Experimental study of Cu2ZnSn(Se,S)4 thin films for solar cell applications

Jessica Engman
Abstract

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Cu2ZnSn(Se,S)4 (CZT(Se,S)) has recently been shown to be a promising material to use in thin film solar cells. It has a band gap of between 1eV (CZTSe) and 1.5eV (CZTS). CZT(Se,S) solar cells have reached 10% efficiency.

The aim of this project was to find an effective way to selenise metallic Cu, Zn, Sn films in order to produce Cu2ZnSnSe4 (CZTSe) films, without destroying the metallic molybdenum (Mo) back contact. Another aim was to make films containing both Se and S and to study the possibility to achieve a controlled S/Se ratio in the films. Selenisation and sulfurisation reactions were carried out in quartz ampoules and samples were characterized using scanning electron microscopy, x-ray diffraction and energy dispersive microscopy.

Since Mo reacts rapidly with Se, experiments with selenisation and sulfurisation of plain Mo films were performed. The time and temperature dependence of the thickness of the reacted layer was studied, and it was found that Se reacts much faster with Mo than S does. Pre-sulfurisation of Mo appeared to hinder Se from reacting with the Mo.

The next step was to react precursor films to make CZTSe and CZT(Se,S) absorber layers. For mixed Se and S samples, the result is the same as for plain Mo samples; pre-sulfurisation, or inclusion of S in the precursor layer, can prevent selenisation of the Mo. The S/Se ratio was controlled with reaction time.

The best efficiency of 3.2% was obtained for a CZTSe sample while the best CZT(Se,S) sample gave 2.3%.
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1 Introduction

One of the most promising solar cell types manufactured today is the Cu(In, Ga)Se$_2$ (CIGS) solar cell. Efficiencies up to 20.3% have been reached by Jackson et al. [1]. However, the price of indium is high because the world demand is at the moment higher than the supply, resulting in higher costs for producing CIGS solar cells. For that reason, attempts are being made to produce solar cells with similar properties but without indium. In theory Cu$_2$ZnSn(Se, S)$_4$ (CZT(Se,S)) is a very good candidate; its characteristics are very similar to those of CIGS and hopefully the same methods can be used to produce it. Cu, Zn, Sn, S and Se are also non toxic, abundant materials and environmentally friendly to use. In figure 1.1 the crystal structure of Cu$_2$ZnSnSe$_4$(CZTSe) can be seen.

![CZTSe kesterite crystal structure](image)

Figure 1.1: CZTSe kesterite crystal structure. From [2].

IBM has set the efficiency record for CZT(Se,S) solar cell devices to 9.7% and they were produced with a “slurry based coating method”, which is a non-vacuum process [3].

1.1 Aim

The aim of this project is to find a good way to selenise metallic Cu, Zn, Sn films in order to produce Cu$_2$ZnSnSe$_4$ films without destroying the metallic back contact of molybdenum. Another aim is to attempt to make films containing both Se and S.
2 Theory

In this section basic solar cell theory is explained as well as specific theory of CZT(Se,S). The selenisation/sulfurisation process and the analysis techniques are also discussed.

2.1 Solar cells in general

The basic principle for a solar cell is that incident photons excite electrons which can deliver an output power when connected over a load. The cells work as p-n junctions but with an added current from the photoelectrons. A p-n junction is a p- and an n-type semiconductor put next to each other. Close to the intersection electrons from the n-type material fill the holes of the p-type material creating a depletion area where there is no free charge. This creates a built-in field over the junction. Photons excite electrons and the junction causes a current to flow. In a CIGS or CZT(Se,S) solar cell the absorber layer is the p-type material and the buffer layer and front contact are the n-type materials.

2.1.1 Solar cell efficiency

The sun emits photons with a spectrum of wavelengths between 100nm and $10^6$nm, which corresponds to energies between 12.4eV and 1.24meV. However, the intensity varies significantly between the different wavelengths, see figure 2.1. The red line is the irradiance of a black body at 5800K, which corresponds to the irradiance of the sun. After the photons enter the atmosphere some wavelengths are absorbed by, for example, ozone and water vapour. Then the spectral irradiance has the characteristics of the black line. AM1.5 means the irradiance at 1.5 atmospheric thicknesses and is an average irradiance over the United States of America over a period of one year [4].

In a single band gap solar cell there is a trade off between absorbing many photons and getting high energy electrons. Photons with energies below the band gap will not be absorbed and photons with energy above the band gap provide no increase in efficiency; they only heat the solar cell.

In 1961, Shockley and Queisser predicted the famous maximum efficiency of solar cells to be about 30% [5]. It was calculated considering single band gap solar cells. The maximum efficiency turned out to be with a band gap of between 1.1eV and 1.4eV. The efficiency of produced solar cells depends more on the quality of
the materials than the exact band gap. The theoretical maximum efficiency has not been reached but solar cells based on Si or GaAs have both reached efficiencies around 25%.

## 2.2 CZT(Se,S) solar cells

CZT(Se,S) has a band gap of about 1eV to 1.5eV [6]. The band gap depends on the Se/S ratio which can be varied to control it. The calculated value for the band gap of pure CZTSe is 0.96eV and for pure CZTS it is 1.5eV for the kesterite structure [2]. Kesterite is the name of the type of crystal structure shown in figure 1.1.

CZT(Se,S) solar cells consist of several different layers, see figure 2.2, which can be deposited in many different ways. The layers are very thin, in the micrometer scale, so they are deposited on a substrate. Here it is soda lime glass(SLG) but it can also be made from different materials. The CZT(Se,S) is the p part in the p-n junction in the solar cell. A buffer layer of CdS and a front contact of ZnO act as the n part. The layers can be deposited as described in section 3.3. The best solar cells of this type are the ones containing both Se and S in the absorber layer. The previously mentioned record cell from IBM of 9.7% is made with both Se and S with a $\frac{S}{S+Se}$ ratio of about 0.4. The record for pure CZTSe is 3.2% [7] and for pure CZTS it is 6.7% [8].

### 2.2.1 The role of molybdenum

The back contact is positioned between the absorbing layer and the substrate the solar cell is deposited on. The back contact is a metal with good conductivity and high optical reflectivity to reflect photons back to the absorber layer.

The back contact used in this study is made of molybdenum, or Mo. It is used
because it is known to work very well for CIGS solar cells. A big reason for that is that Se reacts relatively slow with Mo compared to other similar metals.

2.2.2 MoSe₂ and MoS₂

When a metallic Cu, Zn, Sn precursor is selenised or sulfurised by heating the sample in an atmosphere of Se or S vapour, the Se or S also react with the Mo layer underneath. If too much of the Mo is reacted the resistance of the Mo will be too high to conduct the current needed for a working solar cell. This is because MoSe₂ and MoS₂ are semiconductors. For CIGS solar cells it is known that a very thin layer of MoSe₂ between the Mo and the absorber layer increases the efficiency of the cell. Since there is a difference in band gap level between the absorber and the MoSe₂ the MoSe₂ behaves as a mirror for the electrons and reduces back-surface recombination [9], it also gives a better ohmic contact.

When Mo is reacted with Se or S the resulting layer of MoSe₂ or MoS₂ is about 400% or 340%, respectively, thicker than the Mo layer, calculated with the difference in densities between the materials and assuming isotropic expansion. Because of this it is easy to see if Mo has been reacted or not from SEM cross sections. Figure 2.3 shows the crystal structure of MoS₂.

Possible ways to reduce the growth of MoSe₂ and MoS₂ are by adjusting temperature and pressure since the reactivity depends on both of those and the stability
of the product which is different for MoSe$_2$ and MoS$_2$. Time affects the extent of the reaction. It is also possible to use another material which is less reactive as a kind of barrier to decrease the reaction rate.

Se diffuses through MoSe$_2$ easily and reacts more of the Mo underneath [11]. There are two kinds of diffusion mechanisms, interstitial and substitutional diffusion. In interstitial diffusion atoms squeeze between the atoms in the lattice and take positions that are not lattice sites. In substitutional diffusion atoms from neighboring positions jump to vacant places in the lattice. Atoms always vibrate and each time they are closer to a vacancy or another position that they can jump to there is a possibility that they will change place. The vibrational energy of an atom is about $3kT$, so, if a sample is heated up, the atoms have more energy and the oscillation amplitude is increased, thus the possibility of jumping is greater and the diffusion rate increases. There are more lattice defects in grain boundaries resulting in more vacancies atoms can jump to; so the diffusion rate is much higher in grain boundaries than in the grains. The diffusion rate varies a lot between different elements and depends on the orientation of the material; in interstitial diffusion it requires less energy to squeeze between atoms if there is more space between them. The interstitial diffusion rate depends on the size of the atoms since small atoms disturb the lattice less than big ones.[12]

For selenising and sulfurising molybdenum, different growth directions (c-axis either parallel or perpendicular to the Mo, see figure 2.3 for definitions) could have a big impact on reaction rate. If the c-axis of the MoS$_2$ or the MoSe$_2$ is parallel to the surface of the Mo the spacing between the atoms is bigger than if it is perpendicular, thus interstitial diffusion requires less energy and is more likely to occur.

2.3 Analysis Techniques

For analysing the samples several methods were used. They are described briefly in this section. To analyse the most promising samples they were made in to solar cells as described in section 3.3 and then analysed with IV and QE measurements as described below.

2.3.1 SEM

A Scanning Electron Microscope (SEM) is used to take high resolution images with magnifications up to 500 000 times for the best microscopes. A very focused electron beam scans across the surface and a detector detects secondary electrons which have been scattered out of the material. The detector counts the electrons emitted from a specific point and from that count an image of the scanned area is produced. A bright area in a SEM image means that many electrons were scattered from there. The reason SEM has such high resolution is that the incident electrons have very short wavelengths, about 3000 times as short as light in optical microscopes. Typical resolution for a SEM is 5nm [13]. The SEM used for this study is a LEO 1550.
2.3.2 EDS

An Energy Dispersive X-ray Spectrometer (EDS) is used to see the elemental composition of a sample. A beam of charged particles (electrons in this case) is scanned over the surface of a sample and excites inner shell electrons. Electrons from outer shells recombine to the hole and the excess energy is released in the form of x-rays. The energy of the x-rays is element specific so by measuring it the elemental composition is known. For this study a LEO 440 with an EDAX detector is used for the EDS measurements. Quantitative compositional measurements for Cu, Zn and Sn were calibrated by Rutherford backscattering spectrometry (RBS) and x-ray fluorescence (XRF) measurements.

2.3.3 XRD

X-Ray Diffraction (XRD) is used to acquire structural information of a sample, such as which crystalline phases exist. X-rays are directed at the sample surface and a detector collects the diffracted x-rays. Because of the short wavelength of x-rays it is possible to see a diffraction pattern that arises from x-rays being diffracted at atom planes in the lattice. The spacing between the layers will determine the reflection angle $2\theta$ of the beam. Intensity peaks will arise at different angles and with several peaks the compounds can be determined by comparing the peak positions with a database. The diffraction angle, the number of peaks and their intensity depend mostly on the crystal structure, symmetry and lattice constants. It is often easy to determine the compounds that are present since one can match several peaks with a reference. It can be a problem if some materials have peaks that overlap with other material peaks. The program used to identify the peaks in this study is called EVA.

By varying the angle of the incident beam the x-rays penetrate to different depths. With a bigger angle it is possible to see the material composition deeper in to the sample. In this work gracing incidence (GI) is mostly used (with an angle of 1°). All XRD graphs shown are measured with GI. Some samples have also been measured with $\theta - 2\theta$.

From XRD graphs it is possible to calculate the layer spacing $d_{hkl}$, using Bragg’s law: $\lambda = 2d_{hkl}sin\theta$. The wavelength of the incident x-ray of the Siemens D5000, which is the XRD used for the measurements in this study, is $\lambda = 1.540562\text{Å}$. hkl is the direction of the normal of the lattice planes. $2\theta$ is the angle of reflection resulting from the hkl plane.

When both $d_{hkl}$ and hkl are known the following formula can be used to calculate the lattice parameters a,b and c: $(\frac{1}{d_{hkl}})^2 = (\frac{h}{a})^2 + (\frac{k}{b})^2 + (\frac{l}{c})^2$. The definition of the lattice parameters can be seen in figure 1.1. For CZT(Se,S) it is known that a=b.

2.3.4 IV measurements

IV measurements are done to see how efficient a solar cell is. The cell is contacted at the back contact and at the front contact on the surface and a voltage is applied.
The voltage over the cell is varied from -0.5V to 1V and the resulting current is measured. If the cell is covered so that the measurement is done in the dark it can be seen if the cell behaves as a diode or not, i.e. an effective p-n junction has been made and the current only flows in one direction. When the cell is illuminated with AM1.5 the efficiency of the cell is measured. In figure 2.4 an example of an IV curve is shown. The fill factor, FF, can be calculated with \( V_{mp} \times I_{mp} \). * in the figure is where there is maximum power (V*I) which gives \( V_{mp} \) and \( I_{mp} \) (mp=maximum power). \( V_{oc} \) is the open circuit voltage under illumination and \( I_{sc} \) is the current achievable when the device is short circuited under illumination. Then the efficiency can be calculated with \( \eta = \frac{FF \times V_{oc} \times I_{sc}}{P} \), where \( P \) is the incident power from the light source.

![Figure 2.4: An example of an IV curve.](image)

The light source used is a halogen lamp with an intensity calibrated to give the same short circuit current density \( (J_{sc}) \) as obtained under AM1.5 one sun \((1kW/m^2)\). The lamp might heat the solar cells and that would reduce the efficiency, so the solar cell is placed on a water cooled peltier element to keep it at 25°C.

### 2.3.5 QE measurements

Quantum efficiency measurements are carried out to see the percentage of the incident photons that excite an electron that adds to the current. The wavelength of the incident photons is varied between about 350nm to 1300nm.

An estimate of the band gap can be made by extrapolation from the onset of a squared QE curve. The energy of the wavelength where the linear fit of the long wavelength drop of the curve crosses the x-axis is the width of the band gap, see figure 2.5. It is calculated with \( E[eV] = \frac{h \lambda}{q} \), which corresponds to \( E[eV] = \frac{1240}{\lambda} \), where \( \lambda \) is the wavelength in nanometers at the x-axis.

### 2.3.6 Gibbs triangle

To illustrate the material composition in a ternary alloy the Gibbs triangle is used which is a ternary phase diagram. In this report a Gibbs triangle with Cu$_2$S, ZnS and SnS$_2$ is used, see figure 2.6, as well as a triangle with Cu$_2$Se, ZnSe and SnSe$_2$. Both triangles are used but the S containing one is used here only to describe how
Figure 2.5: A QE curve with a linear fit of the decrease in the long wavelength section.

...the composition is of only SnS$_2$ the position in the diagram would be the top corner of the triangle. At the bottom edge there is no SnS$_2$. In the right side corner there is only Cu$_2$S and along the left edge there is no Cu$_2$S. The circle in the middle is the composition for a CZTS single phase. Outside this area additional phases (ZnS, Cu$_2$S, Sn$_2$S, Cu$_2$SnS$_3$, Cu$_2$SnS$_4$) as well as CZTS will form.

Figure 2.6: A ternary phase diagram for CuS, ZnS and SnS$_2$, taken from [14].
3 Experimental

The experimental setup for making the samples and for making solar cells will be explained in this chapter. The experimental studies can be divided into three main sections:

1. Selenisation and sulfurisation of molybdenum substrates. This is done to determine the maximum temperature and time that can be used without destroying the substrate.

2. Selenisation and sulfurisation of Cu, Zn and Sn films to give pure CZTSe or CZTS films.

3. Mixed selenisation and sulfurisation to give CZT(Se,S) films.

The molybdenum substrates are made by sputtering Mo on SLG (Soda Lime Glass).

3.1 Precursors for CZT(Se,S) films

Precursors of Cu, Zn and Sn are made by co-sputtering on the Mo-coated SLG. The machine used is a von Ardenne CS6005 which has room for two targets. One target of a Cu/Sn alloy and one of Zn or ZnS is used. The ratio of Zn can therefore be controlled by changing the power ratio between the targets. The composition of the precursors are measured with XRF in most cases and EDS in some. Selenisation and sulfurisation is done in the ampoules described in section 3.2 of this chapter.

3.2 Selenisation and sulfurisation in ampoules

To selenise or sulfurise a sample (either a Mo substrate or a metallic Cu, Zn, Sn precursor film) it is put in about 10cm long quartz ampoules together with a selenium bead of about 4mg or a sulfur piece of about 2mg and is then sealed under vacuum of $0.9 \pm 0.1$ Torr. The ampoules had been cleaned in an ultra sonic bath at 60°C with detergent before the samples were put in. The ampoules are then heated in a furnace to different temperatures between 400°C and 550°C and kept there for up to 60 minutes, see figure 3.1. The heat is then turned off and the samples cooled down in the furnace. An example of a temperature profile can be seen in figure 3.2.
CZT(Se,S) films develop larger grains and make better solar cells if produced in higher temperatures, but according to Abou-Ras et al. about 550°C is a critical temperature where the MoSe$_2$ layer thickness increases rapidly [11]. In conclusion, high temperatures are desirable to make good solar cells but then there is a risk of completely selenising the Mo. To get an idea about how long it takes for a sample to be selenised or sulfurised at different temperatures several tests were performed where the ampoules with samples in them were put in to a furnace and heated to temperatures between 400°C and 550°C. The analysis techniques described in section 2.3 were used to see how much of the Mo had been selenised or sulfurised.

![A quartz ampoule with sample after heating.](image)

**Figure 3.1**: A quartz ampoule with sample after heating.

![Cool down time for ampoules when stopped at 500°C.](image)

**Figure 3.2**: Cool down time for ampoules when stopped at 500°C.

### 3.2.1 Pressure in the ampoules

The pressure in the ampoules is calculated with the ideal gas law: $p[Pa] = \frac{NkT}{V}$, where $N$ is the number of particles, $k$ is the Boltzmann constant, $T$ is the temperature in Kelvin and $V$ is the volume of the ampoule. The composition of molecules in S- and Se-vapour at 500°C in a saturated atmosphere is shown in table 3.1. Based on the table it is possible to calculate the total number of particles; $N$. For sulfur, $N$ is $0.166n$ and for selenium it is $0.221n$, where $n$ is the total number of atoms.
Table 3.1: Ratio of molecules in vapour for S and Se, from [15] and [16] respectively.

<table>
<thead>
<tr>
<th>S</th>
<th>Ratio [%]</th>
<th>Se</th>
<th>Ratio [%]</th>
</tr>
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<td>Se</td>
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</tr>
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The vapour pressures of S and Se are taken from [17] and [18], respectively, and at 500°C they are about 1605Torr for sulfur and 42Torr for selenium. There are no selenium grains available that were small enough to give a pressure of less than the vapour pressure in the ampoules in this study, so all ampoules used for selenisation has a pressure of 42Torr at 500°C. The maximum for sulfur, on the other hand, is very high and the size of the sulfur pieces will make a difference. Pieces between 1.1mg and 2.7mg are used in these experiments and the pressure they produce in an ampoule at 500°C is presented in graph 3.3. The pressure for Se is also shown in the graph. Most Se pieces are 3mg or bigger so the pressure is only indicated for 2.5mg and above. Because the maximum vapour pressure is reached the pressure is independent of the sample size.

Because of the low maximum pressure for Se it is not a problem to keep the conditions similar between experiments with Se. For S it is much harder; a small difference in weight will result in a significant difference in pressure and the scale used to weigh the sulfur pieces in the experiments was only reliable in the 0.5mg-range which gives an uncertainty of about 25Torr.

Figure 3.3: The pressure of Se and S in the ampoules depending on how much was put in, in mg, and on temperature.
3.3 Making solar cells

Solar cells were made from some of the selenised and sulphurised precursors using the CIGS standard process which can be found in [19]. Cu, Zn and Sn are sputtered on the Mo and then selenised and sulphurised in about 500°C in ampoules to make CZT(Se,S). A buffer layer of CdS is deposited using CBD (Chemical Bath Deposition) which gives a CdS layer of 50-70nm and a front contact of ZnO is sputtered in the von Ardenne. Some cells are made by sulphurising the Mo before sputtering the precursor layer and some cells are made by changing the Zn target to a Zn/S target in the sputter process to have S in the precursor. The efficiency of the solar cells is tested with IV and QE measurements. These two methods are described in section 2.3.4 and 2.3.5, respectively.
4 Results

In this chapter all the results are presented and discussed. First results from selenising and sulfurising only the Mo are presented and then selenising and sulfurising metallic precursors. As part of the analysis solar cells are made of some metallic samples and the result from that is also shown here. The Mo layer is about 400-500nm thick before selenisation or sulfurisation.

4.1 Selenisation and sulfurisation of Mo

Table 4.1 shows the samples used for the Mo experiments. Samples M1 to M15 are selenised or sulfurised Mo samples. M13 to M15 are both selenised and sulfurised in different orders or at the same time. M16 to M21 are sulfurised in a tube furnace with a lower pressure of S and presence of argon. All ampoule samples are heated to the indicated temperature in the table in 60 minutes. The time column in the table indicates for how long the sample is kept at that temperature. 0min means that the sample is heated up for 60 minutes and then the heater is turned off immediately when the goal temperature is reached and the sample is allowed to cool down.

SEM images of Mo-substrates sulfurised and selenised at different temperatures can be seen in figure 4.1. The images show that more of the Mo is selenised and sulfurised at higher temperatures and at longer times. There is a big difference in how thick the layers of MoSe$_2$ and MoS$_2$ are at different times and temperatures. At 500°C everything is selenised after 60 minutes and the film starts flaking off. The selenisation at 450°C, 500°C and 550°C is compared to sulfurisation at the same temperatures and it is clear that the Mo sulfurises much slower than it selenises.

In figure 4.2 and 4.3 the XRD graphs for some selenised and sulfurised samples are shown. It is clear that the selenised samples consist of Mo and MoSe$_2$ and the sulfurised of Mo and MoS$_2$. By comparing the peaks for the MoSe$_2$ and the MoS$_2$ between the samples it is clear that lower temperature and less time gives smaller peaks. Smaller peaks means less of that material so this result is consistent with that of the SEM cross sections. Meanwhile, at lower temperature and shorter time the Mo peaks are bigger, which is consistent with the thin MoSe$_2$ and MoS$_2$ layers seen in SEM. The intensity of the Mo peaks is related to the thickness of the overlying MoSe(S)$_2$ layer since it is mainly the upper part of the film that is seen in low angle (1°) GI measurements. The Mo peaks are much stronger in the
<table>
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<th>Time[min]</th>
<th>Temp[°C]</th>
<th>Pressure[Torr]</th>
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</tr>
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</tr>
<tr>
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<td>M16</td>
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Table 4.1: List of samples made from Mo substrates.

Sulfurised samples compared to the selenised samples, consistent with the SEM images. The MoS$_2$ reference in the XRD graph for sulfurised samples indicates that there should be a peak at 14.5 which, according to the reference data, should be a [002] peak. This peak is missing in $\theta - 2\theta$ XRD measurements which indicates that the film is oriented with the c-axis parallel to the surface.
Figure 4.1: Selenisation and sulfurisation of Mo for 60 minutes (a to c) and 0 minutes (d to i) at three different temperatures.
Figure 4.2: XRD graph of the selenised Mo samples.

Figure 4.3: XRD graph of the sulfurised Mo samples.
In graph 4.4 the layer thickness of the MoSe$_2$ and MoS$_2$ is plotted against temperature at different times. It is clear that both time and temperature has a significant impact on the thickness of the MoS$_2$ and the MoSe$_2$. At all temperatures there is a clear difference in the layer thickness for 0 and 60 minutes. This goes against the result of Abou-Ras et al. who concluded that the growth rate of MoSe$_2$ depends on selenisation temperature and not on time [11] for temperatures of 450°C. However, their experimental setup was a bit different as they could control the temperature of the Se source and the substrate separately thus having better control over the pressure of Se. They also report that their c-axis is perpendicular to the surface at temperatures below 550°C which limits the growth. In this study the c-axis is parallel to the surface which means it is easier for Se atoms to diffuse through the MoSe$_2$ layer, thus reacting faster. At 580°C Abou-Ras et al. grew layers with the c-axis parallel to the surface but the reaction rate in this study is still much faster. Their pressure of Se was much lower which can explain this difference.

![Figure 4.4: Thickness of the MoS$_2$ and MoSe$_2$ depending on temperature and dwell time.](image)

4.1.1 Mixed selenisation and sulfurisation of Mo

To investigate the different interactions between Mo and Se or S, Mo samples were treated in two stages; first with Se then with S and vice versa. Some samples were made with Se and S at the same time in the ampoule. As can be seen in figure 4.5 there is a big difference in how much of the Mo that has been reacted between the different samples. When the Mo is first selenised then sulfurised the reacted layer is about 800nm thick (4.5a) but when it is the other way around the layer is only about 150nm thick (4.5b). The sample that is made with both Se and S in the ampoule at the same time is very similar to the one made with S first (4.5c).
The piece of Se used produce a pressure of 42Torr in the ampoules while the sulfur ones give about 75Torr.

In figure 4.6 the XRD pattern of the mixed Se and S samples are compared to the pure Se or S samples. The top red line is a selenised sample and the bottom green one is a sulferised. The black line is first selenised at a pressure of 42Torr then sulphurised at 83Torr and the graph shows that the MoSe$_2$ does not change to MoS$_2$. The blue line is from a sample that is selenised and sulphurised at the same time but with a higher pressure of S in the ampoule. The resulting film consists of Mo and MoS$_2$. The purple line is a sample that is first sulphurised at 66Torr then selenised at 42Torr and also here the resulting film is the same as an only sulphurised sample. The intensity of the peaks in the XRD reflect the thickness of the layers seen in the SEM images. M13, which has relatively high peaks, has the thickest reacted layer. M14 and M15 both have thin reacted layers and have low peaks. The black line drawn in the image of M14 is to clarify where the interface between the Mo and the MoS$_2$ is.

(a) M13, Se -> S, 0min, 500°C (b) M14, S -> Se, 0min, 500°C (c) M15, S+Se, 0min, 500°C

Figure 4.5: SEM images of the mixed samples on Mo.

4.2 Sulfurised Mo to prevent selenisation

Since the function of the back contact of Mo will be lost if too much of the Mo is reacted with S or Se some more tests are performed to further investigate if the sulfurised Mo can be used to prevent selenisation. The results from the samples that are both selenised and sulphurised indicate that the sulfurised Mo prevents the selenium to react with the Mo, see figure 4.5. For that reason Mo was sulfurised at different pressures and then selenised to see if this is a good way of controlling the selenisation of Mo.

4.2.1 Sulfurising the Mo

MoS$_2$ films are prepared in two ways; first in ampoules as previously described and also in a tube furnace where larger samples can be sulfurised. However, in the tube furnace much lower pressures of sulfur are used, about 0.008Torr. The resulting films are mainly still Mo with about 50nm of MoS$_2$ on top, see figure 4.7 a, c and e.
4.2.2 Selenising the MoS$_2$

The selenisation of the MoS$_2$ is performed in the same way as before in ampoules. Three samples are made in the tube furnace, producing three different thicknesses of MoS$_2$. The samples are selenised at 500°C for 0 minutes. Figure 4.7 shows SEM images of the unselenised samples next to the selenised ones. a, c and e are the samples sulfurised in the tube furnace and the ones next to them is after selenisation. The thickness of the selenised layer is the same thickness as the previously made only selenised sample (4.1e). Thus the sulfurised Mo from the tube furnace does not stop the selenisation. Figure 4.7h and 4.7g shows the sample first sulfurised in an ampoule, then selenised. In this case the selenisation seems to be stopped or slowed down indicating that there is a difference in how the MoS$_2$ grows in the tube furnace compared to the ampoules. Another explanation could be the formation of a surface barrier layer, such as an oxide.
Figure 4.7: SEM images of the Mo/MoS$_2$ samples before and after selenisation.
4.2.3 Summary

For the mixed samples MoS$_2$ seems to be blocking the Se from reacting with the Mo. Otherwise the reacted layer would be much thicker if the Mo could react with the Se, as shown in image 4.1e. MoSe$_2$ peaks would also show up in the XRD graphs. Because of the big pressure difference between the Se and S it is not so unexpected that S is the element of the two that reacts with the Mo in the sample with Se and S at the same time.

It is possible to use S to block the reaction of Mo with Se, but there are conditions when it does not work as shown when Mo is sulphurised in the ampoules compared to being sulphurised in the tube furnace. A reason can be the growth direction of the MoS$_2$; if the c axis is parallel to the surface the spacing is much larger between the atoms so it becomes easier for Se atoms to diffuse through but if the c axis is perpendicular to the surface it is harder for the Se to go through. The main differences between the ampoules and the tube furnace is the sulfur pressure, which is much higher in the ampoules, and that there is presence of argon in the tube furnace. These differences could cause the MoS$_2$ to grow in a different way but there are no indications that the films have different orientation from the XRD measurements. There could also be a barrier layer, such as an oxide, on the surface on the samples made in the ampoules. Further investigation should be carried out to understand this process. Using this approach should enable preparation of CZTSe samples without destroying the Mo substrate.
4.3 Selenisation and sulfurisation of precursors for CZT(Se,S) absorber layers

Metallic Cu, Zn, Sn precursors are selenised and sulfurised to produce absorber layers for solar cells. It is also interesting to see if there is a difference in how much of the Mo is reacted when it is covered with a metallic precursor. Phase diagrams are presented to show what happens to the metal composition of the precursor after selenisation or sulfurisation.

Table 4.2 shows a list of all samples discussed in this chapter. A to L are selenised metallic precursors, M to O are sulfurised and the rest are different variations of mixed Se and S samples. Sample V, W, X, Y, Aa and Ab all have S in the precursor and X, Z, Aa and Ac have sulfurised Mo under the precursor. P1 to P7 are the precursors used. P1 to P6 are Cu, Zn and Sn containing precursors and P7 also contains 10-15% sulfur.

<table>
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Table 4.2: List of samples made from metallic Cu, Zn, Sn precursors.

4.3.1 Selenisation of Cu, Zn, Sn precursors

Even with the metallic Cu, Zn, Sn precursor on top the Mo selenised about as fast as on substrates with only Mo. As can be seen in figure 4.8 there is a clear temperature dependence of the thickness of the MoSe2. At 0 minutes at 500°C very little Mo has been selenised and the grain size is fairly big; see figure 4.8a.
After 30 minutes at 500°C and at 550°C there is little or no Mo left and thus it will not work properly as back contact for a solar cell. These samples are made from a precursor layer that was 460nm before selenisation. So, as seen in the pictures, the layer becomes about four times as thick after the reaction. The samples with bigger grains are a bit thinner.

Figure 4.8: Selenisation of metallic precursors at two different temperatures and three different times.

Top view SEM images are taken of sample D and sample L for comparison. Image 4.9 shows a nice surface for the sample D; there are very few holes and the reasonably large grains are evenly distributed over the surface. Sample L has larger grains but the MoSe₂ layer is very thick and there seems to be a lot of holes. Because sample D has quite large grains and few holes solar cells are made with the same temperature and the same amount of time (500°C for 0 minutes), see section 4.4.1.

When the samples are selenised the composition of the metals change. SnSe can be lost from the film by evaporation and transmission electron microscopy (TEM) studies of a selenised sample show that Cu can become incorporated in the MoSe₂ layer underneath (see figure 4.12), this has also been seen by other groups [20]. TEM studies also indicate that ZnSe forms on the surface of the sample.

The composition before and after selenisation can be seen in the Gibbs triangle in
Figure 4.9: Top views of two selenised metallic precursors at different temperatures.

Figure 4.10; the measurements are done with EDS. The samples that are originally furthest away from stoichiometry change the most in composition, they appear to lose Sn and Cu and become more Zn rich. So the samples probably evaporate SnSe during selenisation and the Cu moves to the MoSe$_2$. ZnSe might also be forming on the surface. EDS measurements are surface sensitive so there would appear to be less Cu if it is positioned further back in the sample. The Zn content appears to increase because the Sn and Cu content decreases and because it might be present as ZnSe on the surface.

In figure 4.11 the XRD graphs of the selenised metallic samples are shown together with the reference patterns for CZTSe, SnSe$_2$ and Mo. In EVA there is no reference for Cu$_2$ZnSnSe$_4$ so Cu$_2$ZnSnS$_4$ is used with changed lattice parameters (a and c). That will give a correct reference since Cu$_2$ZnSnSe$_4$ and Cu$_2$ZnSnS$_4$ have the same structure and the lattice parameters a and c are the only thing that differs between them. The back contact of Mo is seen only in the last line because that measurement was done at a higher angle than the others. Samples D, L, F, G and K are the closest to stoichiometry and to the SnSe$_2$ phase in the Gibbs triangle.
(4.10) and those five are also the only samples containing that phase. The SnSe$_2$ phase is the only thing varying between the selenised metallic samples in the XRD graph. The ZnSe and Cu$_2$SnSe$_4$ peaks overlap with CZTSe peaks so they can not be investigated with XRD.

Figure 4.10: The change in metallic composition of the selenised samples. Precursors P1 to P6 are selenised, giving films A to L.
Figure 4.11: XRD graph of the selenised metallic samples.

Figure 4.12: TEM image of sample I with buffer layer and front contact, courtesy of J.T. Wätjen.
4.3.2 Sulfurisation of Cu, Zn, Sn precursors

For comparison metallic Cu, Zn, Sn precursors are also reacted with sulfur. The metallic precursor on top of the Mo seems to stop sulfur more than selenium so at high temperatures less Mo is sulfurised compared to the substrates with only Mo; compare figure 4.13a and 4.13b. The precursor for sample 4.13a was 460nm thick and the one for 4.13c was 310nm. At 550°C for 60 minutes the sample grows to five times as thick after sulfurisation and in 500°C for 0 minutes it gets about three times as thick.

![Sulfurised metallic precursors and a sulfurised Mo reference.](image)

(a) M, S, 60min, 550°C  (b) M9, S, 60min, 550°C on Mo  (c) N, S, 0min, 500°C

(d) N, S, 0min, 500°C top view  (e) N, 5kX  (f) N, 150X

Figure 4.13: Sulfurised metallic precursors and a sulfurised Mo reference.

The change in metal composition after sulfurisation compared to before can be seen in figure 4.14. The close to stoichiometric samples change in about the same way as the selenised samples while the Zn-rich samples appears to lose Zn. In the XRD graph, 4.15, both of the samples contain Cu₂ZnSnS₄, Mo and SnS₂. The precursors were both close to the SnS₂ phase in the Gibbs triangle. The red bottom line is a selenised Mo sample and is there for reference.
Figure 4.14: The change in metallic composition of the sulphurised samples.

Figure 4.15: XRD graph of the sulphurised metallic samples.
4.3.3 Mixed selenisation and sulfurisation of precursors

Several variations of mixed samples are made. Some are made with metallic precursors that were selenised and sulfurised in different orders or at the same time. Two samples are made by sulfurising the Mo before sputtering the precursor and then selenising it (Z and Ac), some by changing the Zn target to a ZnS target in the sputter to get S in the precursor without heating it (P7 precursor series) and two by a mix of the two last methods (X and Aa).

The mixed precursor samples all look very different, see figure 4.16 and 4.17. Sample P (mixed S+Se) has a flaky composition with some big flakes on the surface (4.19m). There is no visible MoSe$_2$ or MoS$_2$ layer. The first selenised then sulfurised sample R has small grains and a thick MoSe$_2$ layer. The sulfurised (N) and first sulphurised then selenised (Q) samples both have a thick Mo layer remaining but look a bit uneven on the top view. The selenised only (G) and the sulfurised only (N) samples looks like expected from earlier images and are shown as reference. Z looks quite similar to the selenised sample (4.8a) but with bigger grains. X and V both have two distinct layers and much of the Mo left. To see if the layers can merge V was sealed in an ampoule of 0.9Torr and annealed for 12 hours. The layers then disappeared and the results is nice big grains in sample W, 4.17d.

XRD graphs of the samples with double layers can be seen in 4.18. The difference between before and after annealing in 12h, that is the difference between V and W, is that V has SnSe$_2$ peaks and W does not. X and V give very similar results and they also look similar in the SEM images.

In figure 4.19 top views are shown for some of the samples. All samples look very different but the structure the sample gets the first time it is reacted seems to stay. Sample R, which is selenised then sulfurised has similar structure to sample G, which is only selenised. Sample Q shows the same relation to sample N but for sulfur. The flaky composition of sample P is also seen in the top view.

The change in metal composition can be seen in the ternary phase diagram 4.20.

The XRD graph 4.21 illustrates that the mixed samples have a variety of compositions between CZTSe and CZTS. The selenised sample with sulfurised Mo under the precursor (Z) and the sample with S in the precursor (Y) both comprise of CZTSe in the absorber layer. No sample is purely CZTS but the first sulfurised then selenised sample (Q) has double peaks, one for a mixed CZT(Se,S) phase and one for CZTS phase.
Figure 4.16: SEM cross sections of the mixed metallic precursor samples. Sample preparation given in table 4.2.
Figure 4.17: SEM cross sections of the mixed metallic precursor samples. Sample preparation given in table 4.2.

Figure 4.18: XRD graph of the samples with double layers.
Figure 4.19: SEM top views on mixed samples and references on metallic precursors.
Figure 4.20: Ternary phase diagram for the mixed selenised and sulfurised samples.

Figure 4.21: XRD graph of the mixed selenised and sulfurised metallic samples.
Figure 4.22: XRD graph of the mixed selenised and sulfurised metallic samples zoomed in over peak [112].

Figure 4.23: XRD graph of the mixed selenised and sulfurised metallic samples zoomed in over peak [220] and [312].
From the XRD graphs it is possible to calculate the lattice parameters \( a \) and \( c \) as described in section 2.3.3. \( hkl \) for the peaks have been taken from [7] and [21]. Assuming that there is a linear change in lattice parameter from CZTS to CZTSe as S is exchanged to Se, the S/Se ratio in a mixed sample can be estimated. The measurements are done with low angle GI which means that there can be small peak shifts in the results which gives a small error in the calculations. No separate determination of S/Se ratio is available. Therefore this method is valuable in spite of the existing uncertainties. The result for \( a \) and \( c \) as well as the volume of the unit cell and the S/(Se+S) ratio can be seen in table 4.3.

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<th>S P[Torr]</th>
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<th>( c[\text{Å}] )</th>
<th>( V[m^3] )</th>
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<td>5.43</td>
<td>10.93</td>
<td>3.22 ( \times 10^{-28} )</td>
<td>92</td>
</tr>
<tr>
<td>V</td>
<td>42</td>
<td>-</td>
<td>5.66</td>
<td>11.29</td>
<td>3.61 ( \times 10^{-28} )</td>
<td>8</td>
</tr>
<tr>
<td>W</td>
<td>42</td>
<td>0 (12h)</td>
<td>5.63</td>
<td>11.26</td>
<td>3.58 ( \times 10^{-28} )</td>
<td>16</td>
</tr>
<tr>
<td>X</td>
<td>42</td>
<td>-</td>
<td>5.66</td>
<td>11.33</td>
<td>3.63 ( \times 10^{-28} )</td>
<td>4</td>
</tr>
<tr>
<td>Y</td>
<td>42 (1h)</td>
<td>-</td>
<td>5.68</td>
<td>11.32</td>
<td>3.65 ( \times 10^{-28} )</td>
<td>0</td>
</tr>
<tr>
<td>Z</td>
<td>42</td>
<td>-</td>
<td>5.68</td>
<td>11.32</td>
<td>3.65 ( \times 10^{-28} )</td>
<td>0</td>
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Table 4.3: Calculated lattice parameters. *) Has a double peak which is not considered in the calculations.

There are two samples that are first selenised then sulphurised and two that are made in the reverse order. Q and R are both made with ampoules for 0 minutes at 500°C and S and T are made the same way but the second time it is reacted in an ampoule it is kept at 500°C for 60 minutes. The samples made for 60 minutes are more reacted then the 0 minute ones. It is clear by looking at the table values that the time and the pressure matters for the final result. The pressure of S is about 50% higher than for Se in the ampoules and for all samples that are reacted with both S and Se the result is more sulphurised than selenised.

### 4.3.4 Summary

The Mo is selenised as fast with metallic precursor as without but with sulfur less of the Mo is reacted with the metal precursor layer on top. Also here the temperature and the time matters for the thickness of the MoSe2 and the MoS2 layers. Samples reacted for longer times or increased temperature have slightly larger grains of CZT(Se,S). For the mixed samples the result is the same as for only Mo samples (see section 4.2)); the S is reacting with the Mo and not Se. Z, X and V all have bigger grains than other samples. W has the biggest grains seen in this study after annealing for 12 hours. By using a precursor that contains sulfur
(sample W) or by sulfurising the Mo substrate before precursor deposition (sample Z), good quality CZTSe films can be made without selenising the Mo back contact too much. The result from the selenised then sulfurised and the sulfurised then selenised samples indicate that it is possible to control the composition of Se and S by varying the time the samples are kept at high temperatures.

4.4 Solar cell devices

Solar cells are made to see if the samples that showed large grains and a thick layer of Mo in the SEM images and that showed CZT(Se,S) composition in the XRD graphs also make good solar cells. The whole device consists of SLG as substrate, Mo as back contact, Mo+Se or Mo+S (some of the Mo is selenised/sulfurised), CZT(Se,S) as absorber layer, CdS as buffer layer and ZnO as front contact. They are made as described in section 3.3.

4.4.1 Selenised or sulfurised absorber layers in solar cells

Based on previous results solar cells are produced with metallic precursors that are selenised in 500°C for 0 minutes. That temperature and time produces large grains (4.8a) and the films cover the surface well (4.9a and 4.9b). Samples are made with different compositions according to graph 4.24. After the buffer layer and front contact have been deposited it is no longer possible to measure the Cu, Zn and Sn composition of the absorber layer with EDS so there are no composition measurements for the reacted precursors.
Figure 4.24: Composition of the samples made in to solar cells.
The resulting IV-curves are shown in figure 4.25 and QE measurements are shown in graphs 4.26. The efficiencies of the cells are determined from the IV curves, which are automatically calculated in the program used to measure. From the IV-curves and QE-graphs it is clear that I and K give the best results with high efficiencies and high QE-values, see table 4.4. The performance of the other samples is limited by low QE-values and fill factor (FF) and the efficiencies are low or zero. A $V_{oc}$ of zero and a fill factor (FF) of about 25% means that the sell is shunted. The efficiency of I of 3.2% is the same as the previously set record by Zoppi et al. [7] for a CZTSe device.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Efficiency[%]</th>
<th>Band gap[eV]</th>
<th>$V_{oc}$[V]</th>
<th>$J_{sc}$[mA/cm²]</th>
<th>FF[%]</th>
</tr>
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<tbody>
<tr>
<td>E(P2)</td>
<td>0.0</td>
<td>1</td>
<td>0.03</td>
<td>3.70</td>
<td>25.27</td>
</tr>
<tr>
<td>F(P3)</td>
<td>0.1</td>
<td>1</td>
<td>0.05</td>
<td>4.06</td>
<td>25.36</td>
</tr>
<tr>
<td>H(P4)</td>
<td>0.0</td>
<td>0.95</td>
<td>0.07</td>
<td>1.77</td>
<td>27.01</td>
</tr>
<tr>
<td>I(P5)</td>
<td>3.2</td>
<td>1.05</td>
<td>0.39</td>
<td>20.61</td>
<td>40.01</td>
</tr>
<tr>
<td>K(P6)</td>
<td>0.9</td>
<td>1</td>
<td>0.21</td>
<td>14.80</td>
<td>27.96</td>
</tr>
<tr>
<td>N(P3)</td>
<td>0.0</td>
<td>-</td>
<td>0.01</td>
<td>0.34</td>
<td>24.38</td>
</tr>
</tbody>
</table>

Table 4.4: Efficiency and QE-values of the selenised or sulfurised samples.

The band gaps in the table are measured from the QE curves as described in section 2.3.5. The values (all are approximately 1 for the selenised samples) compares well with literature for CZTSe.
Figure 4.25: IV-curves for the selenised or sulfurised samples.

(a) E (Se), $V_{oc}=0.03$, FF=25.27%

(b) F (Se), $V_{oc}=0.049$, FF=25.36%

(c) H (Se), $V_{oc}=0.071$, FF=27.01%

(d) I (Se), $V_{oc}=0.389$, FF=40.01%

(e) K (Se), $V_{oc}=0.21$, FF=27.96%

(f) N (S), $V_{oc}=0.008$, FF=24.38%
Figure 4.26: QE-curves for the selenised samples.
To get an idea of why I and K work so much better than the other cells SEM images were taken of the samples before the buffer layer or front contact was deposited, see figure 4.27. The layers for all samples but H looks very similar to each other but with the difference that the CZTSe layer is more than 200nm thicker and the Mo layer 80nm thinner for sample I than any of the others. The difference in thickness is not so big before selenisation and has not been explained.

![SEM images](image)

(a) E  (b) F  (c) H  (d) I  (e) K  (f) N

Figure 4.27: SEM images of the selenised or sulphurised solar cells without buffer layer or front contact.

Figure 4.28 and 4.29 shows top views of some of the samples. In the first figure it is hard to see any big differences between the samples but when zoomed out differences appear; the structure of the surface differs greatly. There should not be holes or conducting phases, such as Cu₅Se or CuSnSe, in the film since then it will not work as a diode. The top view images does not reveal any holes and XRD measurements does not indicate presence of Cu₅Se. CuSnSe can not be seen with XRD since its peaks overlap with the CZT(Se,S) peaks. Therefore it is difficult to
explain the poor performance of some of the devices, but it could be due to the very thick MoSe$_2$ layers.

![SEM top views of some of the selenised or sulfurised solar cells without buffer layer or front contact.](image)

**Figure 4.28:** SEM top views of some of the selenised or sulfurised solar cells without buffer layer or front contact.

### 4.4.2 Mixed selenised and sulfurised absorber layers in solar cells

A series of solar cells with both S and Se are made to see what impact the order of selenisation and sulfurisation has on the solar cell. Ab and Aa are both annealed for 12 hours in vacuum before they are made into solar cells to get rid of the double layer seen and discussed in section 4.3.3.

The resulting IV curves can be seen in figure 4.30. All cells but the first sulfurised then selenised sample Q are behaving like solar cells and produce current. That R and P give similar results is expected since the XRD results seen in table 4.3 gives that the sulfur/selenium ratio is the same for the two samples.

QE measurements are made on the working cells, see figure 4.31. R, P and U have a larger band gap and therefore it can be concluded that they contain more sulfur. Ac, Ab and Aa have QE curves that behave more like CZTSe with a smaller band gap. Ab and Aa all have quite good quantum efficiency, both over 70%.

The efficiency of the cells, the maximum QE values, the band gaps (calculated from the QE graphs with the method described in section 2.3.5) and the S/(Se+S) ratios can be seen in table 4.5. The S/(Se+S) ratios for Ac, Ab and Aa are
calculated from XRD graphs of Z, Y and X, respectively, which are samples made with the same method. Band gaps close to 1 should be CZTSe and close to 1.5 should be CZTS which matches the results from the XRD measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Efficiency [%]</th>
<th>Band gap [eV]</th>
<th>S/(Se+S)</th>
<th>V_{oc} [V]</th>
<th>J_{sc} [mA/cm²]</th>
<th>FF [%]</th>
</tr>
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<tbody>
<tr>
<td>R(P3)</td>
<td>0.9</td>
<td>1.38</td>
<td>85.2</td>
<td>0.55</td>
<td>4.08</td>
<td>40.11</td>
</tr>
<tr>
<td>P(P3)</td>
<td>0.3</td>
<td>1.39</td>
<td>85.2</td>
<td>0.22</td>
<td>4.39</td>
<td>33.45</td>
</tr>
<tr>
<td>U(P5)</td>
<td>0.5</td>
<td>1.18</td>
<td>-</td>
<td>0.33</td>
<td>4.27</td>
<td>37.45</td>
</tr>
<tr>
<td>Ac(P6)</td>
<td>1.1</td>
<td>0.98</td>
<td>0</td>
<td>0.22</td>
<td>18.47</td>
<td>29.97</td>
</tr>
<tr>
<td>Ab(P7)</td>
<td>1.7</td>
<td>1.03</td>
<td>0</td>
<td>0.27</td>
<td>18.38</td>
<td>33.22</td>
</tr>
<tr>
<td>Aa(P7)</td>
<td>2.3</td>
<td>1.03</td>
<td>4.1</td>
<td>0.30</td>
<td>19.10</td>
<td>41.05</td>
</tr>
</tbody>
</table>

Table 4.5: The band gap of the solar cells with good QE curves.
(a) R, selenised then sulfurised, $V_{oc}=0.551$, FF=40.11%

(b) Q, sulfurised then selenised, $V_{oc}=0.006$, FF=11.93%

(c) P, sulfurised and selenised at the same time, $V_{oc}=0.217$, FF=33.45%

(d) U, selenised then sulfurised, $V_{oc}=0.327$, FF=37.45%

(e) Ac, selenised Mo then selenised precursor sputtered with S then selenised, $V_{oc}=0.218$, FF=27.97%

(f) Ab, precursor sputtered with S then selenised, $V_{oc}=0.272$, FF=33.22%

(g) Aa, sulfurised Mo then precursor sputtered with S then selenised, $V_{oc}=0.296$, FF=41.05%

Figure 4.30: IV-curves for the mixed samples.
(a) R, selenised then sulfurised

(b) P, sulfurised and selenised at the same time

(c) U, selenised then sulfurised

(d) Ac, sulfurised Mo then selenised precursor

(e) Ab, precursor sputtered with S then selenised

(f) Aa, sulfurised Mo then precursor sputtered with S then selenised

Figure 4.31: QE-curves for the working mixed cells.
4.4.3 Summary

Working solar cells are successfully made based on both CZTSe and CZT(Se,S) absorber layers. The efficiencies vary a lot between the cells and is difficult to correlate to the observed morphology or composition. Of the selenised samples, sample I gave the best result which is the furthest from stoichiometry of the samples made in to solar cells but previous studies have shown that Zn-rich and Cu-poor samples gives good solar cells [3][8]. For selenised samples Zn-rich samples are good. For mixed samples many different compositions gave working solar cells. The values of the band gaps calculated from the QE curves agree with literature.
5 Conclusion and suggestions for future work

The purpose of this diploma thesis was to study the selenisation process of Cu, Zn, Sn precursor films and to find a good way of selenising precursors to produce good Cu$_2$ZnSn(Se, S)$_4$ solar cells. This chapter summarizes the results from the study.

A problem with selenising is that Se reacts very well with the molybdenum back contact, much more so than S does. Therefore the study was started with selenising and sulfurising only the Mo. This was done by sealing pieces of glass substrates with a Mo layer in quartz ampoules along with some Se or S and heating them to temperatures between 400$^\circ$C and 550$^\circ$C. After selenisation or sulfurisation a layer of MoSe$_2$ or MoS$_2$ formed on the Mo. The thickness of the MoSe$_2$ and the MoS$_2$ layers increased with increased time and increased temperature. The Se reacted much faster with Mo than S did and thus consuming a lot of the Mo which is needed for a good back contact. The thicknesses were measured with SEM images and structural information with XRD.

To see how Se and S influence each other during the process some Mo samples were both selenised and sulfurised. In samples that were first selenised then sulfurised and samples that were first sulfurised then selenised the second reaction did not change the composition; the first selenised sample still consisted of Mo and MoSe$_2$ even after sulfurisation and vice versa. Some samples were made with Se and S reacting with the Mo at the same time. This gave the same result as a sample that was first sulfurised then selenised. An explanation for this is that there was a higher pressure of S present in the reaction. Samples were also made with lower pressure of S and in the presence of Ar before selenisation. In these cases the MoS$_2$ did not stop the Se from reacting with the Mo. The results indicated that a thin layer of MoS$_2$ can be used to stop Se from reacting with the Mo but that there also are process conditions when this does not happen. Different surface oxidations could also be a possible explanation.

The next step in the study was to selenise and sulfurise metallic Cu, Zn, Sn precursors to see if there is a difference in how much of the Mo is reacted when covered with the precursor for the absorber layer. The results showed that the Mo is selenised as fast with the precursor as without but for sulfur the layer seems to slow down the reaction and less of the Mo is reacted.

In terms of the Cu$_2$ZnSn(Se, S)$_4$ film, samples with longer reaction times or higher temperatures got bigger grains in the absorber layer. For the mixed Se and
S samples the result is the same as for only Mo samples when first sulfurising then selenising; the S is blocking the Se from reacting with the Mo. A reason for that could be that the pressure of S is higher in the ampoule. The samples made with Se and S at the same time also gave a similar result as for the Mo samples; the Mo reacts with the S but not with the Se. However, in the absorber layer about one fourth has been selenised.

It was found that S in the precursor or a MoS$_2$ layer between the Mo and the precursor enabled CZTSe films to be produced without consuming too much of the Mo substrate. The mixed Se and S absorber layers all looked very different and no clear pattern was visible. The sample that had the largest grains and seemingly no holes was made by incorporating S in the sputter process when the precursor was deposited and then selenising it at 500°C for a short time. Afterwards it was annealed in vacuum for 12h at 500°C. How much the absorber layer was selenised or sulfurised was compared between the samples. The results indicate that it is possible to control how much the absorber layer of a sample is selenised or sulfurised. If a sample is first selenised and then sulfurised the composition can be controlled by varying the time of the second process.

Solar cells were made and characterised by IV and QE measurements. It was difficult to correlate the measured efficiencies with the SEM and XRD measurements but some promising efficiencies were achieved for pure CZTSe films and mixed CZT(Se,S) films. The best solar cell made from the selenised samples gave an efficiency of 3.2% and the best mixed sample gave an efficiency of 2.3%.

Based on the results from this study some recommendations for future studies can be made.

- To make a pre-sulfurisation to prevent the Se to react with the Mo is a promising approach and the mechanism for the process should be investigated.

- In this study quite high pressures of Se was used. It would be interesting to see if lower pressures of Se could reduce the substrate selenisation. In ampoules it is difficult to control the conditions so a furnace where temperature can be controlled separately for the sample piece and the Se or S piece would be better.

- The CZTSe and CZTS films have very different morphology which suggests that their reaction processes are quite different. These differences should be understood to help improve processing methods.
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