Investigation of Metallic Dust formed on Steel Substrates in Solar Cell Sputtering Chambers

Jakob Friberg

Materials Engineering, master's level
2019

Luleå University of Technology
Department of Engineering Sciences and Mathematics
Title: Investigation of Metallic Dust formed on Steel Substrates in Solar Cell Sputtering Chambers

Author: Jakob Friberg

Supervisor: Marta-Lena Antti

Date: 2019-09-30

Abstract:

Investigations have been done as of why dust particles appear in a circular pattern on the backside of solar cells produced in sputtering chambers at Midsummer AB. An experimental approach was conducted, where solar cells were produced at standard conditions and their backside studied by material analytical methods. The solar cells dust particles were analyzed by energy-dispersive x-ray spectroscopy and x-ray diffraction, deducing that they consisted of iron selenide (Fe$_{0.8}$Se). Furthermore, the dust particles appear due to formation of a thin iron selenide film that cracks and delaminate upon cooling from process temperature to room temperature. Iron selenide film thickness was found by energy-dispersive x-ray spectroscopy to occur in a pattern with radial symmetry with respect to the cell center, correlating with the film delamination pattern. The reason to the film formation was due to selenium reacting with the substrate steel at high temperatures (>400 °C) in deposition chambers having a selenium environment. The film delamination occurs at a critical film thickness at which stresses in the film is high enough for the film to yield and fracture.

It was concluded that iron selenide film formation or delamination must be minimized in order to control dust particle formation. These two phenomena can be mitigated by protective substrate films, change of substrate material, selenium environment optimization or temperature profile optimization and should be researched further to find the most effective and viable solution.
# Table of contents

1. Introduction .............................................................................. 1  
2. Process description................................................................. 1  
3. Problem description..................................................................... 4  
   3.1. Dust particles appearance............................................... 4  
   3.2. Dust particles issues....................................................... 5  
4. Aim............................................................................................. 6  
5. Theory......................................................................................... 6  
   5.1. Vapor deposition............................................................ 6  
      5.1.1. Sputtering............................................................... 6  
      5.1.2. Gas-solid interactions.......................................... 7  
      5.1.3. Midsummer deposition system............................. 10  
   5.2. Film stress and delamination........................................... 10  
6. Experiments and material......................................................... 12  
   6.1. Material............................................................................. 13  
7. Analytical methods..................................................................... 13  
   7.1. Electron microscopy (SEM)............................................. 13  
   7.2. Energy dispersive X-ray spectroscopy (EDS).................. 14  
   7.3. X-ray diffraction (XRD).................................................. 14  
   7.4. Etching & Grain diameter measurement........................ 14  
   7.5. Current-Voltage (IV) measurement................................. 15  
   7.6. Delamination severity index (DSI)................................. 16  
8. Results & Discussion................................................................... 20  
   8.1. Substrate steel characterization...................................... 20  
   8.2. Dust particle characterization....................................... 22  
   8.3. Dust particle formation................................................. 26  
      8.3.1. Film formation....................................................... 26  
      8.3.2. Film cracking....................................................... 32  
   8.4. Steel substrate variation................................................ 38  
   8.5. Dust particle distribution pattern.................................... 43  
9. Conclusion and future perspectives ......................................... 45  
10. Acknowledgement.................................................................... 46  
11. References:............................................................................. 47
1. Introduction

The solar cell industry is a rapidly growing sector with the ongoing shift to renewable energy sources. Silicon based solar cells was initially the dominating type during the onset of the first-generation solar cells. However, since then, other alternative material choices have been developed and brought to the market. The second-generation solar cells, although being around for a while, is becoming a viable alternative to silicon cells. The second-generation is also known as thin-film solar cells, in which Cu(In,Ga)Se₂ (also known as CIGS), CdTe, GaAs, CuZnSn(S,Se)₄ (CZTS) and amorphous silicon (a-Si:H) are some of the more common materials. Typical properties of the second-generation solar cell materials are higher absorption coefficient due to direct bandgap properties, allowing them to be thinner than conventional solar cells while still absorbing the same amount of light. A thinner absorber layer allows less material usage, which is an economical advantage. The disadvantage of thin-film cells is their lower efficiency compared to conventional silicon solar cells. However, lower material usage in thin-film cells may allow a lower cost-per-Watt compared to conventional solar cells.

Midsummer AB is a company based in Stockholm, Sweden that has taken on the role to provide equipment for autonomous, simple and efficient production of thin-film solar cell manufacturing equipment, specifically for CIGS solar cells. The Midsummers process is based on a series of subsequent sputtering processes to create solar cells in a layered structure. The process uses several sputtering chambers created for the size of one single substrate, building up a layered structure one layer at a time for each cell. In each chamber, deposition power, pressure and temperature may be controlled independently. The substrates are transferred between chambers in an un-broken vacuum chain. The result is a flexible method where sputtering parameters can easily be modified for each layer.

2. Process description

To go from substrate to a full solar cell is a complex process involving many steps. Figure 1 describes the process flow from substrate to solar cell module. It also illustrates parts of the process where dust particles are formed and where they create issues. Dust particle formation is exclusively appearing in the cell sputtering part of the process. Issues accompanied with dust particles are primarily seen in the cell sputtering process and during cell module assembly. This study has revolved solely around the cell sputtering part of the process.
Figure 1: Process flow of CIGS solar cell manufacturing. Symbols is given for where dust is forming and where they create issues in the process flow.
A schematic representation of the Midsummer sputtering system is shown in Figure 2. The substrates run through a series of stations denoted as S1, S2, S3, etc. Each station deposits a single layer; in stations S1 through S5 metals for back-contact are deposited, in stations S6 through S18 CIGS for the absorption layer is deposited and in stations 19 through 25 transparent conductive oxides (TCO) for the front-contact are deposited. The complete deposited stack is depicted in Figure 3. Deposition settings such as sputter power, substrate heating, gas pressure and gas flow are independently controlled in each station.

Furthermore, the system contains a heater chamber (HCh) and a cooling chamber (CCh). The heating chamber is present to attain the higher temperature that is required during CIGS deposition (550-650 °C). The cooling station is present to cool down the substrate before depositing of the front contact at 300°C or lower.

In the CIGS stations, an environment containing gas phase selenium is present to protect the sputtering material from selenium impoverishment.

![Figure 2: Schematic overview of the Midsummer sputtering system. Numbers 1, 2, 3, etc. indicate a sputtering chamber. LL denotes “loadlock”, indicating where unprocessed substrates are loaded and completed cells are unloaded. Chamber A and B contains each a rotational servo with 14 arms. Each arm has holders for one substrate that is moved around the machine by rotating the servos [1].](image)

The CIGS is the absorber layer that converts solar energy to electrical energy. This occurs when a photon excites an electron in the valence band to the conduction band. The contact layers are present to create a conductive path for the generated current out of the CIGS to be used in electrical appliances. The steel substrate provides a support for the thin layered structure and is in reality many times thicker than what is seen in Figure 3.
3. Problem description

3.1. Dust particles appearance

The problem that this project revolved around was the formation of dust particles during the cell production. These dust particles are formed on the backside of the substrates in a circular pattern (Figure 4).

Figure 3: Simplified layered structure of a CIGS solar cell. CIGS layer converts solar energy to electrical energy by the photovoltaic effect. The conductive front contact and back contact allows for extraction of electrical current by providing a conductive path for electrons. The stainless-steel substrate functions as a support and conductor. The steel substrate is many times thicker than what is shown in the image.

Figure 4: Cell backside with dust particles in a circular pattern. The central region of the cell backside has no dust particles present and appears completely reflective. Inset image taken with optical microscope of substrate backside showing typical flaking of surface layer. A: Dust particle parallel to substrate surface. B: Partially lifted dust particle. C: Region of delaminated dust particles.
By optical microscope analysis, it is seen that dust particles originate from *delamination of a film on the backside surface*. The dust particle size is in the order of micrometer scale as seen in the inset in Figure 4. Some particles are pivoted away from the surface, and when at a high enough angle, fall off. Optical microscopy images of the surface backside show three characteristic features. Particles attached (A) parallel to the substrate surface, (B) particles partially attached to the substrate surface at an angle, and (C) regions of peeled off particles exposing the underneath substrate. Figure 5 shows an illustration of the 3 different features.

![Diagram showing three types of dust particles](image)

*Figure 5: Scheme of typical features seen at the cracked film on the substrate backside. A: Dust particle parallel to substrate surface. B: Partially lifted dust particle. C: Region of delaminated dust particles.*

These three different features are what makes the cell backside appear dusty. The visible amount of dust depends on if the surface film of the cell backside is cracked and delaminated or not. The more cracked and delaminated the surface layer is, the more dust appears to be on the cell since the incident light is reflected in a diffuse manner. On a clean substrate the reflections are mirrorlike, which can be seen in the center region of the cell backside in Figure 4.

### 3.2. Dust particles issues

The dust particles create problems because they are easily detached from the cells and transferred to other steps in the production chain, or to the ambient environment. The dust particles are seen to detach in the sputter system cooling chamber, the sputter system load-lock or by operators handling the cells. In the cooling chamber and the load-lock, a stream of gas is used to cool the substrate. The force exerted by the flowing gas tends to be enough for the less fixated flakes to detach from the surface. In the cooling chamber, dust particles are pumped into the vacuum pump, causing problems. In the load-lock, a slight overpressure is created during cooling which pushes dust particles out into the ambient environment. A considerable amount of the particles is also left on the substrate after sputtering. This means the particle can be detached mechanically when handled or in contact with other surfaces. The adverse effects that the particles produce are as follows:

- **a) Health hazard**
- **b) Power-supply contamination**
- **c) Vacuum pump contamination**
- **d) Robot contamination**
- **e) Storage contamination**
- **f) Soldering issues**
4. Aim

The aim of this study was to increase understanding of dust particles appearing on the backside of processed solar cells. The research questions were:

1. What is the dust particles composition and phase?
2. Where do dust particles appear throughout the process?
3. What is the cause of appearing dust particles?

It was understood at the start of this project that determining the cause of a gas-solid interaction is an extensive task. To fully answer the third research question was outside of the time frame of this project, and emphasis should be put on that this project aimed to increase understanding towards the cause of the appearing dust particles.

5. Theory

5.1. Vapor deposition

5.1.1. Sputtering

There are many different types of physical vapor deposition methods. A physical vapor deposition method denoted magnetron sputtering is used in Midsummer AB’s cell sputtering system, which is a method commonly used in thin film and coating synthesis. A sputtering scheme is shown in Figure 6. An electrical potential is applied between a cathode and an anode placed in a vacuum. Electrons flowing from the cathode towards the anode hit outer shell electrons of gas molecules, ripping them from their atom which thus become ionized, igniting a plasma. The charged ions are accelerated by the electrical potential towards the surface of a target material. As a result, atoms are ejected from the target due to the high impact energy, i.e. sputtered. The ejected neutral atoms will travel from the target to the opposite side of the chamber and adsorb on the substrate surface.

![Sputtering scheme](image)

*Figure 6: Sputtering scheme where the target and substrate are shown. The focused plasma is depicted as two half-circles close to the target with positive signs. Arrows and black dots depicts the direction of the sputtered target atoms transported towards the substrate surface.*

In magnetron sputtering the plasma is confined by a magnetic field positioned close to the cathode. Due to this the ionization of gas molecules is focused close to the target due to electrons being restricted by the magnetic field, which gives a higher sputtering yield [2]. In conventional sputtering, argon gas is used to create the plasma as it is inert and economically advantageous on an industrial level. However, non-inert gases may be used for reactive
sputtering, where the non-inert ionized gas can react with the target material. This will instead deposit a molecular compound on the substrate.

In Midsummer’s sputtering chambers, CIGS solar cells are built up by stacking multiple films on a steel substrate (Figure 3). The essential parts consist of a back-contact, an absorber layer (CIGS), a buffer layer and a front contact (TCO). The exact functioning of a CIGS cell is not relevant to this study. However, it is important to understand that the performance of a solar cell built in this fashion depend on physical properties inherited by the materials during processing, such as crystallinity, chemical composition, density, adhesion between layers etc. [3]. These physical properties are obviously largely dependent on processing parameters. A change in e.g. substrate deposition temperature or chamber pressure may drastically change how the deposited layer appears and behaves (Figure 7). It is a matter of finely tuning depositing parameters for each layer to acquire the most efficient cell possible.

![Figure 7: Structure zone diagrams as function of (a) temperature \((T_i/T_o)\) and (b) bombarding energy of the impinging species. The image illustrates how the film microstructure changes with temperature or bombarding energy \([4][5]\).](image)

5.1.2. Gas-solid interactions

In the case of this project, it shall be seen that Midsummer’s sputtering chambers are subject of reactions between gas and the solid steel substrate. This makes it important to understand the theory behind this kind of deposition to deduce why these reactions appear in their sputtering system. Gas-solid reactions require multiple scientific fields to be fully understood, such as fluid mechanics, thermodynamics and reaction kinetics. To limit the scope of this thesis, fluid mechanics have been left out of this study.

Thermodynamics is important to understand what reactions that are possible, where a central concept is Gibbs free energy \((\Delta G)\). The equation of Gibbs free energy (equation \((5-1)\)) states that Gibbs free energy is a combination of the enthalpy \((H)\) and entropy \((S)\) of the system. Theoretically speaking, it is the maximum of reversible work that can be done by a closed thermodynamic system at constant pressure and temperature. In practice it can be seen as the amount of available energy in the system and the magnitude of Gibbs free energy provides a way of calculating the thermodynamic driving force of a process in the system.

\[
\Delta G = \Delta H - T\Delta S \tag{5-1}
\]

The concept of Gibbs free energy can be developed further, taking into account mixing of chemical compounds. By doing this, the Gibbs free energy can be calculated for different ratios of the chemical compounds involved and also for different temperatures. The result is what is called a phase diagram that presents the thermodynamic preferential compounds to be formed.
at a specific temperature and chemical composition. This is an indispensable tool in understanding reactions in a system of different chemical compounds.

Furthermore, reaction kinetics is important to consider in gas-solid interactions. Homogenous reactions between the gas molecules themselves may occur in the bulk of the gas, forming different intermediate molecules before interacting with the solid.

Reactions between gas molecules or formed intermediate molecules and solid surfaces are denoted heterogenous reactions. The molecules are initially adsorbed to the substrate surface, meaning that molecules are bonded to the surface only by weak van der Waals forces. After this, the molecules are typically decomposed into smaller species. At this point the molecules may migrate on the surface before finding a preferential site. At the site a chemical reaction takes place between the molecule and the solid molecules, forming a chemical bond. The reverse process of adsorption may also occur, denoted desorption. This may occur both before and after decomposition, indicating that both reactant species and by-products may desorb from the surface.

The theories behind these phenomena are many and have a long history. A simplified way of understanding adsorption is by isotherm adsorption theory, developed by Langmuir. In this theory, the surface is modeled as a finite amount of surface sites (N) and the coverage of these sites is denoted as $\Theta$. The Langmuir isotherm adsorption is described by equation (5-2):

$$\Theta = \frac{kp_i}{1 + kp_i}$$  \hspace{1cm} (5-2)

where $k$ is the ratio of equilibrium constant of adsorption and desorption $(k_{abs}/k_{des})$ and $p_i$ is the partial pressure of the gas that adsorbs on the surface. A plot of the Langmuir equation can be seen in Figure 8 showing how it changes with pressure or adsorption coefficient.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{langmuir.png}
\caption{Pressure as a function of coverage as described by the Langmuir isotherm equation. Pressure can be exchanged for adsorption coefficient to see how surface coverage changes with this parameter [6].}
\end{figure}

The rate of reactions occurring, and therefore deposition rate, between the gas and the surface is proportional to the surface coverage of reactional species. Therefore, it is important to understand how surface coverage change with different parameters.

Concerning temperature and deposition rate, the dependence is generally seen to have a three-region relationship. This is seen in Figure 9, showing deposition rate at different temperatures for an exothermic and an endothermic reaction. The three regions are named after the limiting
factor for the reaction rate. (1) Thermodynamically limiting region, (2) mass transport limiting region and (3) chemical reaction limiting region.

In the chemical reaction limiting region the chemical reaction rate is low because temperature is low. The supply of new reactant molecules is faster than the time it takes for the molecules to react with the surface. Therefore, the deposition rate is governed by chemical reaction rate.

In the mass transport limiting region, the reaction between surface and reaction species occurs faster than the supply of new reaction species. It is considered that the boundary layer has a clear concentration gradient of reaction species. As the temperature to deposition rate slope is lower in this region, the dependence on temperature becomes lower. However, there is other means of controlling deposition rate than by temperature. Deposition rate is inversely proportional to the pressure, which means that it can be controlled by changing the system total pressure. Alternatively, gas flow velocity can be varied to control mass transport close to the surface.

In the thermodynamically limiting region the Gibbs free energy can be used to understand how deposition rate is affected. For an exothermic reaction, the Gibbs free energy becomes less negative as temperature increase. This leads to a lower thermodynamic driving force for the reaction to happen. For an endothermic reaction, the Gibbs free energy becomes more negative. However, homogenous reactions in the gas itself begin to be more favorable and consequently reactions in the gas occurs instead of reactions between the gas and the surface.

Thus, gas-solid interactions are largely dependent on how the gas flows in the chamber, temperatures at which it happens and pressure. It is also equally important to consider the particular gas and substrate material used as the thermodynamics and kinetics of this particular gas-solid system affect deposition rate[6][7]
5.1.3. Midsummer deposition system

In the cell sputtering system, reactive sputter deposition is occurring on the front side of the substrate. However, chemical reactions will occur on the backside of the substrates. Gas used in the sputtering process reacts with the substrate backside. The result is an unwanted biproduct in form of a thin film formation on the substrates backside. Figure 10 shows a simplified scheme of the reactions.

![Scheme of the how both sputtering and chemical vapor deposition occur on substrates processed in the cell sputtering system.](image)

**Figure 10:** Scheme of the how both sputtering and chemical vapor deposition occur on substrates processed in the cell sputtering system.

5.2. Film stress and delamination

Thin film cracking and delamination is occurring due to stress produced in the film. Hutchinson et al. [8] have made a comprehensive summary of how stresses distribute in thin films and how to interpret failure modes of said thin films. Stresses arising in thin films are suggested to have three different origins: intrinsic, thermal and mechanical. Intrinsic stress originates from the chemical reaction. The exact causes to this stress are generally not theoretically quantified as it is dependent on grain growth, defect annihilation, phase transition, evaporation, etc. Thermal stress appears during temperature change in substrate and film that have a different thermal expansion coefficient (CTE). Mechanical stress appears due to mechanical loading of a material.

Hutchinson categorizes failure modes of films which occur when the stress in the film is too large. There are tensile and compressive failure modes that both can produce different types of cracking and delamination. However, generally cracking appears in tensile modes while buckling followed by cracking appears in compressive modes. A general criterion for failure mode propagation $\Omega$ can be expressed as in equation (5-3):

$$\Omega = \frac{h\sigma^2}{ET}$$  \hspace{1cm} (5-3)

where $h$ is the film thickness, $\sigma$ is the stress, $E$ an elastic modulus and $T$ a fracture toughness. This is a general notion and different approaches exist concerning which stress, elastic modulus and fracture toughness modes to employ dependent on encountered film issues and behavior.

Furthermore, it is discussed how thermal stress may arise in mismatched CTE between substrate and film. In this it is assumed that the thickness of the film is many times smaller than the thickness of the substrate, leading to the argument that the substrate imposes its in-plane strain on the film ($\varepsilon_s = \varepsilon_f$). The governing equation is as follows:
\[
\Delta \sigma_{\alpha\beta} = \frac{E \Delta \alpha \Delta T}{1 - \nu} \delta_{\alpha\beta}
\]  

(5-4)

where \( E \) is an elastic modulus, \( \alpha \) is the coefficient of thermal expansion, \( T \) is temperature, \( \nu \) is the Poisson’s ratio and \( \delta \) Kronecker’s delta. This equation makes it possible to understand if a deposited film will experience compressive or tensile stresses and their magnitude.
6. Experiments and material

To characterize the dust particles, a range of analytical methods and tests were used. Initially, energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) were used on detached dust particles to determine their chemical composition and phase.

It was quickly understood the importance of measuring how the thickness of the delaminated film evolved throughout the process. Cross-sectional samples of full solar cells were prepared by mounting and polishing to be analyzed by scanning electron microscopy (SEM). However, in all cases, the film had delaminated during sample preparation and was situated far away from the substrate or rotated (Figure 11). Or it broke during sample polishing. Ultimately, EDS was proven to be the most practical method to estimate film thickness.

![Steel substrate backside](image)

*Figure 11: Cell cross-section showing the cell backside region with encircled cross-sections of dust particles. The dust particles have delaminated from the cell surface.*

It was equally important to track how delamination progressed throughout the process. To measure delamination, an optical analysis method denoted as *delamination severity index* (DSI) was developed. This provided a means of quantifying the delamination.

To track this progression of film formation and delamination throughout the process, a test was created where the process was stopped mid-run. Since all stations at all times is occupied by a substrate, it resulted in a series of cells where one cell only had been sputtered in the first station of the process. The next cell had only been sputtered in the first and second station of the process. The cell after this had only been sputtered in the first, second and third station, and so on. This ultimately created a series of cells that had an increasing amount of dust particles present on the backside of cells.

When a better understanding of the dust particle formation had been acquired, variations of sputtering parameter were made. The variations were that of turning the selenium environment on and off, changing the substrate material and sputtering at a lower temperature as seen in Table 1.
Table 1: Overview of tests done with different variations of sputter parameters.

<table>
<thead>
<tr>
<th>Variations</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate material</td>
<td>-                   Steel A, Steel B and Molybdenum-coated Steel A</td>
</tr>
<tr>
<td>Selenium environment</td>
<td>-                   Selenium environment turned on and off</td>
</tr>
<tr>
<td>Sputtering temperature</td>
<td>-                   Cells sputtered at 400 °C in CIGS stations</td>
</tr>
</tbody>
</table>

6.1. Material

Different substrates were used as part of a test to see how dust particle formation varied. The Midsummer solar cells use a ferritic stainless steel of AISI 430 standard. Chemical composition can be found in Table 2.

Table 2: Table of chemical composition for substrate steel as specified by suppliers. Both suppliers claim to follow an AISI 430 standard. Chemical composition values for the AISI 430 standard is included in the table as reference.

<table>
<thead>
<tr>
<th>(at%)</th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>S</th>
<th>P</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AISI 430 [9]</strong></td>
<td>0.12</td>
<td>16-18</td>
<td>1.0</td>
<td>1.0</td>
<td>0.75</td>
<td>0.030</td>
<td>0.040</td>
<td>-</td>
</tr>
<tr>
<td><strong>Supplier A</strong></td>
<td>0.12</td>
<td>16-18</td>
<td>1.0</td>
<td>1.0</td>
<td>0.75</td>
<td>0.030</td>
<td>0.040</td>
<td>-</td>
</tr>
<tr>
<td><strong>Supplier B</strong></td>
<td>&lt;0.12</td>
<td>16-20</td>
<td>&lt;1.00</td>
<td>&lt;1.00</td>
<td>-</td>
<td>&lt;0.030</td>
<td>&lt;0.040</td>
<td>0.30-0.80</td>
</tr>
</tbody>
</table>

To test if dust particle formation depended on supplier, the same steel was ordered from different suppliers and compared. Additionally, a third variation on substrate steel was used, where the steel from supplier A was coated with a thin film of molybdenum on the backside.

Figure 12: Surface appearance of Steel A, Steel B and Steel A coated with Molybdenum. Respectively from the left. Observe that Steel B has a lower surface finish and therefore looks blurry. The substrate coated with molybdenum does not have any visible change in appearance.

7. Analytical methods

7.1. Electron microscopy (SEM)

A Hitachi S4800 was used during the project, detecting morphological features. Morphology of backside particles could be identified at different positions on the cell for different sputtering
parameters or steel types. This was done both on lateral surface and on cross-sections of the sputtered cells.

7.2. Energy dispersive X-ray spectroscopy (EDS)

EDS was used for analyzing single dust particle composition. It was also used to measure element spatial distribution on the cell as an estimation for how the backside film thickness evolve. Measurements were done directly on the backside of as-deposited cells and on dust particles detached from the cells as illustrated in Figure 13.

![Diagram showing EDS analysis on steel substrate and carbon adhesive.](image)

Figure 13: EDS analyze were done on dust particles directly on the steel substrates (left) and on detached dust particles (right).

The analysis done on detached dust particles directly on carbon adhesive gave the absolute chemical composition of the dust particles. Analysis done on backside of cells as-synthesized resulted in distribution of elements spatially. Due to the low thickness of the film the electron beam penetrated both the film and the steel substrate, which had to be considered since both the steel and the film contained iron and chromium. It was seen in results that selenium content measured with EDS directly on the cells backside correlated well with dust particle thickness measurements. Therefore, this type of measurement was deemed to be an estimation of the film thickness. No absolute value of the film thickness could be found, however a quantitative value that could be compared between cells could be found.

For cell backside measurements, a chemical composition profile was made. Approximately 10 measurements were done with 5 mm spacing, starting from the cell edge and running towards the cell center.

7.3. X-ray diffraction (XRD)

A Bruker D8 with Cu Ka radiation was used to investigate phases present in the dust particles and steel differences between providers and pre-/post-sputtering. A 2-theta scan ranging from 10 to 90° was used. By analyzing the angles at which diffraction peaks appear it was possible to identify a fingerprint pattern of the dust particles which could be matched to a specific phase of the dust particle compound.

7.4. Etching & Grain diameter measurement

Electro-etching was used to reveal grain boundaries of the substrate steel used. After experimentation, it was found that 10% oxalic acid revealed the grain structure in the clearest
manner. Samples were etched by submersing the samples into the oxalic acid for 80 seconds while under a 5V potential.

### 7.5. Current-Voltage (IV) measurement

An essential method of characterizing solar cells are IV-curves, where I represents current and V represents voltage. A solar cell is illuminated with an artificial solar illumination source calibrated according to AM1.5 standard [10]. While exposed to the simulated sun, a sweeping voltage is applied while measuring the responding current. The resulting curve is an IV-curve, from which important parameters used in solar cell characterization can be extracted. These parameters are short circuit current (I_{sc}), open circuit voltage (V_{oc}), maximum power point (P_m), shunt resistance (R_{sh}), series resistance (R_s), efficiency (n) and fill factor (FF). An example of an IV curve can be seen in Figure 14.

![IV curve diagram](image)

**Figure 14**: Current-Voltage curve of a solar cell together with the power curve. I_{sc} and V_{oc} are marked, as well as V_m, I_m marking the point for maximum power (P_m). The marked striped rectangle indicates the area created by V_m and I_m [11].

I_{sc} denotes short-circuit current and is the maximum current output from the cell and it corresponds to the current at zero voltage in the IV curve. V_{oc} denotes the open circuit voltage and is the maximum voltage available from the cell and it corresponds to the voltage at zero current in the IV curve. P_m denotes the maximum power point in the IV curve.

The parameters R_s and the R_{sh} can be estimated at V_{oc} and I_{sc}, commonly by fitting a model considering the complete curve. When doing this it is seen that R_s and the R_{sh} are dependent on the slope at V_{oc} and I_{sc}, respectively. A flat slope at I_{sc} indicates a high shunt resistance and a steep slope at V_{oc} indicates a low series resistance. The two types of resistance can be seen as losses in the solar cell. The losses from series resistance are due to material properties and contact surfaces. The losses arising from shunt resistance can be seen as small currents leaking through the cell, taking another path than through the complete cell. This gives an indication that there are defects and impurities in the material. The effect of this is sites inside the cell where excited electrons can recombine instead of having to travel through the external circuit before recombining.

15
Furthermore, there is the fill factor and the efficiency. The fill factor is defined in equation (7-1).

\[
FF = \frac{P_m}{V_{OC} \times I_{SC}}
\]  

Looking at Figure 14, it can be seen as the ratio of the rectangular area that is marked at maximum power \((V_m, I_m)\) and the rectangular area that the cross product of \(V_{OC}\) and \(I_{SC}\) forms. As the maximum power point approaches the value of \(V_{OC} \times I_{SC}\), the series resistance of the cell decreases and the shunt resistance increases, leading to a better performing cell.

The cell efficiency is calculated by creating a ratio between the maximum power output \((P_m)\) and the incident optical power density. The incident optical power density is found by knowing the incident radiation flux supplied by the test lamp and the area of the cell exposed to the radiation [11][12].

### 7.6. Delamination severity index (DSI)

The DSI method is an estimation of the amount of delamination occurring on the cell backside. It is designed to quantify the dark and bright regions seen in optical microscope (Figure 15). The method is built on the correlation between number of dark and bright regions visible in optical microscopy and the visible amount of dust on the cell backside under inspection. The visible amount of dust depends on if the surface film of the cell backside is cracked and delaminated. The more cracked and delaminated the surface layer is, the more there appears to be dust on the cell since the incident light is reflected in a diffuse manner.

Partially lifted dust particle flakes appear as dark particles in optical microscope because light that hits their surface are not reflected into the microscope lens due to their angle. Peeled-off areas instead have a bright appearance due to the fact that steel substrate reflects a large amount of light into the lens. Dust particles that are parallel to the substrate surface display a brightness somewhere in between that of partially lifted particles and peeled-off region. The method was realized by thresholding microscopic images taken in an optical microscope at 50X magnification (Figure 15). This extracts all the pixels with a value higher than or lower than a threshold value.
If measuring area of dark regions below a certain grayscale threshold, essentially what is being measured is the number of partially lifted dust particles that have a pivot angle higher than a certain value (Figure 16). The magnitude of this angle can be seen as the severity of delamination as it increases throughout the delamination process. Measuring areas of bright regions can be interpreted as the continuation of this delamination process where particles have fully delaminated.

This is assuming that other properties that may influence light interaction is kept the same, such as surface structure and material. However, it was found that backside dust particles have a rather consistent structure and element composition. When measuring the bright regions, what is being measured is simply the number of peeled-off dust particles. If the area of both the dark and bright regions are put together, it can be seen as an estimation of how many dust particles on the cells backside that have a pivot angle higher than a certain value or that are fully peeled off. It will be seen later in this chapter that this parameter is a possible way of estimating amount of delamination.

After thresholding an image it is possible to extract how many pixels that make up the dark regions (green masking) and bright regions (red mask). With the particles masked it is possible to compare particle area with total area. This is named:

$$DSI = \frac{\text{Green and red masked pixels}}{\text{Total image pixels}}$$

The DSI method is completely built around the correlation that the area of bright and dark particles observed in microscope increase with the amount of visibly estimated increase in dust. This, of course, gives a subjective aspect to the method. The DSI algorithm parameters were adjusted by letting an external source grade multiple groups of cells as having a low, medium or high amount of dust. The amount of dust present on the cell is mainly judged on how wide the inner region is and how visible the shimmering is (consult Chapter 7.2 for a description of the dust particle regions). The DSI algorithm parameters were then configured to generate a low DSI value for cells with low amounts of dust and vice versa for high amount of dust. Images below show substrates in macro-perspective (Figure 17) and in micro-perspective (Figure 18) as analyzed by DSI.
Since there is a distribution of dust particles over the cell it was decided to measure multiple points to create an average DSI value of the cell. Four points turned out to be a reasonable compromise between statistical significance and measurement-time. Measurement points were situated 20 mm from the cell edge as this is where cracking and delamination of the backside film initiates. A figure of measurement points on the cell backside can be seen in Figure 19.
DSI measurements were done on cells with various dust amount to test the repeatability of the method. Figure 20 shows a boxplot of this, that strengthens the reliability of the DSI method. Each cell was remeasured with the DSI method 3 times. The precision of the method was reliable with a maximum deviation of 0.3 %.

Figure 20: Results from repeatability measurements of DSI done on 40 cells with various dust amount. Y-axis gives average difference between DSI measurement on the same cell.
8. Results & Discussion

8.1. Substrate steel characterization

Steels substrates from two different suppliers, complying with AISI 430, were analyzed with EDS and XRD to allow comparison of substrates before and after the process. The chemical composition measured by EDS is given in Table 3. EDS analysis was used to specify the chromium content more precisely than what was provided by steel suppliers.

Table 3: Chromium content for substrate steel from different providers acquired with EDS analysis.

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Cr (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>18.0</td>
</tr>
<tr>
<td>B</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Figure 21 shows XRD spectrum of XRD analysis done on substrate steels. XRD results of both supplier A and B steel show overlapping diffraction peaks for 2-theta angles 44.5°; 64.9° and 82.1° corresponding to the (110), (200) and (211) plane, respectively. XRD fitting matched the steel as an AISI 430 ferritic steel, which was the same as specified by both providers.

Y. Yu et al. [13] did a study on steels with varying chromium content, where it is seen in XRD spectra how peak ratios change with different Cr content. The peak intensity ratio for A and B matches well with type 430 ferritic steel analyze made by Y. Yu et al [13]. Intensity ratios may also change due to different residual stresses generated by, e.g. roll directions [14]. Between suppliers A and B, the (200) plane has a lower intensity for the A steel, which may be due to variations in residual stresses from deformation.
Figure 21: XRD pattern measured for substrate steels. Marginal peaks at 43, 62 and 78 degrees are equipment artifacts according to experienced operator.

Figure 22 shows substrate steel electro-etched with 10% oxalic acid at 5V for 80 seconds. Etching revealed grain boundaries for steels from provider A and B. The average grain diameter of the steel from provider B was double that of provider A (Table 4).

Figure 22: Microscopic images after substrate steel etching from provider A(left) and provider B(right). Round particles are contaminants from the etching process.
Table 4: Average grain diameter estimated by etching and optical microscopy.

<table>
<thead>
<tr>
<th>Substrate steel grain diameter</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain diameter (μm)</td>
<td>7.3</td>
<td>14.3</td>
</tr>
</tbody>
</table>

Figure 23 presents how surface roughness of the two provided steel differs. Steel from provider A has a smoother surface than that of provider B.

Figure 23: Steel substrate surface of supplier A and B, left and right respectively.

8.2. Dust particle characterization

Figure 24 presents the typical appearance of a standard cell backside. What can be seen in general is four different colored regions with radial symmetry with respect to the cell center. An outer darker region, a white region, an inner region where the dust has a shimmering appearance and a center region where no significant difference in appearance is seen compared to the original steel substrate surface.
Both the inner and outer region show cracking and delamination of the surface layer while the surface layer in the white region is cracked but does not delaminate. In the center region, no cracking nor delamination is seen. For cells with low amount of dust, the inner region typically decreases in width and flaking becomes less severe, which can be seen by it having less shimmering, and in some cases, no shimmering. For high amount of dust, the width of the inner region increases. At the same time the white region decreases in width as the inner and outer region blend together. The center region also decreases in size as the inner region increases in width. Figure 25 presents a closer look on the four cell backside layer regions.

The outer region displays no cracking nor delamination and looks no different from the substrate steel surface. The inner region has flaking and peeled off dust particles, which gives it its shimmering appearance. The white region is a cracked surface layer with occasional dust particles sitting at an angle, but no peeled-off dust particles. It appears hazy white because it has an uneven surface, but less uneven than the inner region. The outer region has a cracked surface layer that has a larger number of pivoted dust particles compared to the inner region,
but generally no peeled off flakes are seen. This region also has micropores and deformation in the film, appearing as dark dots in Figure 25. This is likely why this region appears much darker than the other regions. Typically, the flake diameter is in the 10-50 μm range depending on distance from cell edge. The circular distribution pattern of the dust particles is hypothesized to be due to the design of the chambers, resulting in a temperature profile on the substrate’s backside. Difference in temperature may lead to different reaction rates which could create variations in the backside film thickness and morphology.

Considering the dust particles chemical composition, an analysis was done on dust particles with EDS and XRD. EDS found that dust particles detached from the cells consisted of iron (Fe), chromium (Cr) and selenium (Se). Considering that a selenium containing environment is present in parts of the process, this was a reasonable result. Table 5 presents chemical composition found with EDS. Dust particles are mainly made up of selenium.

Table 5: Characteristic composition of dust particles measured with EDS on backside surface of a standard cell.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>(at %)</td>
<td>40</td>
<td>8</td>
<td>52</td>
</tr>
</tbody>
</table>

From XRD data, fitting against an international center for diffraction data (ICDD - PDF-4.0) found the best fit to be a main phase of Fe₆₋₈Se and a secondary marginal phase of Cr₂Se₃. If considering that the stochiometric ratios achieved from XRD and that compositional EDS data is correct, the ratio calculation suggests that the proportion of phases is approximately 93 at% Fe₆₋₈Se to 7 at% Cr₂Se₃. Judging from the Cr₂Se₃ peaks in Figure 26, a Cr₂Se₃ ratio of 7 at% seems to be too high. Quantification in EDS equipment is a complex task, and parameters such as absorption, fluorescence and back scattering affect the detected signal. The signal of Cr may be overestimated and therefore the calculated phase ratio from EDS results may be lower than 93 to 7 in favor of Fe [15]. This could explain why the Cr₂Se₃ peaks found in the XRD analysis are rather low (Figure 26). To get an exact answer to this question a Rietveld refinement analysis [16] must be done. However, this is a difficult task with low intensity peaks. Therefore, exact ratio of the 2 phases are not exactly known.
In SEM, the surface morphology of flakes varies over the cell surface. It is possible to see how the aspect ratio of plate-like crystallites changes when moving from the cell edge towards its center. Figure 27 shows SEM images taken at 1, 5 and 10 mm from the cell edge.

Furthermore, dust particle thickness depends on cell position, while dust particle composition did not. This is shown in Table 6. The thickness difference is seen in the next chapter to correlate with EDS measurements done directly on the cell backside.
Table 6: Composition and thickness of dust particles measured with EDS on backside surface of a standard cell.
Measurements made 5 mm, 15 mm and 25 mm from the cell edge.

Dust particles composition and thickness

<table>
<thead>
<tr>
<th>Distance from cell edge</th>
<th>Fe</th>
<th>Cr</th>
<th>Se</th>
<th>Dust particle thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mm</td>
<td>35.3</td>
<td>7.3</td>
<td>57.4</td>
<td>170</td>
</tr>
<tr>
<td>15 mm</td>
<td>37.3</td>
<td>7.7</td>
<td>56.0</td>
<td>323</td>
</tr>
<tr>
<td>25 mm</td>
<td>37.0</td>
<td>7.3</td>
<td>55.7</td>
<td>230</td>
</tr>
</tbody>
</table>

8.3. Dust particle formation

As has been seen in previous chapters, the dust particles originate from the cracking and delamination of a thin film on the cell backside. This film formation and film cracking are the two premises required for dust particles formation. This chapter discusses the two phenomena and their causes. The list below presents an overview of the chapter.

- Film formation
- Film cracking
  - Non-matching thermal expansion coefficients
  - Temperature gradient
  - Phase changes
  - Cell bending

8.3.1. Film formation

The film chemical components consist of selenium, iron and chromium. Iron and chromium are present in the steel pre-process, while that selenium is dependent on the selenium environment, which is seen in Figure 28. EDS analysis showed signal from selenium on the cell when a selenium environment was present during the deposition, while without it there was no significant backside content of selenium detected. This is seen in Figure 28, where two EDS profiles measured from the edge of the cell and towards the cell center are shown.
It was found that for cells processed at 400°C and below, no significant dust particle formation was found, nor Se content by EDS analysis. It shows that there may be a kinetic relationship at play in the reaction mechanism. E.g. a certain temperature may have to be reached to have a chemical reaction between the steel and selenium. However, further studies on selenium-steel interactions at elevated temperatures is needed in order to understand this. This would involve fluid mechanics and studies of reaction mechanisms to understand fully how molecules are distributed and reacting with the steel, which was outside the time range of this study.

The flaking of the film is also dependent on the selenium environment, as seen in Figure 29 which shows the severity of delamination as indicated by the DSI value. When eliminating the selenium environment, the delamination is seen to drop to lower values. The reason to why DSI does not drop to 0 is because of a limitation in the algorithm. As can be seen in Figure 30, there is no delamination or film formation occurring on the surface. However, defects in the steel substrate appears as dark elongated spots. The algorithm interprets this as partially delaminated particles. Therefore, the DSI is not 0 when no delamination is occurring.

In Figure 30, the same optical microscope images of dust particles that the DSI algorithm has analyzed is shown. The images are on cells having been sputtered with and without selenium environment.
Figure 29: Boxplot of delamination severity (DSI) for cells deposited with and without selenium environment. When selenium environment is turned off, DSI drops to zero baseline values indicating that no delamination is occurring on the cell backside.

Figure 30: Optical microscope image of cell backside deposited with selenium environment off (left) and selenium environment on (right). When selenium environment is off, no signs of delamination or film formation is seen. Only dark elongated spots are seen which are defects from the steel manufacturing process. When selenium environment is on, partially delaminated dust particles is seen as circular dark regions, indicating that delamination is occurring.

As described in the experimental section of the report, tests were made where the process was stopped mid-run. This made it possible to follow the progression of dust formation and delamination throughout the process. Cells having been through a low number of stations had a low amount of delamination, while cells having been through several or all stations saw an increasing amount of delamination. More precisely, the typical increase of delamination for
each station is given in Figure 31, determined by the DSI method. Station numbers are denoted S9, S10, S11 etc. and represents stations seen in Figure 2. Remark that ICC and CCh signifies “intermediate chamber” and “cooling chamber”, respectively. Cells having passed only through the initial part of the process had no significant amount of delamination detected, but as the number of process stations increased, the delamination increased.

Figure 31: Delamination data of 3 different series of cells run through the process up until the station indicated by x-axis and then stopped, followed by a cooldown to room temperature in vacuum and unload through load-lock.

ICC and CCh signify “intermediate chamber” and “cooling chamber”, respectively.

The trend shows an increased delamination from S10 to the cooling chamber (CCh). This correlates with the increasing iron selenide film thickness. After CCh, there is a large rise in delamination which is fixed around a constant value until S22, where it decreases abruptly to values comparable to those before CCh. Microscopic images from the data used are shown in Figure 32. S20 has a lot of darker areas (tilted flakes) while S16 and S25 has a significantly lower number of dark areas. This trend was observed for multiple test runs.
From EDS data it was discovered that selenium content was not uniformly distributed, when moving from the edge towards the center of the cell as seen in Figure 33. Remark that these measurements were done directly on cell backsides, giving signal from both the Fe-Se film and the bulk substrate steel. The maximum content of selenium appears between 5-15 mm from the cell edge, which is at the interface of the white and inner region of the particle pattern (Figure 24). The selenium content converges to values comparable to what is seen at the cell edge when moving beyond 30 mm from the cell edge. When comparing with cells having passed only partly through the process (Figure 33, b), it could be seen that cell S9 had a low amount of selenium present on the surface, while for cell S17 the selenium content was as high as a standard fully deposited cell (S25). Measurement done on cell S1 to S7 found no significant selenium content in any position on the cell.

However, nucleation sites were visible in SEM images of cell S7 (Figure 34), indicating that growth of the Fe-Se film likely have started already at this point.
Nucleation of iron selenide grains was seen to occur homogenously over the substrate surface, except for defects, where crystallites are arbitrarily oriented (bright crystallites in Figure 35; S9). Substrate steel defects are visible for S9 but not for cells in S17 and S25, because the growing Fe-Se film has covered them. This suggests that the thickness is higher in S17 and S25 compared to S9.

Figure 36 shows part of a region with peeled-off reaction layer. In areas with the reaction film peeled-off there is no significant Se content found with EDS analysis, although nanometer scaled structures are present on the surface. These could either be residues from the peeled off Fe-Se film or the surface undergoing reaction with selenium again, that are not large enough to be detected by the EDS analysis. EDS analysis found the Cr content to be 15 at% in this area, which is 3 at%-units lower than for the original substrate content. However, in cross-sectional analysis, no trend of lower Cr content was found along the thickness of the substrate. Thus, the detected Cr impoverishment seem to only occur close to the substrate surface. Surface in peeled-off areas had a distinct cracked pattern similar to the pattern of grain boundaries.
fact, diameter and shape of the cracked shapes are comparable to the diameter and shape in grains revealed in the substrate steel analysis (Figure 22, \(d_{\text{mean}} = 7 \text{ um}\)).

Based on the results it can be argued that selenium atoms are mainly reacting with the steel between S7 and S17, which is a reasonable result when considering that a selenium contained environment is present in S6 to S17. It could not be proven that selenium had reacted with the steel surface in S6, although it is very likely. When comparing Se content and dust particle thickness (Table 6) on different positions on the cell backside, the thickness and Se content both increase from 0 to 10-15 mm from cell edge, after which they begin to decrease again. This is an indication that varying Se content measured on an as-synthesized cell backside is related to the thickness of the cell backside film, meaning that the EDS measurements made on cell backsides is an indirect measurement of the cell backside film thickness. It can both be seen that the Fe-Se film do not have a homogenous thickness over substrate and that the Fe-Se film thickness increases between S6 and S17. Furthermore, EDS and SEM data acquired in peeled-off areas indicates that a low Se content is present, which indicates that delamination does not occur between S6 and S17, where a selenium environment is present. A higher Se content should be found in peeled-off regions if they were to become peeled-off where a selenium environment is present. In fact, results discussed further into this chapter of the report suggests that it is likely that delamination happens during cooling. This result further strengthens this argument.

Thus, as a conclusion for this chapter, selenium content increases in stations having a selenium environment (S6-S17) and therefore also the iron selenide film thickness. The results also suggest that delamination of particles increase as the iron selenide film thickness increases. If the amount of selenium reaching the substrate backside in the stations with a selenium environment could be minimized, the dust particle formation could be minimized. This could be done by having a less concentrated selenium environment or preventing selenium from reacting with Fe on the substrate backside.

8.3.2. Film cracking

Film thickness

The film thickness is related to the cracking of the film. Cracking appearing in a certain station could be because a critical film thickness is needed to produce a cracking failure mode. The
dust particles formed have distinct and peculiar shapes. The dust particles are not completely even but often elongated and curved in some direction, as can be seen in the inset figure in Figure 4 and in Figure 25 (inner region). It is known from delamination studies of thin films that extraordinary patterns is formed when thin film cracks, as summarized by G.Gioia et al. [17]. Notably buckling cracking patterns, which occur when the film stress is compressive, produce these peculiar cracking patterns. The model proposed in [17] models that film cracking patterns form from destabilized blisters propagating delamination in some direction to reduce energy. Blisters can be seen as local circular regions where the thin film is elevated above the substrate surface but is still intact. In turn, nucleation of blisters have been suggested to occur at defects in either the film, substrate or interface [18]. The buckling does in turn produce a driving force for the adjoined interface crack to propagate. Hutchinson et al. [8] categorized failure modes for tensile and compressive stresses. For compressive modes, there are 2 modes called buckling and edge delamination. The same study presents a general criterion with which the failure modes may be deemed to propagate or not. This is expressed in equation (5-3) mentioned earlier:

$$\Omega = \frac{h\sigma^2}{ET}$$

(5-3)

where \( h \) is the film thickness, \( \sigma \) is the stress, \( E \) an elastic modulus and \( T \) a fracture toughness. This is a general notion and different approaches concerning which elastic modulus and fracture toughness modes to employ have been studied depending on encountered film issues and behavior. Another phenomenon that has been presented by N.Matuda et al [19] is how blister size and the cracking pattern depend on film thickness. This has been hypothesized by multiple authors [18][20][21] to be a direct result of larger dimensions when scaling the film thickness, and was clearly shown by means of a film thickness gradient by N. Matuda et al [19]. Figure 37 presents the dust particle diameter measured for different stations in the cell sputtering system and for different positions on the cell. The dust particle diameter correlates with the dust particle thickness and EDS measurements as seen in Table 6 and Figure 37, respectively. Dust particle diameter is the same for S17 and S22, since film thickness do not increase after S17. The reason to the decreases in dust particle diameter in S25 is due to a second cracking occurring. This is also why DSI decrease after S22, as dust particles seem to be positioned more parallel to the substrate surface with the second cracking. However, why this is happening is subject to further research.
Figure 37: Dust particles diameter as a function of station number (a) and as function of distance from cell edge (b). Dust particle thickness data extracted from Table 6.

Equation (5-3) and the dust particles dimensional data aid to understand how increasing film thickness may be one of the reasons to that the film starts cracking with increasing station number, since there is evidence that film thickness is increasing with stations. The other factor to consider is build-up of stress in the film. A number of suggestions to stress contributors were presented in the beginning of this chapter, which are discussed below.

**Coefficient of thermal expansion (CTE)**

Difference in thermal expansion coefficients is a common cause of film cracking, which is possible when considering this property for stainless chromium steel and Fe$_{0.8}$Se (Table 7 shows CTE for Fe$_{2}$Se$_{8}$ which is believed to be close to that of Fe$_{0.8}$Se).

*Table 7: Table of volumetric expansion coefficient for Fe$_{2}$Se$_{8}$ and AISI 430 stainless steel.*

<table>
<thead>
<tr>
<th></th>
<th>Fe$<em>{2}$Se$</em>{8}$</th>
<th>AISI 430</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt; 370 ^\circ$C</td>
<td>88.7 *</td>
<td>31.3**</td>
</tr>
<tr>
<td>$&gt; 370 ^\circ$C</td>
<td>51.9 *</td>
<td>31.3**</td>
</tr>
</tbody>
</table>

* *Extracted from [22], ** Extracted from [9], assuming isotropic properties

If the film thickness is many times thinner than the substrate thickness ($h<<H$) the substrate will govern the in-plane strain of the film, meaning that $\varepsilon_s = \varepsilon_f$ [8]. The retraction during cooling of Fe$_{2}$Se$_{8}$ is 2.5 and 1.5 times larger than that of the substrate steel below 370$^\circ$C and above 370$^\circ$C, respectively. The resultant stress in the film due to thermal expansion will thus be tensile as illustrated in Figure 38.
Temperature gradient
Another possible reason to explain film cracking is stresses generated due to temperature gradients created when rapidly cooling. Cells are cooled by a low temperature gas stream incident on the surface backside in the cooling chamber. In general, metals have a high thermal conductivity which means that stresses due to a thermal gradient in metals will be low, but for a semiconductor as iron selenide this may not be the case. However, the backside film display cracking even when cooled slowly without the cooling station. This effect was deemed to not be significantly contributing to the backside film cracking and delamination.

Phase changes
A phase change may lead to volume changes which could produce compressive stresses in the film or crystal lattice mismatch which could build up either compressive or tensile stresses depending on the severity of the mismatch. It is known from XRD and EDS analysis that the phase present on the cell backside after cooling is Fe$_{0.38}$Se (53.3 at% Se), with a NiAs-crystal structure. The Fe-Se system has a phase diagram with various phases in the range of 50 to 55 at% Se, depending on temperature. This is the range in which the stoichiometry of the Fe$_{0.38}$Se is found.

The maximum temperature of the cell during deposition is 600-700°C before cooling to 100°C. Considering the phase diagram in Figure 40 constructed by H. Okamoto et al. [23], it is possible to see that δ is the thermodynamically favorable compound for 600°C [24][25]. At 370°C there is a reaction of δ to γ' with a thin region accommodating both δ and γ'. However, the γ' phase has been seen to only appear for certain temperature profiles and it is thus ambiguous if it will appear [26]. The transitions at 300°C from γ' to βFeSe$_s$ and at 180°C from βFeSe$_s$ → αFeSe$_s$ are second order transformations accompanied with re-ordering of vacancies, where βFeSe$_s$ and αFeSe$_s$ are defined as superstructures due to this [26][27][28][29]. This superstructure is used to describe the crystal cell of the material. Since the crystal cell may have several different iron vacancies that is ordered in a specific way, the original crystal cell is not enough to describe the system. The crystal cell is therefore expanded to a superstructure that consists of multiple original crystal cells ordered in a specific way so that the vacancy structuring is shown.
The differences in crystal structure between the phases are mainly that between δ, β and the remaining phases. The δ has a hexagonal NiAs-type crystal structure, the β has a tetragonal PbO-type crystal (Figure 39) and the remaining are of the NiAs-type described with a superstructure.

\[ \delta \rightarrow \gamma \rightarrow \beta Fe_3Se_8 \rightarrow \alpha Fe_3Se_8 \] or \[ \delta \rightarrow \beta Fe_3Se_8 \rightarrow \alpha Fe_3Se_8 \]. In Table 8, the theoretical density of the different phases has been calculated with help of lattice parameters from a various of studies on FeSe. The β phase was also calculated as it may be present depending on chemical composition.

Thus, spanning from 700 to 100°C the likely phase changes are either $\delta \rightarrow \gamma \rightarrow \beta Fe_3Se_8 \rightarrow \alpha Fe_3Se_8$ or $\delta \rightarrow \beta Fe_3Se_8 \rightarrow \alpha Fe_3Se_8$. In Table 8, the theoretical density of the different phases has been calculated with help of lattice parameters from a various of studies on FeSe. The β phase was also calculated as it may be present depending on chemical composition.

![Figure 39: (a) Illustration of the PbO-type crystal [30], where dark and grey atoms represent Fe and Se, respectively. (b) Illustration of the NiAs-type crystal [31], where dark and grey atoms represent Se and Fe, respectively.](image)

![Figure 40: Fe-Se phase diagram [23]](image)
Regarding the $\delta$, there is a considerable density difference (15\% higher) compared to the other phases. Thus, if transition is happening at 370°C there will be an increase of the volume occupied by the film, assuming that thermodynamic equilibrium is attained. However, cooling comprises a temperature change of 550°C in less than 20 seconds. This means cooling rates of 29°C/s at minimum. There has been done very limited analysis on how Fe-Se phase changes depends on cooling and heating rates, making it difficult to estimate the resulting phase change. Furthermore, XRD analysis in this study could only evoke that the dust particles had a NiAs type hexagonal structure at room temperature when unloaded from the machine. Thus, there exists an ambiguity as to what phases are present at high temperature inside the machine, and if the rapid cooling allows formation of the Fe-Se superstructures by arranging of Fe vacancies and would need further study to confirm. Yet, considering the reaction films tendency to buckle, it is possible that this particular phase change is a factor in the cracking mechanism.

*Table 8: Crystalline parameters and calculated theoretical densities of phases.*

<table>
<thead>
<tr>
<th>Phase</th>
<th>System</th>
<th>Lattice parameter (nm)</th>
<th>Angle</th>
<th>Mass/Vol (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$</td>
<td>Hexagonal</td>
<td>0.3694 - 0.5846 - -</td>
<td>$\alpha$ $\beta$ $\gamma$</td>
<td>6.479 [22]</td>
</tr>
<tr>
<td>$\beta$FeSe$_3$ 3c</td>
<td>Hexagonal</td>
<td>1.253 0.7234 1.765 - -</td>
<td>-</td>
<td>5.609 [27]</td>
</tr>
<tr>
<td>$\alpha$FeSe$_3$ 4c</td>
<td>Triclinic</td>
<td>1.253 0.7236 2.354 89.8 89.4 90.0</td>
<td>-</td>
<td>5.570 [28]</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Tetragonal</td>
<td>0.377 - 0.553 - -</td>
<td>-</td>
<td>5.696 [32]</td>
</tr>
</tbody>
</table>

Furthermore, the mismatch of crystal lattice may be a contributor to stress. Comparing steel and Fe-Se film crystal lattice, the interface is body-centered cubic (BCC) to hexagonal both above and below 370°C.

**Cell bending**

Another factor to consider is the bending of cells. When exiting the process, cells are concavely bended with respect to the cell backside. However, this is not due to the Fe-Se film, since its thickness is many times smaller than the substrate thickness (200-300 nm to 150 μm). The stress imposed by the Fe-Se film on the substrate will not be significant. Additionally, the cell bending has not been noted to correlate with dust particle amount present on the backside. The bending is rather thought to be due to the front side solar cell deposition. Thus, since the concave bending of cells is not a result of the Fe-Se film itself, it will contribute to generation of compressive stresses in the backside surface film.

To conclude on the stress generation, the significant contributing factors to Fe-Se film cracking are thermal expansion coefficient mismatch, cell bending and phase change. The first mentioned contributes to tensile stress while the latter ones contribute to compressive stress. It is possible to summarize the contributing factors as in (8-1). Absolute value of stresses is included to indicate if stresses are compressive or tensile. The residual stress variable is included to indicate that other additional stresses may be present. However, they have been deemed to not play an as important role in regard to the cracking and delamination.

$$\sigma_{film} = \sigma_{residual} - |\sigma_{cellbending}| - |\sigma_{phase change}| + |\sigma_{CTE}|$$  \hspace{1cm} (8-1)
8.4. Steel substrate variation

Tests with three different substrate steels were made. Steel from supplier A, supplier B and steel from supplier A coated with molybdenum on the backside. As seen in previous sections, the supplied steels were of similar standard (AISI 430). The steel from supplier A and supplier B is the original and the alternative steel, respectively, and will be denoted steel A and steel B in this sub-chapter, respectively.

It was seen that the backside film on steel B did not crack as extensively as the backside film on steel A. Comparing optical microscopic images, cracking is not seen on cells made on steel B (Figure 41).

![Figure 41: Microscopic image of cell backside on steel A and steel B. Both steels have a iron selenide film present. The film is cracked on steel A but not on steel B.](image)

The steel B backside film does not crack and delaminate because the built-up stress in the film is lower than a critical value. Either this critical value is higher than that for steel A, and therefore no cracking is seen because the film can handle more stress. Or the steel B has comparable critical stress as steel A, but stresses are lower in steel B. A lower stress level could be due to, e.g. lower film thickness.

As a matter of fact, lower Se content is found on steel B backside, indicating a lower Fe-Se film thickness (Figure 42). Hence, it cannot be confirmed that the film on steel B is at a lower stress level and, due to this, does not crack and delaminate. Since this cannot be confirmed, it is only speculative to discuss if the film on steel B can handle higher stress than the film on steel A. An experiment where cracking is studied on steel B when it has attained as high film Fe-Se film thickness as steel A should therefore be done for further studies.
To verify that the lower reaction rate on steel B was not simply due to a lower deposition temperature, the substrate temperatures for all cells were tracked (Figure 43). It was found that steel B generally had slightly higher substrate temperature readings. However, this was measured with pyrometers that base their readings on emissivity of the substrates. This is a problem because steel B has a rougher surface, which may affect the emissivity of the substrate. Therefore, the data in Figure 43 have an unknown error.

Figure 43: Substrate temperature for cells produced with substrate steel A and B. The temperature is normalized to standard substrate temperature.
Furthermore, steel B affects the efficiency of cells which is also important to take into account. Looking at Figure 44, it is seen that steel B has a slightly lower efficiency. At this point it is difficult to tell the exact reason to this. It could be its rougher surface, undetected contamination in and on the steel, different residual stresses or other reasons. This is something that needs to be researched further. However, it is an important result as it clearly shows that substrate material affects efficiency, which may be a suggestion for a future solution to the dust particle issue.

![Cell efficiency graph](image)

*Figure 44: Cell efficiencies for substrate steel A and B. A slightly lower efficiency is found for steel B.*

Considering the steel coated with molybdenum, no visible dust particles were present on the cell backside. This can be seen in Figure 45. This indicates that no delamination is occurring for substrates coated with molybdenum.
EDS profiles seen in Figure 46, showed that no selenium was detected on the cell backside and therefore no iron selenide film was present on the cell backside surface, which explains why no delamination was detected in optical microscopy and with the DSI algorithm.
It has been suspected that molybdenum coated on the substrate backside could affect the deposition temperatures, resulting in a lower cell efficiency. Therefore, substrate temperature was tracked for some different thicknesses of molybdenum coating. A clear correlation between cell temperature and molybdenum coat thickness was found as presented in Figure 47. A thicker molybdenum coating appears to reduce the deposition temperature as expected. However, for very thin films of molybdenum, the temperature is comparable to that of standard cells, while still preventing selenium reaction on the substrate backside. This proves that the lower selenium content is simply not only due to a lower substrate temperature. It appears that a molybdenum coating protects the steel surface, somehow preventing selenium from reacting with the steel substrate.

Interestingly, the protective effect occurs also for very low molybdenum coating thickness (1 kJ). It is believed that the molybdenum coating at such a low value is not a film fully covering the substrate surface but rather islands of molybdenum. This could be a sign that the protective effect is already active at low molybdenum content on the surface. Considering these results, it gives reason to test if bulk molybdenum stainless steel could substitute the current substrate material.
What can be drawn as conclusion is that the backside surface of steel B displays a lower reaction rate with selenium compared to steel A, even though sputtering chamber parameters are identical. Since composition and phase of the two steels have been proven to be comparable, these properties can be rejected as influencing factors. What has been seen to differ between the two steels are surface roughness and residual stress, which are both results from steel processing. Further studies are recommended on how these parameters affect Fe-Se film formation.

Considering the molybdenum coated steel, it can be concluded that it is possible to minimize the selenium-iron reaction by blocking the selenium from reaching the iron. It seems that the reaction rate between molybdenum and selenium is slower, and therefore no molybdenum selenide film forms. This is a promising result that indicate two important facts. Firstly, that the iron-selenium reaction may be blocked by a protective film. Secondly, it gives motivation to test if molybdenum steels, that generally is in a lower price range compared to chromium steels, have a similar effect on the dust particle formation.

8.5. Dust particle distribution pattern
The area with the highest selenium content, and thus highest film thickness, correlates with the regions where cracking is seen (approximately 5-25 mm from the cell edge). This is also the region where the initial signs of dust particles are seen when tracking the delamination while progressing through the process. It was also possible to see that when doing EDS profiles on various positions on the cell, they follow a radial symmetry. This is illustrated in Figure 48, showing the S25 EDS profile from Figure 33 rotated around the cell center.
Figure 48: EDS profile seen in Figure 33 superposed and rotated around the cell center so as to illustrate how the iron selenide film thickness follow a similar radial symmetry as the dust particle delamination pattern.

These results show that film delamination and film thickness are correlated. It suggests that delamination starts in this area because the film has attained the critical thickness. Therefore, the dust particle delamination pattern is a scheme of the film thickness distribution and demonstrates macroscopically how the film thickness has a radial symmetry in respect to the cell center.

As to why the film thickness has a radial symmetry with respect to the cell center has been a subject of speculation. It is at this point known that the selenium reacts with the steel at the highest rate in the inner region, since this is where the selenium content is the highest. As mentioned earlier, temperature is believed to influence the selenium-steel reaction rate. It is likely, due to sputter chamber design, that a temperature profile is present on the cell. Therefore, it is possible that the dust particle pattern is a result of the substrate heating pattern. This is something that should be investigated in further studies.
9. Conclusion and future perspectives

Based on the research results it can be concluded that dust particles present on the solar cells backside consist of a compound of iron selenide and a marginal fraction of chromium selenide. XRD analysis found the stoichiometric ratios of the two phases to be Fe$_{0.80}$Se and Cr$_2$Se$_3$.

The two critical steps of dust particle formation are film formation and film delamination accompanied with cracking. The compound has been shown to form as a thin film on the substrates, which at a critical thickness crack and delaminate when being cooled down to room temperature from deposit temperature. The distinct dust particle distribution pattern correlates with the thickness profiles, having a radial symmetry with respect to the cell center. Film formation occurs in stations where selenium is present in the cell sputtering system, whereas delamination occurs when cells are cooled down to 100 °C or lower. The reason to cracking and delamination is hypothesized to be due to cell bending, phase change, thermal expansion coefficient mismatch, or a combination of all three parameters, generating stress in the Fe-Se film. The exact contribution of each parameter is subject to further investigation. Furthermore, it has been shown that using a substrate steel from a different provider results in a thinner iron selenide film on the substrate backside. This substrate steel has a rougher surface, although it is not proven that the surface roughness is the governing parameter for the thinner iron selenide film.

Coating a steel with molybdenum resulted in no iron selenide film forming on the substrate surface. EDS analysis found no evidence of selenium present on the substrate surface.

A primary recommendation for Midsummer AB towards a solution is to investigate molybdenum’s ability to counter the dust particle formation. Result showed that a very low amount of selenium had reacted with substrates coated with molybdenum, and thus no dust particles were present. Based on these results, a recommendation to Midsummer AB would be to investigate if either molybdenum-coated substrate or molybdenum-rich steels are alternatives to the currently used substrates.

The second recommendation is related to the temperatures and selenium environment in station 6 to 18. It has been seen throughout the study that the iron selenide film is affected by cell temperature and selenium environment in considered stations. One suggestion is to investigate if a temperature profile can be designed in station 6 to 18 that minimizes selenium reaction. E.g. by keeping a lower temperature than normal in the initial stations, while still allowing high performing cells to be created, by keeping a higher temperature than normal in the later stations. The other suggestion is to optimize the selenium environment in said stations, e.g. by lowering the selenium environment concentration.

The final recommendation is to investigate how steel properties directly related to steel processing conditions (e.g. surface roughness) affects selenium-steel reaction rate, as it may be a method to control dust particles amount.
10. Acknowledgement

This project was made possible by the division of materials science in Luleå University of Technology and Midsummer AB. I would like to show my gratitude to my supervisors, Dr. Erdal Suvar for his great support, guidance and patience throughout the whole project, and to Prof. Marta-Lena Antti for providing me support in material analysis and making this project possible.

I would also like to thank all the helpful people working on the Midsummer AB facilities, showing me the ropes and providing me guidance in order to finish this project.
11. References:


