Surface Passivation of CIGS Solar Cells by Atomic Layer Deposition

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Abstract

Thin film solar cells, such as Cu(In,Ga)Se₂, have a large potential for cost reductions, due to their reduced material consumption. However, the lack in commercial success of thin film solar cells can be explained by lower efficiency compared to wafer-based solar cells. In this work, we have investigated the aluminum oxide as a passivation layer to reduce recombination losses in Cu(In,Ga)Se₂ solar cells to increase their efficiency. Aluminum oxides have been deposited using spatial atomic layer deposition. Blistering caused by post-deposition annealing of thick enough alumina layer was suggested to make randomly arranged point contacts to provide an electrical conduction path through the device. Techniques such as current-voltage measurement, photoluminescence and external quantum efficiency were performed to measure the effectiveness of aluminum oxide as a passivation layer. Very high photoluminescence intensity was obtained for alumina layer between Cu(In,Ga)Se₂/CdS heterojunction after a heat treatment, which shows a reduction of defects at the absorber/buffer layers of the device.
Dedicated to my beloved family...
Acknowledgment

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List of acronyms

$Al_2O_3$  Aluminum Oxide, Alumina

ALD  Atomic Layer Deposition

$CIGS$  $Cu(In,Ga)Se_2$

c-Si  Crystalline Silicon

EQE  External Quantum Efficiency

FF  Fill Factor

FTIR  Fourier Transform Infrared Spectroscopy

GPC  Growth Per Cycle

$I_{sc}$  Short-Circuit Current

I-V  Current-Voltage

PECVD  Plasma-Enhanced Chemical Vapor Deposition

PL  Photoluminescence

PV  Photovoltaics

$R_s$  Series Resistance

$R_{sh}$  Shunt Resistance

SEM  Scanning Electron Microscopy

SE  Spectroscopic Ellipsometry

SLG  Soda-Lime Glass

SRH  Shockley-Read-Hall

TCO  Transparent and Conducting Oxide

TMA  Trimethylaluminum

$V_{oc}$  Open-Circuit Voltage
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1 Introduction

In order to make a significant contribution to the low-carbon economy while ensuring the energy security in the future, efficiency of renewable sources has to increase while there is a necessity to decrease the costs per watt peak. Solar photovoltaics (PV), which converts solar energy to electricity is a reliable technology with higher potential, less noise and less required maintenance after installation, compared to other types of renewable energy sources. While most of research done in the field of PV is focused on wafer-based silicon solar cells, there has been less commercial success on thin film solar cells in terms of electronic defects and device physics.

Thin film solar cells based on hetero-junctions of direct band gap semiconductors, such as $\text{Cu(In,Ga)}\text{Se}_2$ (CIGS), have more complex nature and require rapid research and development growth to meet their peak in technology, i.e. reaching optimal energy efficiency. Thin film solar cells have advantage of less material consumption, wide range of deposition techniques, possibility to install on large areas in any shape or structure and lower cost per watt. Equal or better theoretical efficiency of thin film solar cells compared to other types of PV, as shown in Figure 1.0.1, make them more feasible to be used on industrial scales.

![Figure 1.0.1: Research cell efficiencies record at 2013 [1].](image)

One novel way to improve the efficiency of solar cells is to decrease the recombination losses by passivation of surface and bulk defects. Recombination is the opposite of generation. While
in generation electron-hole pairs are created, in recombination electron-hole pairs are lost. Recombination can be caused by dangling (unsaturated) bonds, defects states or impurities at a semiconductor surface or bulk, which can be partially repaired by hydrogen passivation or applying a doping profile or fixed charges which are present at functional thin films. Recombination losses cause decrease in the open-circuit voltage ($V_{OC}$), as shown in Eq. (1.0.1) [11]:

$$V_{OC} = \frac{n k T}{q} \ln \left( \frac{I_L}{I_0} + 1 \right),$$  \hspace{1cm} (1.0.1)

where $n$ is the ideality factor, $k$ is the Boltzmann constant, $T$ is the temperature in Kelvin, $I_L$ is the light-generated current and $I_0$ is the saturation current, which shows the surface recombination process and is the main parameter affecting $V_{OC}$.

Decreasing the open-circuit voltage can affect the efficiency according to Eq. (1.0.2):

$$\eta = \frac{FF \ast V_{OC} \ast I_{SC}}{P},$$  \hspace{1cm} (1.0.2)

where $\eta$ is the energy efficiency, $FF$ is the fill factor, which is a measure of the squareness of the current-voltage ($I - V$) curve, $V_{OC}$ is the open circuit voltage, which shows degree of recombination in the device and is related to the absorber band gap, $I_{SC}$ is the short circuit current due to absorption of photons and collection of light-generated carriers and $P$ is the total power of the incident light.

Among several types of functional thin film layers to be deposited on $c-Si$ (crystalline silicon) solar cells that decreases the surface recombination losses, aluminum oxide ($Al_2O_3$) has been found the most promising one. $Al_2O_3$ thin films grown by atomic layer deposition (ALD) have shown better passivation results compared to other deposition techniques such as plasma-enhanced chemical vapor deposition (PECVD) and reactive sputtering. ALD has emerged to be one of the most powerful techniques in thin film deposition and has been proven to be an attractive way in several PV applications.

In this study, the focus is on a potential way to increase efficiency of $CIGS$ thin film devices, using $Al_2O_3$ deposited by spatial ALD. Spatial ALD has higher deposition rate and higher throughput than the conventional ALD.
2 Literature Review

In this chapter, state-of-the-art methods of passivation of c-Si solar cells will be discussed, continued with an introduction to atomic layer deposition, spatial atomic layer deposition, and CIGS solar cells.

2.1 Surface Passivation

Achieving higher efficiencies in silicon solar cells has been the subject of extensive investigation for many years. Reducing the surface and bulk recombination rates (passivation) is proven to significantly improve the c-Si solar cell efficiency. Surface recombination, plays a more dominant role in cell efficiency, particularly when surface to volume ratio is increased due to reduction of cell thickness for sake of reducing the manufacturing cost.

The mechanism of surface passivation can be defined by the Shockley-Read-Hall (SRH) [3] equation:

\[ U_s = \frac{(n_s p_s - n_i^2) v_{th} N_{it}}{n_s + n_1 + p_s + p_1}, \]

(2.1.1)

where \( U_s \) is surface recombination rate \( \frac{1}{\text{cm}^2 \text{s}} \), \( n_s \) and \( p_s \) are electron and hole surface densities, respectively, \( N_{it} \) is interface defect density \( \frac{1}{\text{cm}^2} \), \( v_{th} \) is electrons thermal velocity, \( n_1 \) an \( p_1 \) are statistical factors, \( \sigma_p \) and \( \sigma_n \) are hole and electron capture cross sections, respectively and \( n_i \) is intrinsic carrier concentration. As can be concluded from Eq. (2.1.1), the surface recombination rate can be decreased by reduction of either interface defect density \( (N_{it}) \) or charge carrier densities \( (n_s, p_s) \) at the silicon surface. The interface defect density is reduced by passivation of the defects, impurities or dangling bonds, which is called chemical passivation. In this case, dangling bonds and defects present at the surface will be passivated by adding hydrogen or a thin film layer. A reduction of the charge carrier density can be obtained using field effect passivation by adding a material that causes an intrinsic charge density. This is called field effect passivation.

Traditional ways of passivation are divided into two categorizes: high temperature and low temperature methods. High temperature method is using thermally-grown SiO\(_2\) on the surface, in which hydrogen released during the growth, causes chemical passivation of dangling bonds at surface. Low temperature method is done either by PECVD of \( a-SiN_x : H \), or deposition of \( a-Si : H \). As Dingeman et al. [3] have shown, surface passivation using Al\(_2\)O\(_3\) is the combination of both chemical and field effect passivation that results in reduction of defect density as well as charge carrier densities.

The formation of negative charge in alumina has been well studied in the literature and native defects inside Al\(_2\)O\(_3\) such as oxygen interstitial \( (O_i) \) and aluminum vacancies \( (V_{Al}) \) are
known to be responsible for negative charge formation in $\text{Al}_2\text{O}_3$. Figure 2.1.1 shows a schematic band-diagram of $\text{Si}/\text{Al}_2\text{O}_3$ interface with thin $\text{SiO}_x$ layer in between, which is formed when adding the alumina layer on top of the silicon [2].

The surface recombination velocity is a factor that is used to measure the quality of surface passivation. The surface recombination effective velocity upper limit is defined by Eq. (2.1.2), assuming infinite bulk lifetime:

$$S_{eff} \leq \frac{d}{2\tau_{eff}}, \quad (2.1.2)$$

where $S_{eff}$ is the effective surface recombination velocity, $d$ is the substrate thickness and $\tau_{eff}$ is the effective lifetime of minority carriers.

### 2.2 Atomic Layer Deposition

The popularity of using ALD over conventional methods for growing thin films, goes back to its ability to deposit precise, uniform, low temperature and self-terminating layers of desired material. The *self-termination* property can be defined as reactants ability to stop automatically when they all react with the prepared sites. This property allows to deposit at most one monolayer in each half cycle even if the dosage time is more than what is required.

Each ALD deposition consists of the following steps: (1) deposition of the first reactant, (2) purge of the non-reacted reactants and volatile products from the first step with inert gas, (3) deposition of the second reactant and (4) purge of the non-reacted reactants and volatile products from the third step. The most common way of manufacturing $\text{Al}_2\text{O}_3$ using ALD is by using Trimethylaluminum/water ($\text{AlMe}_3/\text{H}_2\text{O}$) as reactants, since $\text{H}_2\text{O}$ is the most frequent oxygen source, and Trimethylaluminum (TMA) has been known to be the best source of aluminum due to its high self-termination property. The complete cycle of $\text{Al}_2\text{O}_3$ deposition using ALD is illustrated in Figure 2.2.1.

ALD can be categorized into two methods: thermally driven ALD and plasma-assisted (P-A) ALD. The conventional thermally driven ALD takes place in substrates from room temperature up to $350 \, ^\circ C$ and commonly uses water or ozone as oxidant. In the P-A ALD, the substrate is exposed to the high reactive oxygen radicals generated by plasma, which eliminates the need for high temperature substrate. The use of P-A ALD can therefore make the deposition process applicable on wider ranges of substrate materials. P-A ALD has gained popularity in recent years owing to their improved material properties, such as better film density resulting in reduced purge steps, better electrical properties, less impurity content and higher growth per cycle (GPC). GPC is defined as the slope of the film thickness as a function of the number of ALD cycles, which can be interpreted as a given amount of material to the substrate per cycle [12].
is the key parameter in ALD. Another key advantage of P-A ALD is the ability to monitor and gain information from the plasma during the process, which can be used for optimization of the process. However, since new species can be formed during the plasma step, the plasma-assisted ALD could be more complex in terms of controlling the surface chemistry [13]. A low-temperature ALD of $\text{Al}_2\text{O}_3$ was studied by Groner et al. [14] for deposition of thermally-fragile substrates, such as organic, polymer or biological materials. In low-temperature $\text{Al}_2\text{O}_3$ ALD, low surface roughness, little change in GPC and density, increased $\text{H}_2$ concentration, increased ALD cycle time and longer purge step to remove water are observed.

$\text{Al}_2\text{O}_3$ films deposited by ALD yields the best surface recombination quality compared to the films deposited by other techniques such as PECVD and reactive sputtering. Figure 2.2.2 shows a comparison of surface recombination velocities obtained with spatial ALD, PECVD and reactive sputtering. ALD performance. The excellent surface passivation after firing step indicates the excellent firing stability for ALD layers. Firing is an essential step in industrial type c-Si solar cells with screen-printed metallization. Along with better surface passivation quality in ALD, more dense $\text{Al}_2\text{O}_3$ layers can be obtained by ALD. A thickness of 5 – 10 nm $\text{Al}_2\text{O}_3$ deposited by ALD can give a good passivation result, whereas in PECVD, minimum of 25 nm $\text{Al}_2\text{O}_3$ is required for surface passivation [15].

![Figure 2.2.1: Atomic Layer Deposition cycle of $\text{Al}_2\text{O}_3$][3].

![Figure 2.2.2: Effective surface recombination velocity (SRV) results for spatial ALD, PECVD and reactive sputtering on p-type Si wafers before and after firing at $800^\circ\text{C}$][4].
A schematic structure and process flow diagram for PERC (Passivated emitter and rear cell), is shown in Figure 2.2.3. This type of PERC crystalline silicon solar cell, with the point-contacted, rear passivated either with $\text{Al}_2\text{O}_3$ or $\text{Al}_2\text{O}_3/\text{SiO}_x$ stack layer, have a high potential for future high-efficiency silicon solar cells. In a study by Schmidt et al. [5], excellent surface passivation achieved by ALD of $\text{Al}_2\text{O}_3$ has been shown for the first time in the device level for PERC cells. It should be noted that $\text{SiN}_x$ anti reflection layer deposited on top of the emitter, also acts as a front surface passivation layer, since it has large density of fixed positive charges.

Figure 2.2.3: PERC c-Si solar cell, rear-passivated by alumina, left: process flow diagram, right: structure [5].

Although passivation has shown promising results in increasing the efficiency in c-Si solar cells,
not many methods have been investigated in other types of solar cells. Table 2.2.1 summarizes the passivation techniques of common solar cells.

Table 2.2.1: Passivation methods for different types of solar cells.

<table>
<thead>
<tr>
<th>Solar cell type</th>
<th>Passivation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIGS</td>
<td>Surface Sulfurization using wet process [16]</td>
</tr>
<tr>
<td></td>
<td>Passivation of grain boundary defects by Na [17]</td>
</tr>
<tr>
<td>CdTe</td>
<td>ZnS, CdZnTe [18]</td>
</tr>
<tr>
<td></td>
<td>(Al_2O_3, SiO_2, ZrO_2) [19, 20], (Nb_2O_5) [21]</td>
</tr>
<tr>
<td></td>
<td>ALD of (Al_2O_3) [22]</td>
</tr>
<tr>
<td></td>
<td>Silanization by trichloromethylsilane [23]</td>
</tr>
<tr>
<td>DSSC(TiO_2)</td>
<td>Adding guanidinium to the electrolyte [24]</td>
</tr>
<tr>
<td></td>
<td>Addition of specific molecular adsorbents to the electrolyte ([25], [26], [27])</td>
</tr>
<tr>
<td></td>
<td>Addition of (CO_2, Li_2CO_3,) or (K_2CO_3) to the electrolyte [28]</td>
</tr>
<tr>
<td></td>
<td>Chenodeoxycholic acid (CDCA) [29]</td>
</tr>
<tr>
<td></td>
<td>Poly (ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) [30]</td>
</tr>
<tr>
<td>Organic solar cells</td>
<td>(MoO_3) film [30]</td>
</tr>
<tr>
<td></td>
<td>Ultra thin gold film [31]</td>
</tr>
<tr>
<td></td>
<td>ITO treatments by acids or a chemically bonded monolayer [32]</td>
</tr>
</tbody>
</table>

### 2.2.1 Spatial Atomic Layer Deposition

The drawback of ALD is its low deposition rate due to the time consumed in each purge step, which makes it expensive and not applicable for industrial use (requirement of 2000-3000 wafers per hour for c-Si [6]). Using spatial ALD is one way to increase the deposition rate to reach high throughput rates. The time-based separation of precursor gases in ALD is substituted by spatial separation of half reactions in spatial ALD. This technique increases the deposition rate by a large factor (10^2). As illustrated in Figure 2.2.4, every precursor is confined in a specific zone. Moving the substrate underneath the reactor makes each substrate to be sequentially in contact with the precursor zones. The role of the gas bearing (\(N_2\) in case of \(Al_2O_3\)) is to make frictionless movements between the substrate and the reactor and separation of precursor flows [33]. In this method, the growth rate can be increased up to 70 \(\text{nm} \text{min}^{-1}\), where as in conventional ALD, the growth rate has been measured up to 2 \(\text{nm} \text{min}^{-1}\) [34]. Spatial ALD can be used not only in surface passivation of solar cells, but also in encapsulation deposition of solar cells, OLED industry, buffer layers in CIGS solar cells, patterning and roll to roll industry for flexible applications.
Despite the high market share of c-Si solar cells, the necessity to have more cost effective cells has introduced the thin film solar cells with low material consumption. Thin film solar cells are flexible, more lightweight and are more attractive to the building industry.

In this report, the focus will be on CIGS, which is among CuInSe$_2$ based solar cells that have shown the longest stability and efficiency among other types of thin film solar cells [10]. The most common CIGS device structure consists of five thin layers on a glass substrate, as depicted in Figure 2.3.1. Among several types of substrates used, soda lime glass (SLG) has been proven to be the most suitable one, since it has better match with Mo (Molybdenum) back contact, in terms of thermal expansion coefficient, and it contains sodium.

Diffusion of sodium from SLG through Mo layer is known to have significant effect on the efficiency of CIGS devices. This effect is mostly related to passivation of grain boundary defects, increased carrier density and crystal orientation change through the Na incorporation in CIGS layer [17]. Mo, has been chosen as a back contact layer, since it acts inert in the whole device fabrication steps, except for formation of MoSe$_2$ during Mo deposition is believed to create an ohmic contact between Mo and CIGS.

CdS buffer layer, acts not only as a heterojunction partner to CIGS layer, but also prevents oxidation of CIGS layer. It is also responsible for band-gap alignment and lattice matching. Intrinsic ZnO’s most important role as an additional buffer layer, is believed to be reducing the shunt paths between back and front contacts in CIGS devices [35]. Al-doped ZnO acts as a front layer and TCO (transparent and conducting oxide). A simple process flow for making the CIGS cell is shown in Figure 2.3.2 [36].
2.3.1 CIGS Deposition Techniques

CIGS absorber layer can be fabricated using several techniques. Three-stage co-evaporation is the most common commercial method and has shown the highest conversion efficiency record for thin films (20%). This technique, which has been introduced by US National Renewable Energy Laboratory (NREL) is done by co-evaporation of pure elemental metals, (In, Ga, Cu) in presence of Se vapor in different substrate temperatures [10]. One varied version of the co-evaporation, is a process in which the substrate temperature is constant during the whole deposition, instead the copper flux changes from poor phase to rich phase [37]. The drawback of co-evaporation method is its high price and efficiency decrease for larger scale substrate areas, in which desired deposited flux is harder to achieve.

Another commercial technique for fabricating CIGS absorbing layer is selenization. In this two-step process, metallic precursor layers can be deposited in various ways such as sputtering, evaporation and electro-deposition and then react in Se atmosphere at high temperature. The advantage of selenization method over co-evaporation is its fast fabrication. However, lower conversion efficiencies have been reported by using this method. Among the selenization sources, \( \text{H}_2\text{Se} \) has been found to be the most efficient but also the most toxic one [10].

Chemical vapor deposition (CVD) is another CIGS deposition method, which is done in variety of formats and is not in the commercial phase yet. Atmospheric pressure metal organic CVD (AP-MOCVD), Plasma-enhanced CVD (PECVD), Low pressure metal organic CVD (LP-MOCVD) and Aerosol assisted metal organic CVD (AA-MOCVD) are different types of CVDs used for CIGS deposition. Table 2.3.1 provides a summary of the mentioned CVD methods used for deposition of CIGS [10].
Table 2.3.1: Different types of CVD used for deposition of CIGS [9, 10].

<table>
<thead>
<tr>
<th>Type of CVD</th>
<th>Precursor used</th>
<th>Characteristics</th>
<th>Advantage</th>
</tr>
</thead>
</table>
| **PECVD**   | Cu: Cu(hfac)$_2$  |                 | Low $T_{dep}$
|             | In: In(hfac)$_3$ | Plasma is used for dissociating gases | |
|             | Se: 4-methyl-1,2,3- selenadiazole | Complicated in terms of plasma reactor | |
|             | Carrier gas: H$_2$ |                 | High deposition rate |
| **AP-MOCVD**| Cu: Cu(hfac)$_2$  |                 | |
|             | $N(CH_3)_3$      | Uses metal-organic as precursor source | Low $T_{dep}$ |
|             | $NH(C_2H_5)_3$   |                 | |
|             | In: In(CH$_3$)$_3$, In(C$_2$H$_5$)$_3$ | Atmospheric pressure | |
|             | Se: H$_2$Se      |                 | |
| **LP-MOCVD**| Cu(Se$_2$CNCH$_3$C$_6$H$_{13}$)$_2$ | Uses metal-organic as precursor source | |
|             |                 |                 | |
|             | In[Se$_3$CNCH$_3$C$_6$H$_{13}$]$_3$ | Deposited films have rough surface | |
| **AA-MOCVD**| Cu[SeP(CHCH$_3$CH$_3$)$_2$]$_2$N$_3$ | Precursors are deposited on substrate in aerosol phase | Low cost |
|             | In[SeP(CHCH$_3$CH$_3$)$_2$]$_2$N$_4$Cl | Deposited films have rough surface | |

2.3.2 Recombination in CIGS Solar Cells

The SRH recombination mechanism through defects is the dominant recombination mechanism in CIGS devices. The reason behind the large number of defects at CIGS absorber layer is the poly-crystalline nature of this layer. Fermi level pinning, is a problem at interfaces caused by high concentration of defects, which pins the fermi level far from either conduction or valence band and results in loss in $V_{oc}$ [38, 39]. One method in increasing the CIGS cells efficiency is to reduce the recombination losses.

The basic energy band diagram of the ZnO/CdS/CIGS and main recombination paths are shown in Figure 2.3.3. Before being illuminated, diffusion of electrons from n-type CdS to p-type CIGS in dark, causes positively charged part of CdS and negatively charged part of CIGS, space charge region (SCR) and $V_{bi}$ (built-in potential) in hetero-junction to be made. When illuminated from the TCO layer side, photons with enough energy to excite (energy higher than band-gap of absorber) will cause excitation of electrons to the conduction band of CIGS, leaving holes in the valence band. Several recombination paths are involved in CIGS after electron/hole generation, which are shown in Figure 2.3.3 and summarized in Table 2.3.2 [40]. It should be noted that the CIGS/CdS interface recombination is not dominant in devices with CdS as a buffer layer, since it introduces minimum quantity of interface defects due to good lattice matching with CIGS layer. On the other hand, in devices based on Cd-free buffers, interface recombination at CIGS/buffer is substantial. Although CdS as a buffer layer has shown more

$^1$Deposition temperature
efficiency compared to other types of buffers, the use of toxic Cd in solar cell is undesirable from environmental point of view [41].

Buffer/window interface recombination is not shown in the figure, since this recombination path can be neglected due to wide band gap of buffer and window layers (3.3 eV and 2.45 eV for \(i-ZnO\) and \(CdS\), respectively).

![Figure 2.3.3: Basic energy band diagram of ZnO/CdS/CIGS under illumination and dominant recombination paths at CIGS. Vertical arrows indicate how electrons from the conduction band \((E_c)\) recombine with holes from the valence band \((E_v)\).](image)

Table 2.3.2: Charge transport processes involved in CIGS.

<table>
<thead>
<tr>
<th>Number shown in Figure 2.3.3</th>
<th>Related charge transport process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Recombination path at (CIGS/Mo) interface</td>
</tr>
<tr>
<td>2</td>
<td>Recombination path at bulk</td>
</tr>
<tr>
<td>3</td>
<td>Recombination path at SCR</td>
</tr>
<tr>
<td>4</td>
<td>Recombination path at (CIGS/CdS) interface</td>
</tr>
</tbody>
</table>

Similar to c-Si solar cells, in CIGS solar cells recombination has large effect on \(V_{oc}\) of the device. As it has been discussed before, reduction in surface recombination has been achieved in c-Si cells by adding a passivation layer, in which \(Al_2O_3\) layer deposited by ALD is the most preferred one. In an experiment done by Hsu et al. [42], \(Al_2O_3\) thin films deposited on CIGS surface showed increased photoluminescence (PL) results. This PL enhancement is due to the passivation of the surface recombination [42].

In this study, complete CIGS devices will be made with alumina layer, in order to measure the effect of alumina as an interface passivation layer on the overall behavior and efficiency of the devices.
3 Methodology

All experiments in this study are performed with a rotatory spatial ALD at atmospheric pressure, discussed in Section 3.1. Furthermore, the work in this thesis is divided into the following parts:

1. Since measuring $\text{Al}_2\text{O}_3$ characteristics on CIGS is not straightforward, dependency of $\text{Al}_2\text{O}_3$ film properties on main kinetic parameters and post-deposition annealing effect on $\text{Al}_2\text{O}_3$ layer are measured on $\text{Si}$ substrates (Section 3.2).

2. Passivation of the CIGS devices, which starts with fabrication of base-line CIGS devices and continues with depositing $\text{Al}_2\text{O}_3$ by spatial ALD reactor, using the experimental map developed at first part. The complete devices are characterized with I-V, PL and EQE measurements (Section 3.3).

3.1 Spatial ALD Experimental Settings

“The TMA and water inlets are incorporated in a round reactor head surrounded by exhaust zones, as shown in Figure 3.1.1a. Holes in the inlets deliver the reactive gasses to the substrate. The inlets are surrounded by gas bearing planes. The reactor head is mounted on top of a rotating substrate table, as shown in Figure 3.1.1b. The gas bearing is formed by flowing pressurized $\text{N}_2$ through small holes (0.2 mm diameter) located on the gas bearing surface. When placed over the substrate, a gap between the substrate and gas bearing planes of $\sim 20 \mu\text{m}$ is formed. The corresponding gap height between substrate and inlets is $\sim 200 \mu\text{m}$. The entire construction is mounted in a convection oven, capable of heating up to $400^\circ\text{C}$. The rotating substrate table is connected to a servo-motor by a drive-shaft through a hole in the bottom of the oven. The reactive gases, gas bearing and waste gas lines are connected to the reactor from an opening in the top of the oven. The $\text{N}_2$ for the gas bearing is preheated to the same temperature as the oven. The gas bearing pressure is controlled by a reducing valve. The TMA and water are evaporated from bubblers, with argon as carrier gas, and transported through heated lines to prevent condensation. The gas flows through the bubblers and dilution lines are controlled by flow controllers. The bubblers are heated by thermostatic water baths to control the vapor pressure of the precursors. The waste gas containing TMA vapor residue and reaction products is sent to a scrubber connected to the central exhaust. The waste gas containing water vapor is sent directly to the central exhaust. The reactor inlets are 3 cm long, 1 cm wide and start 3 cm from the center of the reactor head. The reactor head has a diameter of 150 mm. Round substrates with diameters of 150 mm or 200 mm and (semi-)square $15.6 \times 15.6 \text{ cm}^2$ wafers can be mounted” [6].
3.2 Film Properties of $\text{Al}_2\text{O}_3$ as a Function of Main Kinetic Parameters

TMA and water have been used as the metal and oxygen precursors, respectively to make the monolayers of $\text{Al}_2\text{O}_3$ by rotating the substrate, which is a 150 mm double-sided polished Si wafer. The deposition temperature is varied between 150$-250^\circ$C, and water bubbler is heated at 50$^\circ$C. TMA metal precursor was obtained by feeding 30 sccm (standard cubic centimeter) argon flow through the TMA bubbler and diluting with 1470 sccm Ar. Flow of 0.25-1 slm (standard liter per minute) for water was used through the water bubbler. The rotation frequency has been varied between 30-300 rpm. For measuring the thickness and refractive index, spectroscopic ellipsometry (SE) has been used.

The GPC as a function of inverse of rotation frequency, deposition temperature and water concentration has been measured for the first set of experiments. Exposure time ($t$) is determined by dimensions and geometry of the injector and relative speed of substrate according to Eq. (3.2.1) and is proportional to the inverse of rotation frequency [43].

$$t = \frac{W}{2\pi r \nu}, \quad (3.2.1)$$

where $W$ is the precursor inlet width, $r$ is the radius at which the thickness is measured and $\nu$ is the rotation frequency.

Fourier transform infrared spectroscopy (FTIR) measurements have been done on all samples covered with $\text{Al}_2\text{O}_3$, to check the composition of the films. The next experiment was to study the post-deposition annealing ($250^\circ$C and $450^\circ$C) effect on $\text{Al}_2\text{O}_3$ deposited wafers to check the blistering formation in these films. Two $c$-$Si$ wafers covered by $\text{Al}_2\text{O}_3$ with different deposition temperatures were chosen (see Table 3.2.1), each diced in 4 pieces and received different experimental conditions. Thickness and refractive index have been measured before...
and after the annealing. Energy dispersive X-ray analysis (EDX) measurement has been done to check the composition ($\frac{O}{Al}$ ratio) of $Al_2O_3$ film after receiving heat treatment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{deposition}}$ ($^\circ\text{C}$)</th>
<th>TMA flow through bubbler (sccm)</th>
<th>water flow through bubbler (slm)</th>
<th>Rotation frequency (rpm)</th>
<th>#Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3</td>
<td>200</td>
<td>30</td>
<td>1</td>
<td>120</td>
<td>1000</td>
</tr>
<tr>
<td>S9</td>
<td>150</td>
<td>30</td>
<td>1</td>
<td>120</td>
<td>1000</td>
</tr>
</tbody>
</table>

### 3.3 Passivation of CIGS devices

#### 3.3.1 Fabrication of CIGS Devices in This Study

All layers required for CIGS device are deposited according to present "baseline" recipe at TNO. SLG substrates were cut, cleaned with de-ionized water, acetone, isopropyl alcohol and blow dried with nitrogen. Each SLG substrate has dimensions of $3 \times 3 \text{ cm}^2$ and 1 mm thickness. Substrates were then coated with a 0.9 $\mu$m thick layer of Mo, deposited by DC magnetron sputtering. 2 $\mu$m CIGS absorbers are deposited by co-evaporation of four elements (Cu,In,Ga,Se) on a heated substrate (550$^\circ$C).

In this deposition method, investigated by Kessler et. al [37], only the Cu flux is changed during the whole deposition, while substrate, In, Ga and Se sources are kept at a fixed temperature. The process is referred to “CUPRO (Cu Poor-Rich-Off)”, since the Cu source temperature is varied in three steps. Setting the Cu source at 1320$^\circ$C at the first step, results in a Cu-poor growth. Raising the Cu source temperature to 1400$^\circ$C will result in Cu-rich growth at the second step. Finally the Cu source will be off so the film can go back to Cu-poor stage. The CUPRO process has larger grains compared to single-stage co-evaporation process. Figure 3.3.1 shows measured temperatures from thermocouples related to all metal sources during the CIGS growth.

The substrate is mounted 40 cm above the sources, and is heated by infrared lamps placed on top of it. The elemental sources shown in Figure 3.3.2 are placed in such a way that they point the center of Mo-coated SLG.

Figure 3.3.2: Elemental sources used in co-evaporation tool.
3.3. PASSIVATION OF CIGS DEVICES

CHAPTER 3. METHODOLOGY

Figure 3.3.1: Temperature of metal sources vs. time during the CIGS growth in the CUPRO process.

Cross-section scanning electron microscopy (SEM) image of typical CIGS layer on Mo, deposited based on the CUPRO recipe is shown in Figure 3.3.3.

Figure 3.3.3: SEM image of a typical CIGS layer on Mo, deposited based on the CUPRO recipe at TNO. The thickness of the absorber layer is 2 µm.

The p-n junction was completed by depositing 50 nm thick CdS film by chemical bath deposition, immediately after the CIGS growth to prevent oxidation of CIGS layer. Two layers of RF magnetron sputtered ZnO (70 nm intrinsic ZnO followed by 300 nm n-doped with Al) were added to act as a TCO layer and make the complete CIGS device. Copper grids were evaporated through an aperture mask with co-evaporation tool and finally cells with an area of 0.5 cm² each, were defined by mechanical scribing.

3.3.2 Depositing Al₂O₃ by Spatial ALD

Detailed experimental steps for deposition, using the rotatory spatial ALD are described in Section 3.1. The thickness of the Al₂O₃ layer has been modified depending on the experiment, using the optimal precursor concentration and rotational frequency for growing Al₂O₃ at saturated ALD regime (obtained in Section 3.2). Passivation layers were added between Mo and CIGS.
layers for some samples to investigate the Mo/CIGS interface passivation, while it was added between CIGS and CdS layer for other samples to investigate the possibility of passivation of CIGS/CdS interface defects. Since alumina layer is dielectric, a proper way to make contact between the layers has been required to provide a path for charge carriers flow through the cell. There are several ways to make contacts on a dielectric layer, like local etching and using laser ablation. Local etching may damage the layers, and using laser ablation adds cost to the whole process. In this study, we investigated the possibility to use blisters formed during the annealing process to create contacts between layers [8]. Making contacts with subtractive ink patterns was another method tested in this study, as depicted in Figure . In this method, selective permanent ink patterns were made on Mo or CIGS layer before alumina deposition and they were removed with ethanol after alumina deposition. Therefore, the absorber directly contacts the CdS layer or back contact layer depending on the experiment. Schematic diagram of alumina layer location in CIGS device with contacts is shown in Figure 3.3.5.

![Figure 3.3.4: Schematic representation of contact point opening with subtractive ink patterns.](image)

In order to measure the effectiveness of the passivation layer, I-V measurements have been done on all complete CIGS devices. PL and external quantum efficiency (EQE) measurements have been done on the samples with alumina between CIGS and CdS to investigate passivation of the defects and overall behavior of the device after adding an insulator film between the p and n layers.

![Figure 3.3.5: Schematic representation of the investigated samples, left: Mo/CIGS/CdS , middle: alumina passivation layer between CIGS and CdS with contacts, right: alumina passivation layer between Mo and CIGS with contacts.](image)
3.4 Characterization

3.4.1 \( Al_2O_3 \) Film Growth Characterization

3.4.1.1 Spectroscopic Ellipsometry (SE)

SE measures thin film thickness and optical properties such as refractive index. This optical measurement works with the change in the polarization of light when interacting with the substrate [44]. In this study, SE was done on alumina layer on top of Si substrate in the 300-1000 nm range (the reflectometer light beam has been placed on the same spot for all the samples). A two-layer model was defined, consisting of a substrate layer with measured optical properties before alumina deposition. The optical properties of alumina layer are described by a Cauchy model. Refractive indexes are measured at 632 nm.

3.4.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR shows surface chemistry by shining a beam containing many frequencies of light at once and measuring the frequency absorption. In this study, FTIR measurement has been done to check aluminum oxide film composition.

3.4.1.3 Energy Dispersive X-ray analysis (EDX)

EDX measurement identifies both presence of elements in the film as well as their quantitative composition. EDX is done by bombarding focused beam of electrons on the sample and measuring the emitted X-ray spectra. Since each atom has a unique atomic structure, the peaks on the EDX map identify the elemental composition of the sample [45]. In this study, EDX measurements have been done on samples, to check possible changes in film composition after annealing.

3.4.2 CIGS/CdS and CIGS Cell Characterization

3.4.2.1 Current-Voltage Characterization (I-V)

I-V measurement is the most common characterization method for solar cells in which the I-V behavior of the cell is recorded, and exhibits the diode curve. Solid-state-based solar cells are fitted by either one-diode or double-diode equivalent circuits, since ideal solar cells act like diode in dark. For chalcopyrite-based solar cells like CIGS cells, normally single-diode circuit is being used to interpret the I-V characteristics. Figure 3.4.1 shows a typical single-diode equivalent circuit for CIGS cells, which consists of a current photo-generator connected in parallel to a diode (p-n hetero-junction) and a shunt resistor \( R_{sh} \), all series with a series resistor \( R_s \). \( R_s \) and \( R_{sh} \) are representative for bulk and contact material resistance, and any partial shorting across the junction, respectively.

Using I-V measurements, efficiency, FF, \( V_{oc} \), \( I_{sc} \), \( R_{sh} \) and \( R_s \) can be deduced. Figure 3.4.2 shows a typical I-V curve for a CIGS cell. Decreased shunt resistance will decrease \( V_{oc} \). By measuring the slopes of I-V curve at \( V_{oc} \) and \( I_{sc} \), it is possible to approximate \( R_s \) and \( R_{sh} \), as
for ideal solar cells, $R_{sh}$ and $R_s$ are infinity and zero, respectively. Figure 3.4.3 shows how the I-V measurements were done in this study.

![Figure 3.4.1: Equivalent circuit of a solar cell, using one-diode model.](image)

Eight sets of complete CIGS devices were investigated. Four sets had alumina between Mo and CIGS, with different conditions, while the other four had alumina between CIGS and CdS, as already discussed in Section 3.3.2. In each set one device without alumina layer is used as a reference. The standard condition applied during the I-V characterization was illumination of 100 mW cm$^{-2}$ illumination, at temperature of 25°C and the standard global AM 1.5 spectrum.

### 3.4.2.2 Photoluminescence (PL)

PL measurement is a technique used for characterization of defect states, impurity and crystal quality in the CIGS absorber layer. Generally large PL intensities show good interface properties [46].

Four SLG samples covered with CIGS and CdS thin films with a size of 30 $\times$ 30 mm$^2$ were investigated. Three of the samples had alumina layer between CIGS and CdS, with different conditions, while one of them, without the alumina layer was used as a reference. The PL of the samples at 1.1 eV ($\sim$1127 nm) with a SpectraPro 2300i monochromater was measured. An excitation wavelength of 532 nm (green laser) with a YAG laser (CrystaLaser LC) of 25 mW was used. Since the PL-intensity varies with x-y-position of the CIGS sample, each sample was measured at various spots ($7 \times$) around the middle of the sample with a shutter time of 0.2
3.4. CHARACTERIZATION

3.4.3 I-V measurement for a $3 \times 3$ CIGS device.

seconds. The total PL-peak from 1000 nm to 1400 nm was integrated for each PL measurement to get the PL-peak intensity. Subsequently, the PL-intensities of each samples were averaged and normalized with respect to the reference sample.

3.4.2.3 External Quantum Efficiency (EQE)

In EQE, a solar cell is illuminated with monochromatic light and the $I_{sc}$ is measured. By measuring the spectral response of the cell, information about both optical and electrical losses as a function of wavelength can be derived. Ideally EQE result of 1 should be obtained regardless of wavelength, which means every incident photon would result in an electron-hole pair and is separated by the p-n junction. Factors which result in non-ideal EQE curves are shown in Figure 3.4.4 [7]. Region $I$ is responsible for absorption in TCO and buffer layer, while reduced absorption at longer wavelength (region $II$ and $III$) shows worse collection of minority carriers at back of the solar cell, indicating shorter diffusion length of minority carriers. The band-gap of the absorbers in our samples is estimated from the long wavelength value, where approximately a 20% EQE is observed [47].

Figure 3.4.4: Different regions of the EQE plot for a CIGS solar cell, accounting for losses reducing the device output [7].
4 Results and Discussion

4.1 Film Properties of $Al_2O_3$ as a Function of Main Kinetic Parameters

Figure 4.1.1 shows the GPC and refractive index as a function of water concentration, knowing the rate-limiting behavior of water half-reaction in spatial ALD reported by Poodt et al. [48]. It shows the increase in saturation behavior of the GPC by increasing the water concentration. Higher refractive index at more water concentration indicates slightly higher mass density. Data was fitted using Langmuir isotherm (Eq. (4.1.1)). Langmuir isotherm shows coverage as a function of partial pressure. A value of 1.89 for "$K$" was obtained through the fit.

\[
GPC/GPC_{sat} = Kp/(1 + Kp).
\] (4.1.1)
4.1. FILM PROPERTIES OF AL$_2$O$_3$  

CHAPTER 4. RESULTS AND DISCUSSION

Figure 4.1.1: Alumina growth per cycle and refraction index as a function of water concentration at fixed TMA concentration of 30 sccm, deposition temperature of 200°C and rotation speed of 120 rpm, data was fitted using Langmuir isotherm $Kp/(1 + Kp)$, with fit parameter $K = 1.89$.

For the next parts, water concentration has been set at sufficiently high value to meet the self-limiting regime of ALD (1 slm). Figure 4.1.2 shows the GPC and refractive index of Al$_2$O$_3$ as a function of inverse of the rotation frequency (proportional to the cycle time), for deposition temperature of 200°C at fixed water concentration of 1 slm and TMA concentration of 30 sccm. A fast increase in thickness is observed in the unsaturated regime, and the GPC reaches its saturation value at low $1/f$, showing the self limiting behavior of ALD. This means when ALD reaches its saturated regime, increasing precursor exposure time will not have any effect on GPC. A lower refractive index at shorter time scales indicates less mass density in shorter times. The data was fitted with Eq. (4.1.2), shown as a solid line in Figure 4.1.2 (bottom). A value of 0.24 for "a" was obtained through the fit.

$$\frac{GPC}{GPC_{sat}} = 1 - \exp[1 - a\sqrt{t}].$$  (4.1.2)
Figure 4.1.2: Alumina growth per cycle and refractive index as a function of $1/rotational frequency$ at fixed water concentration of 1 slm, TMA concentration of 30 sccm and deposition temperature of 200°C, data were fitted using $GPC/GPC_{sat} = 1 - \exp[1 - a\sqrt{t}]$, with fit parameter $a = 0.24$.

Figure 4.1.3 shows the GPC and refractive index as a function of deposition temperature. An increase in GPC is observed when increasing the temperature up to 250°C, showing a high reactivity of $H_2O$ at higher temperatures. For $T_{dep} > 250°C$, GPC starts to decrease slightly.

These results are consistent with literature [3] for thermal ALD shown in Figure 4.1.4. A lower refractive index at lower deposition temperature is due to the decreased density and the increased impurity levels [14].
4.1. FILM PROPERTIES OF $\text{Al}_2\text{O}_3$

CHAPTER 4. RESULTS AND DISCUSSION

Figure 4.1.3: Alumina growth per cycle and refraction index as a function of deposition temperature at fixed water and TMA concentration of 1 slm and 30 sccm, respectively, and rotation speed of 120 rpm.

Figure 4.1.4: Influence of deposition temperature on GPC [3].

We have measured the absorption of our samples using FTIR to study the binding structure of the $\text{Al}_2\text{O}_3$ films. All samples showed a similar behavior regarding the formation of $\text{O} - \text{H}$ surface hydroxyl groups, overlap of out-of-plane $\text{O} - \text{H}$ bending vibrations and $\text{Al} - \text{O}$ vibrations shoulders after deposition of $\text{Al}_2\text{O}_3$ [49]. Figure 4.1.5 shows an FTIR spectrum for a 100 nm thick as-deposited alumina layer on Si substrate.
Figure 4.1.5: FTIR spectrum of 99.6 nm thick as-deposited alumina film on Si. Other ALD conditions: deposition temperature of 300 °C, rotation speed of 120 rpm, water partial pressure of 1 slm, TMA partial pressure of 30 sccm. The peak at 935 nm is related to $O-H$ surface hydroxyl group. The shoulder at lower frequency band is the overlap of out-of-plane $O-H$ bending vibrations and $Al-O$ vibrations.

Post-deposition annealing of samples described in Table 3.2.1 is done in the next part. Comparing the thickness and refractive index of samples with different deposition temperature before and after annealing, it was observed that after 450 °C annealing, the samples have lower thickness and higher refractive index as shown in Figure 4.1.6. This observation indicates densification and higher mass density of the alumina film after receiving heat treatment.
4.1. FILM PROPERTIES OF $\text{Al}_2\text{O}_3$

CHAPTER 4. RESULTS AND DISCUSSION

Figure 4.1.6: Post deposition annealing effect on thickness and refractive index of c-Si wafers covered by $\text{Al}_2\text{O}_3$ for deposition temperatures $150^\circ\text{C}$ and $200^\circ\text{C}$.

EDX tests were done on annealed samples to compare the $\frac{\text{O}}{\text{Al}}$ ratio of samples with and without annealing treatment. Figure 4.1.7 shows the EDX results for one of the samples.
CHAPTER 4. RESULTS AND DISCUSSION

4.1. FILM PROPERTIES OF AL$_2$O$_3$

Figure 4.1.7: An example of EDX result for annealed alumina layer with 8 kV voltage limit (sample S3). ALD conditions are water concentration of 1 slm, TMA concentration of 30 sccm, deposition temperature of 200 °C and rotational frequency of 120 rpm.

The samples annealed at 250 °C showed $\frac{O}{Al}$ ratios around 1.65, which suggests the hydroxyl surface coverage of the films in lower temperature. Annealing at higher temperature (450 °C) resulted in $\frac{O}{Al}$ ratios of around 1.5, which is representative for stoichiometric Al$_2$O$_3$ (Table 4.1.1). Less $\frac{O}{Al}$ ratios are related to dehydroxylation and decreasing of AlOH and Al(CH$_3$)$_x$ surface species. Closer $\frac{O}{Al}$ ratio to the stoichiometric Al$_2$O$_3$ in higher temperatures suggests higher mass densities of alumina film, which is consistent with the results already shown in Figure 4.1.6. In other words, more incorporated hydroxyl groups, result in films with lower mass density compared to the films annealed at higher temperatures with lower hydroxyl groups and higher mass density. These results are in line with the fact that wide variety of Al$_2$O$_3$ phases exist in different deposition temperatures, which are summarized in Figure 4.1.8.

Table 4.1.1: $\frac{O}{Al}$ for samples annealed at 250 °C and 450 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\frac{O}{Al}$ ratio after annealed at 250 °C</th>
<th>$\frac{O}{Al}$ ratio after annealed at 450 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3</td>
<td>1.639</td>
<td>1.509</td>
</tr>
<tr>
<td>S9</td>
<td>1.649</td>
<td>1.507</td>
</tr>
</tbody>
</table>
The samples annealed at 450°C showed blisters (local film delamination) as shown in Figure 4.1.9. Blister formation in Al₂O₃ layer is related to an external load in the presence of an stress caused by difference between thermal coefficient of Al₂O₃ layer and the substrate. The external load in this case is the pressure caused by the interface accumulation of H₂ from the bulk on the Al₂O₃, being an effective gas diffusion barrier due to its amorphous characteristics [50, 51].

In a study by Vermang et al., it has been discussed that in case of blistering, no additional contact opening step may be needed to create semiconductor-metal contact in thick enough (≥ 10 nm) Al₂O₃ layers [8]. In this work, we have investigated the possibility of using blisters as
an alternative way of making contacts between the CIGS cell layers, as depicted in Figure 4.1.10. Current ways of contact opening such as using laser ablation on dielectric and laser-fired contacts after metallization, add extra costs to the production line, which is undesirable on industrial scales.

Figure 4.1.10: Schematic representation of contact point opening with blisters caused by post-annealing of alumina layer as suggested in [8].
4.2 I-V Results

Table 4.2.1 and 4.2.2 present the normalized $V_{oc}$, normalized efficiency and normalized FF driven for each device type made in this study. On every $30 \times 30 \text{ mm}^2$ device, all cells with area of $0.5 \text{ cm}^2$ were measured and the best working cells are reported. For each set of experiments, one un-passivated CIGS device was made in the same run as the reference sample. The $V_{oc}$ and efficiency of each device were averaged and normalized with respect to the reference sample.

Table 4.2.1: Overview of the normalized cell characterization results for $\text{Al}_2\text{O}_3$ passivated cells between Mo and CIGS, with and without contacts with respect to the un-passivated reference sample made at the same run.

<table>
<thead>
<tr>
<th>Device type</th>
<th>Sample #</th>
<th>Normalized $V_{oc}$</th>
<th>Normalized efficiency</th>
<th>Normalized FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passivated with 10 nm alumina</td>
<td>1.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Passivated with 10 nm alumina +</td>
<td>1.2</td>
<td>0.87</td>
<td>0.63</td>
<td>0.74</td>
</tr>
<tr>
<td>ink contact</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Passivated with 10 nm alumina +</td>
<td>1.3</td>
<td>0.90</td>
<td>0.88</td>
<td>0.89</td>
</tr>
<tr>
<td>more ink contact</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Passivated with 20 nm alumina +</td>
<td>1.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>annealed at 450°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Characteristics represented in Table 4.2.1, belong to the samples with the alumina layer between Mo and CIGS for Mo/CIGS interface passivation. In case of no contact opening on the alumina layer (sample 1.1), efficiency has not been observed, which is due to the blockage of the carrier collection through the back contact from the absorber layer. Although making contact with subtractive ink patterns as discussed in Section 3.3.2 (samples 1.2 and 1.3), enables the carrier collection, no gain in $V_{oc}$ has been observed. This can be explained by the fact that in hetero-junction solar cells maximum generation is done in electric field of the absorber. Therefore, not so many carriers are generated close to the rear-surface and as a result CIGS surface recombination will not play a major role on decreasing the $V_{oc}$. However, if thinner layers of absorbers are made for sake of reduction in material consumption and deposition time, recombination losses in rear-surface of CIGS increase and adding a passivation layer may result in an improvement in $V_{oc}$. Furthermore, since alumina layer is acting as a diffusion barrier layer, it prevents the diffusion of Na from SLG to CIGS layer. As it has already been discussed in chapter 2.3, Na plays an important role in increasing $V_{oc}$ of CIGS devices due to grain boundary passivation. Attempt to make contact with blisters by annealing sample 1.4 has failed, which shows 20 nm alumina layer is not thick enough for blister formation.
Table 4.2.2: Overview of the normalized cell characterization results for $Al_2O_3$ passivated cells between $CIGS$ and $CdS$, with and without contacts with respect to the un-passivated reference sample made at the same run.

<table>
<thead>
<tr>
<th>Device type</th>
<th>Sample #</th>
<th>Normalized $V_{oc}$</th>
<th>Normalized efficiency</th>
<th>Normalized FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passivated with 5 nm alumina</td>
<td>2.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Passivated with 10 nm alumina</td>
<td>2.2</td>
<td>0.85</td>
<td>0.59</td>
<td>0.72</td>
</tr>
<tr>
<td>+ ink contact</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Passivated with 50 nm alumina</td>
<td>2.3</td>
<td>0.89</td>
<td>0.90</td>
<td>0.97</td>
</tr>
<tr>
<td>+ annealed at 450°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Passivated with 50 nm alumina</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.2.2 shows I-V results on samples made with alumina layer between $CIGS$ and $CdS$ with different conditions. Sample 2.1 without any contact openings showed no efficiency due to blockage of charge carriers flow through the cell. Sample 2.2 with ink contacts showed very low $R_{sh}$, derived from the slope of I-V curve in Figure 4.2.1. Low normalized FF in sample 2.2 is caused by low $R_{sh}$. Leakage and shunting between $CIGS$ and $CdS$, which causes low $R_{sh}$ is a result of damaging the $CIGS$ layer by making contact opening with ink. Another reason for the low $R_{sh}$ in all experiments in Table 4.2.2, is because of the rotatory spatial ALD used in this study, which is ideally suitable for $150 \times 150 \text{ mm}^2$ samples. However, since the co-evaporation tool used to deposit $CIGS$ layer can handle samples up to $100 \times 100 \text{ mm}^2$, a sample holder for two $30 \times 30 \text{ mm}^2$ samples was used in ALD, which caused mechanical contact between the substrates and the reactor head. Therefore, scratches were made on all samples, which result in imperfection and impurities and can cause undesired conducting paths in the absorber layer.

![I-V result for a passivated cell in experiment 2.2](image1)

![I-V result for a reference sample in the same run](image2)

Figure 4.2.1: Left: I-V result for a passivated cell in experiment 2.2 Right: I-V result for a reference sample in the same run.

In sample 2.3 with annealed passivation layer, no gain in $V_{oc}$ has been observed. However, having working cells with around 7% efficiency while applying 50 nm dielectric layer between the p-n junction, shows the feasibility of using blisters as contacts. This result can be used when considering making cells with alternative Cd-free buffers as discussed in Section 2.3.2. In $CIGS$ devices based on Cd-free buffers, reducing the $CIGS/buffer$ interface recombination is the first step in improving cells. One way for minimizing the interface related losses in these cells...
could be using a passivation layer between CIGS and buffer layer to reduce the imperfections at the junction. Blister formation during the post deposition annealing can be used as a suitable way to make contacts. Figure 3.3.3 shows cross-sectional images of one of the cells in sample 2.3. Defects shown on top of the CIGS layer are responsible for low $R_{sh}$ in this sample, and decreased FF, mainly caused by scratches made by ALD tool.

It should be noted that due to the major problems with sputtering tool during the study, only one set of devices was made for all the experiments. To make more reproducible results and draw more accurate conclusions, more samples need to be made in future studies.

Figure 4.2.2: Left: cross-sectional images of CIGS device made in experiment 2.3. Right: magnified defect in top of the CIGS layer, mainly caused by scratches from ALD tool.
4.3 PL Results

Table 4.3.1 and Figure 4.3.1 show a summary of the normalized PL-measurements on CIGS/CdS samples with and without alumina in between as already explained in section 3.3.2. Since CdS layer in transparent to light in the measured PL intensity range, the principle emission peak is from the CIGS layer.

Table 4.3.1: Summary of normalized PL at 1.1 eV.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Sample #</th>
<th>Normalized PL</th>
<th>Emission peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-passivated reference</td>
<td>D</td>
<td>1</td>
<td>1127 nm, 1190 nm, 1300 nm</td>
</tr>
<tr>
<td>Alumina layer between CIGS and CdS (50 nm, annealed)</td>
<td>B</td>
<td>16.2</td>
<td>1160 nm, 1132 nm</td>
</tr>
<tr>
<td>Alumina layer between CIGS and CdS (50 nm)</td>
<td>A</td>
<td>1.4</td>
<td>1146 nm, 1250 nm</td>
</tr>
<tr>
<td>Alumina layer between CIGS and CdS (10 nm)</td>
<td>C</td>
<td>1.3</td>
<td>1157 nm, 1106 nm, 1260 nm</td>
</tr>
</tbody>
</table>

As shown in Figure 4.3.1 the normalized PL intensity enhancement in CIGS/CdS with alumina in between (annealed) by a factor of 16, comparing to CIGS/CdS un-passivated reference is observed. An example of a PL measurement in sample D and B is presented in Figure 4.3.2.
Next to a dominant peak at \(~1127\) nm we also see weak defect-related PL peaks at \(~1190\) nm, and \(~1300\) nm, as indicated by the arrows in the graph. In sample B peak at 1300 nm is being decreased. Improved PL intensity at 1.1 eV and decrease of defect-related peak at 1300 nm may be related to several reasons. Either defect concentration at the junction has been reduced or the dangling bond at the surface have been terminated. In both cases, decrease of the non-radiative recombination leads to higher emissions, showing higher carrier life time.

![Figure 4.3.2: Example of a Photoluminescence measurement in Left: Reference sample, Right: Sample with alumina between CIGS/CdS, annealed at 450 °C for 30 minutes](image)

To check if the annealing effect itself is responsible for increased PL, standard CIGS device were made, and annealed at 450 °C for 30 minutes after the CIGS deposition, no working cell has been observed for this sample which could be due to oxidation of CIGS layer. This result is in line with the experiment done by Hsu et. al, in which annealing the reference samples at 250 °C did not have any effect on PL intensity [42]. It could be interpreted that post annealing of “alumina” can improve the passivation of CIGS/CdS interface. In other words, alumina is the main cause of higher PL intensity, not the annealing itself.
4.4 EQE Results

Figure 4.4.1 shows EQE plots on complete devices with and without an alumina layer between CIGS and CdS. The overall behavior of the cell after adding 50 nm insulator between the p and n layers is similar to the reference sample. For wavelengths $> \sim 550$ nm, there is a downward shift in EQE values for the sample with alumina layer between CIGS and CdS, which is mainly due to the interface region and indicates shorter diffusion lengths for minority carriers. An slight increase in the band-gap of the device is observed, shown in Figure 4.4.1. Short current densities of 32.7 mA cm$^{-2}$ and 30.3 mA cm$^{-2}$ were calculated by integrating the EQE plot over the whole wavelength range for CIGS/Al$_2$O$_3$/CdS and CIGS/CdS respectively. Decreased short current density and increased band gap when adding alumina may have been caused by diffusion of aluminum into the space charge region of absorber while annealing, reducing the space charge region width in the absorber.

![EQE plots comparison](image-url)

Figure 4.4.1: Right: The external quantum efficiency of the CIGS reference solar cell compared to CIGS solar cell with 50 nm alumina between CIGS and CdS layers, annealed at 450°C for 30 minutes. Left: Shift of effective bandgap values estimated from 20% QE value (shown by arrows).
5 Conclusions and Recommendations

The purpose of this study was to investigate the effect of alumina deposited by spatial ALD as a passivation layer to reduce recombination of photo-generated minority carriers in CIGS solar cells. Two approaches were tried, adding an alumina layer between Mo and CIGS to investigate Mo/CIGS interface passivation and adding an alumina layer between CIGS and CdS to investigate the possibility of passivation of CIGS/CdS interface defects. Since alumina layer is an dielectric, finding a proper way to make contacts in device was required.

The differences between the reference samples and the ones with additional alumina layer, in I-V, PL and EQE characteristics have been studied. Higher PL intensity in case of alumina layer between CIGS/CdS demonstrated that the recombination at CIGS/CdS can be improved by applying alumina layer. The feasibility of using blisters caused by post deposition annealing as randomly arranged point contacts to provide the conduction through the cell has been shown. Making thinner layers of absorber and measuring the effectiveness of alumina film as an effective rear-passivation layer can be investigated in future studies. In this case, since alumina is acting as a diffusion barrier layer, extra supply of Na is required.

Measuring the passivation effect on efficiency by making complete devices with alternative Cd-free buffer layers along with an alumina layer between CIGS/buffer can also be investigated in future studies. Showing reproducibility of the results by making more samples on larger substrates is recommended, since larger numbers of small cells are required for statistically representative measurements.
Bibliography


