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Stability of zinc oxide deposited by novel techniques for CIGS solar cells

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Stability of zinc oxide deposited by novel techniques for CIGS solar cells

Bart Platier

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Abstract

In this study intrinsic zinc oxide (ZnO) is investigated as a nucleation layer for aluminum doped ZnO (AZO) for the application in CIGS solar cells. A variety of i-ZnO layers is deposited by means of thermal atomic layer deposition (TH-ALD), plasma-assisted atomic layer deposition (PA-ALD) and chemical vapor deposition by an expanding thermal plasma (ETP-MOCVD) under two different reaction chamber pressures. These layers were characterized with atomic force microscopy (AFM), spectroscopic ellipsometry (SE), x-ray diffraction (XRD) and four point probe (FPP). From these measurements can be concluded that different layers are grown to serve as starting layers for the AZO layer.

Stability for CIGS solar cells is still an issue. The efficiency of the solar cell drops due to degradation of the ZnO layers. The change over time of these layers are investigated for different novel deposition techniques. Thanks to this study these changes are better understood. The change of resistivity is caused by species at the grain boundaries and changes of the ratio between oxygen absorption and desorption at the surface. Big material changes are not the cause of the degradation of the material. The susceptibility to change in resistivity can be related to the microstructure of the material.
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1 Introduction

1.1 ZnO in CIGS solar cells

Zinc oxide (ZnO) is considered a promising material due to its wide direct band gap (3.37 eV at room temperature) and large exciton binding energy (60 meV). These interesting properties are the major driving force behind the research on ZnO as a material for light emitting devices and for transparent or high temperature electronics.\(^1\) ZnO can furthermore be doped by other elements to form transparent conducting oxides (TCO’s). Heavily doped ZnO films are used as transparent and conductive electrodes in solar cells.

ZnO based TCO’s are used for example in CIGS solar cells. The absorber layer in CIGS solar cells is made of copper, indium, gallium and selenium or sulfur (CIGS). The direct band gap of this material varies from 1.04 to about 1.68 eV depending on the ratio of indium and gallium.\(^2\) Due to intrinsic defects in the CIGS is the layer p-type doped. The light enters the solar cell from above, passing the window layer stack (window). The window of a CIGS solar cell consists out of three layers: the n-doped layer, the thin i-ZnO layer and the buffer layer. The top layer is made of aluminum doped ZnO (AZO). The incorporation of the aluminum in this layer is the main cause of the n-type doping. The AZO layer is the thickest layer of the window and therefore the most important for the transmittance of the light. An optical transmittance of more than 80% in the visible region is required for the AZO layer.\(^3\) Due to the high transmittance of the window layer stack light reaches the CIGS layer.

Photons will excite electrons in this layer. The heterojunction in the solar cell is formed between the absorber layer and the window, this junction is the cause of the attraction of excited electrons in the CIGS into the window layers. The CdS layer in a CIGS solar cell acts as a stepping stone electrically and optically between the CIGS and the ZnO layers. The quality of the p-n junction of the solar cell is determined by this layer. The layer is deposited by chemical bath deposition (CBD) and is typically 50 to 70 nm thick. Replacement of the CdS is preferred for the following three reasons; the deposition of the CdS is the only wet step in the production of the CIGS solar cell, the toxicity of the Cadmium and the low band gap of the CdS. Several zinc based buffer layers are tested to replace this CdS layer. The excited electron is transported to the AZO layer and now the second function of the layer become clear. The AZO layer act as a front contact for the current collection. A resistivity of less than \(10^{-3} \Omega\cdot\text{cm}\) is required for the AZO layer as a contact for the current collection.\(^3\) The i-ZnO layer prevents electrons in the AZO layer from shunting. This layer is no longer required if the zinc based buffer layer has a high enough resistance, but the TCO will be deposited on a zinc based layer in all cases. See Figure 1 for a micrograph and a schematic drawing of a CIGS solar panel.

\(\text{Figure 1: A micrograph and a schematic of a CIGS solar cell thin film stack. The light is absorbed in the p-type CIGS layer.}\)
1.2 Properties of ZnO

Under normal conditions undoped, doped ZnO and most of the ZnO based alloys crystallize in the wurtzite structure. See Figure 2 for an image of the crystal structure of ZnO. Crystallographically disturbed regions are caused by transitions of crystal orientation; these regions are called grain barriers. Most grains are not properly connected to another which causes an increase of the resistivity. The conductivity of a material is also influenced by doping. Intrinsic defects can be caused by removal or displacement or lattice atoms. These defects can be caused by deviations in the ratio of reactants while depositing the ZnO, possible intrinsic defects are vacancies, interstitials and antisites. Many defects can contribute to the conductance of the material by creating charge carriers and constitute intrinsic dopants. Defects can also decrease the mobility of charge carriers and therefore decreasing the conductivity. Defects and impurities are common in intrinsic ZnO which is referred to as unintentional doping. This unintentional doping causes the ZnO to be n-type. Note that obtaining p-type doping is still a problem for ZnO.

Figure 2: Perspective view perpendicular to the c axis of ZnO in the wurtzite structure.

Extrinsic doping is changing the material electrical properties by adding small amounts of elements of a different valency. The conductivity of a material can be changed by orders of magnitude using extrinsic doping. In recent studies hydrogen is proposed as a very important dopant in ZnO, because it is used in most growth processes. Elements that can be used for improvement of the film resistivity in the film of ZnO are for instance boron and aluminum. For n-type doping the additional electron is not required for bonding and is therefore available for conduction. The concentration of dopants in a semiconductor determines the charge carrier concentration. The long wavelength cutoff also depends on the charge carrier concentration. Free electrons are able to reflect incoming light above a certain wavelength according to Drude theory. Therefore there is a tradeoff between high conductivity and good transmittance of a material. Another material property that determines the conductivity is the electron mobility.

ZnO possess a wide energy band gap (3.37 eV) and is therefore transparent for wavelengths longer than 350 nm. Changing the band gap of ZnO is possible by adding MgO or CdO. When all states near the conduction band are populated the band gap of a semiconductor increases, this effect is called the Burnstein-Moss shift.

1.3 Stability of ZnO

The stability of ZnO for CIGS is still an issue. At the moment it is even possible to deposit flexible CIGS solar cells, but as for all ZnO CIGS solar cells the efficiency decreases due to stability problems of the ZnO. The conductivity of ZnO films increases when they are exposed to illumination above the band gap of ZnO. Oxygen desorbs from the surface by the UV light. This reduces the surface electron depletion region leading to enhanced photoconductivity. When samples are stored
in vacuum the desorbed oxygen is pumped away and therefore the oxygen depletion may persist for as long as the films are kept in vacuum. The oxygen may be totally eliminated from the surface of the film when stored in vacuum, the resistivity of the films stored in vacuum will be lower than for the films exposed to air for the same UV photon flux. Another possible cause of aging is caused by absorption water vapor at the grain boundaries, leading to an enhanced scattering of carriers and also trapping of free carriers and therefore reducing carrier mobility and carrier concentration.\textsuperscript{(15)}

1.4 Thin Film Deposition

Thin film deposition is applying a thin film on a substrate or on an earlier deposited layer. There are many techniques to deposit thin films. Each of these techniques has their own advantages. The following techniques are covered here: atomic layer deposition and chemical vapor deposition by an expanding thermal plasma.

1.4.1 Atomic Layer Deposition

The deposition process of thin films with atomic layer deposition (ALD) consists of several steps. The process of depositing ZnO will be described to explain the technique. In the first step the surface is exposed to diethyl zinc (DEZ) and the precursor reacts with surface. The absorbed DEZ will not react with additional precursor, which causes the self-limiting character of ALD. When the reaction of the precursor is saturated a purge step follows to remove the remaining unreacted DEZ and the by-products of the reaction. The third step is the exposure to water or a plasma as an oxidation source to react in a self-limiting way with the absorbed DEZ surface groups. The last step of the process is a second purge to remove the remaining oxidizer and the by-products of the reaction.

After the last step of the cycle the process can start all over again. The difference between thermal ALD (TH-ALD) and plasma-assisted ALD (PA-ALD) is that the oxidant is a plasma at PA-ALD. Increased choice of reactants, larger temperature window and improved temperature window are a selection of the possible advantages when using a plasma.\textsuperscript{(16)} See Figure 3 for a schematic representation of a PA-ALD and TH-ALD cycle.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Schematic representation of thermal ALD cycle (with H\textsubscript{2}O dosing) and plasma-assisted ALD cycle (with O\textsubscript{2} plasma exposure). The deposition of ZnO is given as example. (a) self-limiting absorption of precursor on the surface (b) purge step to remove the by-products and excess precursor (c1) thermal ALD: the surface is exposed to reactant molecules that react in a self-limiting way to the surface (c2) plasma-assisted ALD: the surface is exposed to plasma that react in a self-limiting way to the surface (d) another purge to remove the by-products and excess reactant or plasma.}
\end{figure}

The growth rates of ALD films are in general lower than for films deposited by other techniques like evaporation or sputtering. Due to the self-limiting reactions ALD may be the preferred method for depositions which need high material quality, high uniformity, precise growth control and an excellent conformality.\textsuperscript{(17) (18) (19)} Research is done to optimize the deposition of ZnO
and get a better understanding of the process. One of the goals is to find other precursors and oxidizers to get more control over defects, doping and crystal structure.

1.4.2 Chemical Vapor Deposition by an Expanding Thermal Plasma

The expanding thermal plasma metalorganic chemical vapor deposition (ETP-MOCVD) technique works in a different way than ALD. The reactants enter the reaction chamber at the same time with ETP-MOCVD, for this reason the precise flows of precursors and reactants plays a much bigger role than by ALD. The cascade arc plasma source generates a plasma in a nondepositing carrier gas, in this case argon. This high pressure plasma expands supersonically through a nozzle in a low-pressure reactor; the electron temperature is reduced due to this expansion. The ionization reactions after the expansion can be neglected because of the low temperature of the electrons. The plasma source operates as an argon-ion source. The precursors are injected symmetrical and at different positions in the reactor chamber. Reactive species causes growth of ZnO on the substrates on the temperature controlled substrate holder.

Deposition of good material is possible even at low substrate temperatures; therefore ETP-MOCVD can be used for future flexible electronics applications. Currently the optimized deposition rate is approximately 1 nm/s, but a deposition rate of over 5 nm/s for well conductive and transparent ZnO films should be possible.

Depending on the pressure in the reactor chamber the growth mode is different. At high pressure the grains are pyramid-like and at low pressure the grains are pillar-like for undoped ZnO and Al doped ZnO. The abbreviations of these depositing conditions are respectively HP-ETP-MOCVD and LP-ETP-MOCVD. The films deposited under low pressure conditions are smoother. AZO films that are deposited by means of HP-ETP-MOCVD are characterized by a high roughness and a large sheet resistance gradient with film thickness. For HP-ETP-MOCVD deposited AZO films the effective resistivity decreases with an increase of the film thickness due to increased electron mobility. See Figure 4 for a cartoon of the tentative growth model for the initial and final growth of the ZnO films for the low (a) and high (b) pressure conditions.

![Figure 4: A cartoon of the initial and final growth of the ZnO films (a) for low pressure in the reaction chamber and (b) for high pressure conditions by means of ETP-MOCVD. The arrows represent the direction of the grain development.](image-url)
1.5 Aim of this Project

This project is part of bigger project. The aim of the bigger project is to control and understand the properties of ZnO for CIGS solar cells better to obtain a fast technique to deposit high quality ZnO. ZnO used as transparent front contact is often doped by aluminum to achieve sufficient carrier density for high conduction. The transparency decreases with an increase of the carrier density, therefore it is desirable to have large grains to increase mobility of the electrons. One of the possible methods to control the grain size of the AZO layer is to deposit on top of an intrinsic ZnO layer deposited by another method. In the bigger project the goal is to deposit the AZO layer on top of i-ZnO.

The aim of this project is to deposit a variety of i-ZnO layers to test as nucleation layer. The layers deposited by means of TH-ALD, PA-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD need to be characterize, to understand the differences of the growth of the AZO layer during the bigger project. The stability of CIGS and the AZO layers needs to be better understood to keep the good efficiencies. During this project the aging of i-ZnO will be investigated. The resistivity of i-ZnO is mostly influenced by the grain boundaries; therefore big chances in resistivity can be expected due to small changes at the grain boundaries.

1.6 Approach

The i-ZnO layers with a thickness of 50 nm need to be deposited by means of TH-ALD, PA-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD on c-Si with a top layer of thermal oxidized silicon SiO$_2$ substrates. These films need to be characterized as deposited to able to interpret the differences of the changes over time. The samples are stored under four different conditions and characterized again after a certain time. An ultraviolet and air treatment is performed and afterwards the samples are characterized again.
2 Experimental Details

2.1 The i-ZnO layer

2.1.1 Deposition of the i-ZnO layer

The 50 nm i-ZnO layers were deposited on c-Si, SiO₂ and glass substrates using one of the following techniques TH-ALD, PA-ALD, LP-ETP-MOCVD or HP-ETP-MOCVD. The experimental conditions that were used during the depositions are found in Table 1 and Table 2.

*Table 1: Deposition conditions for the i-ZnO layer with TH-ALD and PA-ALD.*

<table>
<thead>
<tr>
<th></th>
<th>TH-ALD</th>
<th>PA-ALD</th>
</tr>
</thead>
<tbody>
<tr>
<td>cycles</td>
<td>241</td>
<td>423</td>
</tr>
<tr>
<td>temperature</td>
<td>150 °C</td>
<td>150 °C</td>
</tr>
<tr>
<td>wall temperature</td>
<td>180 °C</td>
<td>150 °C</td>
</tr>
<tr>
<td>DEZ dose</td>
<td>50 ms</td>
<td>50 ms</td>
</tr>
<tr>
<td>DEZ purge</td>
<td>5 s</td>
<td>1 s</td>
</tr>
<tr>
<td>oxidation dose</td>
<td>H₂O for 20 ms</td>
<td>O₂ plasma for 12 s</td>
</tr>
<tr>
<td>oxidation purge</td>
<td>10 s</td>
<td>6 s</td>
</tr>
</tbody>
</table>

PA-ALD needs more cycles to deposit the desired 50nm i-ZnO than TH-ALD, because of the smaller growth per cycle of PA-ALD. The wall temperature was accidentally set to 180 °C during the thermal ALD deposition, but this is not expected to make a difference for the properties of the films.

*Table 2: Deposition conditions for the i-ZnO layer with LP-ETP-MOCVD and HP-ETP-MOCVD.*

<table>
<thead>
<tr>
<th></th>
<th>LP-ETP-MOCVD</th>
<th>HP-ETP-MOCVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>deposition time</td>
<td>3.1 min</td>
<td>8.68 min</td>
</tr>
<tr>
<td>substrate temperature</td>
<td>200 °C</td>
<td>200 °C</td>
</tr>
<tr>
<td>Ar flow</td>
<td>1000 sccm</td>
<td>1000 sccm</td>
</tr>
<tr>
<td>arc current</td>
<td>50 A</td>
<td>50 A</td>
</tr>
<tr>
<td>Ar pressure</td>
<td>2.1 bar</td>
<td>2.1 bar</td>
</tr>
<tr>
<td>Ar pressure DEZ flow</td>
<td>50 sccm</td>
<td>50 sccm</td>
</tr>
<tr>
<td>DEZ flow</td>
<td>3.5 g/h</td>
<td>9.0 g/h</td>
</tr>
<tr>
<td>oxygen flow</td>
<td>1000 sccm</td>
<td>100 sccm</td>
</tr>
<tr>
<td>roots pump valve position</td>
<td>40</td>
<td>5 + manual</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>0.17 mbar</td>
<td>1.8 mbar</td>
</tr>
</tbody>
</table>

Only a few samples were placed on substrate holder per deposition run to achieve good uniformity with ETP-MOCVD, so several depositions were needed. The samples were heated for at least ten minutes to 200 °C to ensure all starting conditions were equal. The deposition rate of HP-ETP-MOCVD is lower than for LP-ETP-MOCVD, which is the reason for the longer deposition time. The pressure in the reaction chamber is higher during HP-ETP-MOCVD depositions as described earlier in paragraph 1.4.2. A valve was opened manually for the high pressure conditions.
2.1.2 Characterization of the i-ZnO layer

The films were analyzed with atomic force microscopy, spectroscopic ellipsometry, x-ray diffraction, profilometer and four point probe to determine the properties of the i-ZnO layer. A short description is given of these techniques.

2.1.2.1 Atomic Force Microscopy

Atomic force microscopy (AFM) is a method for determining the surface topography of a sample beyond the limits of optical microscopes. A probe is held several nanometers above the surface using a feedback mechanism. The interactions between the probe and surface are causing height differences of the probe which are recorded while the sample is scanned. Software is able to create a topographic image from the gathered information. This image can be used to determine for instance the position of atoms or calculate the root-mean-squar (RMS) roughness.

2.1.2.2 Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is an optical technique to determine dielectric properties of thin films. Linearly polarized electromagnetic radiation falls onto the sample, after reflection the radiation passes a second polarizer and falls in the detector. The detector measures the change of polarization: the phase shift of the beam is given by $\Delta$ and the change of the amplitude by $\Psi$. The desired information must be extracted from a model. For example the following film properties can be extracted from the model of a thin film: thickness, refractive index, roughness and uniformity. The photon energy range of the incoming light depends on the used apparatus. For this experiment an SE with Near Infra-Red extension (SE-NIR) and an SE with Ultra Violet extension (SE-UV) were used. Both of the SE’s were mounted on a gonio stage, the information extracted out of the model is more accurate when the sample is measured at different angles.

2.1.2.3 X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive technique that reveals information about the crystallographic structure and orientation of materials. The technique is based on constructive interference of monochromatic X-rays and the crystalline sample.

2.1.2.4 Profilometer

Profilometer is a method to determine the profile of the surface of a sample. The sample is moved relative to the stylus of the profilometer. The stylus follows vertical variations of the surface. The height of the deposited layer is determined by removing the deposited layer locally and determining the height difference between the deposited layer and the substrate. This technique was used to determine the required deposition time for ETP-MOCVD films.

2.1.2.5 Four Point Probe

Four point probe (FPP) is a technique to determine the resistivity of semiconductors. The voltage is measured between the inner two probes while passing a current on the outer two probes. The film must be deposited on an insulated substrate to determine the resistivity. The results of these measurements need to be corrected for finite thickness and finite width.\(^{(25)}\)
2.2 Change over Time

2.2.1 Storage of the Samples

The films were stored under four different conditions; light-vacuum, dark-vacuum, light-air and dark-air. The samples were stored in plastic containers to protect the film from dust. Aluminum foil was wrapped around the samples which were not to be exposed to light to block all radiation. The storage containers of films which were not to be exposed to air were stored in a transparent vacuum bell jar.

2.2.2 Characterization the Change of the Samples

The samples were characterized with four point robe and spectroscopic ellipsometry. These techniques are described in paragraph 2.1.2.2 and 2.1.2.5. Measurements were performed regularly on two spots on each sample. The measurements were performed on two spots to be able to determine the spread in the properties.

2.2.3 UV Treatment

To accelerate the effects of normal light on the films a UV lamp was used to irradiate the films. During the treatment the films are exposed to air. The distance between the films and the ozone lamp was approximately 25 cm. The power consumption of the ozone lamp is 4W.
3 Results and Discussion

3.1 i-ZnO Layer

In this section the material properties of the i-ZnO layers are discussed. The thickness of the i-ZnO film is determined by modeling the data obtained by the SE measurements. The thicknesses of the films deposited by means of TH-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD were approximately 50 nm. The samples deposited by PA-ALD were not uniform in thickness. The thickness of these films on SiO$_2$ substrates was determined on five spots and was between 33.88±0.11 and 50.84±0.06 nm. Not all measurements to characterize the PA-ALD films were performed, because the films were not suitable for this experiment. Results of measurements that are given of PA-ALD deposited films are performed in the region of the spot with a thickness of 50.84±0.06 nm.

3.1.1 Structural and Morphological Properties

All films were crystalline. The films deposited by TH-ALD had more orientations than the ETP-MOCVD deposited films. See Figure 5 for the results of the XRD measurements performed on the TH-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD deposited films on a SiO$_2$ substrate. The TH-ALD deposited film on SiO$_2$ had peaks for the (100), (002), (101) and (110) orientation. The ETP-MOCVD deposited films only have a peak for the (002) orientation, these peaks were higher than the peak (002) peak of the TH-ALD film. The films deposited by mean of TH-ALD were more random oriented than the film deposited by ETP-MOCVD. The orientations of TH-ALD correspond with the literature for ALD grown film, except for the missing (103) orientation in the deposited films. Interestingly the relative intensities of the orientations do match. The preferential growth of ZnO in the (002) orientation of ETP-MOCVD is also consistent to the literature. The (002) orientation is not preferential in the powder spectrum and therefore can be concluded that the film is really preferential in the (002) orientation. See Table 3 for the net heights of the peaks for the (002) orientation of the XRD measurements.

Table 3: The net heights of the peaks for the (002) orientation of the XRD measurements. of the TH-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD deposited films on a SiO$_2$ substrate.

<table>
<thead>
<tr>
<th>deposition condition</th>
<th>net height (counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TH-ALD</td>
<td>1188.3</td>
</tr>
<tr>
<td>LP-ETP-MOCVD</td>
<td>2559.2</td>
</tr>
<tr>
<td>HP-ETP-MOCVD</td>
<td>2117.4</td>
</tr>
</tbody>
</table>
Figure 5: A graph of the results of the XRD measurement of the i-ZnO films deposited with TH-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD on a SiO\textsubscript{2} substrate. The TH-ALD deposited film has more different orientations than the ETP-MOCVD deposited films.

The roughness of the films was calculated from the AFM images. The TH-ALD deposited layers had the lowest RMS roughness and of the ETP-MOCVD deposited films at the high pressure conditions the highest RMS roughness, see Table 4 for the values of the RMS roughness. The PA-ALD deposited films were not analyzed with AFM. The size of the grains is determined by line analyses of the images of the AFM measurements. The grains of the TH-ALD deposited films are the smallest, followed by the grains of the LP-ETP-MOCVD deposited films and the grains of the HP-ETP-MOCVD deposited films are the biggest.

Table 4: The RMS roughness and the grain size of the TH-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD deposited i-ZnO films on a SiO\textsubscript{2} substrate.

<table>
<thead>
<tr>
<th>deposition condition</th>
<th>RMS roughness (nm)</th>
<th>grain size by AFM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TH-ALD</td>
<td>1.7</td>
<td>55±5</td>
</tr>
<tr>
<td>LP-ETP-MOCVD</td>
<td>1.9</td>
<td>78±5</td>
</tr>
<tr>
<td>HP-ETP-MOCVD</td>
<td>5.2</td>
<td>94±5</td>
</tr>
</tbody>
</table>

Films deposited by means of TH-ALD have high uniformity and low roughness and small grains, this is consistent with the literature.\(^{(27)}\) In the literature HP-ETP-MOCVD deposited films have big pyramid-like grains with a high roughness, unlike films deposited under low pressure conditions which have smaller pillar like grains and a low roughness.\(^{(24)}\) The roughness of the ETP-MOCVD deposited films is consistent with the literature.

The XRD data is also used to estimate the grain size of the films. The Full Width at Half Maximum (FWHM) is determined of the (002) peak and the Scherrer equation is used to calculate the grain size. The grain size is estimated at respectively 25 nm, 27 nm and 26 nm for TH-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD. The error is estimated at 5 nm. The difference with the results of the grain size determined from the AFM images can be explained by different forms of the grains for the...
different deposition techniques. On the AFM images it is only possible to determine the width and length of a grain, it is not possible to determine the height. Another explanation for the differences between the results of the AFM and XRD measurements is; XRD does not take in account grain defects. The HP-ETP-MOCVD deposited films have biggest grains on the surface.

3.1.2 Electrical Properties

The four point probe measurements were performed to determine the resistivity of the films on SiO$_2$ and glass. The HP-ETP-MOCVD films had the lowest resistivity, followed by the films deposited with TH-ALD. The LP-ETP-MOCVD films had the highest resistivity. See Table 5 for the exact values of the resistivity and sheet resistance for the films deposited on SiO$_2$, all values were corrected for thickness and sample size. The resistivity values for the films on glass were similar as for the SiO$_2$ substrates.

Table 5: Resistivity of the TH-ALD, PA-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD deposited films on SiO$_2$ corrected for thickness and sample size. The error in the resistivity is determined by calculating the standard deviation of the sample.

<table>
<thead>
<tr>
<th>deposition condition</th>
<th>resistivity ($\Omega \cdot \text{cm}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TH-ALD</td>
<td>0.0146±0.0003</td>
</tr>
<tr>
<td>PA-ALD</td>
<td>28±6</td>
</tr>
<tr>
<td>LP-ETP-MOCVD</td>
<td>24±6</td>
</tr>
<tr>
<td>HP-ETP-MOCVD</td>
<td>0.015±0.002</td>
</tr>
</tbody>
</table>

The resistivity of the TH-ALD and HP-ETP-MOCVD deposited films are comparable to values given in the literature.  

The resistivities of the films deposited by means of ETP-MOCVD under the low pressure reaction chamber conditions are extremely high. A possible explanation is given in paragraph 3.2.2.2 for this high value.

The low resistivity of the HP-ETP-MOCVD deposited layer can be explained by the large size of the grains. Because of the large grain size the electrons will probably have a high mobility. The films grown under low pressure conditions have pillar-like grains.  

3.1.3 Optical Properties

The real part of the refractive index $n$ of the samples was extracted from the SE measurement data, see Figure 6 for a graph of the real part of the refractive index of the films. There are little differences in the refractive indices of the films deposited by means of the different techniques, but the overall behavior is the same.

The reported refractive index of ZnO for photon energy of 3.18 eV is 2.4.  

The depression process for the PA-ALD films was far from optimized, therefore it is better not to make any far-reaching conclusions.
Figure 6: A graph of the real part of the refractive index $n$ of the four i-ZnO layers versus the photon energy.

The imaginary part of the refractive index $k$ indicates the amount of absorption loss when light propagates through a material. The imaginary part of the refractive index was extracted from SE measurement data. The difference in $k$ in the NIR region was minimal. See Figure 7 for a graph of $k$ versus the photon energy of the four deposited i-ZnO layers. There is a little deviation in shapes and the peak intensities of the four lines in the graph.

Figure 7: A graph of the imaginary part of the refractive index $k$ of the four i-ZnO layers versus the photon energy.
A Tauc plot for direct band gap materials was used to determine the band gap of the films.\textsuperscript{[32]} Note, that the Tauc plot for direct band gap materials is different than for indirect band gap materials. See Figure 8 for the Tauc plot. The band gap of the i-ZnO films is a little different for the four deposition conditions. The band gap of the LP-ETP-MOCVD, HP-ETP-MOCVD, TH-ALD and PA-ALD deposited films were respectively 3.26 eV, 3.26 eV, 3.25 eV and 3.28 eV. The band gaps of these films were lower than the 3.37 eV according to the literature. Explaining the difference between the literature and the results is at this moment not possible. The PA-ALD deposited films have the highest band gap, but should have the lowest the Burnstein-Moss shift.

3.1.4 Overview

The results of the grain size for the different measurement techniques are contradicting. The XRD measurements show similar grain size for the different deposition techniques, meanwhile the AFM images show a variation in grain sizes. This can be explained by the form of the grains. Only the length and width of the grain can be estimated from the AFM images.

The PA-ALD deposited films are not fully characterized because of the bad uniformity. The high resistivity is probably caused by oxygen interstitials. The TH-ALD deposited films have many small grains, therefore electrons need to pass many boundaries. The films have a low resistivity due to well connecting grain boundaries. These grain boundaries are well connecting thanks to the good uniformity and conformality of films deposited with ALD. The films deposited by means of LP-ETP-MOCVD have many small grains and low roughness. The films grown by means of ETP-MOCVD have big grains; therefore the electrons have higher mobility and the film lower resistivity.

The differences in the optical properties of the material are very little. At this moment there are difficulties explaining the differences in the measured band gap and known band gap for ZnO. See Table 6 for an overview of properties of the i-ZnO layers deposited by means of TH-ALD, PA-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD on a SiO\textsubscript{2} substrate.
Table 6: Thickness, roughness, grain size, resistivity and band gap of the i-ZnO films deposited by means of TH-ALD, PA-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD on SiO$_2$. N.M. is the abbreviation for not measured. The error in the resistivity is determined by calculating the standard deviation of the sample.

<table>
<thead>
<tr>
<th>deposition condition</th>
<th>thickness (nm)</th>
<th>roughness (nm)</th>
<th>grain size by AFM (nm)</th>
<th>resistivity ($\Omega$*cm)</th>
<th>band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TH-ALD</td>
<td>45.5±0.1</td>
<td>1.7</td>
<td>55±5</td>
<td>0.0146±0.0003</td>
<td>3.25</td>
</tr>
<tr>
<td>PA-ALD</td>
<td>50.8±0.1</td>
<td>N.M.</td>
<td>N.M.</td>
<td>28±6</td>
<td>3.26</td>
</tr>
<tr>
<td>LP-ETP-MOCVD</td>
<td>45±1</td>
<td>1.9</td>
<td>78±5</td>
<td>24±6</td>
<td>3.26</td>
</tr>
<tr>
<td>HP-ETP-MOCVD</td>
<td>42±1</td>
<td>5.2</td>
<td>94±5</td>
<td>0.015±0.002</td>
<td>3.28</td>
</tr>
</tbody>
</table>

3.2 Change over Time

3.2.1 Spectroscopic Ellipsometry

The films are characterized with SE on a regular basis on two spots for each sample. The differences in the samples are very little over time. From these measurements, it can be concluded that any changes in the resistivity should not be related to large material changes. See Figure 9 for a graph of the change of dielectric function $\varepsilon_2$ of the i-ZnO film deposited by means of LP-ETP-MOCVD. There is only a small variation in the dielectric function of the film after two weeks of exposure to light in vacuum.

![Graph of dielectric function $\varepsilon_2$](image)

Figure 9: A graph of the dielectric function $\varepsilon_2$ of the i-ZnO films deposited by means of TH-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD on SiO$_2$ versus the photon energy. There is only a small variation in the dielectric function after two weeks of exposure to light in vacuum.

3.2.2 Electrical Properties

The resistivity of the samples is determined by four point probe on the same two spots for each sample. This technique is expected to be most sensitive. The symbols in the graph represent the change over time of the resistivity of the measuring spots and the lines are the weighted averages of the change of resistivity.
3.2.2.1 Thermal Atomic Layer Deposition

The average resistivity of the films as deposited is 0.0146 ± 0.0003 Ω·cm. See Figure 10 for a graph of the resistivity of TH-ALD films versus time. The resistivity of the samples exposed to light decreases till the reaction is saturated. The resistivity of the dark samples increases, but the sample stored under dark-air condition increases faster. After 23 days the films are exposed to UV and air for 1.5 hours. The resistivity of the dark films decreased during the treatment. The change of resistivity by the treatment of the light exposed films is negligible.

![Figure 10: A graph of the resistivity to the resistivity as deposited of the samples versus the time. The thermal atomic layer deposition deposited samples were stored under four different conditions. The symbols represent the change of the spot. The line represents the change of the average resistivity as deposited. The purple bars in the graph represents ultraviolet and air exposures. The duration of the first exposure was 1.5 hours and the second 2 days.](image)

After the UV and air exposure the films are stored under the same conditions as for the treatment for 33 days. The resistivity of the dark films increased again, but the increase of the resistivity of the dark-air film is the biggest. The resistivity of the light exposed films is approximately the same after the 33 days. The films are exposed again to UV and air, but this time for two days. The resistivity of all four samples decreased by the longer treatment, but the decrease is bigger of the samples with an increased resistivity. It is consistent with the literature that the vacuum stored films have a higher conductivity than the films stored in air with the same light conditions. The biggest decrease of the average resistivity is 34.6% for the light-vacuum film.
3.2.2.2 Low Pressure Chemical Vapor Deposition by an Expanding Thermal Plasma

The average resistivity of the films as deposited is 24 ± 6 Ω·cm. The conductivity of the sample which is stored in dark and exposed to air decreased. The variation in the resistivity of the two spots of the sample as deposited was quite big. The film might not be uniform which can be the cause of the big differences between the two spots during the experiment. The resistivity of the other three films decreased during the storage. The decrease is the biggest for the light exposed films. The decrease of dark-vacuum film cannot be explained by the literature. Assuming that the film is oxygen rich; the desorbed oxygen is pumped away, resulting in a higher mobility. The conductivity of all films decreases by the UV and air treatment of 2 days. See Figure 11 for a graph of the change resistivity of the samples over time. The biggest decrease of the average resistivity is 98.6% for light-air film.

Figure 11: A graph of the resistivity to the resistivity as deposited of the samples versus the time. The low pressure expanding thermal plasma deposited samples were stored under four different conditions. The symbols represent the change of the spot. The line represents the change of the average resistivity as deposited. The purple bar in the graph represents ultraviolet and air exposure. The duration of this exposure was 2 days.
3.2.2.3 High Pressure Chemical Vapor Deposition by an Expanding Thermal Plasma

The average resistivity of the samples as deposited is $0.015 \pm 0.002 \ \Omega\cdot\text{cm}$. During storage the resistivity of the light exposed films decreases, the change of the film stored in vacuum is the biggest which is consistent with the literature. The conductivity of the in dark stored films decreases. After 17 days the films are exposed to UV and air for 2 days. The resistivity of all samples decreased during the treatment. The resistivity of the dark samples decreased more to the resistivity as deposited than the light exposed films due to UV and air exposure. The dark-vacuum film decreased the most in resistivity over the experiment, the resistivity dropped with 46.7%.

![Figure 12: A graph of the resistivity to the resistivity as deposited of the samples versus the time. The high pressure expanding thermal plasma deposited samples were stored under four different conditions. The symbols represent the change of the spot. The line with symbol represents the change of the average resistivity as deposited. The purple bar in the graph represents ultraviolet and air exposure. The duration of this exposure was 2 days.](image)
3.2.3 Transmission storage Container

The samples are stored in plastic containers during the experiment. To determine the absorption of the covers of the storage containers a UV-SE is used to perform a transmission measurement. See Figure 13 for a graph of the transmission versus the photon energy. The red line in the graphs symbolizes the average band gap of the ZnO films.

![Graph of transmission through storage container cover versus photon energy](image)

**Figure 13:** A graph of the transmission through a storage containers cover versus the photon energy of the i-ZnO layer on SiO$_2$, measured with SE-UV. The red line is the average band gap of the ZnO films.

The cover has a high transparency for photon energies below 4 eV and the transparency decreases rapidly for photon energies above 4 eV. The cover blocks almost all light above 4.5 eV. The films can be exposed to UVA and UVB while being stored in the storage container. Light of above the band gap of ZnO can penetrate the container.

3.2.4 Overview

The conductivity of films increases by exposure to light. A transmission measurement is used to determine that photons with energy above the band gap of ZnO can penetrate the storage containers cover, see paragraph 3.2.3. Therefore it is plausible that UV light is responsible for the decrease of resistivity during the experiment. The conductivity of the films stored in vacuum is higher than the films stored in air. The films in vacuum can not re-absorb the desorbed oxygen, because the desorbed oxygen is pumped away. Therefore there is a lower amount of oxygen on the surface which results in less chance of electron scattering and trapping. This leads to higher electron mobility and a higher charge carrier concentration.\(^{(13)}\)

The opposite happens with the dark-air samples. The increase of resistivity is caused by the absorption of oxygen, water or for instance carbon dioxide by the films. This leads to electron scattering and trapping and therefore to higher conductivity.
The films that are stored under dark and vacuum conditions are not exposed to possible causes for the change of the materials. Therefore the change of resistivity is most likely caused by exposure to light and air during the measurements.

The properties of the films are determined during their characterization. For LP-ETP-MOCVD deposited films it is known that they have large open grain boundaries, species enter these grain boundaries and decreases the conductivity of the film. The resistivity of the films deposited by means of LP-ETP-MOCVD had a very high resistivity as deposited, which explains the big decrease compared to the other films. The TH-ALD films are less susceptible for ambient water, because the films are dense and have good uniformity. Therefore there is less chance that ambient species enter the grain boundaries. The HP-ETP-MOCVD deposited films have big grains, therefore the electrons do not have to pass a lot of grain boundaries. Therefore the effect of water on the grain boundaries is probably smaller than for the LP-ETP-MOCVD films. See Table 7 for an overview of the properties of the films deposited by the four different techniques. For an interpretation of these results see Figure 14 for a cartoon of the ZnO films.

Table 7: Thickness, roughness, grain size, resistivity, the maximum decrease of resistivity and the band gap of the i-ZnO films deposited by means of TH-ALD, PA-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD on SiO₂. N.M. is the abbreviation for not measured.

<table>
<thead>
<tr>
<th>deposition condition</th>
<th>thickness (nm)</th>
<th>roughness (nm)</th>
<th>grain size (mm)</th>
<th>resistivity (Ω*cm)</th>
<th>Δ resistivity (%)</th>
<th>bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TH-ALD</td>
<td>45.5±0.1</td>
<td>1.7</td>
<td>25±5</td>
<td>0.0146±0.0003</td>
<td>-34.6</td>
<td>3.25</td>
</tr>
<tr>
<td>PA-ALD</td>
<td>50.8±0.1</td>
<td>N.M.</td>
<td>N.M.</td>
<td>28±3</td>
<td>N.M.</td>
<td>3.26</td>
</tr>
<tr>
<td>LP-ETP-MOCVD</td>
<td>45±1</td>
<td>1.9</td>
<td>27±5</td>
<td>24±6</td>
<td>-98.6</td>
<td>3.26</td>
</tr>
<tr>
<td>HP-ETP-MOCVD</td>
<td>42±1</td>
<td>5.2</td>
<td>26±5</td>
<td>0.015±0.002</td>
<td>-46.7</td>
<td>3.28</td>
</tr>
</tbody>
</table>

Figure 14: A cartoon of the ZnO films deposited by means of (a) ETP-MOCVD under the low pressure reaction chamber condition, (b) ETP-MOCVD under the high pressure condition and (c) TH-ALD.
4 Conclusion

One of the aims of this project was to deposit different i-ZnO layers with a thickness of 50 nm and to characterize them. Three different layers are grown by means of TH-ALD, LP-ETP-MOCVD and HP-ETP-MOCVD. The TH-ALD films have small grains and is more random oriented. The TH-ALD films have a small RMS roughness and are very dense. The films deposited by means of LP-ETP-MOCVD have also a small roughness like the TH-ALD deposited films. The LP-ETP-MOCVD films have a preferential growth direction in the (002) direction. The films deposited under low pressure conditions have columnar crystals. The high number of grain boundaries electrons need to overcome due to the columnar crystal results in a low electron mobility. This is consistent with the high resistivity of the LP-ETP-MOCVD films. The films deposited by means of HP-ETP-MOCVD have big roughness and big grains. The films have preferential growth in the (002) direction. The resistivity is approximately the same as the resistivity of the TH-ALD deposited films. The properties of the deposited thin layers of i-ZnO are the same as for thick layers described in literature.

The deviations in aging of films can be explained by the differences in properties of the films. The columnar structure of the LP-ETP-MOCVD deposited films makes it very susceptible for water at the grain boundaries. The resistivity of the films deposited by the other techniques is less influenced due to the lower amount of grain boundaries or the denser film. The TH-ALD films are very dense and therefore it is difficult for water to penetrate the grain boundaries. Increasing the resistivity of these films is more difficult than for the LP-ETP-MOCVD films. Transport of electrons is not hindered by a lot of grain boundaries in the HP-ETP-MOCVD deposited films, because the films have big grains. The influence of species at the grain boundaries is smaller because of the lower amount of grain boundaries.

The decrease of resistivity of the films by light is consistent with the literature. Light above the band gap of the ZnO was able to penetrate the storage containers. This light causes oxygen to desorb from the surface. This reduces the surface electron depletion region leading to enhanced photoconductivity. The resistivity of the films could be lowered by an UV treatment, even for the films with already saturated reactions during the storage conditions.

The high resistivity of the LP-ETP-MOCVD deposited films can be explained by a high level of oxygen in the film. The decrease of the resistivity dark-vacuum film is possibly caused by the high level of oxygen desorption, the oxygen is pumped away in the vacuum condition resulting in a decrease of the amount of oxygen in the film.
5 Epilogue

Over the last years I lost my interest in physics, because of all the other amazing things in the world. During my internship at PMP I rediscovered my interested in physics. I want to thank Harm for his guidance, his humor and his positivity. I want to thank Mikhail for his contribution and guidance during the ETP-MOCVD depositions and Adriana for her guidance during this project. At this moment I am not sure what I want to do in my professional career, but what I do know is that I want to finish the Applied Physics master and specializing in Plasma Physics and Radiation Technology. After this master I will see what option I like most, but what I learned during this time at PMP is that research can be great fun. I want to end this epilogue with thanking all the other people for their help and the good time here at PMP.
Bibliography


