Thin film zinc oxide deposited by CVD and PVD

Frank U Hamelmann
Bielefeld University of Applied Sciences, Campus Minden, Artilleriestraße 9, 32427 Minden, Germany
E-mail: FHamelmann@fh-bielefeld.de

Abstract. Zinc oxide is known as a mineral since 1810, but it came to scientific interest after its optoelectronic properties found to be tuneable by p-type doping. Since the late 1980’s the number of publications increased exponentially. All thin film deposition technologies, including sol-gel and spray pyrolysis, are able to produce ZnO films. However, for outstanding properties and specific doping, only chemical vapor deposition and physical vapor deposition have shown so far satisfying results in terms of high conductivity and high transparency. In this paper the different possibilities for doping will be discussed, some important applications of doped ZnO thin films will be presented. The deposition technologies used for industrial applications are shown in this paper. Especially sputtering of aluminium doped Zinc Oxide (ZnO:Al or AZO) and LPCVD of boron doped Zinc Oxide (ZnO:B or BZO) are used for the commercial production of transparent conductive oxide films on glass used for thin film photovoltaic cells. For this special application the typical process development for large area deposition is presented, with the important trade-off between optical properties (transparency and ability for light scattering) and electrical properties (conductivity). Also, the long term stability of doped ZnO films is important for applications, humidity in the ambient is often the reason for degradation of the films. The differences between the mentioned materials are presented.

1. Introduction
Zinc oxide is used as a material for centuries, known as a white powder and used as a pigment for paints (“chinese white”). Also for some other industrial applications zinc oxide is used. The electro-optical properties were first used for Ag based low emissive coatings in heat protective windows [1]. The common method for deposition of dielectric coatings for architectural coatings is reactive DC magnetron sputtering [2, 3].

Another important application of thin film zinc oxide films on large areas is using the fact, that ZnO is a wide band gap semiconducting material that can be doped. Good results can be found for n-type doping with aluminium, boron, gallium. Such doped ZnO can be used as transparent conductive oxide, especially important for thin film solar cells [4, 5, 6]. First results were obtained by Siemens Solar for the development of CIS (copper, indium, sulphur) based solar cells [7, 8]. Further development of this low pressure CVD was done at University of Neuchatel [4] with a commercial use by Oerlikon Solar, Switzerland [5]. In this case, the CVD precursors are diethyl zinc (DEZ) with water vapor for oxygen delivery. For doping, boron is introduced to form boron doped zinc oxide (BZO). The low deposition temperatures and high growth rates are suitable for production of TCO substrates.
with good transparency at low sheet resistance, and a unique film texture for efficient light trapping, which is needed for silicon based thin film solar cells.

The second technology for large area ZnO transparent conductive oxides is sputtering. The doping is usually done with aluminium (AZO). The development of high rate sputtering processes [9, 10] was commercialised by Applied Materials [11, 12]. For light trapping, the flat films were treated in a wet chemical etching process using HCl, craters are etched into the AZO film. Large area deposition up to six m² was achieved with this technology.

In this paper results of both technologies are shown: BZO and AZO films produced on industrial coating systems, and discuss the structural differences of the resulting films with a focus on the special features of BZO.

2. Method
The presented results have been measured in the laboratory on BZO and AZO films produced by production sized deposition systems on 1.4 square meter float glass substrates). The BZO films were deposited on the Oerlikon TCO-1200 LPCVD coating system, which a shortened version of the commercial product, consisting of a loadlock with pre-heating of the substrate, the deposition chamber with a three zone hot plate to keep the surface temperature constant on the whole substrate area, and an unloadlock for controlled cooling of the substrate. The temperature range used was between 150 and 190°C with a total pressure of typically 0.5 mbar. Mass flow controllers allow the flow of the precursors (DEZ and water vapor) through a showerhead. Diboran diluted in hydrogen was used for the doping. It must be noted that this system needs cleaning of the chambers, because some deposition occurs also on non-heated parts like the showerhead nozzles. To control the status of the chamber, a standard recipe was used before any other depositions. The commercial system consists of additional deposition chambers, so the throughput is multiple times higher.

The sputtered AZO films were deposited on a R&D sputtering system of Leybold Optics, suitable also for substrates up to 1.4 square meter. The system contains a loadlock for radiative preheating of the substrate, a deposition chamber for DC magnetron sputtering metal films (aluminium and silver) and a separate chamber for oxide films, including DC magnetron for AZO and RF magnetron for silicon oxide. An additional chamber allows several deposition runs at constant substrate speed (oscillating deposition). HCl etching can be performed in a modified glass washer constructed by RENA, containing a bath with 0.5% HCl solution. The speed of the substrate and the pH value of the solution and its temperature control the etching rate.

Films are characterized for thickness and sheet resistance on the whole substrate area with a self constructed x-y table measuring optical reflexion in the visible range and resistance with a 4-point probe. For further analysis, samples are cut into smaller pieces at several fixed spots of the full size substrate.

3. Results
A series of boron doped zinc oxide samples has been prepared with different deposition times, while all other deposition parameters were kept constant. The substrate temperature was fixed at 175°C, the DEZ/H2O ratio at 0.8 and the DEZ/B2H6 ratio was 0.25 (2% B2H6 diluted in hydrogen). The corresponding film thickness was 1.8 µm after 12 minutes, giving a deposition rate of about 2.5 nm/s. The linearity of the deposition after a short time for initial nucleation has been shown before [13]. The sheet resistance for the 1.8 µm film is about 7 Ω/sq. Figure 1 shows the development of the surface structure for each additional minute of deposition. The growth of the polycrystalline structure with pyramid shaped surface can be seen. From the SEM images, the average area of each pyramid was calculated, the square root gives the value of the surface feature.
Figure 1. Development of BZO surface structure with time: SEM images.

Figure 2. Correlation of surface feature size with haze.

Figure 2 shows the feature size as a function of deposition time, as it can be expected the correlation is linear. The graph of the haze at 600 nm wavelength as a function of film thickness is included as well, and shows a similar slope. The haze was calculated from transmission measurements of UV-vis spectrometer with and without integrating sphere. It gives the amount of diffuse scattered light to total transmitted light. This is an important value for the light scattering abilities of the film. However, it must be noted that the angular distribution of the scattered light is important as well, but this haze does not take it into account.
Another series of samples was prepared with variation of diborane flow in a wide range. As it can be seen in figure 3 (right), the sheet resistance is saturated at 3 sccm gas flow, while the film thickness is mainly unaffected. This can be explained by hall measurements that show the carrier concentration saturates, while the mobility of carriers decreases at higher levels of doping gas flow. This decrease in mobility may be explained by scattering at ionised impurities in the film [4]. However, from SEM images it can be seen that the feature size at high doping gas flows decreases slightly, while the haze decreases in a linear way from over 30% to 10% (left). To explain this, a rough estimation of the optical constants was done from reflection R and transmission T values of the films. The results in figure 4 show in fact a strong influence of the optical constant from the doping gas flow. This has to be taken into account for all measurements based on the knowledge of the optical constants, like the determination of film thickness by optical reflectometry. For a more precise determination, spectral ellipsometric measurements would be useful.

While the BZO and AZO films are comparable in terms of transmission and sheet resistance [13], their structure is different. The orientation of the LPCVD produced BZO depends on the temperature, the conditions for the best growth of the material with respect to the application as TCO at temperatures around 175°C leads to c-axis parallel to the surface, (110)-plane is main direction as it
can be seen in the XRD measurements shown in figure 5. The sputtered AZO shows clearly a different behaviour, the main direction is the (002)-plane, c-axis is perpendicular to the surface.

![Figure 5. XRD results of BZO and AZO.](image)

Another important difference is related to the light scattering abilities of the films. It must be noted, that the surface structure of the AZO films depends on the sputter parameters and the etching process. The results shown here were not optimized. As other authors have shown [14], this concept has room for further improvements. However, some of the developments in laboratory will be difficult to scale up for mass production. Figure 6 compares the angular distribution of the light scattering at 633 nm wavelength (left) and the haze (measured as mentioned before). To compare the results, three different commercially available TCO substrates with fluorin doped tin oxide are presented also. These commercial products are produced with an APCVD process in the float line of glass manufacturers. It can be seen, that the AZO has similar light scattering properties to the commercial SnO:F samples, the BZO has improved properties, the scattering is increased for all angles, while the AZO has only improved scattering in small angles, while it is reduced for the most important large angles. The resulting haze is higher for BZO in the whole for silicon solar cells relevant spectral area between 400 and 1100 nm.

Due to the structural differences of BZO and AZO, the long term behaviour of the material is different. As published elsewhere [15], the BZO shows a connected network of voids, where diffusion of small ions can take place. It has also been shown [16], that exposure of the films to damp/heat (80% rel. humidity, 80°C for several hours) leads to an increased depletion layer that surrounds the crystals. Such behaviour could not be found for sputtered AZO. Such films proved to be stable in accelerated aging tests for a long time without any need for encapsulation [17]. Table 1 shows the results of a damp-heat test for 48 hours for different doped BZO films. It is found that highly doped films are more stable than low doped films.

**Table 1.** Sheet resistance of BZO before and after damp-heat test for 48 hours.

| Sample     | Resistance before DH | Resistance after DH |
|------------|----------------------|---------------------|
| 0 sccm Diboran | 84 Ω/sq.           | 3.5 MΩ/sq.          |
| 0.9 sccm   | 15.3 Ω/sq.          | 1100 Ω/sq.          |
| 1.9 sccm   | 8.0 Ω/sq.           | 214 Ω/sq.           |
| 3.4 sccm   | 6.6 Ω/sq.           | 26 Ω/sq.            |
| 4.9 sccm   | 7.0 Ω/sq.           | 12.5 Ω/sq.          |
Another interesting effect is related to a post deposition treatment of BZO samples with a UV lamp with an emission of 185 and 254 nm. Such lamps are used for surface cleaning, since they also produce ozone in air ambient. A reasonable decrease of the sheet resistance could be found in samples with all doping levels. A lot of tests have been performed with different experimental conditions. It turned out, that the ozone production of the lamp does not influence this effect, since the UV treatment showed an even stronger decrease of the sheet resistance when the BZO sample was kept in vacuum. Also the addition of other gases to the process showed only a decrease of the effect, probably due to higher absorption of the UV light. The reduced sheet resistance turned out not to be completely stable, if the sample is heated to temperatures as used for solar cell deposition, the sheet resistance increases slightly but stabilized on a lower level compared to the as deposited values. It must be noted, that this

**Figure 6.** Angular distribution of light scattering (left) and haze at 600 nm wavelength (right).

**Figure 7.** Variation of sheet resistance by treatment with UV light for different doped BZO films.
effect does not occur on AZO samples, and also no effect could be seen for commercial SnO:F substrates. The mechanism of the UV treatment is still unclear, since the optical properties of the samples are not changing at all. Test of a UV treatment of BZO samples before a deposition of amorphous silicon solar cells showed a reasonable improvement of the fill factor, while open current voltage and short circuit current are not changed. The resulting relative improvement in efficiency was in the range of 10%, it is not clear if this is only a result of the lower sheet resistance, the contact between ZnO and silicon may also be improved by this treatment. The UV treatment has the potential to be included in a production process, it can be easily included in a deposition line at low costs. Further investigation can identify the process, and optimize the process with respect to the needed time.

4. Conclusions
Thin films of doped zinc oxide produced with deposition systems suitable for industrial mass production have been investigated. Boron doped zinc oxide (BZO) produced by LPCVD at 175°C shows some unique features for the use as transparent conductive oxide used for thin film silicon solar cells. The native surface texture that can be tailored by the deposition conditions results in excellent light scattering properties, in combination with high transparency and low surface resistance. The major disadvantage of this material is the sensitivity to humidity, for long term operation a good encapsulation is required, otherwise a degradation causing increased sheet resistance may be the result.

The structure of BZO is different from aluminium doped zinc oxide, deposited by DC magnetron sputtering. The AZO has a compact film structure, different crystal orientation. The as deposited films are flat. A surface roughness can be provided by an additional wet etching step in diluted HCl. This technology still has some potential for improvements, the surface structure can be tailored by sputter parameters and etching process details. The films are stable even in humid ambient.

An interesting effect was shown for BZO with post deposition UV light treatment. The sheet resistance of the film can be reasonably lowered by some irradiation of UV light. This effect has the potential to be included in mass production processes. Further investigation is required for this.

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