Since Mo and S overlap in the x-ray methods it is difficult to measure the sulfur content in the thin CZTS films on top of the Mo-coated glass (which is the standard substrate for CZTS solar cells). For the precursor samples, it can be an alternative to make the measurements on samples sputtered on Si substrates, but then it has to be assumed that the growth of the films is similar on the two different substrate materials. For the XRF case, we have not managed to make a calibration for sulfur content, since the sputtered sulfur-containing binaries generally do not stick well to Si.

In EDS, for thicker samples, an alternative is to decrease the beam energy enough to not penetrate down to the Mo layer. The problem with lowering the voltage is that the intensity for the Zn-line is lost. However the sulfur content can be determined in comparison with, for example Sn, as a S/Sn ratio and then the rest of the metal composition can be taken from measurements at higher acceleration voltages. In Figure 6 it is shown that both these techniques work for our films, here exemplified on a precursor sputtered at 300 °C. The higher temperature was chosen since it could be argued that the difference in growth between the Si and the Mo-coated glass should increase with higher temperature. However, as shown later, in Figure 10, the real temperature difference between the substrates seems to be small, and thus it is more likely that the growth is similar.
2.3.6 Comparisons

2.3.6.1 Discussion of the composition calibration

To date, we have used several different composition calibrations, because continuous improvements, both in the thickness series and in the calculations, have been made. Three of the calibrations are compared in Table 11. The calibration used in the papers included in this thesis is referred to as C_120511.

The first calibration was done with a Zn-series which was both very rough and contained a lot of oxygen and was therefore not easy to interpret in RBS. A new Zn-series was sputtered and much smoother films were achieved. The amount of oxygen is however hard to estimate due to the channeling effect in the RBS measurements. For both C_120511 and C_130322 it was assumed that the films contain 4-5 % oxygen, but since the number of incoming ions was set on the height of the film peak this is very uncertain. To investigate the influence of this assumption, a comparison between simulating the Zn-films as pure metal or including 4-5 % of oxygen was made. The result can be seen in Figure 7 as the difference between the red and the blue markers. The simulation without oxygen gives on average 3 % higher areal density of Zn which means that the amount of Zn given for any measured unknown piece also increases by roughly 3 %.
Table 11 Comparison of the resulting composition value of the reference piece 7950a21 for different calibrations. 
C_120511 is used as the reference in the papers included in this thesis.

<table>
<thead>
<tr>
<th>Name</th>
<th>Details</th>
<th>Cu [at%]</th>
<th>Zn [at%]</th>
<th>Sn [at%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_original</td>
<td>Rough Zn-series.</td>
<td>45.78</td>
<td>26.05</td>
<td>28.16</td>
</tr>
<tr>
<td>C_120511</td>
<td>Less rough Zn-series, including attenuation correction.</td>
<td>48.47</td>
<td>21.49</td>
<td>30.04</td>
</tr>
<tr>
<td>C_130322</td>
<td>Same RBS data as C_120511 but refined simulation, subtracting the full background (not only the mask), calculating the attenuation with integral and increased the thickness with 1/cos(45°).</td>
<td>47.80</td>
<td>22.45</td>
<td>29.75</td>
</tr>
<tr>
<td>C_Rossendorf</td>
<td>Sample on Si from the same sputtering run measured by RBS and PIXE in HZB Rossendorf</td>
<td>47.08</td>
<td>23.21</td>
<td>29.71</td>
</tr>
</tbody>
</table>

Another uncertainty is the signal from the mask. In C_130322 the full background was removed for the respective substrates, based on an average of several measurement of the mask together with the bare substrate. The background signal from the substrate will be slightly attenuated through the film and this is not accounted for with this method. In C_120511 only the added signal from the mask is subtracted. The difference between subtracting the full background values and only subtracting the signal from the mask can be seen in Figure 7 when comparing the red and the purple markers. For the reference piece the difference is about 3 % in Sn content but since the measured pieces are generally thicker, the difference for the unknown samples is generally only 1-2 %. The difference in Cu and Zn content is negligible.

The use of the mask in the thickness series calibration also means that only measurements with the mask will give correct areal densities. Densities as in Paper I and II can therefore only be calculated from the XRF measurements made with the mask. Also, since the areal density is used in the calculation of attenuation correction, this will not be correct for the pieces measured without the mask. The "thickness" is overestimated by about 60 % which means that the Cu and Zn XRF signals are overcompensated with 2-3 %. In the phase diagram this looks like a decrease of Sn. A similar difference is shown in Figure 7 as the difference between the red and the green markers, which is a comparison between assuming the XRF detector sitting right over the sample (green), or, as it is in reality, with an angle of roughly 45° (red), which makes the apparent thickness increase by about 40 %. The C_120511 calibration is calculated without the angle correction.

Also in Figure 7b it can be seen that there is a difference in composition when measuring with mask (rings) or without (crosses) on the same sample. Both measurements have their problems, measuring with the mask gives lower counts and the added Sn-background and the correction of this therefore causes uncertainties. For the measurements without the mask, the attenuation correction is not properly calculated and the absolute values are incorrect since the original calibration was done with the mask.

As mentioned before, the best linear fit of the thickness series values does not go through zero as would have been expected from the simple assumption that, for example, no copper in the film would mean zero XRF signal, besides the background. The offset from zero is not consistent for the different elements, as seen from Table 7 and Table 12, which points against that it should be a systematic error. The difference between using the best fit and forcing the equation to go through zero can be seen when comparing the red and the orange markers in Figure 7.
Comparing the $R^2$-values shows that the quality of the fit, as expected, is degraded, see Table 12. When looking at the offset in XRF counts, Table 12, it seems likely that the reason the equation does not go through zero could be an offset, not a change in slope. This could arise from a non-perfect background correction or, in the case of Zn, additionally, the assumption that there is oxygen in the thickness series.

Table 12 Comparison of quality of linear fit with and without setting the intercept to zero. Also shown is the intercept in the case of best fit.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Best fit</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intercept at</td>
<td>+7</td>
<td>+35</td>
<td>-8</td>
</tr>
<tr>
<td>XRF axis $R^2$</td>
<td>0.9998</td>
<td>0.9993</td>
<td>0.9980</td>
</tr>
<tr>
<td><strong>Setting intercept to zero</strong></td>
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<td>$R^2$</td>
<td>0.9996</td>
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Figure 7 Part of the CZTS phase diagram with comparison between different calculations for the reference piece 7950a21 (a) and sample B2 from paper II (b). The pale colored markers are from the calculations without attenuation correction. The red markers are the C_130322-values. For the blue markers it is assumed that the Zn thickness series does not contain any oxygen (4-5 % is assumed in C_130322). The purple markers show the value when only subtracting the extra mask signal instead of the full background. The green markers shows the composition if not taking into account the extra thickness the XRF-detector sees due to its position with roughly 45° angle to the sample. The orange markers show the difference between using the best linear fit to the RBS-XRF thickness series values, or forcing the curve through zero. In (b) the rings are from a measurement with the mask and the crosses are from a measurement without the mask.
2.3.6.2 EDS

The EDS system used in this thesis is an EDAX included in a LEO 440 SEM. The instrument has been calibrated with a range of pure elemental samples (not specifically Cu, Zn and Sn) and is run with the standard software. Comparing composition measurements from this system with XRF measurements, made without mask, generally yields a Zn-richer, more Cu-poor composition from the EDS. Compared to the stoichiometric metal composition (Cu:Zn:Sn=50:25:25) the Cu is on average 1-2 at% lower and Zn 1-2 at% higher while the Sn-value is generally quite well matching.

Larger differences can be seen when measuring on graded samples where EDS generally gives a higher value for the element that is accumulated towards the surface. This is due to the smaller information depth for EDS compared to XRF.

2.3.6.3 RBS at Helmholtz Zentrum Rossendorf

To verify our composition calibration, samples were sent for composition measurements to Helmholtz Zentrum in Rossendorf. Six samples with varying metal composition were sent, three of them were pure metal samples and three also contained 15-20 % sulfur, since they were sputtered with a ZnS target instead of Zn. The samples were analyzed with RBS using a 1.7 MeV He⁺ beam with the detector at 160°. To obtain the ratio between Cu and Zn, the samples were also analyzed with PIXE using a 3 MeV H⁺ beam.

In the pure metallic samples, gradients in the sample made the evaluation complicated and the results are uncertain.

For the sulfur containing samples the results from Rossendorf gave 1.2-1.4 at% lower Cu-content, 0.4-0.8 at% higher Zn-content and 0.7-1.0 at% higher Sn-content compared to our XRF measurements without mask on the same samples, see also the comparison in Table 11.

Comparing the absolute values from the RBS measurement at Rossendorf with the RBS measurement done here on samples from the same sputtering run as the reference piece 7950a21, we find that their combined areal density is 3 % lower for Cu and Zn and 7 % lower for Sn.

2.3.6.4 XAS at Helmholtz Zentrum Berlin

To compare to the absolute areal densities from RBS, we sent two samples for measurement with x-ray absorption spectroscopy (XAS) by Helmholtz Zentrum Berlin at beamline X at DORIS, HASYLAB @ DESY in Hamburg. The beam was monochromatized by a Si(111) double crystal monochromator. The intensity of the monochromatic x-ray beam was measured by ionization chambers placed before and after the sample. The initial intensity I₀ and transmitted intensity I were measured at several energies around the absorption edge of each element of interest. The difference between the intensities is proportional to the areal density of the specific atom species according to the same law responsible for the attenuation in XRF (Equation (6)).
Since the measurement was done in transmission mode, a thin Mo-coated glass (100 µm thick cover glass D 263® M from Schott) was used as substrate. This glass however contained a large amount of Zn and therefore only the Cu and Sn content of the films could be measured.

One of the samples sent was sputtered in the same run as precursor C1 from Paper II. When comparing the areal densities from our XRF measurement with mask, to the areal density from XAS, the latter gives roughly 20-30 % higher values. Relatively, XAS gave a slightly higher Cu/Sn-ratio than our measurement on the sample, Cu/Sn=1.97 compared to Cu/Sn=1.82. For the second sample measured, the Cu/Sn-ratio was 1.57 from XAS and 1.50 from our measurement with mask.

2.4 Conclusions

Precise composition measurements are challenging. To find the relative difference between two samples is often possible but to find the absolute change or composition is much more difficult. Here we have described some of the difficulties with finding the absolute value but also shown that we have a good idea of the relative changes between the samples.

The largest uncertainty in our XRF-measured compositions is in Zn-content, mostly due to the problem with fitting the spectra from RBS. For the example sample in Figure 7b, the variations are on the order of ± 1-2 at%, depending on the choices in calculation. For samples with composition close to stoichiometric, this is the level of uncertainty we can expect. The Sn-content is the second most problematic due to the extra Sn in the mask calls for a large background correction. The fact that attenuation of Sn differs a lot from that of Cu and Zn also makes the relative Sn-value uncertain. From the example sample we see that the variations on Sn-content also are on the order of ± 1-2 at%. The Cu value varies least, about ± 0.5-1 at% for the example sample in Figure 7b. Currently these variations are roughly on the same order as the variations we have from the process. An example of this is that we, from ten consecutive sputtering runs, with the same settings, had variations of maximum 1.5 at% for Cu, 2 at% for Zn and 1 at% for Sn. The calibration presented in this thesis have helped us to improve our solar cell process and increased our knowledge of the implications of composition measurement on CZTS films. However, the calibration could be further refined, especially to pin-point the correct Zn and Sn values.

The measured sulfur content seems to be satisfactory when Si substrates are used for the precursors. If an absolute measurement of sulfur would be needed, it should in theory be possible to do a thickness series of a sulfur containing compound and measure it in RBS in a similar way as described above. However, some work with finding a compound which adheres well, on for example Si, and that is stable enough in the ion beam, would have to be done. Also, the substrate for XRF measurement would in these cases have to be something other than Mo-coated glass, due to the overlap between S and Mo.

The absolute numbers agree quite well between the two RBS measurements and the thickness series calibration (with mask) while the results from XAS are less consistent.
3 Sputtering

3.1 Introduction

Sputtering is a physical vapor deposition technique. The process takes place in a deposition chamber which is evacuated with a pump system to a low pressure. In the chamber the substrate is placed together with one or more solid material targets containing the elements wanted in the films. When letting in a controlled amount of gas and applying a high potential on the target, the gas gets ionized and a plasma is created. Since the ions have a charge they are pulled towards the target, which acts as a cathode, and when they hit it, target atoms are ejected (sputtered). These ejected atoms will end up on all surfaces in the vacuum chamber including the substrate intended to be coated. Several factors will influence the properties of the final film, such as pressure in the chamber, distance between the substrate and the target, deposition rate and additional heating of the substrate. The typical energy of the sputtered atoms is a few eV and this energy input to the growing film provides significant improvement in the film quality compared to evaporation, where energy input is lower. Moreover, magnetron sputtering is a scalable technique, widely used for production of thin films.

Using several targets at the same time makes it possible to create films with several elements and variable composition. This is referred to as co-sputtering. It is also possible to add a gas which reacts with the target material and forms compounds, this is denoted reactive sputtering. Reactive sputtering can be performed either only in the reactive gas or in a mix of reactive gas and the normal inert working gas. The composition of the deposit can be varied by changing the power on the targets and the fraction of reactive gas.

The voltage applied to the target can either be constant (DC sputtering) or applied with a frequency (pulsed DC sputtering or RF sputtering). The different types are used depending on the conductivity of the target. If the target is insulating, a charge will be accumulated at the surface and eventually lead to a sudden electrical breakdown and cause an arc discharge. In pulsed DC and RF sputtering this is avoided by turning the voltage off or reversing its direction, for short times, meaning that the surface is discharged and a large charge is never built up. A disadvantage with pulsed DC and RF sputtering is that the equipment is more expensive. For RF sputtering, the deposition rate is also substantially lowered. This requires longer deposition times, which are undesirable from a production point of view. Long deposition times also means a higher degree of contamination in the films because, even at the low pressures used in sputtering, there will always be small amounts of oxygen and other contaminants adsorbing on the surfaces and thus being incorporated in the films.
3.2 Experimental

3.2.1 Characterization techniques

The techniques used to measure material properties (besides composition) of the reactively sputtered films, with emphasis on the implications when measuring on CZTS material, will be briefly discussed in the following chapter.

3.2.1.1 Raman spectroscopy

Raman spectroscopy uses the fact that atoms bonded together vibrate with certain frequencies. When laser light is incident on a sample, a fraction of it gets inelastically scattered and shifted in wavelength. The amount of the shift is connected to which atoms are involved in the vibration and how they are arranged and a given material therefore has a certain pattern of shifts, corresponding to peaks in the Raman spectrum. Commonly, the wavelength of the laser light used is in the visual range and, since this light does not penetrate far into the material, it makes the technique very surface sensitive.

![Raman spectrum](image)

Figure 8 Typical Raman spectra from CZTS (measured on the annealed sample B2 in Paper II) using a laser with excitation wavelength of 514 nm. A strong peak is seen at 336 cm$^{-1}$ and weaker contributions at 164, 252, 286, 350, 363 and 372 cm$^{-1}$. At roughly double the value of the main peak its weaker second order peak is seen.

Raman spectroscopy on CZTS gives a spectrum as in Figure 8. The peak positions and intensity distribution is unique for CZTS but several secondary phases, such as SnS$_2$, Sn$_2$S$_3$ and most of the Cu-Sn-S-compounds, have peaks in the same region and can therefore seldom be excluded by this technique. ZnS also overlaps with CZTS but when using a laser in the UV-range it gives a resonant excitation and can therefore be confirmed or excluded. SnS and several Cu-S-compounds can be distinguished clearly with Raman spectroscopy using a green laser, for example with an excitation wavelength of 514 nm.
The measurements in this thesis were done with a Reinshaw system at an excitation wavelength of 514 nm.

### 3.2.1.2 X-ray diffraction

X-ray diffraction (XRD) is an x-ray analysis method that can be used to find the structure of crystalline materials. A crystalline material is arranged in a lattice where atoms have certain positions depending on the structure of the material. This ordering also creates planes of atoms and thus a distance between planes. When shining x-rays at a crystalline material the waves will interact with the planes and the intensity of the outgoing x-ray will differ depending on the angle of the incoming x-rays, the angle of the detector and the distance between the atomic planes. Plotting the intensity versus the angle will give a specific pattern for a certain structure, called a diffractogram. Patterns can be calculated from the structure of a material but there is also a library with measured samples to compare with. However, the reference patterns are usually recorded on powders, and applying this technique to thin films has additional challenges, such as thin films giving low intensities or that thin films can be affected by the substrate they have been grown on, giving a preferential orientation or strain in the films that alters the diffractogram.

![XRD diffractogram from a CZTS thin film (top) and a sputtered precursor (bottom).](image)

Due to the similarity in structure between CZTS, ZnS and several CuSnS-compounds, many of the peaks in these patterns overlap. ZnS is the simplest structure of these and therefore has fewest peaks. The pattern for CZTS has additional peaks, which are unique for CZTS, meaning that it is difficult to exclude the presence of ZnS in CZTS by XRD, but possible to confirm the presence of CZTS in a film.
Several Sn-S and Cu-S compounds are also possible to distinguish in XRD and since the x-rays penetrate through the whole film it is possible to detect secondary phases in the bulk and at the back contact if the amount is large enough.

The measurements in this thesis were done with a Siemens D5000 system.

### 3.2.1.3 Stress measurements

Stress in films can cause delamination, cracks and changes in the structural and electronic properties. It is therefore important to measure and control the stress in thin films. Several approaches can be used to measure the stress. One way is to look at the shift of peaks in XRD, because the stress will affect the distances between the atomic planes, hence shifting the peak position. However, peak shifts in XRD could also have other origins, such as off-stoichiometry or impurities. A more direct way of measuring the stress is to look at the difference in flatness of a sample, before and after deposition. If the substrate is bendable enough and the stress in the film is high enough, it will cause the whole sample to warp slightly. Measurement of the flatness can be done either with a mechanical approach, such as with a profilometer, or with light, either from the side, looking at the reflection, or from the top, looking at the interference patterns. In this project the profilometer approach was chosen and the measurements were done with a Veeco Dektak 150.

The most common substrate to use for such measurements are Si-wafers, but since the growth, and therefore stress, could be different on different substrates, we chose to use Mo-coated thin glass slides (100 µm thick cover glass D 263® M from Schott). In this way we can ensure the results are relevant to the films produced on Mo for solar cells. In the case of Si-wafers, it is often assumed that the untreated wafer is flat but in the case of our substrates the glass had a curvature already before the deposition, and it was therefore important to measure the curvature also before. The measurement was made along two directions, perpendicular to each side of the quadratic glass piece, and was individually compared to the respective values after the precursor deposition. The curvatures were fitted by a least squares method. The resulting radii were used to calculate the stress, $\sigma$, with Equation (8) from [26], where $r_{\text{pre}}$ and $r_{\text{post}}$ are the radii before and after the precursor deposition, $E$ is the Young modulus for the glass (72.9 kN/mm$^2$, given by the manufacturer), $\nu$ is the Poisson ratio for the glass (0.208, given by the manufacturer) and $t_s$ and $t_f$ are the thickness of the substrate and film respectively.

$$\sigma = \frac{1}{6} \left( \frac{1}{r_{\text{post}}} - \frac{1}{r_{\text{pre}}} \right) \frac{E \cdot t_s^2}{1-\nu \cdot t_f}$$

### 3.2.2 Sputtering setup

The sputtering system used for deposition of the precursors is shortly described in this chapter. The system was limited to two target positions and therefore the three metals had to be combined into two targets. Due to the low melting point of Sn and its good miscibility with Cu, a CuSn-alloy target was chosen. This allowed easy control over the Zn content in the films, but the
Cu/Sn-ratio was, in theory, determined by the specific target composition. Two different CuSn-alloys were used, one with composition Cu: 67 at% and Sn: 33 at% (purity 99.99 %) and one with Cu: 65 at% and Sn: 35 at% (purity 99.999 %). To incorporate sulfur in the precursors, H₂S (purity 99.5 %) was used as a process gas solely or together with Ar. Both targets were operated in constant power mode with pulsed DC with a frequency of 20 kHz, which was supplied by two Huttinger PFG 3000 DC power supplies equipped with Advanced Energy Sparc-le 20 pulsing units. The insulating ZnS surface layer on the Zn-target (purity 99.994-99.995 %) was sufficiently thin not to cause arcing problems at this frequency. The film depositions were performed in a Von Ardenne CS600 sputtering system with two magnetrons and a front side heater, all facing the substrate at an angle of 45° at 160 mm distance. The targets were 102 mm in diameter and 6 mm thick. The base pressure was below 10⁻⁴ Pa. The maximum setting for the radiative front side heater was 500°C, yielding a maximum temperature at the substrate of approximately 300 °C, as can be seen in Figure 10.

![Figure 10 Temperature measurement by thermocouples incorporated in two different substrates.](image)

Three different substrates were used for depositions: soda-lime glass (SLG) for profilometer thickness measurements, silicon wafer for sulfur content measurement and Mo-coated SLG for the other characterization techniques and solar cell fabrication.

### 3.2.3 Device fabrication and characterization

The solar cells prepared in this thesis used SLG as the substrate. Onto this substrate a Mo back contact was DC sputtered. The back contact is typically 350 nm thick and has a sheet resistance of 0.6 Ω/square. The precursor film was then deposited on top of the Mo. To prepare solar cells the sample was then annealed in a tube furnace. The annealing temperature was 560 °C and a static argon atmosphere of 350 mbar was used. No extra sulfur was added and the annealing time was 3 min. When the piece had cooled down, it was etched in a 5 wt% potassium cyanide solution for 2 min and then coated with a CdS buffer layer by chemical bath deposition (CBD). The CBD solution comprised of 1.1 M ammonia, 0.100 M thiourea, and 0.003 M cadmium acetate.
and the pieces were kept in the solution for 8 min and 15 s at 60 °C, yielding a CdS film thickness of about 50 nm. The samples were then cleaned with DI-water, dried and loaded into a sputter for the deposition of the transparent front contact, a 90 nm intrinsic ZnO layer and then a 350 nm thick layer of Al-doped ZnO. The final step was a Ni/Al/Ni metal grid contact, evaporated through a mask to a thickness of about 3000 nm.

The final solar cells were characterized by quantum efficiency (QE) measurements and current-voltage (IV) measurements. The QE setup was calibrated with two externally measured Si and InGaAs solar cells from Hamamatsu. In the IV measurements the sample was placed on a temperature controlled stage and illuminated with a tungsten halogen lamp. To minimize the error from mismatch between the halogen lamp and the AM1.5 spectrum, the intensity of the lamp was adjusted to yield the short circuit current from the QE, after correcting the value from the QE for grid shading.

### 3.3 Results and discussion

In this section we present and discuss the results from the included papers. The sputtering process and the resulting films are investigated, as well as the influence of sputtering parameters on solar cell performance.

#### 3.3.1 Process curve

In reactive sputtering the target surface can be affected by the reactive gas used. The changed surface can in turn affect the deposition rate and target voltage, if run in constant power mode. To describe these changes, measurements at different reactive gas flows can be made and put together in a process curve. Figure 11 shows a process curve for our system and the target voltage and deposition rate, for different H₂S/Ar-ratios is presented. The process curve is included in Paper I and thoroughly described there. In conclusion it shows that the Zn-target is affected at a lower gas flow, indicating that this target is sulfurized first. This agrees with ZnS having a more negative free energy of formation than Cu-S and Sn-S compounds. The abrupt transition indicates high reactivity and a large difference in sputtering yield between Zn and ZnS. The CuSn-transition from metal to compound mode is more gradual and the voltage continuously increases over a large range of H₂S-flows.

On the right axis in Figure 11 the metal content in four samples, deposited with the different settings indicated in the graph, is shown. It can be seen that the deposition rate decreases both from the Zn- and the CuSn-target, but at different rates, agreeing well with the metal-to-compound transition types observed with the voltage measurement.
3.3.2 Structure of the sputtered films

In XRD, samples sputtered at high H₂S-flow show the pattern from a zinc blende structure, see example in Figure 9. These peaks are common for CZTS [27], Cu₂SnS₃[28,29,30] (CTS) and sphalerite ZnS with small shifts. None of the weak reflections specific for CZTS or CTS are observed. Following the notation introduced in [31], this pattern is hereafter referred to as Σ. There is also an unidentified shoulder just below the main peak.

In Raman typically a clear but broad peak around 335 cm⁻¹ is seen for the samples sputtered at high H₂S-flow. Peak fitting with Lorentzian curves gives good agreement for four peaks between 200 and 500 cm⁻¹, see Figure 12. The resulting peak positions for the weaker contributions are around 256 cm⁻¹, 290 cm⁻¹ and 354 cm⁻¹. According to [32], Raman scattering from CZTS should show three peaks at 285, 336 and 362 cm⁻¹ where the middle peak is most intense. Several IR peaks are also reported and the one at 255 cm⁻¹ agrees well with our peak fitted at 256 cm⁻¹. The other peak positions suggested from the fit are close to the three Raman frequencies reported and have similar intensity distribution. CZTS is therefore a plausible match for the result. However, as described in [33] several other compounds have intensities in the same range, such as ZnS, Cu₂SnS₃ and Cu₃SnS₄, and cannot be ruled out.

Figure 11 Process curve for co-sputtering CuSn and Zn in a pressure of 0.67 Pa and a total flow of 20 sccm (the H₂S flow shown on the x-axis was complemented with Ar-flow to a constant sum of 20 sccm). Samples were prepared with the conditions indicated by the letters at the top (all other parameters were kept constant). The dotted/dashed lines and the right axis show the metal content of these samples, measured by XRF and converted to areal density by the RBS calibration.
Figure 12 Raman spectrum from a precursor film (sample D in Paper I) with fitted curves showing suggested peak positions for the main peak at 332 cm\(^{-1}\) and broad overlapping peaks at 256, 290 and 354 cm\(^{-1}\). The grey curve is the resulting curve from the peak fit and the red crosses are experimental data.

Sputtering quite commonly yields non-equilibrium phases and as discussed in Paper V we suggest that the sputtered precursors have a non-equilibrium phase with S-ions in the zinc-blende configuration and the metal ions randomly ordered at the cation sites. This would fit the XRD and Raman responses where a ZnS structure is observed with XRD but Raman suggests that each S atom is surrounded by 2:1:1 Cu:Zn:Sn, as in the kesterite structure. A random ordering of the cations would also mean a range of slightly different S environments causing a broadening of the Raman peak. Also in Paper V, Raman spectra were recorded using a 325nm (UV) excitation wavelength and this measurement strongly suggests the absence of the ZnS phase in the precursor, which is the pattern seen in XRD. When examining these precursors with transmission electron microscopy (TEM) they look homogenous and no indication of more than one phase is found, see Figure 13. These results support the hypothesis of a disordered structure for the as-sputtered films.

Figure 13 Bright field image and EDS mapping by TEM. The distribution of elements within the precursor is very homogeneous and no indication of different phases can be found.
3.3.3 Effect of sputtering pressure

A small study of process pressure was made in Paper I. Two different pressures, 0.67 and 1.33 Pa, and three different H$_2$S/Ar-ratios were compared. The films were generally very similar at the two different pressures. The only difference seen was at 10 sccm H$_2$S and 20 sccm Ar where the XRD for the 1.33 Pa setting shows two very broad peaks at around 28.6° and 42.5°. When the process pressure was decreased to 0.67 Pa, an additional peak at 36.3° appeared in the XRD pattern. The peak matches the close packed plane for elemental Zn [34] and could indicate that this setting did not supply high enough partial pressure of sulfur to completely react the Zn at the substrate. The two broad peaks match the most intense peaks from sphalerite ZnS [25] and several CuSn-phases, for example Cu$_{40}$Sn$_{11}$ [35], respectively. This agrees with the process curve which indicates that the Zn-target at this point should be fully sulfurized while the CuSn-target still is in transition between metallic and compound mode.

3.3.4 Effect of substrate temperature

The substrate temperature during deposition is predicted to affect the morphology and stress in the film due to increased surface mobility of the arriving atoms [36,37]. Two temperature series were prepared in Papers I and II respectively. The substrate temperature was varied between room temperature and about 300 °C and several properties were affected. The composition changed both in Cu/Sn-ratio, Zn/(Cu+Sn)-ratio and sulfur content. Comparing the raw XRF signals from the metals, it was clear that the difference was mainly due to a decrease of Zn- and Sn-content with increasing temperature. This is probably due to the high vapor pressures of Zn and SnS. The lower sulfur content at higher temperatures can also be assigned to the high vapor pressure of S$_2$.

Since different compositions also could affect several other properties of the film, the second series (Paper II), was designed to give three controlled compositions at three different substrate temperatures, using different CuSn-alloy targets and varying the powers to the magnetrons, yielding in total nine samples. The sulfur loss was however not compensated for, resulting in lower sulfur content in the high temperature samples.

The decreasing deposition rate at higher temperature naturally yields thinner films. However, using the areal densities from the XRF measurement together with the sulfur content from EDS and the thickness, the film densities were calculated for the samples in the temperature series, and it was shown that the thickness decrease could not only be attributed to fewer atoms in the film, but that the high-temperature films are also denser. The generally low density values retrieved for the precursors, compared to the CZTS powder references, are not surprising for films that are sputtered at this rather low temperature [37].

Comparing SEM images (Figure 14) of the samples sputtered at different temperatures, with a general structure zone model (SZM) for sputtering (Figure 15) [36], the low temperature depositions exhibit features of zone 1-zone T with a columnar structure and rounded surfaces. The high temperature deposition appearance is closer to zone T-zone 2 morphology with faceted surfaces and angled grain boundaries within the film. When calculating the approximate
ratio of substrate temperature and melting temperature for these depositions it agrees well with what is expected from the SZM.

![Image 14 Films sputtered at different substrate temperatures; left: 40 °C, middle: 180 °C, right: 300 °C. The film is thinner and the surface increasingly faceted with higher temperature.](image)

![Image 15 Structure zone model from [37] showing the characteristics of films sputtered at different conditions. T is the substrate temperature and $T_m$ the melting temperature of the material, both measured in K.](image)

From XRD, all depositions show the $\Sigma$-pattern and the unidentified shoulder just below the main peak at 28°. However, the intensities of the peaks changes within the series in a way that indicates that the film becomes more oriented towards the (111) (for ZnS) or (112) (for CZTS) planes with higher temperature. This kind of texture, with the closest packed plane horizontal to the substrate, is common for sputtered films [36]. A (200) pole figure was recorded with XRD, which confirmed that the film had a (111)/(112) preferred orientation.

### 3.3.5 Stress in the sputtered films

Stress measurements were made on the two temperature series prepared for Papers I and II, and the deflection of thin glass substrates shows compressive stress for all samples, except one which has an unusual morphology. For the series with constant deposition parameters there is a weak trend showing lower stress values for higher temperature, but these are also the samples with the highest copper content. For the constant composition series there is a slight correlation
between high copper content and lower stress but no trend with temperature. A further possible explanation for the stress variations in the constant composition series is that the copper rich samples were made from a different sputtering target and at a higher deposition rate, which theoretically should increase compressive stress [37], the opposite to what is seen here. Additionally, direct comparisons of stress levels in films deposited from different targets is not straightforward, since the angular distribution of the energetic species changes overtime as the target is eroded, resulting in different growth conditions.

Using XRD for residual stress measurements on a sample which had high stress and weak preferred orientation showed good agreement with the curvature measurement, but when applying this method on samples with more texture it was apparent that the strong preferential orientation made the XRD measurement uncertain.

Differences in stress values can also give rise to peak shifts in XRD, although several other factors, such as composition and phase mixture, could also have an influence on the peak position. For the measured samples, all the visible Σ-peaks are slightly shifted to lower angles while the peaks from the Mo-back contact are well aligned. The shifts in the (111)/(112) peak are about 0.1-0.3 degrees compared to ZnS or CZTS (28.531° and 28.4502° respectively [24,25]). Combining the results from the two series we conclude that at least some of the peak shift comes from the Cu/Sn-ratio since the samples with the most stoichiometric Cu/Sn-ratio have peaks closer to the powder reference. However, there is probably also a contribution from stress since the sample with unusual morphology, which showed a small positive stress, also had by far the smallest peak shift.

### 3.3.6 Annealing and solar cell results

In Paper II the precursors were annealed and solar cells were made from the sample set. The films sputtered at room temperature had cracks after annealing and the cells produced from this material were shunted. The samples that were sputtered on heated substrates gave much better morphology after annealing. The grain size was larger for the more copper rich compositions and also increased slightly with higher temperature. The solar cells had efficiencies between 2-4.5 % with no particular trends with composition or between the two temperatures. However, due to the generally low efficiencies this is an uncertain result and it is possible that it would have been different if, for example, the anneal had been carried out with added sulfur, which currently gives us efficiencies between 6-8 % for the same type of precursors.
Summary

Composition measurements and sputtering of precursors for the thin film solar cell material CZTS have been investigated. A procedure for using sets of samples with different thicknesses measured with RBS to calibrate XRF measurements was explained and pros and cons of this approach were discussed. The composition of a reference sample was determined and could thereafter be used to find the composition of precursors and annealed films with XRF.

The reactive sputtering process, and the resulting thin films, of a CuSn- and a Zn-target sputtered in an H$_2$S atmosphere were investigated and described. A process curve of the system was presented and the influence of sputtering pressure and substrate temperature were investigated. The pressures tested had little influence on the film properties but the substrate temperature affected both composition and morphology, giving less Zn, Sn and S, and a more oriented film with increasingly facetted surface for higher temperatures. The stress in the films was not found to be influenced by the substrate temperature.

The precursors produced with this method are suggested to have a disordered structure with randomized cations, giving a CZTS-like response from Raman spectroscopy but a sphalerite ZnS-pattern from XRD. The films have an excellent homogeneity and it is possible to achieve stoichiometric sulfur content.

The complete steps from precursor, to annealed film, to finished solar cells were investigated for three film compositions sputtered at three different substrate temperatures, yielding in total nine samples. The films sputtered at room temperature cracked when annealed and thus gave shunted solar cells. For the samples sputtered at higher temperatures there are trends in grain size with larger grains for higher copper content and also slightly larger grains for higher temperatures. However, no connection between this and the electrical properties of the solar cells could be found and all the solar cells from precursors sputtered with substrate heating gave roughly the same efficiencies.
5 Suggestions for future work

Preferably the composition calibration should be redone with larger samples to be able to do the calibration both with and without the mask. This would facilitate measurements of both small and large samples. A new mask that does not contain Sn should then be used. Precautions to avoid channeling in the RBS measurements should also be taken, either the sample holder could be tilted or, even better, the substrate could be changed to an amorphous material but still with few, light elements, for example amorphous SiO$_2$, as was used as the substrate in Paper III.

Regarding the sputtering system, to be able to use three metal targets and thus be more free in terms of metal composition, the front heater, occupying the third target position of the chamber, has been exchanged for a heater in the substrate table. This makes it possible to use three separate elemental metal targets, which hopefully will give a better and easier control of the composition. The first indications are however, that a pure Cu-target does not work well in H$_2$S atmosphere, since a thick and porous Cu-S-layer is created on the surface, causing unstable operation and flakes to fall down on the substrates. An alternative would be to use a Cu-S-target. The conductivity of Cu-S-compounds is generally good which promises for the possibility to sputter the Cu-S-target with pulsed DC.

The change of heater also means the substrates can be brought up to higher temperatures. This enables for the kesterite phase to be crystallized already in the sputtering step. Investigating the transition between the disordered phase and kesterite could be beneficial to understand the creation of the kesterite phase.

Another alternative for sputtering of CZTS is to use a single compound target, which already contains all the elements needed for the film. Ideally the composition of the resulting film should be the same as for the target but due to, for example, high vapor pressure of Zn and SnS, an increased amount of these elements can be needed in the target to compensate for losses and achieve the correct composition in the film. Also, sulfur has a high vapor pressure and it can therefore be necessary to use H$_2$S as a sputtering gas together with the compound target to achieve a fully chalcogen stoichiometric precursor. The downside of using a quaternary compound target is that the composition is not easily changed and the optimal composition should therefore be found before choosing the composition of the compound target.

So far, the best solar cell efficiencies in the literature have been achieved with cells containing both sulfur and selenium. Future experiments could therefore be to include Se in the films. This could for example be done annealing in a selenium containing atmosphere or by sputtering from
compound targets including Se. To use H$_2$Se gas is a possibility but, it is even more poisonous than H$_2$S and therefore needs extremely rigorous safety measures to use.

A suggested reason for the bad performance of the sulfides is a disadvantageous conduction band alignment with the commonly used CdS-buffer. We therefore prepared a series of samples with the alternative buffer material Zn(O,S), for which it, on CIGS, has been shown that the conduction band is tunable in the range of interest. The results indicate that the conduction band alignment indeed was changed but that problems with interface recombination, causing reduced electrical performance, increased with the alternative buffer. Further efforts to improve the interface would be interesting. The initial results will be orally presented on the IEEE Photovoltaic Specialist Conference in Tampa, June 2013.
Sammanfattning på svenska


Eftersom CZTS har ett litet enfasområde är det viktigt att exakt kunna bestämma sammansättningen på filmerna som produceras. En stor del av denna avhandling ägnas därför åt denna uppgift och ett sätt att kalibrera röntgenflourscencemätningar med resultat från Rutherford backscattering mätningar för att kunna göra enkla, precisa sammansättningsmätningar, presenteras.

Eftersom CZTS inte är termodynamiskt stabilt vid höga temperaturer i kombination med låga tryck, så har en tvåstegsprocess för produktion av materialet valts i denna avhandling. Det första steget är reaktiv sputtring där en homogen film med alla de ingående ämnena skapas. Steg två är en kort uppvärmning av filmen för att generera större korn och minska antalet defekter i kristallstrukturerna. I denna avhandling beskrivs framförallt sputtringen i det första steget, bl a så visas en processkurva för systemet. Också hur parametrarna tryck och temperatur påverkar filmerna har undersöks och resultaten indikerar liten skillnad mellan filmer sputtrade vid olika tryck. Substrattemperaturen har dock större inverkan och filmerna blir mer orienterade, ytan mer facetterad och densiteten högre med ökande temperatur.

För en provserie med tre olika substrattemperaturer och tre olika sammansättningar, totalt nio olika prover, så undersöktes hela kedjan, från sputtringsparametrar, till egenskaperna hos den värmebehandlade filmen, till de elektriska egenskaperna hos de färdiga solcellerna. Resultaten visade att filmer sputtrade vid rumstemperatur fick sprickor när de värmebehandlades och solcellerna därför var delvis kortslutna. För de proverna som sputtrats vid högre temperaturer så sågs trenden i kornstorleken hos de värmebehandlade filmerna, både med ökande sputtertemperatur och med ökande kopparinnehåll. Dock fanns ingen koppling mellan detta och de elektriska egenskaperna hos solcellerna.
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List of papers

I. Reactive sputtering of precursors for Cu$_2$ZnSnS$_4$ thin film solar cells
Personal contributions to the article: Material synthesis, characterization and writing.

II. Annealing behavior of reactively sputtered precursor films for Cu$_2$ZnSnS$_4$ solar cells
Personal contributions to the article: Material synthesis, device fabrication, characterization and writing.

III. The effect of Zn$_{1-x}$Sn$_x$O$_y$ buffer layer thickness in 18.0% efficient Cd-free Cu(In,Ga)Se$_2$ solar cells
Johan Lindahl, Jörn Timo Wätjen, Adam Hultqvist, Tove Ericson, Marika Edoff, Tobias Törndahl.
Available online in Progress in Photovoltaics, doi: 10.1002/pip.2239
Personal contributions to the article: Composition measurements with RBS.
IV. Secondary compound formation revealed by transmission electron microscopy at the Cu$_2$ZnSnS$_4$/Mo interface


Personal contributions to the article: Calibration of the composition measurement, part in development of the precursor deposition method used and discussion.

V. Rapid annealing of reactively sputtered precursors for Cu$_2$ZnSnS$_4$ solar cells


Available online in Progress in Photovoltaics, doi: 10.1002/pip.2265

Personal contributions to the article: Calibration of the composition measurement, part in development of the precursor deposition method used and discussion.
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