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Analysis of blister formation in spatial ALD Al2O3 for silicon surface passivation in photovoltaics

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Analysis of Blister Formation in Spatial ALD Al₂O₃ for Silicon Surface Passivation in Photovoltaics

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Abstract

Aluminum oxide ($\text{Al}_2\text{O}_3$) films yield excellent surface passivation of silicon solar cells. However, local delamination of the $\text{Al}_2\text{O}_3$ layer, known as blistering, can occur upon annealing. This recently discovered phenomenon is undesirable for the industrial application of $\text{Al}_2\text{O}_3$ in solar cells. Therefore, the goal of this research is to provide a better understanding of blisters and the formation processes involved. Experiments were conducted to describe their appearance and to study the influence of several parameters on blistering. The experiments are discussed in relation to a suggested physical model.

When investigating the appearance of blisters for single-layer $\text{Al}_2\text{O}_3$, typical blister diameters of 2 to 10 $\mu$m were found with a density in the order of $10^3$ mm$^{-2}$, providing a blister surface coverage of around 1 percent. $\text{Al}_2\text{O}_3$ films, deposited by the Levitrack tool, showed blistering for thicknesses $d>11$ nm after an 800 °C anneal for 30 s. Blistering increased when an $\alpha$-$\text{SiN}_x$:H film was deposited on top, leading to a blister surface coverage of around 6%. AFM measurements revealed identical shapes for different sized blisters, allowing the introduction of the blister volume as a main parameter.

Experimental results revealed competition between diffusion laterally and perpendicularly to the interface. It was concluded that the accumulated blister volume depends on the particle flux diffusing from the $\text{Al}_2\text{O}_3$ bulk towards the Si/$\text{Al}_2\text{O}_3$ interface, but is independent of blister size distribution. Secondary Ion Mass Spectrometry (SIMS) measurements provided hydrogen depth profiles in the film, which showed that the number of hydrogen particles removed from the $\text{Al}_2\text{O}_3$ film strongly exceeds the amount of hydrogen trapped inside blisters. A parameter study on deposition and annealing conditions showed a negligible amount of blistering for films deposited at 150 °C. Also, a strong dependence of blister formation on polishing method was found, most likely caused by differences in surface roughness. Furthermore, the absence of a direct relationship between blister formation and minority carrier lifetime showed that a decrease in lifetime takes place with or without blistering. Finally, a numerical study of the formed physical model was executed to simulate hydrogen profiles in the system. Comparison of the numerical results with the flat profiles found by SIMS, revealed an effusion limited process, which entails that $D_{\text{bulk}} \geq 10^{12}$ cm$^2$/s.

In conclusion, the obtained insight into blistering can guide future research which will be necessary to elucidate the exact reason of blistering and the processes involved.
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Chapter 1

General Introduction

1.1 Photovoltaic Industry

The first modern solar cell was produced in 1954 at Bell Laboratories and had an energy conversion efficiency of 6% [1]. Since this proof of concept, research has made large progress and a large solar cell industry has emerged, that produced 29.7 GW in 2011 [2]. The large commitment to the research was fed by the ever increasing global energy demand and the potential of solar energy to contribute to the decrease of fossil fuel usage. Figure 1.1 shows the annual global solar cell production over the last decade in megawatt peak [2]. It also includes two future scenarios forecasted by the European Photovoltaic Industry Association (EPIA): a moderate scenario and a more optimistic, policy-driven scenario. This graph illustrates the large growth of the industry and the future potential. The growth has lead to a solar energy market with a global economical scale of 82 billion USD in 2010 [3]. In May 2012, the US National Renewable Energy Laboratory (NREL) published a research in which conservative projections were made on the electricity production in 2050 [4]. It was concluded that current techniques are able to achieve a sustainable electricity input to the national US demand of up to 80% by 2050, using only renewable energy produced on US soil. Depending on time and location, solar energy is responsible for a significant proportion of this estimate. These numbers indicate the

![Figure 1.1: The global annual solar cell production in the last decade in megawatt peak and two scenarios for the near future forecasted by the European Photovoltaic Industry Association [2]. The Policy-Driven scenario is based on the assumption that policymakers are able to maintain acceptable market conditions.](image)
potential of solar energy as a renewable resource and justify further research in order to optimize the energy conversion efficiency. Since the work in the Bell Laboratories, the solar cell efficiencies of silicon cells have increased to around 18% for commercial solar cells [5]. At the moment of writing, the industrial record efficiency for a commercial 156x156 mm² solar cell is set by Sunpower with a value of 22.5% using mono c-Si Maxeon cells [6]. Many technological developments have contributed to this efficiency gain. One particular development, surface passivation of silicon solar cells, is central in this work and will be explained in the next section.

1.2 \( \text{Al}_2\text{O}_3 \) for Silicon Surface Passivation

In recent years the excellent surface passivating qualities of aluminum oxide (\( \text{Al}_2\text{O}_3 \)) for silicon solar cells received much attention [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. It was shown that \( \text{Al}_2\text{O}_3 \) is an excellent candidate to transport hydrogen to the \( \text{Si}/\text{Al}_2\text{O}_3 \) interface in order to passivate dangling bonds. Dangling bonds are unbounded electrons present at the surface of a silicon wafer, because of the termination of the silicon lattice [18]. A dangling bond acts as a recombination center for charge carriers leading to a loss of photovoltaic current and a decrease of the cell’s efficiency. This process is illustrated in Figure 1.2, in which the energy conversion of light leads to the creation of electron hole pairs in a solar cell. The dangling bonds present at the non-passivated bottom surface act as recombination centers (Figure 1.2a). Decreasing the amount of dangling bonds (\( D_{\infty} \)) by passivation with hydrogen results in a larger amount of charge carriers flowing into the electrical contacts (Figure 1.2b) [13]. Besides this so-called chemical passivation, the negative fixed charge (\( Q_f \)) of the dielectric \( \text{Al}_2\text{O}_3 \) contributes as well [7, 19, 20, 21, 22]. In p-type silicon solar cells, as many holes as possible should diffuse from the silicon to the bottom contact in order to generate current. By applying \( \text{Al}_2\text{O}_3 \) to the bottom surface, electrons are shielded from this surface by the electric-field created by the negative fixed charges, while holes are attracted. Therefore, the holes are less likely to recombine before they reach the contact. This effect is called field-effect passivation.

In order to activate the passivation of silicon, the \( \text{Al}_2\text{O}_3 \) film needs to receive a thermal treatment [13, 14, 23]. Such an activation anneal allows hydrogen, present in hydroxyl bonds in the \( \text{Al}_2\text{O}_3 \), to move to the

![Figure 1.2: A schematic overview of surface passivation of silicon by \( \text{Al}_2\text{O}_3 \) in a p-type silicon solar cell. In Figure (a) dangling bonds form recombination centers at the bottom surface of the cell. This leads to a loss in current and therefore a loss in cell efficiency. As shown in Figure (b), passivation of this surface by \( \text{Al}_2\text{O}_3 \) leads to a decrease in recombination centers resulting in higher cell efficiencies. A amorphous silicon nitride (a-SiN\(_x\):H) layer is applied for protection of the \( \text{Al}_2\text{O}_3 \) during the contact formation step.](image-url)
Si/Al₂O₃ interface and passivate dangling bonds [13]. An example of the passivation of silicon by Al₂O₃ is shown in Figure 1.3. The plot shows the lifetime of the charge carriers in the substrate as a function of the minority carrier density. When the carriers have a higher lifetime they are more likely to reach the contact and contribute to the power output. The lifetime of the minority charge carriers increases after deposition of Al₂O₃. After the activation anneal of 450 °C for 20 minutes, the lifetime has increased significantly. The use of Al₂O₃ for silicon surface passivation is an alternative for other materials such as silicon oxide (SiOₓ), amorphous silicon nitride (a-SiNₓ:H) or amorphous silicon (a-Si:H) [8, 24, 25]. Of these materials Al₂O₃ shows the best passivating abilities.

1.3 The Levitrack Spatial ALD System

In this project, Al₂O₃ is deposited using the Levitrack, a spatial atomic layer deposition (ALD) tool, developed by the company Levitech. As in any ALD process the substrate surface is subsequently exposed to different precursors [26, 27, 28, 29]. The used precursors are tri-methyl-aluminum (Al(CH₃)₃, TMA) and H₂O. Between each precursor step a nitrogen purge is applied to prevent precursor mixing. The basic ALD process is shown in Figure 1.4 and the basic reactions involved are given by equation (1.1) [7,30, 31]:

\[
\begin{align*}
Al - OH^* + Al(CH₃)_₃(g) & \rightarrow AlO - Al(CH₃)_₂^* + CH₄(g), \\
Al - CH₃^* + H₂O(g) & \rightarrow Al - OH^* + CH₄(g),
\end{align*}
\]

in which surface groups are denoted with an asterisk. In contrast to conventional ALD reactors, spatial ALD separates the precursors and purge gases in space rather than in time [32, 33, 34, 35]. In the Levitrack the silicon wafers float in an aluminum track at atmospheric pressure [33]. The track contains holes in the top and bottom that guide gases towards the moving wafer, as illustrated in Figure 1.5. The wafer is subsequently exposed to Al(CH₃)₃, N₂, H₂O, N₂ while moving through the track, enabling Al₂O₃ deposition. Such a full cycle is repeated over the length of the track leading to a deposition of 0.96 nm Al₂O₃ (8 cycles) for each meter of track length at the standard deposition temperature of \( T_{dep}=200 \) °C. Deposition takes place at the bottom side of the wafer. A nitrogen flow is applied to the top of the wafer to counterbalance the forces on the wafer exposed by the gases injected from the bottom. The wafer is loaded and unloaded by rubber belts transporting them from wafer cassettes into the track and vice versa. A slight angle is applied to the track to...
1.4 Solar Cell Production

The production of a solar cell consists of several specific steps. As an example the process flow for a PERC (passivated emitter and rear) type cell is shown in Figure 1.6 [10, 28, 31]. The design of this cell type is shown in Figure 1.2b. This process starts with the cleaning and saw damage removal step of a p-type silicon wafer. This removes any residues left from the wafer sawing process. When the wafer is clean, the top and bottom surfaces are texturized. This will reduce the reflection of light from the cell’s surface and thus enhances light absorption. Next, phosphorus is diffused into the wafer as the n⁺ emitter of the cell. After the rear side removal step of phosphorus layer a pn-junction is left for this p-type substrate. Subsequently, amorphous silicon nitride (a-SiNₓ:H) is deposited on the front as an anti-reflective coating and top surface passivation layer [36]. Next, the aluminum oxide is deposited. The Al₂O₃ film is deposited on the bottom surface, because that will enable field-effect passivation. On top of the aluminum oxide, amorphous silicon nitride is deposited. This layer protects the Al₂O₃ during the final steps. It also functions as a mirror reflecting IR light that is not completely absorbed back into the cell. After the deposition of these functional layers, laser ablation is used at the bottom, to etch lines in the a-SiNₓ:H/Al₂O₃ stack at the locations were the electrical contacts will be formed. The aluminum contact material is then screen-printed on the front and bottom of the cell. In order to make good electrical contacts, a short, high temperature anneal is executed in a belt furnace. During this so called firing step the electrical contact with the silicon is created. The peak temperature of the firing step is...
around 850 °C. Unfortunately, the firing anneal influences the surface passivation by the Al₂O₃ in a negative way. Although the minority carrier lifetime can still increase after the firing step, the result is not as good as for the optimum, 450 °C, activation anneal. After these production steps, the wafer is ready for integration in a solar module.

1.5 Blistering in Al₂O₃ Films

During temperature treatments of the aluminum oxide layer, unwanted blistering can occur. A blister is defined as a local delamination of the Al₂O₃ film [37, 38]. An example of a blister in an Al₂O₃ film on a silicon wafer is shown in Figure 1.7. In literature several reports on blistering have appeared showing an influence of the temperature step and layer thickness [37, 39, 40]. However, not all aluminum oxide layers seem to lead to blistering after an anneal. Indications exist that the formation of blisters is related to the effusion of hydrogen [37, 41], but the phenomenon is as yet insufficiently understood. Although aluminum oxide films for surface passivation received much attention in previous research, blistering is a more recently discovered phenomenon which is not much addressed in literature. More scientific research is needed to overcome the unwanted situations caused by blistering.
CHAPTER 1: GENERAL INTRODUCTION

1.6 Project Relevance and Goals

Blistering is undesirable in industrial application of Al₂O₃ in solar cells for several reasons. First of all, it might influence the passivating properties of the film. For some type of Al₂O₃ films, the silicon surface passivation is far from optimum after the high temperature firing anneal. It is often suggested that the blisters created during this firing step are responsible for the thermal instability of the passivation [40]. This is, however, still a point of debate and is also addressed in this report. Looking into blistering and their formation processes will reveal more knowledge on their influence on the thermal stability of passivation as well. Blistering can also influence the contact formation step during cell production. As will be shown in chapter two, there is a possibility that a blister bursts open. This creates a pin-hole in the Al₂O₃/a-SiNₓ:H stack, in which uncontrolled electrical contacts can be formed [37]. Blistering is unwanted for a third, more obvious reason. Customers do not accept such defects as they fear a possible influence on the solar cells’ lifespan. Finally, it is unknown whether blistering has an influence on the light absorption of the cells.

The goal of this project is to create more insight into blistering and address many of the aforementioned uncertainties. The experimental approach that is used is such that a maximum amount of information can be obtained on blistering. This implies that the experiments occasionally differ from standard approaches in the solar cell industry. The objective is that this research forms a good starting point for further blister research, which eventually can lead to a high level of understanding and prevention of blistering during the solar cell production. Therefore, the following open questions are addressed and form the guideline for the project. First, the most basic, yet essential, question is asked:

1. What is a blister and how can it be observed?

This question is addressed in chapter two of this report. It contains unknown variables such as shape, size, density, possible manifestations and techniques to observe them. The answer to this question provides a good definition of the defect and the overall system. It also allows the proper observation and quantification of blisters. As we will see, using the right quantities in the experimental analyses is essential for the correct testing of hypotheses regarding blister formation and the parameters involved. Such hypotheses are the focus of the third chapter, in which the central question is:

2. How are blisters formed and which parameters are involved?

Several experiments are executed on causes for blistering and the formation processes involved. A physical model is presented that is linked to experimental results. In this chapter, many relevant issues on the formation of blistering are discussed. A third goal is to elaborate the proposed physical model into a theoretical framework:

3. How can the relevant mechanisms for blister formation be simulated quantitatively?

This question is addressed in the fourth chapter of this report. The goal is to enhance the understanding of the experiments.
Chapter 2

Basics on Blisters

The focus of this research is on the formation mechanisms of blisters in Al₂O₃ and the relevant parameters involved. However, before going into the experiments that unravel these issues it is important to create a good understanding of what blistering actually is and how it can be defined. Understanding the blister’s appearance, shape, height, surface coverage, etc provides an important starting point for further blister studies. Therefore, this chapter contains a literature summary and a system definition, a description of the used observation methods for blistering, an overview of the relevant values describing blisters and the different manifestations of blisters on silicon wafer samples.

2.1 Blisters in Literature and System Definition

Recently, blistering in Al₂O₃ was mentioned in several publications. Richter et al. showed that blisters can occur in Al₂O₃ layers deposited by plasma-assisted atomic layer deposition (PA-ALD) [39]. Applying a firing anneal to these layers resulted in blistering when the Al₂O₃ layer was 10 nm or thicker and the deposition temperature \( T_{\text{dep}} \) was 180 °C or 130 °C. For higher \( T_{\text{dep}} \), blisters were found for 20 nm thick layers. Vermang et al. reported an increase in blistering for increasing anneal temperature of a 30 nm film [37]. The first appearance of blisters in his experiment occurred at an annealing temperature of 350 °C and the largest blisters occurred at a temperature of 500 °C. A layer thickness of 5 nm showed no blistering for annealing temperatures up to 900 °C. Effusion measurements show that during an anneal hydrogen is released from the aluminum oxide in the form of H₂ and H₂O. The effusion signal is related to both diffusion in the layer and surface chemistry at the top surface of the samples. Molecular hydrogen is measured in the mass spectrometer of the effusion setup at temperatures beyond 400 °C [37, 41]. The maximum H₂ effusion takes place around a temperature of 650 °C. These results suggest that blister formation is related to hydrogen species that become mobile in the Al₂O₃ layer at high temperatures.

In the literature blisters are defined as local delaminations of the aluminum oxide layer. Between this Al₂O₃ layer and the silicon substrate an interfacial region exists which contains a small layer of silicon oxide [7, 9, 15, 18, 19, 31, 42, 43]. Tunneling electron microscope measurements show that this interfacial oxide layer is around 1.5 nm thick [9]. It is formed when ALD of Al₂O₃ takes place on the silicon wafer. Scanning electron microscope (SEM) measurements done by Richter et al. indicate that the delamination of a blister in Al₂O₃ occurs at this Si/SiOₓ/Al₂O₃ interfacial region [39]. A schematic overview of this multilayer system is shown in Figure 2.1a. Figure 2.1b shows a schematic illustration of a blister.
2.2 Blister Observation Methods

Optical microscopy is the main tool to study blistering. When looking at a blistered Al₂O₃ layer, the blisters are most often recognizable by the interference patterns at the edges of the blisters. These colored fringes are caused by interference of visible light. An example of these fringes is shown in Figure 2.2. This image contains a 30 nm thick Al₂O₃ layer on top of a Cz p-type silicon surface. The film is deposited in the Levitrack tool and received its thermal treatment in the Levitor RTP system [44]. This rapid thermal processing (RTP) system provides a flexible means to give wafers a well-defined thermal treatment. Details on this thermal treatment and differences with the industrial procedures can be found in Appendix A. Besides blistering, Figure 2.2 also shows other structures of the silicon surface. The block like pattern is caused by the wafer production process. The small black dots are also related to the silicon substrate surface. The locations of the blisters are revealed by the interference pattern. Depending on the height of the blister and the wavelength of the light, constructive and destructive interference causes one color of the white light spectrum, supplied by the microscope, to be dominantly visible. Besides location, this pattern also provides an indication about the blister’s height. By counting the number of fringes of one specific color, the height can be approximated. For this calculation the difference in path length for constructive interference must be evaluated. Note that, the height of the blister is in the order of µm’s while the aluminum oxide thickness is several nanometers [37], as already indicated in Figure 2.1b. Therefore, the actual difference in optical path length is created by the blister’s height and not inside the Al₂O₃ film. For light rays interring perpendicular to the substrate, this leads to the following equation for constructive interference:

\[ m\lambda = 2nH, \]  

(2.1)

in which \( m \) is the number of fringes for a specific color, \( H \) is the blister height, \( n \) is the refractive index and \( \lambda \) is the wavelength of the light. For the estimation of the height it is assumed that the blister is filled with a gas with \( n=1 \). When evaluating the bottom left blister in Figure 2.2, four blue fringes (\( m=4 \)) are visible. If a wavelength of 450 nm is taken for blue light, a thickness of 0.9 µm is found. Note that this is only an estimation since the number of fringes might not be exactly visible. This leads to an accuracy of 0.2 µm. The estimated heights are in good agreement with the values mentioned in literature [37] and confirm the large blister height with respect to the film thickness.

In some cases, normal, bright-field microscopy, is not the best way to visualize blistering. This is most often the case when the blisters are small, when other surface structures are more dominantly visible or when the reflection of the silicon sample is too high to properly see the interference fringes. In such cases dark-field microscopy is a more suitable technique. Dark-field microscopy uses light diffraction rather than reflection as shown schematically in Figure 2.3 [45]. Only light that is scattered by the sample’s surface is transported to the
camera of the microscope. When using this technique, differences in height, such as edges, scratches and blisters, light up. An example of blistering observed by dark-field microscopy is shown in Figure 2.4. We can now clearly see blisters that are otherwise hard to spot without this microscopy technique.

A third technique is a so called Differential Interference Contrast (DIC) filter. This is an advanced microscopy technique creating a pseudo three-dimensional effect. The exact operation of this technique can be found in literature and is outside the scope of this research [45]. An example of a blister observed using a DIC filter was shown in Figure 1.8. In this image, the interference fringes are visible on the sides of the blister. Besides the blister, some surface features of the substrate are visible, similar to those discussed for Figure 2.2. Although this technique leads to a good visualization of larger blisters, it has no added value when identifying and quantifying blisters and is therefore rarely used.

Note that some wafers have a texturized surface to enhance light absorption of the solar cell through scattering. Dark-field microscopy visualizes all of these textures, making it hard to locate other defects, such as blisters. The optimum settings for the microscope differ from sample to sample and one should therefore always consider multiple options.

![Figure 2.2: An example of a bright-field microscopy image of several blisters in an Al2O3 layer. Optical interference patterns reveal the blisters' locations. The image also shows the blocked surface structure of the silicon substrate. The black dots in are related to the silicon substrate as well.](image)

![Figure 2.3: A schematic drawing explaining the differences between bright-field (left) and dark-field (right) microscopy. For dark-field microscopy only scattered light is collected [45]. Therefore, this technique allows a better visualization of height differences on the substrate's surface.](image)
In this research all the pictures were taken using an Olympus MX51 microscope with an UC-30 camera and 5x, 20x, 50x or 100x objectives providing a 2.5x, 10x, 25x or 50x magnification. The additional Olympus software allowed a quantitative measurement of blistering. The parameters reported in literature for describing blistering are size (diameter and area), the blister surface density and the blister surface coverage as shown in Table 2.1. For completeness, the blister volume is added as a new quantity here and this parameter will be explained below. A detailed overview of the calculation of the used variables can be found in Appendix B.

Table 2.1: An overview of the quantities used to describe blister properties.

<table>
<thead>
<tr>
<th>Measure</th>
<th>Symbol</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blister diameter</td>
<td>$D$</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Blister area</td>
<td>$A$</td>
<td>$\mu$m$^2$</td>
</tr>
<tr>
<td>Blister surface density</td>
<td>$n$</td>
<td>mm$^{-2}$</td>
</tr>
<tr>
<td>Blister surface coverage</td>
<td>$S$</td>
<td>%</td>
</tr>
<tr>
<td>Blister volume</td>
<td>$V$</td>
<td>$\mu$m$^3$</td>
</tr>
<tr>
<td>Total blister volume per area</td>
<td>$V_{\text{total}}$</td>
<td>$\mu$m$^3$/mm$^2$</td>
</tr>
</tbody>
</table>

The parameter “blister volume” is introduced in this project for the first time and will appear to be essential in the discussion of the experimental results in Chapter 3. In order to determine the volume, the shape of a blister has to be determined. This is done using an atomic force microscopy (AFM) study. These measurements were executed on films deposited on mirror polished samples. Blister of different sizes were scanned, see Figure 2.5. The graphs show the central cross-sections of the blisters. Note that the vertical axis is stretched with respect to the horizontal one, causing the blisters to appear less flat than in reality. Two complete AFM scans are added to the figure. For most blisters, a similar shape was found. Blister number 3 shows a slightly higher contact angle than the other blisters. The height-radius ratio is added in the bar-plot as an indication for the shape. This ratio has an average value of 0.26±0.02. This shows that the contact angle is more or less similar for different sized blisters. For blister number 4, the shape is fitted to a sphere defined by equation (2.2):

$$H = H_0 + \sqrt{R^2 - x^2},$$

in which $H$ is the height, $r$ is the position and $H_0$ and $R$ are fit parameters. This spherical fit shows very good agreement with the blister’s shape. This allows us to approximate the shape of the blisters using a sphere.
which is cut-off by a horizontal plane, as shown in Figure 2.6. For this model, the volume of the blister is given by equation (2.3):

\[ V = \frac{2}{3} \pi R^3 \left( \frac{3}{2} \left( \frac{H}{R} \right)^2 - \frac{1}{2} \left( \frac{H}{R} \right)^3 \right), \quad (2.3) \]

in which \( R \) is the radius of the sphere and \( H \) the blister height. By using the height-radius ratio of 0.26±0.02 and the model of Figure 2.6, the blister volume can be calculated. For this calculation the blister radius and abovementioned ratio form the input parameters. A detailed overview of the calculation of all parameters is provided in Appendix B.

Figure 2.5: AFM results showing half the central cross-section of several blisters with different diameters. This result shows the similar shape for the different sized blisters. Note that the vertical axis uses a different scale than the horizontal one causing the blisters to appear less flat than they really are. The inserted bar-graph shows the value of the height-radius ratio. This ratio has an average of 0.26±0.02 and is important in order to calculate the blister volume. For two blisters, a visualization of the complete AFM scan is added.

Figure 2.6: A schematic image to describe the blister’s shape. The blister is approximated as the top of a sphere which is cut off by a horizontal plane. This model is using to calculate the volume of the blisters.
CHAPTER 2: BASICS ON BLISTERS

2.3 Description of Typical Blister Values

Before going into the different manifestations of blistering, it is important to develop some understanding of typical values regarding blistering. Although their size and density can differ depending on process condition, this section will provide an overview of the most relevant values found by this research.

Figure 2.7 contains a complete AFM scan showing the actual shape a blister that is 6 µm in diameter. Although other sizes are found, most blisters in this research are between 2 and 10 µm in size. When the Al₂O₃ is capped with silicon nitride, the overall wafer size increases to values around 5 to 20 µm. The surface density of blistering depends on their size and is typically in the order of 10³ mm⁻². This leads to a surface coverage ranging from 0.1 percent to several percents. The blister volume typically ranges from 1 to 60 µm³. Combining this with the blister surface density leads to a total blister volume in the order of [V_{total}] = 10³ µm³/mm². A complete overview of these numbers is provided in Table 2.2.

2.4 Different Manifestations of Blistering

Depending on the process conditions and substrate surface, blisters can manifest themselves differently. The differences are mostly in size and density, but also in distribution and shape. In Figure 2.8 several blistered samples are shown containing blisters of different sizes. For small blisters, dark-field microscopy is used. One can clearly see the number of fringes increasing for larger sized blisters. When a mirror polished substrate is used, the blisters show perfect circular fringes as shown in Figure 2.9a. This, together with the AFM measurements, indicates that the bubble-like shape is determined by surface tension in the aluminum oxide film minimizing the system’s energy, similar to a soap bubble [46]. Although the blisters are circular in nature, they can be influences by edges in the surface, leading to a different shape, as shown in Figure 2.9b. Texturized substrates have a high surface roughness. This leads to distortions in the shape of the blisters. Figure 2.9c shows a blistered surface of a 9 nm Al₂O₃ film on a texturized wafer capped with 70 nm a-SiNₓ:H. The blisters are now larger in size and their shapes are strongly influenced by the surface structure of the silicon wafers. For such texturized wafer the blister’s shape varies, which inhibits the calculation of the blister volume by equation (2.2).

Table 2.2 contains an overview of the physical parameters and their values. The range of values for each parameter is included, as well as typical values mentioned in the previous section. It was found that in some cases blisters tend to form on surface defects such as scratches or edges. Two typical examples are given in Figure 2.10. The blisters in Figure 2.10a are aligned along a line. Such an
alignment is not expected when the formation location of these blisters is random and therefore it indicates that the formation is influenced by substrate surface structure. Figure 2.10b shows blisters formed along the visible grain boundaries of the silicon substrate.

When more extreme process conditions are used, such as a thick $\text{Al}_2\text{O}_3$ film or a long temperature treatment, the pressure inside the blister becomes too high, and the blister can burst. This is observed on any kind of wafer substrate. When this happens, parts of the film are blown away. Some bursted blisters for an $\text{Al}_2\text{O}_3$/SiN$_x$ stack are shown in Figure 2.11. One can clearly see the film sections that are blown off and scattered near the blister.

Table 2.2: An overview of relevant values for the parameters used to describe blisters. Both the spread in measured values and typical values are included. The blister volume for $\text{Al}_2\text{O}_3$/a-SiN$_x$:H stacks could not be calculated since these blisters were produced on substrates with a high surface roughness. This causes blisters to have different shapes causing the assumption of similar shape for different sizes to fail.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Measured values</th>
<th>Typical values for $\text{Al}_2\text{O}_3$</th>
<th>Typical values for $\text{Al}_2\text{O}_3$/SiN$_x$ stacks</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blister diameter</td>
<td>$D$</td>
<td>0.7 - 46</td>
<td>2 – 10</td>
<td>5 – 20</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Blister area</td>
<td>$A$</td>
<td>0.4 - 1700</td>
<td>13 - 80</td>
<td>100 - 300</td>
<td>$\mu m^2$</td>
</tr>
<tr>
<td>Blister surface density</td>
<td>$n$</td>
<td>0 - 300000</td>
<td>40 - 1000</td>
<td>200 - 2500</td>
<td>$mm^2$</td>
</tr>
<tr>
<td>Blister surface coverage</td>
<td>$S$</td>
<td>0 - 11</td>
<td>0.1 - 3</td>
<td>5 - 10</td>
<td>%</td>
</tr>
<tr>
<td>Blister volume</td>
<td>$V$</td>
<td>0.01 - 5100</td>
<td>1 – 60</td>
<td>1 – 60</td>
<td>$\mu m^3$</td>
</tr>
<tr>
<td>Total blister volume</td>
<td>$V_{total}$</td>
<td>0 - 20000</td>
<td>2400 – 15000</td>
<td></td>
<td>$\mu m^3/mm^2$</td>
</tr>
</tbody>
</table>

Figure 2.8: Several blistered samples showing blisters of different sizes. The square columns are present on the silicon substrate. Figure (a) shows small blisters, visualized by dark field microscopy as blue dots. The bigger, bright white circles (visible in (b), (c) and (d) as dark spots) are defects of the silicon surface. Diameters and densities for these images are $D=1.13\pm0.01 \mu m$ and $n=(80\pm3).10^3 \text{ mm}^{-2}$ (a), $D=1.8\pm0.1 \mu m$, $n=(973\pm9).10 \text{ mm}^{-2}$ (b), $D=3.7\pm0.1 \mu m$, $n=1140\pm40 \text{ mm}^{-2}$ (c), $D=7.1\pm0.2 \mu m$, $n=114\pm6 \text{ mm}^{-2}$ (d). The difference between these samples is caused by different layers, as will be explained in Section 3.3.

Figure 2.9: Blistered samples for several types of substrate surfaces. When a smooth, mirror polished wafer is used they show their natural circular shape (a). The shape of blisters can be influenced by surface structures as shown in (b) and (c). In (c), the $\text{Al}_2\text{O}_3$ film is covered with an a-SiN$_x$:H film causing a blue surface color.
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Figure 2.10: Blisters tend to form near surface defects. The blisters in (a) are positioned in a line, indicating a surface feature. In (b) most blisters are positioned near grain edges of the substrate’s surface.

Figure 2.11: This sample shows bursted blisters in an Al₂O₃/a-SiNx:H stack on a texturized silicon substrate. A bursted blister creates a hole and the debris of the layer is scattered on the surface.
Chapter 3

Blister Formation Studies

Now that it is clear what blisters are and how they can be described quantitatively, this research focuses on the second central question as listed in the introduction (Chapter 1):

2. How are blisters formed and which parameters are involved?

As discussed in Section 2.1, recent publications have indicated that blistering is related to hydrogen diffusion in the aluminum oxide film. It has also been shown that layer thickness and annealing temperature are of influence \[37, 39\]. These influences are explored in the following sections for Al$_2$O$_3$ films deposited with the Levitrag tool [33]. First, several experiments are presented that reveal knowledge on diffusion in the thin film system, which is then articulated in a physical model. Secondly, an experiment is discussed which focuses on hydrogen migrating in the system. Next, the deposition and annealing temperatures are varied and associated hydrogen concentration profiles are discussed in relation to blistering. Also a discussion on the relation between the minority carrier lifetime and blistering is included.

3.1 Layer Thickness and Diffusion

To study the influence of hydrogen migrating in the film, several experiments were executed. First, the relation between Al$_2$O$_3$ film thickness and blister formation was explored. In order to do so, a set of p-type Cz wafers was deposited with Al$_2$O$_3$ films with layer thicknesses \(d_1\) varying from 2 to 14 nm. The wafers subsequently received an annealing treatment \(T_1\) of 450 °C for 20 minutes or 800 °C for 30 seconds in the RTP Levitrag system. This tool is already discussed in Section 2.2 and more information can be found in Appendix A. After deposition of \(d_1\), followed by an anneal at 450 °C, no blistering occurred. Wafers annealed at 800 °C showed blisters for an initial layer thickness exceeding 11 nm. The highest surface density \(n\) found on these samples was 40±2 mm$^{-2}$ and the highest average blister diameter \(D\) was 4.2±0.1 µm. These results are shown in Figure 3.1. Note that the overall surface coverage of the blisters in this case is below 0.1%.

These results indicate that diffusion in the film, most probably hydrogen diffusion, is of vital importance. At 800 °C, the hydrogen can easily diffuse in the film, which is not the case for at 450 °C [41]. For thin layers, \(d_1<11\) nm, the hydrogen that is present in the film can diffuse to the sample surface and effuse into the environment. For layers thicker than 11 nm, the hydrogen containing film is thicker, such that the hydrogen is more contained and sufficient amount of hydrogen can get trapped at the Si/Al$_2$O$_3$ interface to form blisters. This leads to the conclusion that a first order approximation of the typical diffusion length of hydrogen in the Al$_2$O$_3$ film is in the order of 10 nm for this 800 °C, 30 second anneal. This value forms an upper boundary, since it is possible that not enough hydrogen was available for blistering in layers thinner than 11 nm. Note, that this estimate is only valid for this specific anneal, since the diffusion coefficient depends on
temperature. Overall, these results show that hydrogen diffusion perpendicular to the interface is of importance for blister formation.

The situation changes when silicon nitride is deposited on top of the Al$_2$O$_3$ before annealing at 800 °C. A sample with 9 nm aluminum oxide and 68 nm a-SiN$_x$:H shows a much higher blister surface density of $300\pm20\text{ mm}^2$ leading to an area coverage of $5.6\pm0.4\%$. For this situation, hydrogen in the thin films cannot escape as easily from the Al$_2$O$_3$ surface, moreover, hydrogen from the silicon nitride might diffuse into the aluminum oxide. As a result, more hydrogen accumulates at the Si/Al$_2$O$_3$ interface resulting in more blistering.

An interesting case-study of the Al$_2$O$_3$/a-SiN$_x$:H sample is shown in Figure 3.2. It shows the sample surface as seen by bright-field microscopy. The blue surface color is caused by the silicon nitride. The white dots are blisters and the striped pattern is the substrate surface structure caused by the sawing of the silicon ingot. A smaller surface structure, caused by texturization, is also visible. A very large blister, is present at the center of the image. It is caused by a macroscopic defect and it is surrounded by a circular area where no blisters are observed. Outside the circle, a large density of smaller blisters is present. Consequently, the large blister appears to form a sink for hydrogen in the lateral direction. This indicates that lateral diffusion lengths are in the order of a 100 µm. Such high lateral diffusion was also indicated by Dingemans et al. [41], who furthermore suggest that it takes place in the interfacial silicon oxide present at the Si/Al$_2$O$_3$ interface.

These two findings, i.e. more blister formation for thicker barrier layers and high lateral transport of hydrogen, illustrate the importance of two competing aspects concerning blister formation. First, there is hydrogen diffusion perpendicular to the interface. This can lead to sufficient hydrogen trapping at the interface which can result in blistering. Secondly, hydrogen can move large distances in lateral direction in the SiO$_x$ layer, thereby changing any hydrogen accumulation that could lead to blistering. In the next section, a physical model is suggested that includes these findings and several new hypotheses.

### 3.2 Proposed Physical Model

In this section, a physical model is proposed that is based on the findings of the experiments. This model also contains conclusions from literature and some assumptions as will be discussed in this section. Even though this model is partially based on findings which are discussed later in this chapter, it is presented here to
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Mechanism 1: Hydrogen diffusion in the Al₂O₃ film

Above results showed that diffusion in the Al₂O₃ film, perpendicular to the interface, is of importance. As discussed in Section 2.1 hydrogen effuses from the film in the form of H₂ and H₂O at annealing temperatures similar to those at which blisters are formed [37, 41]. This indicates that hydrogen is the relevant element for blistering. Additionally, the knowledge on surface passivation by Al₂O₃ also shows the relevance of hydrogen and hydrogen diffusion [7, 8, 9, 10, 11, 12, 13, 14].

Hydrogen is incorporated in the Al₂O₃ film as hydroxyl (–OH) groups [41, 47]. This hydrogen is able to diffuse in the aluminum oxide film either to the Si/Al₂O₃ interface or to the film’s outside surface at high enough temperatures. The precise mechanism and form of this diffusion is unknown. Diffusion measurements on inert gasses (He and Ne) by Dingemans et al. show the influence of film density on the diffusion processes in the Al₂O₃ film [41]. It is stated that the diffusion of such inert gasses depends on an activation energy, E_D, that allows the atoms to move from one site to the next. For hydrogen diffusion, however, the hydrogen atom is bonded in the hydroxyl group. Consequently, a bond breaking energy is necessary before diffusion can take place [41]. Because of these activation energies the diffusion is a thermally activated process.

Since the exact diffusion mechanism is unknown, it is assumed that it is atomic hydrogen diffusing through the film to the Si/Al₂O₃ interface and the sample surface.

Mechanism 2: Chemical passivation of the silicon surface

Hydrogen atoms that reach the interfacial silicon oxide can passivate dangling bonds by forming Si-H bonds. Dangling bonds are primarily present at the Si/SiOₓ interface [48]. However, for high annealing temperatures the Si-H bonds can break \( T_{\text{anneal}} \geq 400 \degree \)C [49, 50, 51, 52]. Therefore, there are two sources of atomic hydrogen in the interface region during an anneal: atomic hydrogen diffusion from the film and atomic hydrogen generated by Si-H bond breaking.

Figure 3.2: Blisters on the surface of a sample containing an Al₂O₃/a-SiNₓ:H stack \( (d_{\text{AlO3}}) = 9 \) nm, \( d_{\text{SiN}} = 68 \) nm). The blue color is caused by the silicon nitride layer. The substrate’s surface structure shows lines due to the wafer sawing step and a smaller structure caused by texturization. Blisters are shown as white dots. A large blister in the center of this image functions as a sink for hydrogen, thereby locally decreasing hydrogen pressure build-up which leads to a decrease in blistering.

provide a preliminary overview of the relevant features and to enhance the reader’s understanding of later discussions.
**Mechanism 3: Creation of trapped species**
The fact that blisters are formed indicates that a certain pressure is built up, causing the film to delaminate. Since Richter *et al.* indicate that the delamination takes place near the Si/Al₂O₃ interface, it is plausible that there are molecules trapped at this interface. When these molecules are not able to diffuse away in perpendicular or lateral direction, their concentration increases. This leads to an accumulation in the interface, which can cause local delamination of the layer. Therefore, it is assumed that a chemical process takes place, involving atomic hydrogen, resulting in these trapped species. The most plausible possibilities for the trapped reaction product are molecular hydrogen (H₂) and water (H₂O). The possibility of these molecules to diffuse through the Al₂O₃ film depends on the film density and the annealing temperature. If such diffusion is impeded, the molecules are confined in the SiOₓ interfacial oxide.

The presence of the chemical reaction is an assumption since no explicit empirical proof is available for this reaction. However, there are several indications that make its presence plausible. First of all, the blisters indicate that a pressure is formed inside the system which causes the delamination. Since atomic hydrogen is able to diffuse from the film to the interfacial silicon oxide it is unlikely that it is not able to diffuse back into the film. Secondly, atomic hydrogen is very reactive and will tend to react to a stable molecule before entering the blister. For sake of the discussion, it is from now on assumed that molecular hydrogen is formed by this reaction and forms the trapped species.

**Mechanism 4: Lateral diffusion**
As concluded from the case study of the Al₂O₃/a-SiNx:H sample, lateral diffusion takes place which is consistent with findings from Dingemans *et al.* and it is suggested that this diffusion takes place in the interfacial silicon oxide [41]. The numbers found in the previous section show that typical diffusion lengths for this lateral diffusion (~100 μm) are much larger than for diffusion in the direction perpendicular to the interface (~10 nm).

From this case study it cannot be specified what species actually diffuses in the lateral direction. It is possible that atomic hydrogen hops from one location to the next and that the reaction to molecular hydrogen, H₂, takes place at defects in the lattice where the blister will be formed. Another possibility is that it is the trapped species themselves that are mobile along the lateral direction.

**Mechanism 5: Accumulation in the interfacial region**
If more and more species are trapped in the interfacial region, the concentration increases. If this concentration is not reduced by lateral diffusion, high pressures build up.

**Mechanism 6: Delamination of the Al₂O₃ film**
A high enough pressure in the interfacial silicon oxide can cause delamination of the Al₂O₃ film, thereby forming a blister. The volume of the blister is filled and the concentration in the interfacial oxide is decreased. Although SEM measurements performed by Richter *et al.* indicate that it is the interfacial oxide where delamination takes place, no hard experimental proof is available [39]. In this project, it is assumed that it is indeed the interfacial oxide where delamination takes place.
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A schematic overview of these mechanisms is shown in Figure 3.3. The features of this model can be summarized as follows:

1. Hydrogen is incorporated in the \( \text{Al}_2\text{O}_3 \) film in the form of hydroxyl groups. This hydrogen is able to diffuse to the surface and the interfacial silicon oxide. It is assumed that this diffusion happens in the form of atomic hydrogen.
2. Atomic hydrogen in the interfacial region can passivate dangling bonds. At temperatures above 400 °C this bond can also break, as indicated by the double arrow in step two of Figure 3.3.
3. The atomic hydrogen from the film is able to react to larger molecules that are trapped at the interface. It is assumed that these trapped species are molecular hydrogen.
4. The interfacial silicon oxide acts as a freeway for the atomic or molecular hydrogen, enabling fast lateral diffusion.
5. During annealing of the system, the amount of molecules trapped at the Si/\( \text{Al}_2\text{O}_3 \) interface can increase. This creates an accumulation of molecular hydrogen in the interfacial region.
6. This accumulation causes delamination of the film at the interfacial silicon oxide causing a blister to be formed. The trapped molecules now fill the blister.

Several of these aspects of the model are addressed by the experiments and will be discussed in the next sections.

3.3 Double Layer Diffusion Experiments

3.3.1. Experimental Design
To further explore the perpendicular diffusion of atomic hydrogen in the film, several hydrogen distributions are created in the \( \text{Al}_2\text{O}_3 \) bulk. This is done by depositing an additional \( \text{Al}_2\text{O}_3 \) layer on the annealed single layer \( \text{Al}_2\text{O}_3 \) samples that were already discussed in Figure 3.1. On these samples \( \text{Al}_2\text{O}_3 \) films were deposited with thicknesses varying between 2 and 14 nm (\( d_1 \)). The second layer thickness (\( d_2 \)) ranges from 28 to 16 nm making the total thickness 30 nm for each sample. This experimental design is illustrated in Figure 3.4a. After the second deposition, the wafers again received an anneal (\( T_2 \)) at 800 °C (30 s). This resulted in several sets of wafers with different \( T_1, T_2 \) combinations.
Depending on the thicknesses of the layers and the used anneals different hydrogen distributions are created in the Al₂O₃ film. Therefore, this experiment allows testing of the influence of diffusion for the different hydrogen distributions on blistering. This leads to the following expectations for the different sets:

- **The T₁=450 °C, T₂=800 °C set:**
  For the first anneal at 450 °C, it is expected that not much atomic hydrogen is removed from the film. Thus, the first layer will still have a rather large hydrogen concentration when the second deposition \((d₂)\) is done. Therefore, the thickness of hydrogen rich Al₂O₃ after the second deposition will be 30 nm for all samples, regardless of \(d₁\). When the second anneal, at 800 °C, is executed and atomic hydrogen diffusion starts taking place a similar amount of atomic hydrogen will diffuse to the interface, leading to a similar amount of blistering.

- **The T₁=800 °C, T₂=800 °C set:**
  For this set, the first anneal at 800 °C removes much hydrogen from the film. By depositing a new, hydrogen rich, second layer, a new source of atomic hydrogen in the film is created. The second 800 °C anneal, enables this new hydrogen to diffuse through the system. It is expected that samples with a large amount of atomic hydrogen close to the Si/Al₂O₃ interface (thin \(d₁\)) will show more blistering than samples with a low amount of new hydrogen and a larger barrier to the interface (thick \(d₁\)). The distribution of hydrogen for these double layer samples and the associated expectations for blistering are shown in Figure 3.4b.

### 3.3.2. Results and Discussion

After the second deposition and temperature treatment, the blistering increased significantly, as shown in Figure 3.5. For the T₁=450 °C, T₂=800 °C set (Figure 3.5a) the average blister diameter increases as a function of initial layer thickness \(d₁\), while the blister surface density decreases. In case of two 800 °C anneals (Figure 3.5b) the average blister diameter shows a minimum for \(d₁=7.2 \mu m\), where the blister surface density shows a maximum. Average blister diameters varying between \(D=0.7±0.1 \mu m\) and \(D=4.0±0.1 \mu m\) are found. Values between \(115±8 \text{ mm}^2\) and \((3.0±0.1) x 10^5 \text{ mm}^2\) were found for the average blister density \(n\). Examples of microscopy images of these samples are shown in Figure 2.9 of Section 2.5.

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**Figure 3.4:** (a) A schematic overview of the double layer experiment. Two Al₂O₃ films with varying thicknesses \(d₁\) and \(d₂\) are deposited on top of each other. The total thickness is 30 nm for all samples. After each film deposition, the system is annealed \((T₁, T₂)\). Because of this design, different hydrogen distributions in the film are created which lead to different expectations for blistering after the second anneal, as shown in Figure (b) for the \(T₁=800 °C, T₂=800 °C\) set. The dashed arrows represent hydrogen diffusion during the second anneal.
For these quantities, no clear trend on $d_1$ is found. However, plotting the blister density $n$ against $D$ reveals a much clearer trend, as shown in Figure 3.6 for the $T_1$=450 °C, $T_2$=800 °C. It shows that small blisters relate to large blister densities and vice versa. The following equation is used to describe this relation:

$$n = \frac{C}{D^N},$$

(3.1)

in which $n$ is the blister surface density, $D$ the average blister diameter, $C$ and $N$ are constants. An empirical fit of these data points to Equation (3.1) shows a power of $N = 2.7\pm0.3$ for the $T_1$=450 °C, $T_2$=800 °C set. $N = 3$ indicates that the surface density multiplied with $D^3$ is constant. This can be interpreted as a measure for the total volume of all blisters per mm$^2$. This interpretation is only justified when blisters of different sizes have a similar shape, which was demonstrated by AFM measurements discussed in the Section 2.2. This allows us to express the amount of blistering in the quantity total blister volume $V_{\text{total}}$ as shown in Figure 3.7.

Figure 3.5: Blister surface density and average blister diameter as a function of the Al$_2$O$_3$ first layer thickness ($d_1$) for (a) the $T_1$=450 °C, $T_2$=800 °C set and (b) the $T_1$=800 °C, $T_2$=800 °C set. Error bars are based on Poisson statistics (1σ) of blister counts of each surface as explained in Appendix B.

Figure 3.6: The relation between blister surface density and average diameter for the dataset with $T_1$=450 °C, $T_2$=800 °C. The lines show the relation $n = C/D^N$ with $N=2.7$ (fit) and $N=3$. The latter reflects that the total blister volume for this set is constant.
For the dataset with $T_1=450 \, ^\circ\text{C}$, $T_2=800 \, ^\circ\text{C}$, the total volume of the blisters is constant and independent of blister size and initial $\text{Al}_2\text{O}_3$ thickness ($d_1$). For the set with $T_1=800 \, ^\circ\text{C}$, $T_2=800 \, ^\circ\text{C}$, there is a higher blister volume, which is constant for $d_1<11\,\text{nm}$ and then decreases rapidly for larger $d_1$. The scattering in the data is most likely related to the reproducibility of the experiment. The given error bars are based on Poisson statistics ($1\sigma$) as explained in Appendix B.

The expectation described in Section 3.1 can be linked to these results for the total blister volume. The $T_1=450 \, ^\circ\text{C}$, $T_2=800 \, ^\circ\text{C}$ set shows a total blister volume which is independent of the first layer thickness. This is consistent with the expectations for this set based on similar amounts of atomic hydrogen being available for all samples. For the $T_1=800 \, ^\circ\text{C}$, $T_2=800 \, ^\circ\text{C}$ set a decrease in blistering was expected for an increasing first layer thickness, $d_1$. This decrease is visible for $d_1>10 \, \text{nm}$. For $d_1<10 \, \text{nm}$, the hydrogen from the second layer is able to reach the interface where it can form blisters. For $d_1>10 \, \text{nm}$ less hydrogen reaches the interface. This is consistent with the data shown in Figure 3.1, where hydrogen near the interface could not escape for thicknesses larger than 11 \, \text{nm}. Interestingly, the total blister volume stays constant for $d_1<11 \, \text{nm}$ in the $T_1=800 \, ^\circ\text{C}$, $T_2=800 \, ^\circ\text{C}$ dataset. This might indicate that blister formation becomes saturated by a yet unknown effect.

In this analysis, the total blister volume appears to be the relevant parameter. It is concluded that, for this type of surface, the total blister volume depends on the atomic hydrogen flux to the interface, but is independent of blister size distribution.

### 3.3.3. Blistering in $\text{Al}_2\text{O}_3$/a-$\text{SiN}_x$:H stacks

In the next experiment, an $\text{Al}_2\text{O}_3$ film is capped with an a-$\text{SiN}_x$:H layer. Such a silicon nitride layer is used in solar industry as a reflective coating and protective layer on top of the aluminum oxide [48]. Because of this layer on top of the $\text{Al}_2\text{O}_3$ film, hydrogen effusion from the $\text{Al}_2\text{O}_3$ surface is blocked. Therefore, it is expected that this will lead to higher concentrations of $\text{H}_2$ at the Si/$\text{Al}_2\text{O}_3$ interface. It might even be possible that atomic hydrogen from the hydrogen rich silicon nitride diffuses into the $\text{Al}_2\text{O}_3$. This results in a higher accumulation at the Si/$\text{Al}_2\text{O}_3$ interface and therefore more blistering. In this experiment, a 70 \, \text{nm} silicon nitride layer was deposited on top of aluminum oxide before on Cz silicon substrates before annealing both layers at 800 \, ^\circ\text{C}. The applied $\text{Al}_2\text{O}_3$ layer thicknesses are 9 \, \text{nm}, 11 \, \text{nm} and 26 \, \text{nm}. Deposition temperatures of $T_{\text{dep}}=200 \, ^\circ\text{C}$ and $T_{\text{dep}}=400 \, ^\circ\text{C}$ were used for the $\text{Al}_2\text{O}_3$ and a-$\text{SiN}_x$:H films, respectively. A microscopy image of the 9 \, \text{nm} and 26 \, \text{nm} sample is shown in Figure 2.10c and 2.12, respectively. Note that the samples used in this experiment have a texturized surface. Since the shape of the blisters is strongly influenced by this texturization, it is not possible
to calculate the total blister volume for these samples. Therefore, the blister surface coverage, $S$, is used for analysis.

The blister coverage for these samples is shown in Figure 3.8 and is much higher than that of samples that are not capped with silicon nitride. This indicates that the a-SiN$_x$:H capping layer leads to a higher molecular hydrogen concentration at the Si/Al$_2$O$_3$ interface resulting in a higher blister surface coverage. It is also possible that for thin Al$_2$O$_3$ films, atomic hydrogen from the a-SiN$_x$:H diffuses through the film to the Si/Al$_2$O$_3$ interface and contribute to blistering, as suggested by Lüder et al. [38]. For these samples it cannot be excluded that blister formation can take place at the Al$_2$O$_3$/a-SiN$_x$:H interface. This could be the case if trapped species are formed at this interface. However, the findings from Lüder et al. indicate that the delamination takes place at the Si/Al$_2$O$_3$ interface [38]. This is also suggested by microscope images of the above discussed samples.

3.4 Experiments on process parameters

3.4.1. Experimental Design
In order to gain more insight into the relevant parameters for blister formation, samples were produced using different process conditions. Two main parameters are varied: the deposition temperature and the annealing temperature. A constant Al$_2$O$_3$ film thickness of 24 nm was used, sufficient for blister formation. For these depositions, semiconductor grade p-type Cz silicon <100> wafers were used. These substrates received different mirror-polishing steps on their front and back side, resulting in a different surface roughness. This introduces the inclusion of surface roughness as an extra parameter. The substrates also received a wet HF etch of 30 seconds prior to deposition. In this experiment, three deposition temperatures were used: 150 °C, 200 °C and 250 °C. A reference sample was included in the experiment. This reference received 24 nm Al$_2$O$_3$ by thermal ALD at $T_{dep}=250$ °C in the OpAL setup from the P&MP group of the Eindhoven University of Technology. After the deposition, the square samples were broken in 9 pieces and annealed as shown in Figure 3.9. Of each piece, the blistering and minority carrier lifetime was measured. Several pieces were also used for AFM, XRR and Secondary Ion Mass Spectrometry (SIMS) measurements.
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3.4.2. Deposition Temperature and Blistering

As concluded from the previous experiments, the hydrogen in the film, incorporated by –OH bonds, and the diffusion properties are key parameters for blistering. By changing the deposition temperature, these properties can be influenced. A change in deposition temperature leads to changes of the film structure and hydrogen concentrations \([41, 53]\). It is shown by Dingemans et al. that the hydrogen concentration in the bulk decreases for increasing deposition temperature, while the film density increases \([41]\). Note that these variables are not independent, since a hydrogen rich film by itself means a less dense film. Three deposition temperatures are used for this experiment (150 °C, 200 °C, 250 °C). Associated blistering results are discussed below.

The total blister volume for each deposition temperature is shown in Figure 3.10, for an 800 °C (30 s) anneal. The TU/e reference sample is included as well. On the horizontal axis the deposition temperature and deposition tool are provided. Strikingly, a negligible amount of blistering is found for \(T_{\text{dep}}=150 \, ^\circ\text{C}\) samples, a result that is reproducible for this deposition temperature. The \(T_{\text{dep}}=200 \, ^\circ\text{C}\) deposited samples show the highest amount of blister volume. For the 250 °C samples the blistering is decreased with respect to the 200 °C

![Figure 3.9: Wafers are deposited at different deposition temperature and then broken into 9 pieces which all received different temperature treatments as indicated.](image)

![Figure 3.10: The total blister volume after an 800 °C (30 s) anneal for several deposition temperatures. A reference sample deposited at the TU/e is included.](image)
ones. The TU/e reference sample shows a bit lower values than the Levitrack 250 °C samples.

These results are discussed in relation to the associated as-deposited hydrogen depth profiles and the as-deposited densities of the Al₂O₃ films, as shown in Figure 3.11. In these plots, a sample deposited at \( T_{\text{dep}}=100 \) °C is included as well. For the density measurements, the \( T_{\text{dep}}=250 \) °C was not measured. The different hydrogen profiles in Figure 3.11a were measured by SIMS and the horizontal axis is normalized to the interface depth. These profiles show several features. Firstly, high concentrations are found at the surface of the samples (depth \( h = 0 \)), caused by contamination from the ambient on top of the Al₂O₃ surface. Near the Si/Al₂O₃ interface (depth \( \approx 0.9 \)) a bump is visible. This is a measurement artifact. When discussing the profiles we will therefore concentrate on the bulk values (0.1 < depth < 0.8). The different hydrogen profiles can be mutually compared with an inaccuracy of 10%. Similar to these hydrogen profiles, the carbon profiles were measured as well and are included in Appendix C. However, these results on carbon in the film showed no interesting features for the analysis of blister formation.

The as-deposited hydrogen concentration of the film decreases when the deposition temperature is increased from 100 °C to 150 °C and further to 200 °C, but then unexpectedly increases again for \( T_{\text{dep}}=250 \) °C. However, the sample deposited at the TU/e, shows the expected decrease in hydrogen concentration for \( T_{\text{dep}}=250 \) °C. It is suspected that the Levitrack 250 °C sample shows untrustworthy results and is therefore excluded from further analysis. The blistering results shown in Figure 3.10 can now be compared to the changes in the hydrogen concentration of the Al₂O₃ film and the film density. For \( T_{\text{dep}}=150 \) °C, almost no blisters are found. If the deposition temperature is increased to 200 °C the blistering increases. This is accompanied by a decreasing hydrogen concentration and increasing film density. Further increase of the deposition temperature to 250 °C shows a lower blister volume.

As discussed earlier in this report, in order to create the pressure build-up leading to blistering, molecular hydrogen has to become trapped at the Si/Al₂O₃ interface. If the molecules can escape through the film, no blisters are expected. This is a possible explanation for the lack of blistering on the \( T_{\text{dep}}=150 \) °C samples. A reduced film density, i.e. less material, might allow the molecular hydrogen to diffuse into the film, thereby decreasing the likelihood for blister formation. This would mean that, although the 150 °C samples have a higher as-deposited hydrogen concentration in the film, less molecular hydrogen is present at the interface. This is consistent with findings of Dingemans et al. which show that Ne atoms, about the size of molecular H₂, are able to diffuse through Al₂O₃ films that are deposited at a low temperature [41]. For a higher

Figure 3.11: Figure (a) shows the as-deposited hydrogen concentration in the Al₂O₃ film as a function of the normalized film depth for several depositions, measured by Secondary Ion Mass Spectroscopy (SIMS). The high concentrations at the samples’ surfaces (depth \( h = 0 \)) are caused by contamination from the ambient. Near the Si/Al₂O₃ interface (depth \( \approx 0.9 \)) a bump is visible, caused by a measurement artifact. The focus is therefore on the bulk values (0.1 < depth < 0.8). Figure (b) shows the associated film densities, measured by XRR and RBS.
deposition temperature of $T_{dep}=200\, ^\circ\text{C}$ the as-deposited hydrogen concentration is lower, but the film density increases. For this case the blistering is the highest. This would mean the density is now sufficient to trap the active species at the interface. The XRR results show that the density indeed increases for increasing deposition temperature. However, it should be noted that the increase in density for $T_{dep}=150\, ^\circ\text{C}$ and $T_{dep}=200\, ^\circ\text{C}$ is only 4%. The error bars shown in Figure 3.11b are based on measurement errors.

These results indicate the presence of a trade-off concerning blister formation. On the one hand the density increases for an increasing deposition temperature. Such higher densities cause the diffusion coefficient of molecular hydrogen to be lower, which results in higher trapping of this molecular hydrogen in the interfacial oxide. On the other hand, the hydrogen concentration in the film decreases for increasing deposition temperature. Therefore, less hydrogen is available to become trapped. This trade-off is visible in the blistering results by the fact that blistering shows a maximum for $T_{dep}=200\, ^\circ\text{C}$. This trade-off was also indicated by effusion measurements by Dingemans et al. [41].

### 3.4.3. Annealing Conditions and Blistering

In the previous section, blistering was discussed in relation to different deposition temperatures. In this section, blistering is compared to the hydrogen profiles after the different anneals. These profiles, together with the total blister volumes for the $T_{dep}=200\, ^\circ\text{C}$ samples, are shown in Figure 3.12a and 3.12b. The total blister volume shows values that are similar after an 600 °C (20 min) and 800 °C (30 s) anneal and somewhat lower after an 450 °C (20 min) anneal. In the hydrogen profiles both the high values at the surface (depth $\approx 0$) as the bump near the interface (depth $\approx 0.9$) are visible again. For the as-deposited sample, the hydrogen content in the bulk is around $8.2\times10^{21}$ atoms/cm$^3$ which is 10 ± 3 atomic percent. After the 450 °C anneal, the concentration has decreased somewhat. Also a local minimum has appeared at low depth ($0.05 < \text{depth} < 0.1$) caused by hydrogen effusion from the surface. For both the 600 °C and 800 °C anneal, the hydrogen concentration in the bulk drops to similar amounts. Although the profiles have dropped significantly there is still a small amount of hydrogen present in the Al$_2$O$_3$ film after the 800 °C anneal. Apparently, these annealing conditions are not sufficient to remove this left over hydrogen from the film.

There are several interesting observations when the hydrogen profiles are compared to the total blister volume. After the 600 °C and 800 °C anneals a similar amount of hydrogen is removed from the film, thereby creating similar amounts of blistering. The small decrease in hydrogen concentration of the 450 °C sample already leads to a significant amount of blister volume. To further investigate these results, the amount of hydrogen in the 24 nm film is determined by integration of the profile. This result is shown in Figure 3.12c for all four profiles. The profiles are integrated over the domain $1\, \text{nm} < \text{depth} < 20\, \text{nm}$ in order to

---

**Figure 3.12:** Figure (a) shows the total blister volume per mm$^2$ of all annealed samples for the $T_{dep}=200\, ^\circ\text{C}$ deposition. Figure (b) shows the associated hydrogen concentration as a function of normalized Al$_2$O$_3$ film depth ($d_{\text{Al}_2\text{O}_3}=24\, \text{nm}$). During the anneals hydrogen is removed from the film. Figure (c) shows the amount of hydrogen available in the film and how much is removed, resulting from integration of Figure (b).
exclude the unrealistic surface and interface values in the profiles from the integration. It is calculated that in the order of \(10^{15} \text{ cm}^{-2}\) hydrogen atoms have diffused away from the 24 nm film after the 450 °C anneal. After the 600 °C and 800 °C anneal this number has increased to \(1.1 \cdot 10^{16} \text{ cm}^{-2}\). This number can be compared with an estimate of the amount of hydrogen atoms inside blisters. By doing so it is possible to determine what ratio of the removed hydrogen species ends up in blisters. Since the total blister volume is known, the amount of molecules inside the blisters can be approximated using the ideal gas law. In order to do so, the pressure inside the blisters is (rather arbitrary) assumed to be 2 atm, i.e. 1 atmosphere above ambient. Filling in these values and using the blister volumes shown in Figure 3.12a provides the numbers as given in Table 3.1.

Table 3.1: This table contains the relevant numbers of the calculations on the number of hydrogen atoms in the thin film system and in blisters. The ideal gas law and the total blister volume, \(V_{bl,total}\), are used to calculate the number of hydrogen atoms in the blisters \(N_{bl}\).

<table>
<thead>
<tr>
<th>(T_{anneal}) (°C)</th>
<th>(V_{bl,total}(10^4 \mu\text{m}^3 \text{ mm}^{-2}))</th>
<th>(N_{bl}(\text{cm}^{-2}))</th>
<th>(N_{removed \text{ from film} (\text{cm}^{-2})})</th>
<th>Ratio ((N_{removed \text{ from film}}/N_{bl}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>450 °C</td>
<td>11.2</td>
<td>2.3 (\cdot) 10^{13}</td>
<td>2.0 (\cdot) 10^{15}</td>
<td>89</td>
</tr>
<tr>
<td>600 °C</td>
<td>17.1</td>
<td>2.8 (\cdot) 10^{13}</td>
<td>1.1 (\cdot) 10^{16}</td>
<td>390</td>
</tr>
<tr>
<td>800 °C</td>
<td>17.9</td>
<td>2.5 (\cdot) 10^{13}</td>
<td>1.1 (\cdot) 10^{16}</td>
<td>462</td>
</tr>
</tbody>
</table>

It is found that in the order of \(10^{13}\) hydrogen atoms are present in the blisters on one cm\(^2\). This leads to the conclusion that a ratio in order of several hundreds more hydrogen atoms are released from the film than that which actually end up in blisters. Even if the assumed pressure is increased by e.g. an order of magnitude, this ratio is still significant. This conclusion is consistent with the fact that the small decrease of the hydrogen profile after the 450 °C anneal leads to significant blistering, since much more hydrogen atoms are available in the film than is contained in the blisters. Whether the excess in hydrogen that is removed from the film is released from the sample surface or is partially incorporated in the interfacial silicon oxide is unknown.

One should keep in mind that atomic hydrogen passivates dangling bonds at the interface region. As mentioned earlier such Si-H bonds can break for temperatures higher than 400 °C [49, 50, 51, 52], forming a potential, alternative, source of atomic hydrogen for blistering. The surface of an ideal <100> silicon lattice contains \(6.8 \cdot 10^{14} \text{ cm}^{-2}\) atoms [54]. If 1% of these atoms is bonded with hydrogen atoms [31, 50, 55] and all these bonds break during the high temperature anneals, almost \(10^{13} \text{ cm}^{-2}\) atoms become available. These numbers indicate that Si-H bond breaking is a small source of atomic hydrogen with respect to that diffusing from the Al\(_2\)O\(_3\) bulk.

From these calculations it is concluded that there is a large excess of hydrogen available in the Al\(_2\)O\(_3\) bulk for blister formation. The amount that is removed from the film is much higher than the amount that ends up in blisters.

### 3.4.4. Surface Structure and Blistering

The silicon substrates are standard one-side polished wafers that are thinned by polishing other side back to the desired thickness. Consequently, each side received a different mirror-polishing step. For each sample the blistering on the the sides, defined as side A and side B, was measured. The outcome of the measurements are shown for the \(T_{dep}=200\) °C samples in Figure 3.13.

The figure shows a large difference in blistering between both sides for all anneals. This means that for similar process conditions, it is possible to create significant differences in blistering depending on the polishing method. Since such differences were not visible for other substrates it is caused by the different polishing methods and not the processing. The differences in surface structure between both sides of the wafer were measured using AFM measurements. These results, shown in Figure 3.14, reveal a clear difference in surface roughness. The root mean square of the roughness is 0.11 nm on side A and 0.62 nm on side B.
Contrary to what was expected, the side with the low surface roughness showed the most blistering, while the rough side showed practically no blistering. Several possibilities exist to explain this result. First of all, it is possible that the flat surface somehow contains specific features that form nucleation sites for the chemical reaction to molecular hydrogen to take place. Another possibility is the difference in surface area caused by the higher roughness. A higher area can accommodate more hydrogen per unit area. Therefore, lateral diffusion might be able to decrease any accumulation more easily. However, a higher area would also mean that more hydrogen is available from the film. A third explanation could be a possible difference in the polishing conditions, other than surface roughness. Although the surface roughness is strikingly different between both sides, the cause could lie elsewhere. Unfortunately, the exact details of the polishing method are unknown and were not made public by the manufacturer. Looking into this issue could be an interesting direction for follow up research.

3.5 Blistering and Thermal Stability of the Lifetime

One of the main reasons to avoid blistering is the expectation that it reduces the surface passivation and therefore the effectiveness of the Al₂O₃ layer. As explained in Chapter 1, the passivating working of ALD Al₂O₃...
is formed by both chemical and field-effect passivation. It is possible that the delamination of the film leads to a higher density of dangling bonds. In this case a blister would create recombination centers and therefore destroy the chemical passivation of the silicon surface.

In order to study a presence of the relation between the minority carrier lifetime and blistering, the lifetime is compared to the surface coverage of blistering for several samples. This is done by plotting the lifetime as a function of the blister surface coverage $S$. If blistering causes a decrease in lifetime, a graph with a negative slope would be expected in this plot.

In Figure 3.15 the lifetime data of the samples is plotted versus blister surface coverage for several process conditions. For each deposition temperature three data points were provided by the different anneals. When looking at the 450 °C annealed samples only, it is clear that no relation can be discerned between blistering and lifetime for these samples. Of these 450 °C data points, a sample with a higher amount of blister surface coverage does not always have a lower lifetime. It should be mentioned that for these 450 °C samples the range in blister surface coverage and lifetime is not very large, meaning that a correlation might be present when covering larger ranges in blister surface coverage and lifetime. The data points also show why $T_{dep}$=150 °C is not the preferred deposition temperature. Although it consistently shows low blistering, it also shows low lifetimes after the activation anneal of 450 °C. This is caused by the low film density which allows atomic hydrogen to be removed from the system quite easily [41]. For higher annealing temperature the lifetime drops for all samples. For $T_{dep}$=200 °C this is accompanied by an increase in blistering. However, for the $T_{dep}$=150 °C sample the lifetime decreases as well, but no increase in blistering is found. This proves that there is a mechanism responsible for thermal instability of the lifetime that is not related to blistering. A plausible reason for the decrease in lifetime is that more Si-H bonds break at the higher annealing temperatures [41, 51, 52]. These results show that for these samples, the decrease in lifetime takes place with or without blistering. Although this does not prove an absence of a causal relationship between blistering and a decrease in lifetime, it does show that blistering is not the only reason for thermal instability of the lifetime.

### 3.6 Conclusion

In this chapter, multiple experiments on blister formation were presented. It was shown that blister formation depends on process conditions and the resulting film. For example, the influence of deposition temperature on the atomic hydrogen concentration and density of the film proved to be essential for blister formation. Also the annealing temperature had a large influence on blistering. By calculating the volume of the blisters, it was
found that much more atomic hydrogen is removed from the film during an anneal, than the amount of hydrogen that ends up in blisters. Also the surface structure proved to be of importance to blister formation. Clearly, diffusion of atomic hydrogen in the film is an important aspect for blistering. When this leads to trapping of molecular hydrogen in the interfacial silicon oxide, depending on the film density and annealing temperature, blisters can form. This trapping is enhanced when an a-SiNₓ:H capping layer is applied on the Al₂O₃ film. Besides diffusion in the film perpendicular to the interface, also lateral diffusion, most likely in the interfacial oxide, was found to be relevant. If it is possible to decrease the concentration of the trapped molecular hydrogen by lateral diffusion, blister formation can be suppressed. The underlying mechanisms as deduced from the experiments presented in this chapter were combined in a physical model that is able to describe blister formation. In the next chapter, a numerical study will be carried out implementing this model to reveal the influences of each mechanism in more detail.
Chapter 4

Physical Model of Blister Formation: Numerical Simulations

In Section 3.2, a physical model for blister formation was presented. This model contains six mechanisms that are considered relevant for blister formation. In this chapter, several of these mechanisms are studied by numerical simulations in order to answer the third central question, as listed in the introduction of this report (Chapter 1):

3. How can the relevant mechanisms for blister formation be simulated quantitatively?

A theoretical framework is build in which the Si/SiOₓ/Al₂O₃ system is represented by several coupled, first order differential equations. The mechanisms of the physical model are implemented in these equations. By numerically solving the differential equations the time-evolution of the hydrogen concentration in the system is determined. Starting conditions are, whenever possible, based on values found in the experiments. With this script, the various mechanisms in the system can be studied separately, thereby creating more insight into the parameters involved and their typical values. The theoretical framework also enables dedicated experiments for future studies.

4.1 Theory and Script Design

4.1.1. The theoretical Model
In this theoretical work, a cross-section of the Si/SiOₓ/Al₂O₃ system, perpendicular to the interface, is evaluated, as showed in Figure 4.1a. Influences in the x-direction are taken into account while it is assumed that the system is uniform in the direction parallel to the interface. The physical model that was presented in Section 3.2 contains six separate mechanisms:

1. Hydrogen is incorporated in the Al₂O₃ film mostly in hydroxyl groups [41, 47]. This hydrogen is able to diffuse to the sample surface and the interfacial silicon oxide.
2. Atomic hydrogen in the interfacial region can passivate dangling bonds. However, at temperatures above 400 °C this bond can also break [49, 50, 51, 52].
3. The atomic hydrogen from the film is able to react to larger molecules that are trapped at the interface. It is assumed that these trapped species are molecular hydrogen.
4. The interfacial silicon oxide acts as a freeway for the atomic or molecular hydrogen, enabling lateral diffusion over several hundreds of microns.
5. During annealing of the system, the amount of molecules trapped at the Si/Al₂O₃ interface can increase. This creates accumulation in the interfacial region.
6. The associated pressure causes delamination of the film and a blister is formed. The trapped molecules now fill the blister.

As mentioned earlier, the hydrogen in the Al₂O₃ film is mostly present in hydroxyl groups [41, 47]. However, it is unknown in what form the diffusion of hydrogen actually takes place. Possibly the hydroxyl bond in the film first has to be broken in order to free the diffusing particle. Also the exact form of the trapped species is unknown. As in the previous chapter it is assumed that it is H₂ that becomes trapped. Furthermore, effusion measurements show that, besides H₂, also H₂O leaves the film’s surface [37, 41]. The exact mechanisms describing the surface chemistry and the diffusion of oxygen are unknown. Therefore, only H₂ that is formed on the surface of the sample and then effuses into the ambient is taken into account and no H₂O formation is included in the model. It is assumed that the system initially contains atomic hydrogen which is able to diffuse through the film and can lead to molecular hydrogen formation at the sample surface and in the interfacial silicon oxide. A detailed discussion of these assumptions can be found in Section 3.2.

4.1.2. Theory and Script Design

Of these six mechanisms, four are taken into account in this chapter: diffusion in the film, passivation of dangling bonds, a reaction to H₂ and H₂ accumulation in the interface. First, diffusion of atomic hydrogen in the film is described and a theoretical framework is formed.

Diffusion in the film is described by evaluating a concentration difference in an infinitely thin slice as shown in Figure 4.1b. For this situation Fick’s laws for diffusion apply [56, 57]:

\[
\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}, \tag{4.1a}
\]

\[
J(x,t) = -D \frac{\partial c(x,t)}{\partial x}, \tag{4.1b}
\]

in which \(D\) is the diffusion coefficient, \(c(x,t)\) is the concentration of the diffusing species in terms of atoms per \(\text{cm}^3\) and \(J(x,t)\) is the particle flux. In the Al₂O₃ system, the atomic hydrogen in the bulk material diffuses to the film’s surface and to the SiOₓ/Al₂O₃ interface. These fluxes, for a film with thickness \(d\), are given by:

\[
J_{\text{bulk-surface}} = -D \frac{\partial}{\partial x} [H](0, t), \tag{4.2a}
\]

Figure 4.1: (a) A sketch of the Al₂O₃/SiOₓ/Si system. The Al₂O₃ layer is defined at \(0 < x < d_{\text{bulk}}\). The surface of the sample is located at \(x = 0\). (b) A sketch of a thin slice of material with a volume \(A \cdot dx\). A difference between the influx \(J(x)\) and outflux \(J(x+dx)\) will lead to a net change in particles contained in the volume.
CHAPTER 4: PHYSICAL MODEL OF BLISTER FORMATION: NUMERICAL SIMULATIONS

in which \([H](x,t)\) is the hydrogen concentration in atoms per \(cm^3\). A first approach to the calculation of these fluxes is done by analytically solving equations (4.1a) and (4.1b) for the following starting profile for the concentration:

\[
[H](x,0) = \begin{cases} 
H_0, & 0 \leq x \leq d \\
0, & x < 0 \land x > d 
\end{cases}
\]  

(4.3)

The analytical, time-dependent solution for this problem is given by equation (4.4) and both the concentration as the fluxes are shown in Figure 4.2.

\[
[H](x,t) = \frac{H_0}{2} \left[ \text{erf} \left( \frac{x}{2\sqrt{D}t} \right) - \text{erf} \left( \frac{-x}{2\sqrt{D}t} \right) \right],
\]

(4.4a)

\[
f(x,t) = -D \frac{H_0d}{2\sqrt{\pi}Dt} \left[ e^{-\left( \frac{x}{2\sqrt{D}t} \right)^2} - e^{-\left( \frac{d-x}{2\sqrt{D}t} \right)^2} \right].
\]

(4.4b)

The figure shows that the fluxes form peaks near the interfaces. For \(t=0\), these peaks are Dirac delta functions and the fluxes at the edges asymptotically approach infinity. This is caused by the infinite concentration gradient in the starting profile of the concentration. Since the system will be solved numerically, this provides a problem for the starting condition at \(t=0\). The outcome will strongly depend on the size of the first time-step. The use of this analytical solution provides another problem, since processes at the interfaces such as effusion can be of influence to the diffusion, but are not included in the analytical derivation.

Therefore, another approach is used. Instead of starting with infinitely thin slices, the bulk and interface are divided into \(n\) and \(m\) sublayers, respectively. Each with a thickness \(d_{\text{bulk}}/n=\Delta x\). The bulk now consists of \(n\) sublayers, denoted with index \(i\), while the interface consists of \(m\) sublayers, with \(m=d_{\text{interface}}/\Delta x\), denoted with index \(j\). The direction of increasing index is parallel to \(x\). The diffusion is then calculated explicitly from the concentration differences between these sublayers. The associated differential equation describing the concentration, in atoms per \(cm^3\), of sublayer \(i\) in the bulk is given by equation (4.5). This equation is the discrete representation of equation (4.1).

\[
\frac{d[H]_i}{dt} = +D_{H,\text{bulk}} \frac{[H]_{i+1} - 2[H]_i + [H]_{i-1}}{\Delta x^2},
\]

(4.5)

in which \([H]_i\) is the atomic hydrogen concentration in atoms \(cm^3\) in sublayer \(i\) and \(D_{H,\text{bulk}}\) the diffusion coefficient of atomic hydrogen in the bulk. This can be rewritten to emphasize the influence of the explicit

Figure 4.2: (a) The analytical solution for diffusion of a rectangular concentration profile in a medium with uniform diffusion coefficient. The associated fluxes near the edges are illustrated in Figure (b). The flux at each edge forms a delta function for \(t=0\). Therefore, the edge fluxes contain an asymptote for \(t=0\) as shown in Figure (c). For these graphs a diffusion coefficient of \(D = 10^{-14} \, cm^2/s\) is used in order to properly illustrate the process.
concentration differences at each side of the sublayer:

\[
\frac{d[H]_i}{dt} = +D_{H,\text{bulk}} \frac{[H]_{i+1}-[H]_i}{\Delta x^2} - D_{H,\text{bulk}} \frac{[H]_i-[H]_{i-1}}{\Delta x^2},
\]

(4.6)
in which each term gives the interaction with one adjacent sublayer.

Now that bulk diffusion is described, effusion to the ambient is considered. Therefore, a surface is defined that contains \( M \) surface sites per cm\(^2\). Atomic hydrogen from the top sublayer is allowed to occupy these sites with rate \( k_M \). It is then assumed that the atomic hydrogen of two of such occupied sites (denoted as \( M+MH \)) is able to effuse as molecular hydrogen as given by:

\[
2MH^* \rightarrow 2M^* + H_2(g),
\]

(4.7)
in which surface groups are denoted with an asterisk. This is implemented by the following differential equations:

\[
\frac{d[H]_{\text{ambient}}}{dt} = +k_{eff,H}[M]H^2,
\]

(4.8a)

\[
\frac{d[M]}{dt} = +2k_{eff,H}[M]H^2 - k_{MH}[M][H]_{i=1},
\]

(4.8b)

\[
\frac{d[MH]}{dt} = -2k_{eff,H}[M]H^2 + k_{MH}[M][H]_{i=1},
\]

(4.8c)

\[
\frac{d[H]_{i=1}}{dt} = -k_{MH}[M][H]_{i=1} + D_{H,\text{bulk}} \frac{[H]_{i=2}-[H]_{i=1}}{\Delta x^2},
\]

(4.8d)
in which \([H]_{\text{ambient}}\) is the molecular hydrogen released from the surface, \([H]_{i=1}\) the atomic hydrogen concentration in highest bulk sublayer, closest to the sample surface, and \([H]_{i=2}\) is the atomic hydrogen concentration in the second highest bulk sublayer. Because any decrease of available empty sites leads to a similar increase in occupied sites \( M+MH \) stays equal to the starting value of \( M \) (i.e. all surface sites are initially empty) over time.

Next, the interfacial processes are included in differential equations. The interfacial silicon oxide is described by \( m \) sublayers given by \( m=d_{\text{interface}}/\Delta x \). Diffusion in the \( x \)-direction is included similar as equation (4.6) in which \( D_{H,\text{bulk}} \) is changed by the diffusion coefficient in the interfacial oxide \( D_{H,\text{int}} \). In order to prevent an unwanted source or sink to appear, the first interfacial sublayer, \([H]_{j=1}\), has to take both diffusion coefficients into account:

\[
\frac{d[H]_{j=1}}{dt} = +D_{H,\text{int}} \frac{[H]_{j=2}-[H]_{j=1}}{\Delta x^2} - D_{H,\text{bulk}} \frac{[H]_{j=1}-[H]_{j=n}}{\Delta x^2},
\]

(4.9)
in which \([H]_{j=1}\) and \([H]_{j=2}\) are the atomic hydrogen concentration of the first and second interface sublayer, respectively, and \([H]_{j=n}\) is the hydrogen concentration in the deepest bulk sublayer.

Hydrogen that reaches the silicon surface \( (x=d_{\text{bulk}}+d_{\text{interface}}) \) is able to passivate dangling bonds. In order to take passivation of dangling bonds into account, two extra concentrations, \([S]\) and \([SH]\), are defined. These are the surface concentration of dangling bonds and passivated dangling bonds in cm\(^{-2}\), respectively. It is assumed that hydrogen available in the deepest interfacial sublayer, \([H]_{j=m}\), is able to react with dangling bonds with a reaction rate \( k_{SH} \). For temperatures higher than 400 °C, Si-H bonds can be broken \([49, 50, 51, 52] \). This reverse reaction is included using an additional rate \( k_S \). Note that in this definition the unit of \( k_S \) (s\(^{-1}\)) differs from that of \( k_{SH} \) (cm\(^3\) s\(^{-1}\)). The following differential equations are included for passivation:

\[
\frac{d[H]_{j=m}}{dt} = -D_{H,\text{int}} \frac{[H]_{j=m}-[H]_{j=m-1}}{\Delta x^2} - k_{SH}[H]_{j=m}[S] + k_S[SH],
\]

(4.10a)
\[ \frac{d[H_{\text{ij}}]}{dt} = -k_{\text{SH}}[H]_{\text{ij}=m}[S] + k_{\text{SH}}[SH] \]  
\[ \frac{d[SH]}{dt} = +k_{\text{SH}}[H]_{\text{ij}=m}[S] - k_{\text{SH}}[SH] \]

in which \([H]_{\text{ij,m}}\) is the atomic hydrogen concentration in the deepest interfacial sublayer.

Next, the reaction to molecular hydrogen in the interfacial region is included. It is assumed that this reaction takes place inside the interfacial silicon oxide (at any location in this interfacial silicon oxide). Therefore, each differential equation for the hydrogen concentration in an interfacial sublayer, \([H]_{\text{ij}}\), is expanded with a reaction term:

\[ \frac{d[H_{\text{ij}}]}{dt} = +D_{\text{H2,int}} \frac{[H_{\text{ij+1}}]-[H_{\text{ij}}]}{\Delta x^2} - D_{\text{H2,int}} \frac{[H_{\text{ij}}]-[H_{\text{ij-1}}]}{\Delta x^2} - 2k_{\text{H2}}[H]_{\text{ij}}^2 \]

in which \(k_{\text{H2}}\) is the reaction rate of molecular hydrogen formation. For this species, no reverse reaction is included. The molecular hydrogen that is formed is represented by its own differential equation for each sublayer:

\[ \frac{d[H_{\text{ij}}]}{dt} = +D_{\text{H2,int}} \frac{[H_{\text{ij+1}}]-[H_{\text{ij}}]}{\Delta x^2} - D_{\text{H2,int}} \frac{[H_{\text{ij}}]-[H_{\text{ij-1}}]}{\Delta x^2} + k_{\text{H2}}[H]_{\text{ij}}^2 \]

in which \(D_{\text{H2,int}}\) is the diffusion coefficient of molecular hydrogen in the interfacial oxide. Similarly to atomic hydrogen, the bulk diffusion of \(H_2\) is included. Therefore, the parameter \(D_{\text{H2,bulk}}\) is introduced as the diffusion coefficient of \(H_2\) in the bulk. Note that effusion from the sample into the ambient is not taken into account for the \([H_2]\) differential equations, since \(H_2\) forms the trapped species near the interface.

In this model the delamination of the film is not explicitly taken into account. The likelihood for a blister to form is, therefore, quantified by the amount of molecular hydrogen trapped in the interfacial silicon oxide. The system now contains \(5 + 2n + 2m\) coupled differential equations:

- 1 equation for the amount of \(H_2\) in the environment,
- 2 equations describing the surface: \([M]\) and \([MH]\),
- \(n+m\) equations describing \([H]\) in the system,
- 2 equations describing the passivation: \([S]\) and \([SH]\),
- \(n+m\) equations describing \([H_2]\) in the system.

The differential equations are numerically solved using the ode15s solver from the matlab library [S8]. An anneal is simulated by assuming constant values for the coefficients, meaning that heating and cooling of the sample is not taken into account and the temperature is reached instantaneously at \(t=0\) s. This assumption is plausible because the temperature treatments for this project are executed using the Levitor system. As mentioned earlier this Rapid Temperature Processing tool reaches very high heat-up and cool down rates. The ramping times are much shorter than the soak-time. Therefore, the temperature profile of the anneal can be approximated as a step function, which is done in the simulations.

The outcome of the numerical calculation is a matrix containing the time-evolution of the concentration in each sublayer. This allows visualization of the hydrogen content in the system as shown in Figure 4.3. In this example the bulk and silicon oxide thicknesses are 24 nm and 1 nm, respectively. A sublayer thickness of 1 angstrom is used meaning \(n=240\) and \(m=10\). This choice resulted from a convergence check, which is discussed in the next section. For this simulation, a diffusion coefficient of \(10^{-13}\) cm\(^2\)/s is taken for atomic hydrogen in the bulk. Furthermore, the profile in the interfacial SiO\(_x\) is flat, since diffusion in this interfacial layer is assumed to be fast with respect to bulk diffusion, as will be explained, along with all other
Figure 4.3: An example of a result from a simulation showing the time-evolution of the atomic hydrogen concentration in the system. The Si/SiO$_x$/Al$_2$O$_3$ system is visualized in a similar way as in Figure 4.1a. The starting value in the Al$_2$O$_3$ bulk is based on the SIMS measurements discussed in Section 3.5. It is assumed that the interface contains no hydrogen at the start. The time-evolution shows effusion at the surface ($x = 0$) and the filling of the interfacial region ($24$ nm $< x < 25$ nm). The interface profile is flat since diffusion here is fast with respect to bulk diffusion, as will be discussed in Section 4.3, along with other details of this simulation.

details, in Section 4.3. An overview of all associated differential equations for this system is provided in Table 4.1 and the complete script can be found in Appendix C.

Table 4.1: An overview of all the differential equations used to simulate the system. For this overview 240 bulk sublayers ($n=240$) and 10 interface sublayers ($m=10$) are used. All sublayers are denoted by the overall index $l$.

<table>
<thead>
<tr>
<th>Index</th>
<th>Differential equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
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<tr>
<td>[MH]</td>
<td>$l=2$</td>
</tr>
<tr>
<td>[M]</td>
<td>$l=3$</td>
</tr>
<tr>
<td>[H] in Bulk top layer</td>
<td>$l=4$</td>
</tr>
<tr>
<td>[H] in Bulk Al$_2$O$_3$</td>
<td>$5&lt;l&lt;243$</td>
</tr>
<tr>
<td>[H] in highest Interfacial layer</td>
<td>$l=244$</td>
</tr>
<tr>
<td>[H] in Interfacial SiO$_x$</td>
<td>$245&lt;l&lt;252$</td>
</tr>
<tr>
<td>[H] in deepest interfacial layer</td>
<td>$l=253$</td>
</tr>
<tr>
<td>Dangling bonds S</td>
<td>$l=254$</td>
</tr>
<tr>
<td>Si-H bonds</td>
<td>$l=255$</td>
</tr>
<tr>
<td>[H$_2$] in Bulk top layer</td>
<td>$l=256$</td>
</tr>
</tbody>
</table>
CHAPTER 4: PHYSICAL MODEL OF BLISTER FORMATION: NUMERICAL SIMULATIONS

<table>
<thead>
<tr>
<th>[H₂] in bulk Al₂O₃</th>
<th>257 &lt; l &lt; 495</th>
<th>( \frac{d[H_2]}{dt} = D_{H_2, bulk} \frac{[H_2]<em>{l+1} - [H_2]</em>{l}}{\Delta x^2} - D_{H_2, bulk} \frac{[H_2]<em>{l} - [H_2]</em>{l-1}}{\Delta x^2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H₂] in highest interfacial layer</td>
<td>l=496</td>
<td>( \frac{d[H_2]}{dt} = D_{H_2, int} \frac{[H_2]<em>{497} - [H_2]</em>{496}}{\Delta x^2} - D_{H_2, int} \frac{[H_2]<em>{496} - [H_2]</em>{495}}{\Delta x^2} + k_{H_2}[H]^2 )</td>
</tr>
<tr>
<td>[H₂] in interfacial SiOₓ</td>
<td>497 &lt; l &lt; 504</td>
<td>( \frac{d[H_2]}{dt} = D_{H_2, int} \frac{[H_2]<em>{497} - [H_2]</em>{496}}{\Delta x^2} - D_{H_2, int} \frac{[H_2]<em>{496} - [H_2]</em>{495}}{\Delta x^2} + k_{H_2}[H]^2 )</td>
</tr>
<tr>
<td>[H₂] in deepest interfacial layer</td>
<td>l=505</td>
<td>( \frac{d[H_2]}{dt} = -D_{H_2, int} \frac{[H_2]<em>{505} - [H_2]</em>{504}}{\Delta x^2} + k_{H_2}[H]^2 )</td>
</tr>
</tbody>
</table>

### 4.2 Convergence

Before the influence of each parameter is studied, the convergence of the numerical method is proven. This is done in two steps. First, the theoretical solution of equation (4.4) is compared to the numerical outcome of a diffusion simulation. For this simulation, a 40 nm thick hydrogen containing layer is defined and the hydrogen is allowed to diffuse into its surroundings. For this diffusion a constant diffusion coefficient is used for all values of \( x \), as was done when deriving the theoretical solution. The outcome of this diffusion is shown in Figure 4.4a. The squares show the numerical solution for several times, while the black lines show the associated analytical outcome. In this simulation, forty sublayers are used. The numerical solution shows perfect agreement with the analytical one. This is also visible in Figure 4.4b, in which the time evolution is shown for \( x = 5, 10, 50 \) and 70 nm. In Figure 4.4c, the difference between the numerical and theoretical solution, defined as \( \delta \), is plotted as a function of the number of sublayers \( n \). The graph shows an oscillating pattern with decreasing amplitude. This graph clearly shows that \( \delta \) converges to zero for increasing \( n \). For \( n=41 (\Delta x \approx 1 \text{ nm}) \), the found delta is already below \( 10^{-2} \).

Next, the convergence of the Si/SiOₓ/Al₂O₃ system is demonstrated. This is done by evaluating the final concentration of a sublayer as a function of the number of layers in the system. A thickness of 24 nm is used for the film and 1 nm for the interface. The values for coefficients will be described in the following section. The concentration for the deepest interfacial sublayer is shown in Figure 4.5 (red line) and it clearly convergences. The difference with the value for \( n=1500 \) is also included (black line). For \( n>200 \), the difference with the final value is lower than 10%. Because of this, and practical reasons such as calculation time restrictions, it is decided that 240 sublayers are sufficient to simulate the 24 nm thick film, meaning \( \Delta x=0.1 \text{ nm} \).

Figure 4.4: Figure (a) shows both the analytical (black lines) and numerical (dots) solution of the diffusion process of a rectangular hydrogen profile in a uniform medium for different times. The rectangle is divided into 200 sublayers (n=200) for this simulation. Figure (b) shows the time-evolution of several of these sublayers for both solutions. In Figure (c), the difference between both solutions, \( \delta \), at \( x=10 \) is plotted as a function of the number of sublayers \( n \).
4.3 Parameter Study

4.3.1. Starting Conditions

In this section, the individual influence of different parameters is studied. First, the starting conditions are defined. A bulk thickness of 24 nm is chosen with an interface thickness of 1 nm. It is assumed that at time $t=0$, the bulk has a constant hydrogen concentration $[H_0]$ and the interface contains no atomic or molecular hydrogen. A value of $[H_0] = 8 \cdot 10^{21} \text{ cm}^{-3}$ is chosen based on SIMS measurements of the as-deposited samples shown in Figure 3.13. For the coefficient, $D_{H,\text{bulk}}$ an estimation is made using the approximation of the typical diffusion length that was found in Section 3.1. The experiments of Section 3.1 revealed a first order approximation for the diffusion length of atomic hydrogen diffusion in the bulk of 10 nm for an 800 °C, 30 second anneal. Squaring this length and dividing it by the time provides an estimation of $D_{H,\text{bulk}} \approx 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for the diffusion coefficient. Although this is a very rough estimate it is not unrealistic. For most simulations the bulk diffusion coefficient is assumed to be a bit higher, i.e. $D_{H,\text{bulk}} \approx 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. An estimate for diffusion in the interfacial oxide is made using the observation of Figure 3.2 in which lateral diffusion was observed. This result showed that the diffusion distance during the anneal is in the order of 100 µm. This number is used for an estimate of the diffusion coefficient for atomic hydrogen in the interface during the 30 second anneal: $D_{H,\text{int}} \approx 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. It was expected that this diffusion takes place in the interfacial SiOₓ. Because diffusion is high in the lateral direction in the SiOₓ it is possibly also quite high for the $x$-direction. Furthermore, the interfacial region is thin compared to the rest of the system. Therefore, it is assumed that the concentration at this interface region is constant. This is implemented in the model by setting the diffusion coefficient in the interfacial sublayers a factor hundred times higher than for bulk sublayers, causing the concentration profile in the interface to be constant (flat profile), so $D_{H,\text{int}} = 100 \cdot D_{H,\text{bulk}}$. Furthermore, it is assumed that surface sites tend to become occupied fast with respect to diffusion, which is implemented by choosing a high value for $k_{MH}$, i.e. $k_{MH}=1 \text{ cm}^3 \text{ s}^{-1}$. The starting value for the surface sites is chosen to be $1$.

Figure 4.5: The final concentration in the last interfacial sublayer (red) as a function of the number of bulk sublayers $n$ employed in the simulations. The difference with the value for $n=1500$ is included (black). The convergence of the system is clearly visible. For $n>200$, 90% of the final value is reached. For this, and practical reasons, $n=240$ is chosen for the simulations described in the next sections.

$^{1}$ For this estimate $l^2/t$ is used in which $l$ is the found diffusing distance and $t$ the annealing time.
10^{14} \text{ cm}^{-2} \) empty ones and zero occupied ones. Usable values for the other parameters are deduced along the way. The values described above are summarized in Table 4.2.

<table>
<thead>
<tr>
<th>( H_0 ) (cm(^{-3}))</th>
<th>( D_{H,\text{bulk}} ) (cm(^2) s(^{-1}))</th>
<th>( D_{H,\text{int}} ) (cm(^2) s(^{-1}))</th>
<th>( k_{\text{MH}} ) (cm(^3) s(^{-1}))</th>
<th>[M] (cm(^{-2}))</th>
<th>[MH] (cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 8 \cdot 10^{21} )</td>
<td>( 10^{-13} )</td>
<td>( 10^{-11} )</td>
<td>1</td>
<td>( 10^{14} )</td>
<td>0</td>
</tr>
</tbody>
</table>

4.3.2. Diffusion and Effusion

In the parameter study the following questions are discussed:

- How does the system evolve over time?
- What is the influence on the concentration profiles of:
  - \( D_{H,\text{bulk}} \) and \( k_{\text{eff,H}} \)?
  - \( k_S \) and \( k_{SH} \)?
  - \( k_{H2} \)?

Figure 4.3 of Section 4.1 shows the evolution of the system over time for \( D_{H,\text{bulk}} = 10^{-13} \text{ cm}^2/\text{s} \) and \( k_{\text{eff,H}} = 10^{-6} \text{ cm}^2/\text{s} \). This diffusion coefficient is chosen to be a factor 10 larger than deduced above for a good visualization of processes, while the effusion coefficient is solely based on proper visualization of the processes and the profiles. An anneal with a duration of 30 seconds is simulated. In this system no passivation and \( H_2 \) formation is taken into account yet. Two processes are clearly visible in the time evolution. First, effusion of hydrogen takes place at the surface of the sample resulting in a decrease of the concentration near \( x=0 \). Secondly, a flux of atomic hydrogen from the bulk fills the interfacial oxide. The interface concentration increases until it is similar to that of the deepest bulk layers. These processes are further studied by variation of \( D_{H,\text{bulk}} \) and \( k_{\text{eff,H}} \). These results are shown in Figure 4.6. The graph only shows the final profiles \( (t=30 \text{ s}) \).

In Figure 4.6a, again effusion takes place at the surface and the interface is filled due to diffusion. For high values of \( D_{H,\text{bulk}} \), more diffusion takes place. This means that the diffusion process is able to flatten the concentration profile faster. This shows that the diffusion coefficient is a measure for the ability of diffusion to flatten any gradient in the profile. This influence of the bulk diffusion coefficient is also indicated by additional SIMS measurements, included in Appendix E. For high diffusion coefficients, the 30 seconds timeframe of the
simulation shown in Figure 4.6 is enough to divide all hydrogen equally and create an almost horizontal profile. The amount of atomic hydrogen lost from the system depends on $k_{\text{eff},H}$. The results in Figure 4.6b show that the effusion coefficient is responsible for the overall height of the profile and only for high effusions rates a slope in the profile appears. Therefore, the effusion coefficient forms a measure for the rate at which hydrogen is removed from the system. These simulations illustrate two basic types of diffusion in the system. If effusion is fast and diffusion slow, the surface concentration goes to zero and steep slopes appear in the profile. The process is now diffusion limited. If on the other hand, diffusion is fast and effusion is slow, the fast diffusion will cancel out all concentration gradients and the height of the flat concentration profile is determined by the value of the effusion coefficient. The process is now effusion limited. For this annealing time, values of $10^{-15}$ cm$^2$/s < $D_{H,\text{bulk}}$ < $10^{-12}$ cm$^2$/s show the relevant regime. If the diffusion is lower than $10^{-15}$ cm$^2$/s, no significant changes occur in 30 seconds. If the bulk diffusion coefficient is larger than $10^{-12}$ cm$^2$/s, no difference with $D_{H,\text{bulk}}=10^{-12}$ cm$^2$/s can be observed since the profile is horizontal. For the effusion-simulations shown in 4.6b, the used domain for $k_{\text{eff},H}$ is [10$^{-7}$, 2.7 · 10$^{-6}$] cm$^2$/s. Figure 3.13 shows flat hydrogen profiles in the bulk measured by SIMS. This indicates an effusion limited process. Compared to the simulations, this would entail that $D_{H,\text{bulk}} \geq 10^{-12}$ cm$^2$/s.

4.3.3. Passivation

Next, passivation is included in the simulations. It is chosen to keep the values for the bulk diffusion coefficient similar to the earlier used value of $D_{H,\text{bulk}}=10^{-13}$ cm$^2$/s. As the starting condition for the number of dangling bonds $[S]$ a value of $6.8 \cdot 10^{12}$ cm$^{-2}$ is used. This number is based on a perfect silicon surface (6.8 · 10$^{14}$ silicon atoms/cm$^2$ [54]) of which 1% forms a dangling bond [31, 50, 55]. Note that no passivated dangling bonds are taken into account at t=0, meaning $[SH] = 0$ cm$^{-2}$. The numerical solution for the surface concentration of available and passivated dangling bonds is shown in Figure 4.7 for two values of the reaction rates $k_S$. These results show that the atomic hydrogen starts to passivate the dangling bonds as soon as it reaches the Si/SiO$_x$ interface. If the reverse reaction happens fast enough, an equilibrium is reached in which not all bonds are passivated. Note the large differences in the order of magnitude of $k_{SH}$ and $k_S$. In the differential equation, $k_{SH}$ is multiplied by $[H]$ and $[S]$, while $k_S$ is multiplied by $[HS]$. Since $[H]$ is in the order of 10$^{21}$, the rate coefficients also differs around this many orders. Consequently, both parameters, $k_{SH}$ and $k_S$, describe different physical processes. $k_{SH}$ describes the rate of a reaction in which two species have to combine, while $k_S$ is the frequency at which a certain bond breaks for a given temperature.

The number of dangling bonds used in these simulations is in the order of $10^{12}$ cm$^2$. Therefore, the maximum number of hydrogen atoms used for passivation is also $10^{12}$ cm$^2$. Note that this can be less if not all dangling bonds are passivated, depending on rate of the reverse, Si-H bond breaking, reaction. This number is much lower than the available hydrogen atoms in the films. Therefore, the inclusion of passivation does not have a visible effect on the hydrogen profiles. This is consistent with the findings of Section 3.4.3, where it was calculated that the bonding of 1% of the silicon surface bonded with hydrogen is insignificant to the number of hydrogen atoms being available in the Al$_2$O$_3$ film.
4.3.4. \( \text{H}_2 \) Formation

Finally, the reaction to \( \text{H}_2 \) is included in the sublayers of the interfacial oxide as provided by equation (4.11) and (4.12). The solution of this system is shown in Figure 4.8. For these simulations it is assumed that the diffusion coefficients for molecular hydrogen are e.g. 2 orders in magnitude lower than those of atomic hydrogen. Figure 4.8a shows that the concentration of atomic hydrogen now stays lower near the interface since molecular hydrogen is created. The molecular hydrogen concentration profile is shown in Figure 4.8b. Because of the low bulk diffusion coefficient for molecular hydrogen, \( D_{\text{H}_2, \text{bulk}} \), diffusion of \( \text{H}_2 \) into the \( \text{Al}_2\text{O}_3 \) film is slow. This causes a high concentration to occur in the interfacial region, thereby showing that indeed molecular hydrogen becomes ‘trapped’ at the interface.

However, since the exact mechanism of the diffusion in the \( \text{Al}_2\text{O}_3 \) film is unknown, it is hard to compare the found values for the diffusion coefficients with literature values. In literature several values for diffusion coefficients of hydrogen species can be found. Doremus et al. report experimental values of \( 10^{-7} \) cm\(^2\)/s and \( 10^{-11} \) cm\(^2\)/s for diffusion of \( \text{H}_2 \) and \( \text{H}_2\text{O} \), respectively, in crystalline alumina at \( T=800 \) °C [59]. Simulations done by Belonoshko et al. showed values of \( 10^{-6} \) cm\(^2\)/s for \( \text{H}_2 \) diffusion in liquid alumina [60]. These values are all several order of magnitude higher with respect to value found by the simulations in this project. Therefore, if the literature values for \( \text{H}_2 \) are used in the simulations, no trapping will occur at the interface and all concentrations are equally spaced in the system. However, the comparison between the values from the simulations and those from literature is poor, since they are measured for different types of aluminum oxide than ALD \( \text{Al}_2\text{O}_3 \). Furthermore, these literature values are determined using permeability tests, which use different techniques than SIMS measurements. Therefore, the literature values might not be based on a similar type of diffusion, i.e. one that involves bond breaking.

An overview of the used coefficients for this, and the other simulations of this chapter, is shown in Table 4.3. In this table the varied parameters are noted bold and underlined. In this table the outline of the parameter study is clearly visible. First, the diffusion and effusion was simulated. Then, passivation and molecular hydrogen formation were added to come to the complete model in which trapping in the interface took place.
Table 4.3: An overview of the used values for all relevant coefficients for the simulations discussed in Section 4.3. The varied parameters are noted bold and underlined.

<table>
<thead>
<tr>
<th>Figure</th>
<th>$D_{H_{\text{bulk}}}$ (cm$^2$ s$^{-1}$)</th>
<th>$D_{H_{\text{int}}}$ (cm$^2$ s$^{-1}$)</th>
<th>$k_{\text{MH}}$ (cm$^3$ s$^{-1}$)</th>
<th>$k_{\text{eff, H}}$ (cm$^2$ s$^{-1}$)</th>
<th>$k_{\text{SH}}$ (cm$^3$ s$^{-1}$)</th>
<th>$k_s$ (cm$^3$ s$^{-1}$)</th>
<th>$k_{\text{H}_2}$ (cm$^3$ s$^{-1}$)</th>
<th>$D_{\text{H}<em>2</em>{\text{bulk}}}$ (cm$^2$ s$^{-1}$)</th>
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<td>$10^{-15}$</td>
<td>$10^{-13}$</td>
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</table>

4.4 Conclusion

In this chapter, a numerical framework was developed to study the suggested physical model by simulations. This numerical script included diffusion of atomic hydrogen in the Al$_2$O$_3$ bulk, effusion at the film’s surface, passivation at the Si/SiO$_x$ interface, the formation of H$_2$ in the interfacial silicon oxide and trapping of this H$_2$ in this interfacial region. In this framework, the Si/SiO$_x$/Al$_2$O$_3$ system was divided into sublayers and the mechanisms mentioned above were included in the differential equations that describe the processes in each sublayer. By doing so, we were able to study the influence of each separate mechanism on the hydrogen species in the system.

The influence of the diffusion and effusion, when relating the data to SIMS measurements of the hydrogen content, revealed an effusion limited process. Furthermore, since an excess of hydrogen is available in the film, no influence of the passivation was found on the concentration profiles for both atomic and molecular hydrogen. Since a uniform film was assumed in the lateral direction, the lateral diffusion did not have to be taken into account in the model in order to create the H$_2$ concentration to pile up in the interface. This shows that, although experiments show that lateral diffusion is present during an anneal, it is not essential to explain blister formation. Finally, it was shown that indeed trapping of molecular hydrogen can take place leading to very high H$_2$ concentrations in the interfacial oxide.
Conclusions and Outlook

In this project, blister formation in spatial ALD Al₂O₃ films was researched. This was done by answering three central questions regarding (1) the shape of the blisters and their observation, (2) the parameters and physical mechanisms that lead to blister formation and (3) the possibility to numerically simulate these mechanisms.

Firstly, several microscopy techniques and an AFM study were used to investigate the appearance and properties of blisters. It was shown that blisters have similar shapes, which could be approximated by using a section of a sphere. This allowed the introduction of the blister volume as a new quantity. The values for this and other quantities were discussed in detail.

Furthermore, experimental results showed that blisters can occur after annealing the film depending on the film thickness, the annealing temperature, the surface of the substrate and the deposition conditions of the Al₂O₃ film itself. From these experiments, it was concluded that blisters are caused by hydrogen diffusion in the film, which can lead to accumulation in the interfacial silicon, leading to blistering. This accumulation depends on the film density and hydrogen concentration. For the first time, the found mechanisms were combined in a physical model explaining blister formation.

Additionally, numerical simulations implementing this model were executed showing the influence of several of the underlying mechanisms. Also the conditions for trapping of molecular hydrogen were studied. The experiments, the model and the simulations provide much insight on what blisters are and which parameters are relevant for their formation.

Since this insight is now available, the focus for future research should be aimed at several open questions that are yet to be answered to provide a more detailed description of blister formation. Firstly, one should focus on which species are trapped in the interface and therefore cause the pressure build-up that leads to delamination of the film. In this project it was assumed that the trapped species was molecular hydrogen. Answering this question would allow important extension of the proposed physical model. Furthermore, similar questions concern both diffusion in the film and diffusion lateral to the interface. Although this work proves that both mechanisms are relevant for blister formation, future studies should focus on the details of the diffusing species, their activation energies and the transport mechanisms.

For such studies, the use of the numerical script shows great potential. A possible experimental approach is to create a slope in the hydrogen concentration in the Al₂O₃ film by means of a very short, high temperature anneal. The numerical model could then be used to fit this hydrogen concentration to that of the actual film measured by SIMS. By doing so, it might be possible to deduce the diffusion coefficient for bulk diffusion of hydrogen. Furthermore, thermal programmed desorption measurements could be simulated with the numerical model designed in this project in order to fit effusion parameters and to obtain knowledge on diffusion in the film. Several other relevant possibilities for future research could be suggested, such as an investigation of the question when blisters are formed during the anneal. The answer to this question would greatly contribute to knowledge on blister formation and could improve the suggested physical model. Another important issue that is yet to be answered in detail is the influence of blistering on the lifetime of the charge carriers and therefore on the efficiency of the solar cell.

Overall, a deeper understanding of blister formation will contribute to strategic decision making in how to prevent blister formation during the solar cell production. Furthermore, the use of the proposed
physical model in combination with research on the aforementioned issues will provide a thorough understanding of the hydrogen dynamics near the Si/Al$_2$O$_3$ interface.
Acknowledgements

For this graduation project, I had the opportunity to work at Levitech BV in Almere. During the year I spent there, I received much support and help from many of my co-workers. Not only did they supervise me while using the equipment, but they were always kind enough to brainstorm and discuss several issues of my research. Therefore, I want to thank the entire Levitech team, both in the Netherlands as in Belgium, for their help. Without their support I would simply not have been able to do this work. A special thanks goes to Ernst for supervising my project. He provided direction and input that was essential for the successful execution of the research. I explicitly want to thank him for providing me with the opportunity to attend the 38th Photovoltaic Specialist Conference in Austin. This formed a goal for my work and a great experience for me as a future engineer. I also gained much relevant learning points by writing the manuscript and making the poster, which are included in this report in Appendix F.

Besides the support I received from the people from Levitech, I was also helped by several persons from the Plasma & Materials Processing group. In particular, the support I received from Wytze, Cristian and Bart was very helpful for my experimental results. Obviously, a special thanks goes to Erwin, whose input and supervision contributed significantly to the project. I found collaborating with both Erwin as Ernst very instructive.

Overall, this project was a great experience for me that provided many new learning points and I enjoyed collaborating with everyone.
References


REFERENCES


Appendix A: The RTP Levitor Tool

In this research all the samples received their thermal treatment in by rapid thermal processing (RTP) in the Levitor tool. This machine is developed for the semi-conductor industry. The Levitor uses heat conduction through a thin gas layer to realize very high heat-up rates [44]. The wafer levitates on a N₂ gas cushion between two heater blocks. The distance between the sample and the heaters is 150 µm. Because of this small distance, conduction of heat takes place very effectively and the sample is ramped up to the set-point temperature quickly. A schematic image of the Levitor principle is shown in Figure A.1a. A typical temperature profile for a silicon wafer processed in the Levitor at 800 °C for 30 seconds is included in Figure A.1b.

As shown in the temperature profile profile, the heat-up rates of the sample are large in the Levitor. Both the heating as the cooling takes only several seconds. It should be noted that, a belt furnace is the preferred choice in solar industry. In such a system, wafers are transported on a belt passing several arrays of heating lamps. This allows the high throughput processing required in solar cell manufacturing. The wafers heat up rates in a belt furnace are lower than in the Levitor. As concluded by this research diffusion of hydrogen in the Al₂O₃ film is of major importance to blister formation. The difference in temperature profile between the Levitor and belt furnace systems forms a limitation when comparing the outcomes of the samples in this project with those done in a furnace belt.

Figure A.1: (a) A schematic overview of a half cross-section of the RTP Levitor tool. Two heater blocks (orange) heat up a wafer (grey) by heat conduction using the gas flowing through the system. Figure (b) shows a typical temperature profile in °C for a silicon wafer in the Levitor, processed at 800 °C for 30 seconds.
Appendix B: Calculating Blister Quantities

Blisters are captured by optical microscopy. From these images the used quantities as shown in Table B.1 are calculated for quantitative analysis of the experiment. First, the blisters are selected using the Olympus Stream software package. Although attempts are done to automate this selection, it proved to be more time effective to do it manually. A screenshot of this process is shown in Figure B.1. Since the magnification used is known, the software is able to automatically provide the diameter and area for each selected blister.

From these measurements the other variables can be determined. From all the counted blisters, the average diameter $D_{av}$ and average surface $A_{av}$ are determined. Their associated errors are given by the $1\sigma$ of the spread in values, calculated using Poisson statistics. From these average values, all the other measures are calculated using the formulas provided in Table B.1. For the volume calculations, the height-radius ratio of 0.26±0.02 is used, as shown in Section 2.3. Figure B.2 shows a schematic image of the shape that is used to approximate the blister and the accompanying variables.

In these equations $D_i$ and $A_i$ are the diameter and area of blister $i$, $N_{\text{photo}}$ and $A_{\text{photo}}$ are the total number of used photos and the area of one photo, respectively. The other symbols are explained by Figure 2.6.

![Figure B.1: A screenshot of the Olympus Stream software package in which several blisters are selected (red circles).](image-url)
Table B.1: An overview of all the used equations for the data analysis including their error calculation.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Equation</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{av}$</td>
<td>$D_{av} = \frac{\sum D_i}{N}$</td>
<td>$\sigma_{D_{av}} = \frac{\sigma_D}{\sqrt{N}}$</td>
</tr>
<tr>
<td>$A_{av}$</td>
<td>$A_{av} = \frac{\sum A_i}{N}$</td>
<td>$\sigma_{A_{av}} = \frac{\sigma_A}{\sqrt{N}}$</td>
</tr>
<tr>
<td>$n$</td>
<td>$n = \frac{N}{N_{photo} \cdot A_{photo}}$</td>
<td>$\sigma_n = \frac{\sqrt{N}}{N_{photo} \cdot A_{photo}}$</td>
</tr>
<tr>
<td>$S$</td>
<td>$S = A_{av} \cdot n$</td>
<td>$\sigma_S = \sqrt{A_{av}^2 \cdot \sigma_A^2 + S^2 \cdot \sigma_{A_{av}}^2}$</td>
</tr>
<tr>
<td>$r$</td>
<td>$r = \frac{D}{2}$</td>
<td>$\sigma_r = \frac{\sigma_{D_{av}}}{2}$</td>
</tr>
<tr>
<td>$H/r$</td>
<td>0.26</td>
<td>0.02</td>
</tr>
<tr>
<td>$H$</td>
<td>$H = 0.26 \cdot r$</td>
<td>$\sigma_H = \sqrt{r_{av}^2 \cdot 0.02^2 + 0.26^2 \cdot \sigma_{r_{av}}^2}$</td>
</tr>
<tr>
<td>$R$</td>
<td>$R = \frac{1}{2H} (r^2 + H^2)$</td>
<td>$\sigma_R = \sqrt{\left(\frac{r}{H}\right)^2 \cdot \sigma_r^2 + \left(\frac{1}{2} - \frac{1}{2} \left(\frac{r}{H}\right)^2\right)^2 \cdot \sigma_H^2}$</td>
</tr>
<tr>
<td>$V$</td>
<td>$V = \frac{2}{3} \pi R^3 \left(\frac{3}{2} \frac{H}{R}^2 - \frac{1}{2} \frac{H}{R}\right)^3$</td>
<td>$\sigma_V = \sqrt{(\pi \cdot H^2)^2 \cdot \sigma_R^2 + (\pi (2R - 1)H)^2 \cdot \sigma_H^2}$</td>
</tr>
<tr>
<td>$V_{total}$</td>
<td>$V_{total} = V \cdot n$</td>
<td>$\sigma_{V_{total}} = \sqrt{V^2 \cdot \sigma_V^2 + n^2 \cdot \sigma_V^2}$</td>
</tr>
</tbody>
</table>
Appendix C: Carbon Depth Profiles

Besides the hydrogen profiles discussed previously, carbon profiles were also measured by SiMS. The carbon profiles for the different deposition temperatures are shown in Figure C.1a. Again the bulk values are discussed since both the surface and interface features are inaccurate. The carbon concentrations in the film are around $2 \times 10^{20}$ atoms/cm$^3$ which is a below 1% atomic percent of the Al$_2$O$_3$ films. Just as for the hydrogen profiles, the carbon concentration decreases for a higher deposition temperature with the exception of the $T_{\text{dep}}=250$ °C sample. Figure C.1b shows the carbon contamination profiles for the different anneals of the $T_{\text{dep}}=200$ °C sample. These plots clearly show that no significant changes in carbon concentration and distribution in the Al$_2$O$_3$ film takes place during an anneal. The hydrogen-carbon ratio was investigated and showed no consistent data. It is therefore concluded that carbon contamination in the film is not directly related to blister formation.

Figure C.1: The carbon concentration profiles in the Al$_2$O$_3$ film as a function of normalized film depth for (a) several deposition conditions (as-deposited) and (b) several temperature treatments for $T_{\text{dep}}=200$ °C deposited samples.
Appendix D: The Script used for Simulating the Blister Formation

The numerical method described in Chapter 4 consists out of 3 scripts. These scripts are included subsequently in this appendix. The first script is called \textit{model\_functions} and contains the differential equations. In this script all parameters, such as starting values for the equations, coefficients and the timespan, are included as arguments. These parameters are defined in the script \textit{model\_solver} which also invokes \textit{model\_functions} using the \textit{ode15s} solver for coupled differential equations from the Matlab library. By running the \textit{model\_solver} script the time evolution of the system is solved and a matrix, \( y \), with the values for each concentration at each time is created. This matrix is then used in the script \textit{model\_visualization} to visualize the concentrations in the system as used in the graphs of Chapter 4.
function dydt = system1_functions(t, y, dx, n_bulk, n_interface, D_H_bulk, D_H_int, k_eff_H, k_H2, D_H2_bulk, D_H2_int, k_SH, k_S, k_MH)

    dydt = zeros(1+2+n_bulk+n_interface+n_bulk+n_interface+2,1);

    %environment H2
    dydt(1)=+k_eff_H*y(2)^2;

    %[MH]
    dydt(2)=+k_MH*y(4)*y(3)-2*k_eff_H*y(2)^2;

    %[M]
    dydt(3)=-k_MH*y(4)*y(3)+2*k_eff_H*y(2)^2;

    %surface H (top bulk layer)
    dydt(4)=-k_MH*y(4)*y(3)+D_H_bulk*(y(5)-y(4))/(dx^2);

    %bulk H (without top bulk layer)
    i=5;
    while i<n_bulk+4
        dydt(i)=-D_H_bulk*(y(i)-y(i-1))/(dx^2)+D_H_bulk*(y(i+1)-y(i))/(dx^2)-2*k_H2*y(i)^2;
        i=i+1;
    end

    %interface H (top interface layer)
    i=n_bulk+4;
    dydt(i)=-D_H_bulk*(y(i)-y(i-1))/(dx^2)+D_H_int*(y(i+1)-y(i))/(dx^2)-2*k_H2*y(i)^2;

    %interface H (without top and bottom interface layer)
    i=n_bulk+5;
    while i<n_bulk+n_interface+3
        dydt(i)=-D_H_int*(y(i)-y(i-1))/(dx^2)+D_H_int*(y(i+1)-y(i))/(dx^2)-2*k_H2*y(i)^2;
        i=i+1;
    end

    %interface H bottom interface layer
    i=n_bulk+n_interface+3;
    j=n_bulk+n_interface+4;
    k=n_bulk+n_interface+5;
    dydt(i)=-D_H_int*(y(i)-y(i-1))/(dx^2)-2*k_H2*y(i)^2-k_SH*y(j)*y(i)+k_S*y(k);

    %Passivation of dangling bonds S
    dydt(j)=-k_SH*y(j)*y(i)+k_S*y(k);
    dydt(k)=+k_SH*y(j)*y(i)-k_S*y(k);

    %surface H2 (top bulk layer)
    i=3+n_bulk+n_interface+3;
    dydt(i)=+D_H2_bulk*(y(i+1)-y(i))/(dx^2);
%bulk H2 (without top bulk layer)
i=3+n\_bulk+n\_interface+4;
while i<n\_bulk+n\_interface+n\_bulk+6
    dydt(i)=-D\_H2\_bulk*(y(i)-y(i-1))/(dx^2)+D\_H2\_bulk*(y(i+1)-y(i))/(dx^2);
i=i+1;
end

%interface H2 (top interface layer)
i=3+n\_bulk+n\_interface+n\_bulk+3;
j=3+n\_bulk+1;
dydt(i)=-D\_H2\_bulk*(y(i)-y(i-1))/(dx^2)+D\_H2\_int*(y(i+1)-y(i))/(dx^2)+k\_H2*y(j)^2;

%interface H2 (without top interface layer)
i=3+n\_bulk+n\_interface+n\_bulk+4;
j=3+n\_bulk+2;
while i<3+n\_bulk+n\_interface+2+n\_bulk+n\_interface
    dydt(i)=-D\_H2\_int*(y(i)-y(i-1))/(dx^2)+D\_H2\_int*(y(i+1)-y(i))/(dx^2)+k\_H2*y(j)^2;
i=i+1;
    j=j+1;
end

%interface H2 bottom interface layer
i=3+n\_bulk+n\_interface+2+n\_bulk+n\_interface;
j=3+n\_bulk+n\_interface;
dydt(i)=-D\_H2\_int*(y(i)-y(i-1))/(dx^2)+k\_H2*y(j)^2;
end
Model_solver

clear all
t0=cputime;
'--------------------------------

%Definition system and variables:
d_bulk=24e-7; % [cm]
n_bulk=240; %number of sublayers in the bulk
dx=d_bulk/n_bulk; % [cm]
d_interface=1e-7; % [cm]
n_interface=round(d_interface/dx); %number of sublayers in the interface

%Definition coefficients [%nm]
%H:
D_H_bulk=1e-13; % [cm2/s]
D_H_int=100*D_H_bulk; % [cm2/s]
k_eff_H=1e-6; % [cm2/s]
k_MH=1; % [cm3/s]

%H2
k_H2=1e-22; % [cm3/s] (2H->H2)
D_H2_bulk=1e-15; % [cm2/s]
D_H2_int=100*D_H2_bulk; % [cm2/s]

%S
k_SH=1e-22; % [cm3/s] (S+H->SH)
k_S=1e-1; % [1/s]

%Start condition
H0=8e21; % [cm-3]
N=6.8e12; % [cm-2] (perfect Si surface = 6.8e14 cm-2)
M0=1e14; % [cm-2]
y0=zeros(1,1+2+n_bulk+n_interface+2+n_bulk+n_interface);
y0(4:round((n_bulk+3)*4/4))=H0;
y0(n_bulk+n_interface+4)=N;
y0(3)=M0;

%domain
tmax=30; % [s]
tspan = [0, tmax]; % [s]

%numerically solving the differential equations:
ode = @(t,y) model4_functions2_for_report(t, y, dx, n_bulk, n_interface, D_H_bulk, D_H_int, k_eff_H, k_H2, D_H2_bulk, D_H2_int, k_SH, k_S, k_MH);
[t,y] = ode15s(ode, tspan, y0); % [s, cm-3]
calc_time=(cputime-t0)/60
Model_visualization

'---------------------------------------------'

y_plots=y;
H0_plots=H0;

%define times to display
t1=round(size(t,1)*0.92);
t2=round(size(t,1)*0.95);
t3=round(size(t,1)*0.985);
t4=size(t,1);

%select solutions for the selected times
yH_1=y_plots(1,4:n_bulk+n_interface+3);
yH_2=y_plots(t1,4:n_bulk+n_interface+3);
yH_3=y_plots(t2,4:n_bulk+n_interface+3);
yH_4=y_plots(t3,4:n_bulk+n_interface+3);
yH_5=y_plots(t4,4:n_bulk+n_interface+3);

yH2_1=y_plots(1,n_bulk+n_interface+6:size(y,2));
yH2_2=y_plots(t1,n_bulk+n_interface+6:size(y,2));
yH2_3=y_plots(t2,n_bulk+n_interface+6:size(y,2));
yH2_4=y_plots(t3,n_bulk+n_interface+6:size(y,2));
yH2_5=y_plots(t4,n_bulk+n_interface+6:size(y,2));

%define horizontal axis in dimension nm
x=0:dx*1e7:(d_bulk+d_interface-dx)*1e7;

%plot graph H
figure
hold on
xlabel('x (nm)');
ylabel('[H] (cm^-3)');
axis([-1 26 0 10e21]);
bulk=[H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots];
x_bulk=0.5:1:23.5;
bar_bulk=bar(x_bulk,bulk,1,'FaceColor',[0.9 0.9 0.9], 'EdgeColor', [0.9 0.9 0.9]);
int=[H0_plots];
x_int=24.5:1:24.5;
bar_int=bar(x_int,int,1,'FaceColor',[0.8 0.8 0.8], 'EdgeColor', [0.8 0.8 0.8]);
hAnnotation = get(bar_bulk,'Annotation');
hLegendEntry = get(hAnnotation,'LegendInformation');
set(hLegendEntry,'IconDisplayStyle','off');
hAnnotation = get(bar_int,'Annotation');
hLegendEntry = get(hAnnotation,'LegendInformation');
set(hLegendEntry,'IconDisplayStyle','off');
plot(x, yH_1,'-bs','MarkerFaceColor','b','MarkerSize',2)
plot(x, yH_2, '-rs', 'MarkerFaceColor', 'r', 'MarkerSize', 2)
plot(x, yH_3, '-ms', 'MarkerFaceColor', 'm', 'MarkerSize', 2)
plot(x, yH_4, '-gs', 'MarkerFaceColor', 'g', 'MarkerSize', 2)
plot(x, yH_5, '-ys', 'MarkerFaceColor', 'y', 'MarkerSize', 2)

hleg1 = legend(['t=', num2str(t(1))], 's', ['t=', num2str(t(t1))], 's', ['t=', num2str(t(t2))], 's', ['t=', num2str(t(t3))], 's', ['t=', num2str(t(t4))], 's');

text(20, 9.6e21, 'Bulk Al_2O_3');
text(20, 9.0e21, 'Interfacial SiO_x');
text(16, 9.7e21, ''); 'BackgroundColor', [0.9 0.9 0.9]);
text(16, 9.1e21, ''); 'BackgroundColor', [0.8 0.8 0.8]);

title(['D_H_bulk=', num2str(D_H_bulk), ' cm^2/s, k_eff_H=', num2str(k_eff_H), ' cm^4/s']);

hold off

%plot graph H2

figure
hold on

x_label('x (nm)');
y_label(['[H_2] (cm^3)']);
axis([-1 26 0 20e21]);

bulk=[H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots];
x_bulk=0.5:1:23.5;
bar_bulk=bar(x_bulk,bulk,1,'FaceColor', [0.9 0.9 0.9], 'EdgeColor', [0.9 0.9 0.9]);

int=[H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots H0_plots];
x_int=24.5:1:24.5;
bar_int=bar(x_int,int,1,'FaceColor', [0.8 0.8 0.8], 'EdgeColor', [0.8 0.8 0.8]);

hAnnotation = get(bar_bulk, 'Annotation');
hLegendEntry = get(hAnnotation, 'LegendInformation');
set(hLegendEntry, 'IconDisplayStyle', 'off');

hAnnotation = get(bar_int, 'Annotation');
set(hLegendEntry, 'IconDisplayStyle', 'off');

plot(x, yH2_1, '-bs', 'MarkerFaceColor', 'b', 'MarkerSize', 2)
plot(x, yH2_2, '-rs', 'MarkerFaceColor', 'r', 'MarkerSize', 2)
plot(x, yH2_3, '-ms', 'MarkerFaceColor', 'm', 'MarkerSize', 2)
plot(x, yH2_4, '-gs', 'MarkerFaceColor', 'g', 'MarkerSize', 2)
plot(x, yH2_5, '-ys', 'MarkerFaceColor', 'y', 'MarkerSize', 2)

hleg1 = legend(['t=', num2str(round(t(1)))], 's', ['t=', num2str(round(t(t1)))], 's', ['t=', num2str(round(t(t2)))], 's', ['t=', num2str(round(t(t3)))], 's', ['t=', num2str(round(t(t4)))], 's');

text(20, 9.6e21, 'Bulk Al_2O_3');
text(20, 9.0e21, 'Interfacial SiO_x');
text(16, 9.7e21, ''); 'BackgroundColor', [0.9 0.9 0.9]);
text(16, 9.1e21, ''); 'BackgroundColor', [0.8 0.8 0.8]);
title(['D_{H_2}, bulk=', num2str(D_H2_bulk), ', cm^2/s'])

figure
hold on
ylabel(['[Si-H] (cm^3)']);
xlabel('t (s)')
plot(t, y(:,n_bulk+n_interface+4), 'r')  % [HS]
plot(t, y(:,n_bulk+n_interface+5), 'b')  % [S]
hold off
Additional SIMS measurements were done on samples containing a 50 nm thick Al$_2$O$_3$ film deposited at 200 °C that received a short anneal (10 seconds) at several temperatures. Although these measurements are outside the scope of this project, they do show an interesting feature regarding hydrogen diffusion in the bulk that is also deduced from the simulations in chapter 4.

The as-deposited sample shows a gradient in the hydrogen concentration in the bulk of the Al$_2$O$_3$ film (0.1< depth < 0.7). After the 450 °C anneal, this gradient has not changed, except for values near the sample’s surface (0.05< depth < 0.2). However, for anneals at 600 °C and 800 °C the gradient in the bulk becomes flatter. Furthermore, the bulk diffusion is thermally activated causing the diffusion coefficient to increase for increasing temperature. Therefore, these graphs indeed show that a higher diffusion coefficient leads to flattening of the hydrogen profile, which is consistent with the findings of Figure 4.6a. Overall, a high diffusion coefficient is able to flatten a concentration gradient more effectively.

However, these measurements also raise new questions that are interesting for future research. For instance, it is remarkable that a gradient is present in the hydrogen concentration profile of the as-deposited sample. This is possibly caused by the deposition conditions of the track. Furthermore, an unexpected bump is visible in the 800 °C profile at depths around 0.75.

Figure E.1: SIMS measurements of samples containing a 50 nm Al$_2$O$_3$ film deposited at 200 °C that received a short anneal (10 s) at several temperatures. The as-deposited film shows a gradient in the bulk (0.1< depth < 0.7) which is flattened by diffusion at high enough annealing temperature.
Appendix F: Contribution to the 38th IEEE Photovoltaic Specialist Conference

During this project, the opportunity was available to present this work on the 38th Photovoltaic Specialist Conference in the first week of June 2012 in Austin, Texas. For this conference a poster was made and a manuscript was written for the conference proceedings. This contribution gained much interest during the conference and also new, interesting knowledge for Levitech was learned. In this appendix both the poster and the manuscript are included so that this report provides a complete overview of the executed work during the project period.