Transparent Conductive Oxides in Thin Film Photovoltaics

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Abstract. This paper show results from the development of transparent conductive oxides (TCO’s) on large areas for the use as front electrode in thin film silicon solar modules. It is focused on two types of zinc oxide, which are cheap to produce and scalable to a substrate size up to 6 m². Low pressure CVD with temperatures below 200°C can be used for the deposition of boron doped ZnO with a native surface texture for good light scattering, while sputtered aluminum doped ZnO needs a post deposition treatment in an acid bath for a rough surface. The paper presents optical and electrical characterization of large area samples, and also results about long term stability of the ZnO samples with respect to the so called TCO corrosion.

1. Introduction
For efficient thin film solar cells transparent conductive oxides (TCO’s) are needed as a front side electrode, since a metallic grid as used in crystalline silicon solar cells cannot be used. Various metal oxides with different doping materials can be used as a TCO. In general, a tradeoff between transparency and conductivity of the TCO must be made. For highest conductivity at lowest optical absorption sputtered indium tin oxide (ITO) is an established thin film material on glass, which can be bought on glass substrates in many sizes. However, this material is expensive and should be replaced for low cost applications such as thin film solar modules. Another established TCO is fluorine doped tin oxide (FTO), which is produced by glass companies in an APCVD process in the floatline. It is available on soda-lime glass and on low-iron glass with a substrate size up to 6 m² (Nippon Sheet Glass). This TCO is important for thin film silicon solar modules, since the FTO shows a native substrate roughness with pyramidal shapes, which is important for the light management in the amorphous silicon. In difference to other thin film solar cell technologies, thin film silicon requires besides high optical transparency and high electrical conductivity a rough surface that is able to scatter light under large angles, without disturbing the growth of the silicon with sharp edges or pinholes.

This paper will show results for another class of transparent conductive oxides, based on zinc oxide. Large area deposition was introduced in the 1980s for Ag-based low emissive coatings (low-E) in energy efficient glazing [1]. Reactive DC sputtering is still today used for these dielectric coatings in architectural glazing [2, 3]. These developments were the basics for the high rate magnetron sputtering of aluminum doped zinc oxide (AZO) [4, 5]. The process of high rate sputtering following by a wet chemical etching to achieve a tailored surface roughness suitable for thin film solar cells was (amongst others) developed at the Institute for Photovoltaics of the Forschungszentrum Jülich, the latest results with a two-step etching process with HCl and HF are described in [6]. The etching creates craters on the surface with the ability of excellent light scattering, as it is needed for high efficiency thin film silicon solar cells. Applied Materials commercialized the sputter/etch process
for their “SunFab” turn key thin film silicon production line [7, 8], which was able to produce solar modules with a size of up to 6 m².

![Layers of a thin film silicon solar cell.

Figure 1.](image)

The second large area deposition strategy for doped ZnO is the low pressure CVD process (LPCVD). The first developments were patented by Siemens Solar in the 1980’s for their CIS thin film solar cells [9, 10]. The University of Neuchatel spent a lot of work to create a low pressure process with boron doping, based on the reaction of diethyl zinc (DEZ) and water vapor at moderate substrate temperatures [11]. This technology was licensed by Oerlikon Solar for their turn key thin film silicon production line “ThinFab” for solar modules of 1.4 m² size [12]. The process delivers a transparent conductive oxide with a pyramidal shaped surface texture that is excellent for light scattering in thin film silicon solar cells. The same process can be used for the creation of the cells back contact. Combined with a white paint as back reflector, this is a highly efficient alternative to the usually used metallic back contact of thin film silicon solar cells. Figure 1 shows the layers of a typical thin film silicon solar cell, with a tandem structure of amorphous (a-Si) and microcrystalline (µ-Si) silicon.

2. Methods
The presented results were obtained in the R&D facilities of the Malibu GmbH & Co KG in Bielefeld, Germany. The boron doped ZnO was deposited on soda lime glass in the TCO-1200 LPCVD system from Oerlikon Solar, the R&D version of their commercial deposition system. The System contains
For the use in 1.4 m² solar modules the homogeneity of the TCO is the most important issue. To get an idea about the distribution of film thickness and sheet resistance, both values are measured on a x-y table with a distance 10 cm for each point.

**Figure 2.** Distribution of thickness and sheet resistance on a 1.4 m² substrate coated with ZnO:B. Statistical data of the sheet resistance distribution are given on the right side.
An automated detailed statistical analysis of the results makes it easy to decide if the distribution is good enough for the purpose. Figure 2 shows an example of a LPCVD produced ZnO:B layer. It can be seen, that the coating on the corners is the too thin, resulting in a too high sheet resistance. A carefully adjusted temperature distribution of the hot plate with its three heating zones is essential for a good homogeneity.

In order to do advanced measurements, the substrates have to be cut into smaller pieces. Figure 3 shows on the left graph the results of a series of LPCVD samples produced with the same parameters at the same growth rate, but at different deposition times. To exclude effects from inhomogeneous thicknesses on the substrate, each sample was taken from the same position on the glass. An almost linear behavior can be seen. Also the development of the sheet resistance is proportional to 1/d as it should be. It must be noted that the thickness estimation is based on reflectivity measurements it needs the proper optical constants to deliver good results. So the resistance measurement is usually more reliable to determine the uniformity of the TCO.

![Figure 3. Film thickness, sheet resistance (left) and transmission (right) at various deposition times](image)

On the right side the corresponding measurements in the UV-vis spectrometer show the increasing absorbance of the films with increasing film thickness. Especially in the IR the absorbance increases strongly. It must be noted, that for amorphous silicon the useable wavelength is between 400 and 700nm, while (micro-) crystalline silicon can convert light up to 1100 nm into electrical energy. Such measurements can also be used to calculate the important wavelength dependent “haze”, the amount of diffuse transmitted light to the total transmitted light (not shown). Many other detailed observations can be made on such small samples to explain the microscopic structure of the material and its electrical, optical and morphological properties and the influence of the deposition parameters on the material. However, the ultimate test for the quality of a TCO sample is the fabrication of cells of complete modules.

Another example of an important parameter for the large area homogeneity of LPCVD produced ZnO:B is shown on figure 4. In this graph the distribution of the sheet resistance on the full 1.4 m² area of the glass substrate is illustrated for two different samples. All parameters were the same during deposition, except the total pressure in the chamber, adjusted by a butterfly valve. While the uniformity is good on the left graph for the sample produced at 1.0 mbar, a lower pressure of 0.5 mbar results in a higher average resistance and a higher standard deviation.

The same experiments as above were performed for sputtered and etched aluminum doped ZnO samples. The distribution of the sheet resistance looks different to the LPCVD samples, and it is even more difficult to achieve good uniformity since two completely different processes are involved. Figure 5 shows the sheet resistance on a 1.4 m² substrate with an AZO thickness of 1000 nm, measured after deposition.
It can be seen that the edges in the direction of the movement in the sputter system (right and left edge on the graph) show a lower resistance than the center. The following etch step makes things even worse, since the etching rate depends on the material a lower uniformity can be expected after etching. The process development for this two-step process takes a lot of time and many runs on full size systems.

**Figure 4.** Distribution of the sheet resistance at various deposition pressure.

| Material     | Effect                              |
|--------------|-------------------------------------|
| ZnO:B        | - no peeling                        |
|              | - strong increasing resistance      |
| ZnO:Al       | - peeling, darkening                |
|              | - no change in resistance           |
| SnO2:F       | - peeling, darkening                |
|              | - no change in resistance           |

**Figure 5.** Distribution of sputtered AZO sheet resistance before and after etching (N.U. = non-uniformity)

**Figure 6.** Accelerated test for TCO corrosion, results.
A very important issue for production quality is the long term stability of modules. Besides the efficiency of the encapsulation one important aspect for thin film modules is about the TCO-glass interface. During operation of the modules a potential between the TCO and the frame of the module of several hundred volts may occur. At high operating temperatures of up to 70 °C the migration of sodium ions from the glass into the TCO can happen, resulting in a destroyed TCO layer after a partly couple of years. This so called “TCO corrosion” was first investigated for SnO2:F coatings in a-Si modules [13], but it is also important for ZnO coatings. It can be suppressed by avoiding frames and/or using inverters with galvanic separation, or using sodium free glass. However, all this is a disadvantage for the system, so other solutions like diffusion barriers may be an option. For accelerated corrosion tests, the TCO sample is contacted at the glass side with a conductive glue. Between TCO and glass a voltage of about 100V is applied, while the whole sample is heated up to 200°C. A small current of some µA can be observed. After 15 minutes the test is finished, and the damage to the TCO can be seen.

Here some major difference between ZnO:Al, SnO2:F and ZnO:B can be seen. While the first two materials show a massive cracking on large parts of the film, but no change in resistance at the undamaged parts, the ZnO:B seems to be undamaged, but the whole film has a highly decreased resistance. In all cases it could be shown, that a silicon dioxide layer of some 10 nm is suitable to reduce the corrosion effects by several orders.

To explain the different behavior in the corrosion test, grazing incidence x-ray diffraction (GIXRD) was used to determine the stress in the films (see figure 7). ZnO:B shows no stress in the bulk film, while SnO2 exhibits tensile stress of 221 MPa, and ZnO:Al high compressive stress of 646 MPa on the glass substrate.

![Figure 7. GIXRD measurement on ZnO:Al film (left) and ZnO:B (right) under 1.5°](image-url)
Further experiments explained the structure of the ZnO:B and the increasing of the resistance. It is well known, that ZnO:B is sensitive to humidity [11, 12]. However, the work at Malibu showed that the LPCVD produced ZnO:B shows a connected network of voids, allowing the diffusion of ions through the bulk material [14] much easier than in more compact material like sputtered ZnO:Al. In addition, it could be shown in [15] that the results of IR reflectivity obtained structures at high wavelength (between 15 and 20 µm) that could not be explained by the standard Drude model (figure 8, left graph).

Figure 9. SEM images of ZnO surfaces, results of AFM imaging (lower right).
The Maxwell-Garnett model however could describe the measurements very well with a depletion layer around the ZnO grains. It can be seen on the right graph of figure 8, that the IR reflection spectra after a damp-heat test (at 80°C and 80% humidity) can be simulated with an increased depletion layer.

Figure 9 shows SEM images of ZnO:B produced at 175°C (upper left), 150°C (upper right) and sputtered ZnO:Al (lower left). It is obvious, that the structure of the 175°C ZnO:B is completely different to the other samples, it shows large pyramidal shapes as needed for light scattering. The analysis of AFM images on LPCVD samples produced at different temperatures shows a transition between 160°C and 170°C in the angle of the surface elements (figure 9, lower right). Additional analysis with XRD showed, that at temperatures of 160°C and lower, the ZnO:B with a uniform orientation in the (002)-plane (c-axis perpendicular to the surface), just like the ZnO:Al does. At temperatures between 170°C and 190°C the crystal orientation is uniform in the (110)-plane (c-axis parallel to the surface), resulting in the pyramidal shapes [11].

As mentioned before, the ultimate test for a TCO is the measurement of the cell or module efficiency in a solar simulator. For the optical performance of a TCO in the cell, the external quantum efficiency is an important tool. Figure 10 shows on the left side the EQE of an a-Si cell on two different ZnO:B substrates. It can be seen, that a higher surface roughness results in a higher current generated between 550 and 700 nm. A similar experiment is shown on the right side for a tandem cell structure (a-Si/µc-Si), the current generated in the bottom cell increases with increasing ZnO:B roughness. However, the generated voltage and fill factor are also important for the resulting efficiency of a cell, and limit the surface roughness.

4. Conclusions
This paper showed some important examples of the development of ZnO as a transparent conductive layer in industrial thin film solar module production. Large area uniformity is as important as the basic understanding of the material and the processes in order to improve the module performance with respect to the production costs.

Acknowledgments
The author thanks the former Malibu R&D team, especially Henning Kurz and Dr. Pavel Prunici.

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