Mesoporous metal oxides for perovskite solar cells

Project report

by

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Abstract

The aim of this project is to produce perovskite solar cells with the use of three different mesoporous metal oxides. By a subsequent investigation of the function of these three systems and a final comparison the purpose is to find out which mesoporous metal oxide offers the best properties and provides the best performance together with the other components in the solar cell compound. In order to be able to determine which of the metal oxides fits best several investigations have to be performed including SEM, Profilometry, UV-VIS measurements as well as IV- and IPCE- measurements.
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2 Purpose of the project

This project aims to investigate the effect of the mesoporous metal oxide in a perovskite solar cell system. Therefore respective solar cells with three different metal oxides are fabricated and subsequently studied by several characterization methods. However, the original aim of this project was to study the interfaces of light absorbing materials on a metal-oxide substrate. The initial intention was to analyse valence band and conduction band offsets between a perovskite material and three different metal oxides in order to be able to draw the corresponding band diagrams. The band offsets are crucial parameters for device performance in perovskite solar cells. The band diagrams should be investigated using X-ray spectroscopy utilizing ESCA instrument at Angström Laboratory. Unfortunately, due to a leakage in the main vacuum chamber of the ESCA instrument the planned measurements could not be performed. The aim of this project consequently changed to the actual production of perovskite solar cells and other measurement opportunities have been consulted to analyse the metal oxides.

3 Introduction and Background Information

3.1 Solar Cells

Nowadays the demand for energy is increasing constantly and solutions have to be found in order to assure those high needs in future. When thinking about such solutions also the climate change and environmental issues have to be taken into account. Therefore, especially renewable energies play a major role and among these the photovoltaic sector is of special interest. The sun is our biggest energy source and the challenge is to convert the provided solar energy into electricity as efficient and cost-effective as possible. Solar cells are devices which can do this conversion directly by absorption of photons and charge separation of the created electron-hole-pairs. In the last years the most important development in the field of photovoltaics have been perovskite solar cells, because it turned out that this new generation of solar cells is able to satisfy both, the demand for high efficiencies and low cost manufacturing. The power conversion efficiency of perovskite solar cells has exceeded 15% in a very short period of research approaching the efficiency of silicon solar cells (1st generation solar cell), which are the dominating solar cells at the market at present and thereby overtaking many other technologies. Besides that, there is a wide range of techniques, solution to vacuum based, which can be used to fabricate the devices.\textsuperscript{[1][2]}
3.2 Perovskite material

The name “Perovskite” is the common term for any type of crystal structure with the general chemical formula – ABX$_3$ (e.g. CaTiO$_3$), in which A and B are cations of different sizes an X is an anion. An example for the perovskite structure can be seen in Figure 1. For interesting perovskites in photovoltaic applications, the large cation A is represented by suitable organic species usually the methylammonium ion (CH$_3$NH$_3$), while the small cation B is Pb and the anion X is a halide (mostly I, Cl or Br). In this way the very efficient organic-inorganic hybrid perovskite materials are created, where methylammonium lead halides (CH$_3$NH$_3$PbX$_3$) are the front-and-centre perovskite materials at the moment. They are very versatile materials as they can be used as light absorber, hole conductor, as a combined light absorber and hole conductor or as a combined light absorber and electron conductor. [3] In this project methylammonium lead triiodide (CH$_3$NH$_3$PbI$_3$) was used as the perovskite material. [4]

![Cubic perovskite crystal structure](image)

This material is very suitable for solar cell applications because of its almost ideal direct bandgap of 1.55 eV (ideal bandgap of GaAs: 1.42 eV) [5] and the good sensitizing property. Most of the incoming light can be absorbed within a layer of only about 2 µm, which makes this material a very promising sensitizer in high efficiency solar cells. [6]

3.3 Development of Perovskite Solar cell

Perovskite Solar cells originate from the architecture of dye-sensitized solar cells, where the perovskite material is deposited on top of a mesoporous TiO$_2$ structure, acting as the sensitizer. In order to understand the function of a perovskite solar cell it is necessary to know how the base technology – the dye-sensitized solar cell – works. In Figure 2 a schematic overview of a dye-sensitized solar cell can be seen.
The dye-molecules adsorbed on the mesoporous TiO$_2$ layer act as the light absorbing material. The mesoporous layer of the wide-bandgap semiconductor TiO$_2$ ($E_g=3.2$ eV) offers a big surface area which enables a higher coverage of dye-molecules and thereby more electron injections. As a substrate for the mesoporous oxide layer and transparent conducting front electrode glass with a conducting film is used (FTO or ITO). The back contact is mostly a thin metal film. The incoming light is absorbed by causing an electron transfer from a low energetic state (HOMO) into a higher energetic state (LUMO) in the dye which leads to the creation of an exciton, a bound electron-hole-pair, which has to be separated. The photo-excited electron is ideally injected into the TiO$_2$ network and transported to the electrode (FTO substrate) by diffusion processes and then forwarded to an external circuit. The hole is transported through the hole-conducting layer. In order to make this charge transfers possible the energy alignment has to fit, which means that the materials for the different parts of the cell have to be compatible to favour the right processes. The oxidized state of the dye is reduced by the electrolyte to make further excitation processes possible and at the counter electrode the electrolyte itself is reduced. Of course recombination processes, which lower the performance of those cells, play a big role in this charge transfer system and are one of the big issues and limitations for efficiency.

The problem with the first perovskite cells produced by substituting the dye molecule with the perovskite material was the stability. Because of the fact that organo-lead halide perovskites are ionic crystals they dissolve in polar solvents and it is not possible to use them together with liquid electrolytes. Therefore solid hole-conductors have to be used instead of the liquid electrolyte. In the samples fabricated for this project the hole-conducting layer is represented by Spiro-MeOTAD. The two major structures of perovskite solar cells developed so far can be seen in Figure 3, on the one hand it is the mesoscopic structure and on the other hand the planar structure.
As previously mentioned the initial prototypes were based on the architecture of dye-sensitized solar cells where the perovskite compound was deposited on top of the mesoporous TiO$_2$ structure (Fig.3a.). More recent works demonstrated that also a simpler geometry is able to convert light with reasonable efficiencies. In the so called planar structure the perovskite layer is sandwiched between a compact thin film of TiO$_2$ and a hole-conducting layer (Fig.3b.).

### 3.4 Energy Alignment and Electronic Structure

Energy alignment between the different materials in the solar cell is a fundamental parameter affecting the function of the system. Bandgaps, relative valence and conduction band positions and offsets are of high importance and have an influence on light absorption and charge separation. The bandgap has to be efficient for absorbing visible light, the conduction band edge of the electron conducting semiconductor has to be a bit lower than the conduction band edge of the absorber to make electron injection favourable. Concerning the hole injection the HOMO of the hole-conducting layer has to be slightly higher than the valence band edge of the absorbing material. Also the total output voltage of the solar cells is defined by the difference between the conduction band edge in the semiconductor and the HOMO in the hole conducting molecule. By choosing different materials all this energy levels can be changed and thereby the performance of the cell improved or downgraded. In this work three systems with varying metal oxides are investigated (TiO$_2$, ZnO and Al$_2$O$_3$). A schematic energy level diagram of TiO$_2$, CH$_3$NH$_3$PbI$_3$ and spiro-MeOTAD as it is the case in one of the three investigated systems can be seen in Figure 4.
Especially the energy band alignment at the interfaces of a sensitizing material is of direct relevance for the materials electrical functions. The most important interface-related quantities that are determined by band alignment are the barrier heights for charge transport, given by the Fermi level position at the interface. The valence and conduction band discontinuities at the interfaces largely define the potential distribution and the current transport through these interfaces, a significant property in semiconductor devices. Unfortunately it was not possible to perform X-ray spectroscopy measurements together with UV-VIS spectroscopy, which would be powerful methods in order to explore those band diagrams and alignments. Instead, devices where produced and both IV- and IPCE measurements performed to analyse the effect of the different metal oxides.

4 Basic Solar cell characterization

Characterization of solar cells can be performed using many different techniques and depending on the method chosen information about different parts of the device is provided. The techniques used in this work are: SEM, Profilometry, UV-VIS, IV- and IPCE-measurements. For each of these methods a short description can be found in the following sections.

4.1 SEM

Scanning electron microscopy is a method based on the scanning of a sample surface with a focused electron beam. Due to the interaction of electrons with the atoms of the sample, a plurality of signals is generated, which return information about the samples surface. In a conventional SEM, the secondary electrons (SE), the backscattered electrons (BSE) and the characteristic X-rays are used for imaging. [9] The SEM-images for this project were acquired on a high resolution Zeiss Leo1550 FEG SEM situated in the clean-room facility of the Ångström laboratory and only the secondary electron signal was used for imaging.
4.2 Profilometry
With this technique heights and surface profiles of the produced layers can be measured. A cantilever is scanned over the sample which registers height variations. The profilometer used in this work was the DektakXT at Uppsala University.

4.3 UV-VIS
In UV-VIS measurements the sample is exposed to light, the wavelengths are scanned over a defined range (VIS to near IR) and absorption, transmittance as well as reflectance can be measured corresponding to the respective wavelength by comparing the transmitted signal measured at the detector with the incident signal. The transmittance $T$ can be used to calculate the absorbance $A$ according to the following equation 1.

$$A = -\log_{10} T$$

(1)

Transmittance $T$ and Reflectance $R$ can be calculated with the following equation 2.

$$A = 1 - T - R$$

(2)

The UV-VIS measurements were carried out on an Ocean Optics HR2000 fiberoptic spectrometer which measures the whole sample spectrum at once using a deuterium and a halogen light source. [3]

4.4 IV-measurements
The IV-curve delivers information about the energy conversion efficiency of a solar cell. For this measurement the sample has to be exposed to a light source with a spectrum which is comparable to the sun’s spectrum. While the sample is illuminated the current is measured as a function of the voltage, which is modified through a variable external load. Important values to get a useful approximation model of the electrical behaviour of the cell are the open-circuit voltage $V_{OC}$ (voltage at zero current) and the short-circuit current $I_{SC}$ (current at zero voltage). A schematic IV-curve can be seen in Figure 5.
The produced power of a solar cell is the product of current $I$ and voltage $V$. If photovoltaic cells were ideal the IV-curve would be a square. Because of the fact that no solar device is ideal, there is a deviation of the measured IV-curve from the theoretical predictions described by the fill factor (FF). This fill factor is expressed as the ratio of the maximum power of the solar cell to the product of $V_{OC}$ an $I_{SC}$. The efficiency of a solar device is described by the following equation 3 where $P_{in}$ is the light intensity.

$$\eta = \frac{I_{SC}V_{OC}FF}{P_{in}}$$ \hspace{1cm} (3)

The measurements were carried out with a Newport solar simulator under simulated solar radiation. A silicon diode served as a reference to calibrate the system. A computer-controlled source meter was used for the measurements. [3]

### 4.5 IPCE-measurements

The IPCE-measurement (Incident photon to current conversion efficiency) is a method to determine photon to current conversion by measuring how efficiently the incident light is converted into electrical energy at a given wavelength (visible range). The wavelength is regulated and scanned through the whole range with a monochromator. The IPCE is given by the following equation 4 with $i_{ph}$ being the photocurrent density and $P$ the light density.

$$IPCE = \frac{hc i_{ph}(\lambda)}{e \lambda P(\lambda)}$$ \hspace{1cm} (4)

If the solar cell is working the generated curve should look like the one in Figure 6. This graph shows that over the range of visible light the conversion of incoming photons to actual current is working well.
This measurement was carried out using a xenon light source together with a computer-controlled monochromator. [12]

5 Experimental part

5.1 Metal oxide development

In this project three different systems of solar cells are fabricated, each with a different metal oxide used: TiO$_2$, ZnO and Al$_2$O$_3$. Because of the fact that the conducting glass substrates (covered with FTO) are purchased and therefore freely available, the first step in the production of the solar cells was to find out how the different metal oxides can be synthesized. For the TiO$_2$-based perovskite solar cell a blocking layer of TiO$_2$ as well as a mesoporous layer has to be synthesized. However, for the solar cells with ZnO and Al$_2$O$_3$ a simpler geometry without a blocking layer is used. The significance of the TiO$_2$ blocking layer in the classical architecture of perovskite solar cells is to prohibit contact between the hole-transporting layer and the FTO layer in order to prevent a short circuit. Since no blocking layer is used together with ZnO and Al$_2$O$_3$ one of the main requirements for these metal oxide layers is therefore a very dense morphology and besides that, the layer has to cover the whole substrate. In the following sections the generation of the metal oxides is described. The recipes for the TiO$_2$ blocking layer and the mesoporous layer where already known as well as the one for Al$_2$O$_3$, but the way of developing the ZnO layer was by trial and error.

5.1.1 TiO$_2$ blocking layer and mesoporous layer

The blocking layer of TiO$_2$ was created by spray-pyrolysis. The precursor solution was produced by mixing TTIP (titanium tetraisopropoxide) with acetylacetone in a ratio of 1:1. Prior to deposition the precursor was diluted 1:9 in isopropanol. Nitrogen N$_2$ served a carrier gas. The FTO-glass substrates were heated on a hotplate to 550°C and then the precursor was deposited using an airbrush. The nozzle was moved over the substrate at a distance of about 10 cm. Several spray cycles were necessary in order to create a thick
enough layer. The TiO$_2$ film is created by the reaction of the precursor solution with atmospheric oxygen at the hot substrate surface. The temperature was kept at 550°C for 20-30 minutes before cooling down. The different steps of spray pyrolysis can be seen in Figure 7.

After the production of the blocking layer the mesoporous layer has to be synthesized. Therefore 100 µl of diluted TiO$_2$ Dyesol 18NRT paste (1:5 by weight in terpinol) is used. After sonicating the precursor solution is spin-coated with 3000 rpm for 30s on the substrates (already covered with the blocking layer), dried at 120°C and after that the sample has to be sintered in an oven or on a hotplate. The sintering steps are listed in Table 1.[10]

<table>
<thead>
<tr>
<th>Step</th>
<th>T / °C</th>
<th>t / min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>320</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>390</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>500</td>
<td>30</td>
</tr>
</tbody>
</table>

5.1.2 Al$_2$O$_3$ layer

The reason why Alumina is one of the metal oxides used in perovskite solar cell production is not clearly obvious, because it is an insulator (E$_g$ > 4 eV) and therefore photoelectrons generated in the perovskite cannot be injected into this material. Nevertheless it turned out that even though Alumina has very different properties compared to TiO$_2$ the solar cell works and Alumina seems to serves as a scaffold for the perovskite layer.

The basis for the synthesizing of the Alumina layer was Aluminium oxide dispersion (20 wt. % in isopropanol). Following a recipe to produce a 400 nm film[13] the dispersion was diluted with isopropanol (1 mL Al$_2$O$_3$, 2 mL ISO), sonicated for 1 h and then deposited by
spin-coating followed by drying on a hotplate at 150 °C for about 30 min. For the spin-coating three different settings were chosen in order to investigate if there are differences in the resulting layers (Table 2). By increasing the rotations per minute it may be possible to decrease the layer thickness. Another parameter controlling the final thickness is the initial concentration of nanoparticles in the dispersion before spin coating, but this parameter was not varied in this work.

Table 2: Spin-coat settings for Alumina layer

<table>
<thead>
<tr>
<th>Settings</th>
<th>pre-step / rpm</th>
<th>main step / rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>3000</td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>4000</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>5000</td>
</tr>
</tbody>
</table>

5.1.3 ZnO layer

Zinc oxide ($E_g$=3.37 eV)\(^{14}\) is a material with very similar properties compared to TiO$_2$ ($E_g$ = 3.2 eV)\(^{15}\) and therefore it is justifiable to use it instead of TiO$_2$. The basis of synthetizing this layer was again a Zinc oxide dispersion (40 wt. % in butyl acetate). The variables in the formation of the precursor solution in this case were the choice of solvent to dilute the dispersion in order to get a thinner layer and improve the viscosity for spin-coating, the ratio of dilution and spin-coat parameters. The first two variables were fixed by choosing ethanol as a solvent and diluting the dispersion in a ratio of 1:2 (1 mL Zinc oxide, 2 mL Ethanol) which later turned out to be a reasonable choice. The precursor solution was sonicated, deposited by spin-coating (settings same as for Alumina, see Table 2) followed by drying on a hotplate at 110°C for about 30 min.

5.2 Solar cell fabrication

After the development of the different metal oxides the actual solar cells were fabricated. The solar cell architecture for the different devices can be seen in Figure 8 and Figure 9. As one can see by comparing figure 8 and 9 in the devices with ZnO and Al$_2$O$_3$ no blocking layer is used.
The different materials used for the solar cell fabrication can be found in Table 3.

<table>
<thead>
<tr>
<th>Function of material</th>
<th>Material used</th>
</tr>
</thead>
<tbody>
<tr>
<td>conducting glass</td>
<td>Glass, coated with layer of transparent electrical conducting fluorine-doped tin oxide (FTO)</td>
</tr>
</tbody>
</table>
| metal oxide (electron-conducting-layer) | – TiO₂ (mesoporous and blocking)  
 – ZnO (mesoporous)  
 – Al₂O₃ (mesoporous)  |
| Perovskite                    | Methylammonium lead iodide (CH₃NH₃PbI₃)                                     |
| HTM (hole-conducting-layer)   | Spiro-MeOTAD                                                                  |
| electrodes                    | Silver (Ag)                                                                   |

The first step in the production process is to dimension the substrates. This size is predetermined by the sample holder in the evaporator in which the samples at the end have to fit. Therefore the sample size was chosen to be 2.5 cm x 1.5 cm and the FTO glass substrates were cut into this dimension with a diamond blade glass cutting gadget.
In order to clean the substrates and thereby avoid contaminations the substrates were put into acetone and then sonicated for about an hour. **The second step** is etching, because on one side of the sample the FTO has to be removed. A wet chemical etching process was utilized using ZnO powder together with hydrochloric acid (4 molar). These two components react and thereby etch the FTO away ($Zn + 2HCl \rightarrow H_2 + ZnCl_2$). First the powder is put onto the sample at the area were the FTO has to be removed and then the hydrochloric acid is dropped on the powder. The chemical reaction takes about 20 min and after that the substrates again have to be sonicated for 1 hour to clean them. The first two production steps are schematically pictured in Figure 10.

![Figure 10: Fabrication steps 1 and 2](image)

**The third step** is the deposition of the metal oxides, which has already been described in the previous section about the metal oxide development (see chapter 5.1). **The fourth step** is the perovskite layer deposition with a two-step method for which a precursor solution has to be prepared. Therefore PbI₂ and CH₃NH₃I (MAI) are dissolved in DMF (Dimethylformamid) and DMSO (Dimethylsulfoxid) respectively. The amounts used of each component are: 461 mg PbI₂, 159 mg MAI, 0.75 mL DMF and 0.25 mL DMSO. The solution is blended and then heated at 70°C with shaking to create a dispersion. Thereafter the dispersion is loaded onto the samples already covered with the respective metal oxide for about 1 min and then spin-coated with 3500 rpm for 30 sec. To finish the perovskite layer the sample has to be heated at 120°C for about 30 min on a hot plate. A sign that the components have reacted and the perovskite crystal structure has been formed is the colour change of the perovskite layer during drying. The appearance of the dispersion before it is dried is yellow, which is an indication for the PbI₂ ($E_g=2.31$ eV) present in the solution. After the sample is put onto the hotplate, the colour quickly changes to dark brown, which means that the perovskite crystal has been formed. There was a difference visible between the perovskite films deposited on the different metal oxides. The colour of the perovskite layer deposited onto the ZnO was clearly brighter and more yellowish than the one on TiO₂ and Al₂O₃.
This could mean that the crystallization has not completely happened or that the layer is much thinner. The two-step deposition method is straight forward to implement but however, the perovskite film is rather heterogeneous and does not have the best quality compared to other methods like the sequential methods or the vacuum-based-approaches.

**The fifth step** is the deposition of the hole conducting layer which in this case is Spiro-OMeTAD. For the production of this solution 40 mg Spiro-MeOTAD is weighed, mixed with 500 µL Chlorobenzol and then 14.25 µL tributyl phosphate (tbp) and 8.75 µL Li-TFSI (lithium bis-trifluoromethanesulfonimide) are added. This solution is again loaded onto the sample already covered with the perovskite for 1 min and then spin-coated with 3000 rpm for 30 sec. The amounts for the components used have to be adhered very precisely, because otherwise it can happen that the perovskite layer gets dissolved which happened in the first cycle of sample production. It turned out that the precursor solution was prepared in a wrong way using too much Chlorobenzol. Before the last step all layers deposited have to be scratched off from a small area (≈3 mm) on the long side of the sample (opposite to the side where the FTO was etched away) in order to allow contact between the FTO and the silver electrode (compare Figure 8/9).

**The sixth and final step** in the fabrication process is the deposition of the electrodes (Silver in this case), for which a metal evaporator is used. A 200 nm film is created by evaporation of the source material silver and a subsequent condensation on the substrate. The evaporator used was a LEICA EM MED020 at Uppsala University. After the execution of all this steps described above the solar cells are finished. An example how the cells look like can be seen in Figure 11.

![Figure 11: Example of solar cell](image)

During the fabrication process UV-VIS measurement have been performed. The results can be found in the following chapter.
6 Results and Discussion

6.1 SEM and Profilometry

After the synthetizing of the three different metal oxides SEM pictures have been made. The aim is to compare them and in addition to analyse the influence of the various spin-coating parameters used. Concerning the SEM pictures it has to be mentioned that their quality is not the best, especially the Al₂O₃ samples. Since metal oxides are not conductive and no sputtering equipment was available the samples were charging a lot and thereby limiting the quality of the pictures. Concerning the thicknesses determined with the Profilometer only the values for TiO₂ blocking layer and mesoporous layer are available.

6.1.1 TiO₂

The SEM pictures of the TiO₂ blocking layer and the mesoporous layer can be seen in the following pictures. The thicknesses received for the two layers can be found in Table 4.

Table 4: Thicknesses of TiO₂ layers

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ blocking</td>
<td>112</td>
</tr>
<tr>
<td>TiO₂ mesoporous</td>
<td>687</td>
</tr>
</tbody>
</table>

Especially for the SEM pictures of the TiO₂ blocking layer excessive charging occurred and therefore no close-up picture could be taken.

a)
In Figure 12 the mesoporous structure of the TiO$_2$ layer can be seen. It provides a huge surface area which is of special importance in the dye sensitized solar cell structure (DSSC), where the dye molecules are adsorbed onto this porous structure. The higher the surface area, the more molecules can be adsorbed, the more photo-electrons can be generated and injected. Since the Perovskite solar cell origins from the DSSC this mesoporous structure is also used in this system, but at the moment researchers are not sure if this mesoporous layer is really necessary. As already mentioned in the introduction it turned out that also the “sandwich architecture” without a mesoporous layer is working.

In Figure 13 the SEM picture of the blocking layer in an overview mode can be found. No closer picture was possible due to charging.
6.1.2 ZnO

For the ZnO layer three different spin-coat parameters have been used which can be found in Table 2. The resulting SEM pictures can be found in the following Figure 14. Concerning the thickness of the ZnO layers unfortunately no data is available.

In picture a) one can see that the ZnO layer is not completely flat, but rather wavy. This is a consequence of the spin-coat procedure. Reasons for that could be a too slow rotation speed or the wrong choice of the solvent (Ethanol) which has an influence on...
the viscosity and flowing property. However, the requirement of a dense morphology seems to be fulfilled and can be seen in b) and c). Comparing the mesoporous structure with the one of TiO$_2$ it is clearly obvious that the ZnO film is less porous. Because of the fact that together with ZnO and Alumina no blocking layer is used, this is not a problem but rather helpful to prevent recombinations and short circuiting.

Figure 15: SEM pictures ZnO; 4000 rpm; different magnifications
As can be seen in Figure 15 the usage of a higher rotation speed (4000 rpm) does not really affect the quality of the film. The wavy character stays the same and when comparing the most magnified pictures one cannot really detect a significant difference to Figure 14.

Figure 16: SEM pictures ZnO; 5000 rpm; different magnifications
Also the increase of the rotation speed to 5000 rpm does not really improve the wavy appearance of this film (see Figure 16), but still the dense morphology is given. Summing up these results the rotation speed is not an important parameter concerning the flatness of the film. One possibility to improve the flatness could be the choice of a different solvent. Nevertheless, the ZnO film covers the whole substrate and shows a dense character which is very important for the function of the solar cells.

### 6.1.3 Al$_2$O$_3$

The Alumina samples were very difficult to measure because of charging. The originated pictures can be seen in the following figures. Again three different spin-coating parameters were applied and the effects are analysed. Unfortunately it was not possible to measure the actual height of the Alumina film, but according to the recipe used, the film is supposed to have a thickness of about 400 nm.
Unfortunately in none of the three pictures in Figure 17 the actual crystalline mesoporous structure can be seen, because it was not possible to focus in such a high magnification mode. What can be said about this Alumina film is that it has a very uniform and flat appearance throughout the substrate and it is covering the whole area. There are no FTO parts visible not even at the borders. So also for this film the requirement of coverage and dense character is fulfilled. The only exception is the border area, where the Alumina film is brittle and dissolving from the substrate. But the important area of the solar cell is the middle area and therefore this defect does not play a big role. In the following pictures the Alumina films with higher rotation speeds can be seen.
Again no relevant differences can be observed. The film looks uniform, dense, it is covering the whole substrate and features defects at the borders.
For the samples rotated at a speed of 5000 rpm (Figure 19) the same film quality is observed as for the previous two. The only things that have improved are the boundary artefacts. The film is still brittle indeed but not dissolving anymore, which indicates that a higher rotation speed seems to have a positive impact on the film quality at the border areas.

6.2 UV-VIS

The UV-Vis measurements where performed several times during the fabrication process with the aim to see if the different films are present on the substrate and to determine the absorption behaviours and band gaps. Even though this UV-VIS measurement is not very accurate it gives an idea about the formation of the different layers. It has to be mentioned that also without this measurement it was clearly visible with the eyes, that the films have been formed. In the following Figure 20 the spectrum of the light source used for the absorption measurement can be seen. The spectrum results from two complementary light sources namely a deuterium lamp for the UV range and a halogen source for the visible range.

![Source spectrum UV-VIS](image)

The absorption spectra were all referenced to the basic material glass with FTO. The wavelength regions smaller than 300 nm and bigger than 1000 nm are irrelevant because those ranges are dominated by noise. The first measurements were performed after the creation of the metal oxides in order to see if a metal oxide layer has been formed or not and in addition to determine the band gap of the respective materials. The absorption spectrum of TiO$_2$ together with a linear fit can be found in Figure 21.
This absorbance curve shows the expected trend. As can be seen in this plot the absorbance starts to increase at around 400 nm, which corresponds to an energy of 3.1 eV. The band gap of TiO₂ that can be found in literature is 3.2 eV and lies in the UV range. To determine a more accurate value for the band gap of TiO₂ a linear fit was performed. With the values obtained for the slope and intercept of the linear fitting curve the value at which the TiO₂ material starts to absorb turned out to be 384 nm. This corresponds to an energy of 3.22 eV and therefore matches perfectly with the band gap for TiO₂ that can be found in literature.

In the next Figure 22 the absorption spectrum of Alumina can be seen.
No absorption can be observed, because the band gap of Alumina is too high and not possible to measure with this UVVIS equipment. It is situated somewhere in the area smaller than 200 nm which is dominated by noise. One possibility to determine this band gap would be X-ray absorption spectroscopy, but for this measurement a synchrotron source needs to be provided.

In Figure 23 the absorption spectrum together with a linear fit of ZnO can be seen.

In this spectrum a sharp absorption increase can be observed. Therefore a linear fit was performed in order to determine the band gap of ZnO. With the values obtained for the slope and intercept of the linear fitting curve the value at which the ZnO material starts to absorb came to be 385 nm. This corresponds to an energy of 3.22 eV and therefore matches perfectly with the band gap for ZnO that can be found in literature and is 3.2 eV.

After these measurements the fabrication process of the solar cells was continued by adding the perovskite layer. In order to see if the perovskite has crystallized again UVVIS measurements were performed and can be observed in the following figures.
In Figure 24 the spectrum of methyl ammonium lead iodide on top of TiO$_2$ can be seen. There are two increase steps recognizable, one at about 750 nm and one at 500 nm. The step at 750 nm (approximately 1.65 eV) arises from MAPbI$_3$ because it matches quite well with its band gap of 1.55 eV and hints that there is a perovskite structure present in the film. The existence of a second step at 500 nm (approximately 2.48 eV) means that PbI$_2$ ($E_g = 2.31$ eV) is still available in the film which indicates that the film has not completely crystallized. The presence of PbI$_2$ is not clear yet. Actually a uniform crystalline structure would be the best for the function of the solar cells, but it has been proved, that some amount of PbI$_2$ present in the perovskite film can improve the performance because of its passivation ability. [1] In the following Figure 25 the absorption spectrum of perovskite on top of ZnO can be seen.
Here the absorbance steps do not have a distinct character and are much weaker. As already mentioned in pervious sectors also the colour of the perovskite on top of ZnO was much brighter than on TiO₂ or Alumina. An explanation for this could be that less perovskite has been formed. Also in Figure 25 you can see a weak step at 500 nm which means that PbI₂ is present. Figure 26 shows the plot for perovskite in top of Alumina.

![Absorption spectrum of perovskite on Alumina](image)

On the contrary to ZnO and TiO₂ in the spectrum of perovskite on Alumina no step originating from PbI₂ can be observed, which indicates that the film has fully crystallized into the perovskite structure.

Summing up all these results the crystallinity of the perovskite film seems to be best on top of Alumina. On top of ZnO and TiO₂ some PbI₂ has remained which leads to the second step in the absorption spectrum. The weakest steps are present in the perovskite layer on top of ZnO which also exhibits a brighter colour compared to the other films. The UV-VIS measurement of the TiO₂ layer is unfortunately erroneous and the results cannot be taken seriously. Also for the measurement of Alumina another method has to be used, since the UVVIS delivers no results.

### 6.3 IV-measurement

In order to find out if the fabricated solar cells are working the IV-curves were measured. All devices showed a very high resistance, but some of them especially those with ZnO delivered promising results. Lots of measurements have been executed and thereby a huge amount of data was collected. In this chapter only the representative results for each metal oxide are presented. A silicon diode served as a reference to calibrate the system.
6.3.1 Solar cell with TiO₂

The results for the original solar cell with TiO₂ blocking layer and mesoporous layer unfortunately were not really promising. All of the tested cells showed a very resistive behaviour which can be seen in Figure 27.

![IV curve of solar cell with TiO₂](image)

Figure 27: IV curve of solar cell with TiO₂

Reasons for this behaviour are versatile. One of them could be contaminations which arise during the fabrication process. Beginning at the substrates over the metal oxide layers to the perovskite and HTM layer, each step entails contaminations because the production is executed in a normal laboratory surrounding where foreign particles are naturally everywhere. More accurate cleaning of the devices during the fabrication could probably improve the function of the cell. Another point is the overlap between the Silver electrode (touching the FTO) and the HTM layer, which was the case in the production of these cells. This condition is not beneficial for the system since the electrons have to overcome additional barriers. More accurate work and more time for the production would definitely favour a better performance.

6.3.2 Solar cell with Alumina

In the following Figure 28 the result for the solar cell with Alumina can be observed. Compared to the previous IV curve this one shows again a resistive behaviour, and not a curve like a solar cell curve should look like. This condition is also confirmed by the bad values for efficiency, $V_{OC}$, $I_{SC}$ and Fill factor.
Table 5: Values from IV measurement Alumina

<table>
<thead>
<tr>
<th>Efficiency / %</th>
<th>$V_{OC} / V$</th>
<th>$I_{SC} / mAcm^{-2}$</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,00112</td>
<td>-0,0015</td>
<td>0,319</td>
<td>0,234</td>
</tr>
</tbody>
</table>

Figure 28: IV curve of solar cell with Alumina

Again ways to improve the performance of these cells could be a more accurate and clean fabrication and a better alignment of the different layers, especially the position of the electrodes can be improved. Another option could be to use a thin TiO$_2$ blocking also together with Alumina in order to avoid recombinations and short circuiting.

6.3.3 Solar cell with ZnO

The most promising results were delivered by this solar cell configuration with ZnO used as a metal oxide. The results can be seen in Figure 29 and Table 6.

Table 6: Values from IV measurement ZnO

<table>
<thead>
<tr>
<th>Efficiency / %</th>
<th>$V_{OC} / V$</th>
<th>$I_{SC} / mAcm^{-2}$</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3</td>
<td>-0,690</td>
<td>6,53</td>
<td>0,51</td>
</tr>
</tbody>
</table>
Figure 29: IV curve of solar cell with ZnO

The efficiency lies at 2.3 % which is a very promising value. The generated voltage is also quite good but the current drops behind. Reasons for the missing current could be recombinations and traps which prevent the charges from reaching the respective electrodes.

6.4 IPCE measurement

Due to the fact that only the solar cell fabricated with ZnO used as the metal oxide showed reasonable results in the IV measurement, the aim was to measure also the IPCE for this particular cell. Several attempts have been mad to get some values out of this measurement, but it was not possible. The generated current was probably not sufficient enough. Therefore no IPCE characterisation is available for the fabricated solar cells.

7 Conclusions

Summing up all the results and experience gained in the course of this investigation it has to be said that Zinc Oxide showed the best performance as a metal oxide in the solar cell. The synthetized layer with the very dense structure as well as the good IV measurement results make Zinc oxide a very promising material. This is not very astonishing as it is a material with very similar properties compared to TiO₂. Nevertheless TiO₂ remains an important material even though the results of the TiO₂ based cells were not the best in the IV measurement. An interesting value would be the valence band offset between the perovskite and ZnO and TiO₂ respectively, which is a crucial parameter. By comparing the obtained values one could figure out which of the
two materials leads to a better solar cell performance. Reasons for the bad performance of the TiO$_2$ based cell have to be searched for in the fabrication process, where lots of things can be improved like the accuracy and cleanliness. Especially the substrates should definitely undergo a more intense and extensive cleaning process. Another suggestion to improve the function concerns the formation of the TiO$_2$ blocking layer. At the end of the fabrication all layers on one side of the device have to be scratched off in order to expose the FTO again. This is a challenge when it comes to scratch off the TiO$_2$ blocking layer because of its hardness and durability. The other layers are easier to get rid of. Therefore it would be much less destructive for the device if the blocking layer would not be present in this area. This could be achieved by capping this area during the pyrolysis process in which the TiO$_2$ blocking layer is established.
8 References


[16]. AHLAWAT, DHARAMVIR SINGH. Study of band gap energy and thermal properties of PBI2 by photoacoustic spectroscopy. Department of Physics, Chaudhary Devi Lal University, Sirsa 125055, India: s.n., 2012.