Degradation studies of aluminium-doped zinc oxide

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ABSTRACT

This paper describes the degradation of sputtered aluminium-doped zinc oxide (ZnO:Al) layers which were exposed to damp heat (85°C/85% relative humidity). The ZnO:Al samples were characterized by electrical, compositional and optical measurements before, during and after damp heat exposure. Hall measurements showed that the carrier concentration stayed constant, while the mobility decreased and the overall resistivity thus increased. This mobility decrease can be explained by the enhancement of the potential barriers at the grain boundaries because of the occurrence of additional electron-trapping sites. X-ray diffraction (XRD) and optical measurements demonstrated that the crystal structure and transmission in the range 300–1100nm did not change, thereby confirming that the bulk structure stayed constant. Depth profiling showed that the increase of the potential barriers was caused by the diffusion of H_2O/OH^- through the grain boundaries, leading to adsorption of these species or to the formation of $Zn(OH)_2$ or similar species. Depth profiling also revealed the presence of carbon, chloride and sulphide in the top layer, which indicates the possible presence of $Zn_5(CO_3)_2(OH)_6$, $Zn_5(OH)_8Cl_2{\bullet}H_2O$ and $Zn_4SO_4(OH)_6{\bullet}nH_2O$. Furthermore, white spots appeared on the ZnO:Al surface during damp heat exposure. The spots contained elements, such as silicon and calcium, which might have migrated from the glass and which reacted with species from the environment, including oxygen, carbon and chlorine.

Introduction

Zinc oxide (ZnO) has been investigated extensively because of the increasing number of possible industrial applications, including gas sensors, transparent electronics and thin-film solar cells. For chalcopyrite-based thin-film PV – such as $Cu(In,Ga)Se_2$ (CIGS) solar cells – aluminium-doped ZnO (ZnO:Al) is used as a front contact, as it is a non-toxic, inexpensive and abundant material. Furthermore, ZnO:Al is very attractive for CIGS, since sputtering allows room temperature deposition, which prevents exposure of the underlying layers to elevated temperatures.

> “ZnO:Al is one of the key parameters in solar panel degradation.”

Knowledge about ZnO:Al degradation is very important in the PV market, where producers give out warranties that panels will still yield 80% of their initial power after 25 years. CIGS PV should therefore be reliable for at least this length of time; however, it has been observed in field testing that CIGS PV often degrades too fast. It was discovered that ZnO:Al is one of the key parameters in solar panel degradation, indicating that the optical and electrical properties of ZnO:Al are not stable for 25 years in the field. Accelerated lifetime testing has demonstrated that water ingress leads to an increase in lateral sheet resistance of the ZnO:Al [1], thereby increasing series resistance in the solar cell; this results in a decrease in fill factor and consequently in efficiency.

Adequate encapsulation can protect solar cells against water ingress. For rigid modules, glass is an excellent encapsulation material, while for flexible modules, expensive inorganic/organic multi-stack materials are often chosen. A CIGS cell with a more stable ZnO:Al front contact can contribute to lower energy costs and accelerate the introduction of flexible CIGS modules to the market. Similar cost and lifetime issues are naturally important for other applications of ZnO:Al. It is therefore necessary to understand and improve the degradation behaviour of ZnO:Al when subject to water ingress.

In order to learn more about the degradation behaviour of ZnO:Al, several studies [2–7] have already tried to simulate exposure in the field, by placing the samples in damp heat conditions (1000 hours' exposure to 85°C/85% relative humidity RH). Some of these studies [2,3] have led to an increased insight into the change in electrical and optical properties caused by degradation. Relationships between these properties and the surface roughness of the substrate [2], deposition temperatures [4], crystallinity [4] and aluminium content [3] have been reported.

Various studies have also provided us with information about the change in the chemical composition of ZnO:Al – it has been suggested that the presence of oxygen along with water promotes ZnO degradation [5], while it is thought that the formation of $Al(OH)_3$ [2,7] and $Zn(OH)_2$ [2,6,7] plays a role in the degradation, since these materials do not conduct electricity. In general, however, although those studies provide an excellent physical picture of the degradation, the chemical behaviour is underexposed and does not yield an unambiguous picture for the influence of layer composition on the film properties.

Many questions about the degradation mechanisms of ZnO:Al therefore still remain unanswered. In order to learn more about the chemical and physical degradation behaviour of ZnO:Al, samples for this study were also submitted to damp heat, and their electrical, compositional and optical characteristics were analysed before, during and after degradation. This information was then used to define the degradation mechanisms in ZnO:Al, knowledge of which can help towards developing more stable ZnO:Al layers.

Full details about the study reported in this paper can be found in Theelen et al. [8].

Samples and degradation conditions

The deposition temperature of the degraded samples was varied: one sample was not intentionally heated, as is mostly the case for CIGS cells (room temperature or 'RT' sample), while another sample was deposited on a substrate heated to 200°C ('200°C' sample), thus reaching the maximal temperature acceptable for deposition on top of a CIGS/CdS stack. These samples allowed us to look at the broadest possible deposition spectrum.

The main differences between the RT and 200°C samples could be found in the thicknesses (620 and 490nm respectively) and grain sizes (0.9 and 1.3μm^2 respectively, measured from the top).

The samples were exposed to 85°C/85% RH for up to 2876 hours. Unless otherwise mentioned, the analyses after degradation were carried out after this period.

Structural and visual changes

In general, no changes in structural properties due to degradation were observed. The grain size and sample thickness, as measured by cross-section helium ion microscopy (HIM), were constant, while X-ray diffraction (XRD) measurements did not show major changes in structural properties as a result of degradation.

> "No changes in structural properties due to degradation were observed."

Visual changes, however, were observed on the surface: optical microscopy and scanning electron microscopy (SEM) revealed small dots and larger stains on the surface (Fig. 1), which increased in size and quantity with exposure time. After approximately 2000 hours, the circle-like dots had diameters of up to 100μm, while the stains, with less defined shapes, had diameters of up to 1mm. After 2182 hours, these blemishes covered approximately 6±1% of the surface.

The nature of these spots was studied by energy-dispersive X-ray (EDX) spectroscopy mapping at 10kV. Naturally, the elements zinc, oxygen and aluminium were encountered, but the less expected elements carbon, silicon and calcium were also observed. The spots and stains seem to consist of mostly calcium and carbon, but oxygen, silicon and aluminium were certainly also present, whereas the zinc has disappeared from these spots.

The distilled water was tested for cations by induced coupled plasma-mass spectrometer (ICP-MS) and showed only the presence of very small quantities of sodium and silicon, and no trace of aluminium and calcium. It is known that aluminium, silicon and calcium can be present in the glass, so these elements might have migrated from it. These migrating cations can be expected to react with H_2O, CO_2 or O_2 from the glass to form carbonates or hydrates. It is proposed that the spots and stains occur when the samples are removed from the climate chamber. The thin water film on the surface can then dry out and form small dots or coffee stains and leave behind salts.

Changes in electrical properties

Hall measurements showed that both ZnO:Al film samples exhibited an n-type behaviour, which is in agreement with the type of conduction associated with these ZnO:Al semiconductors. Fig. 2 illustrates the evolution of the resistivity of the two samples with degradation time. It was observed that the 200°C sample had an initial resistivity of $6\times10^{-4}\Omega$cm, which is a factor of two lower than that of the RT sample. The deterioration of the RT sample was also faster after exposure to 85°C/85% RH, and is therefore more vulnerable to damp heat.

A square-root function of the following form can be fitted to the increase in resistivity of both samples:

$$y = a \times \sqrt{(bt)} + c \qquad (1)$$

As a result, the conductivity automatically follows a $1/\sqrt{(t)}$ trend. The resistivity change can therefore be linked to a diffusion-like process, in which a species from an infinite reservoir diffuses into a semi-porous material. The diffusion of the species in the sample will hence be the rate-determining step, while the reaction between the diffused species and the grain boundary atoms inside the sample is a faster process.

It has been reported in the literature that thick samples have a lower degradation rate than thin samples [4–6]. This is explained either by a diffusion-based degradation process that starts from the surface and gradually deepens into the layer [6], or by a difference in grain sizes or

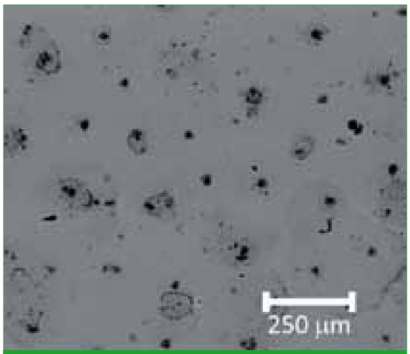


Figure 1. Backscattered SEM image of the RT sample after 2344 hours' exposure at 85°C/85% RH.

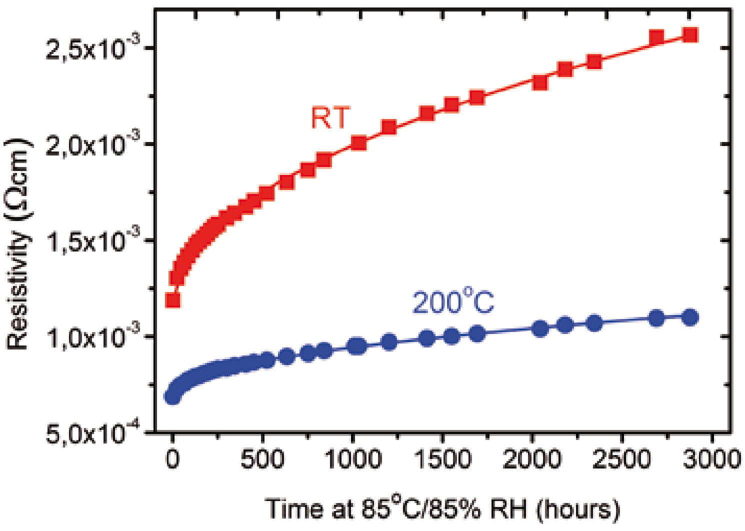


Figure 2. Evolution of the resistivity of the two ZnO:Al samples as a function of time, at 85°C/85% RH, as obtained by Hall measurements.

structures for different thicknesses [5]. In the study reported in this paper, it was confirmed that diffusion controls the resistivity increase.

The difference in resistivity increase between the 200°C and RT samples cannot be explained purely by the difference in thickness, since the samples were respectively 490 and 620nm thick, which cannot account for the large difference in the rate of increase in resistivity. It is therefore proposed that the diffusion rate can be explained by the number of diffusion channels present, for example the grain boundaries.

The Hall mobility and carrier concentration were also measured (Fig. 3). The initial values of both parameters were higher for the 200°C sample than for the RT sample. The mobility measurement for the 200°C sample was 20cm^{2}V^{-1}s^{-1}, whereas it was 16cm^{2}V^{-1}s^{-1} for the RT sample; initial carrier concentrations of approximately 4.5×10^{20}cm^{-1} and 3×10^{20}cm^{-1} were measured for the 200°C and RT samples respectively. These values are in line with those reported in the literature [9].

When the influence of damp heat exposure was studied, a clear change in carrier concentration as a function of exposure time was not visible. The initial and final values of the carrier concentration after degradation only showed a very small decrease, which is within the error margin. It can therefore be concluded that the change in carrier concentration cannot be a major source of the increase in resistivity, which indicates that the bulk of the ZnO:Al grains has a constant composition.

On the other hand, the Hall mobility decreased during the first 1000 hours, but after that time point, the continued decline was slower. This decrease cannot be explained by the white spots, since these mainly occur at the top of the ZnO:Al layer, which will not block lateral electron movement. Furthermore, the size of the spots is a factor of 1000 greater than the grain size, so any influence on the electrical properties would also affect the carrier concentration. The reason for the decrease in mobility should therefore be found within the ZnO:Al layer itself.

Fig. 4 shows the dominant electron-scattering mechanisms in ZnO:Al that limit the mobility, i.e. the potential barriers at the grain boundaries and the ionized impurity scattering in the grains. In the case of the Hall measurements, electrons travel macroscopic lengths and cross several grain boundaries, so the grain boundary density can be a limiting factor of the value of the Hall mobility [10].

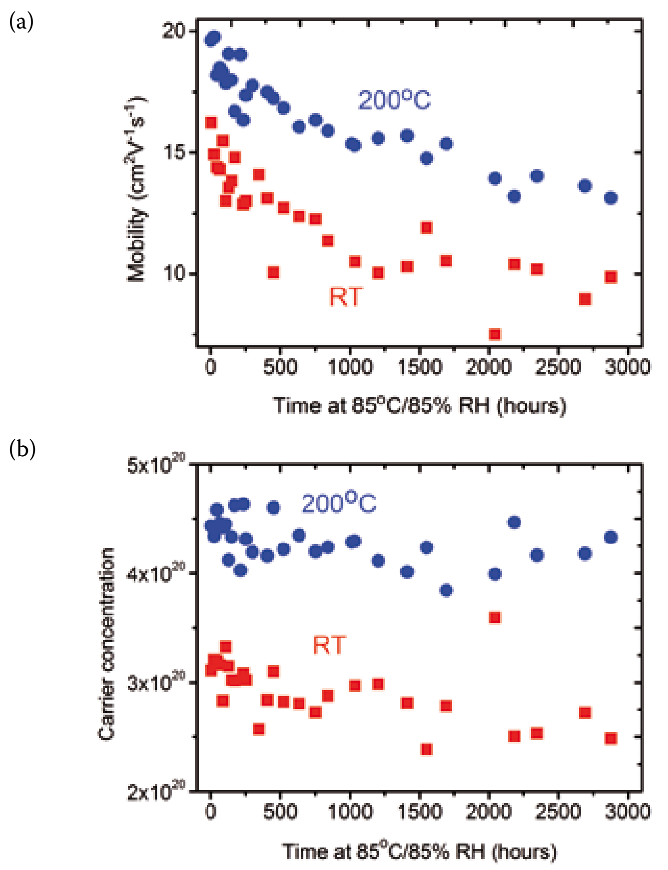


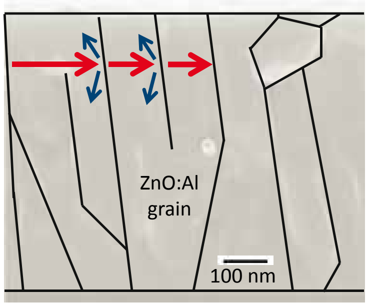
Figure 3. Hall mobility (a) and carrier concentration (b) of ZnO:Al as a function of time, at 85°C/85% RH.

> "It can be expected that the formation of detrimental compounds in ZnO:Al occurs at the grain boundaries and not in the bulk material."

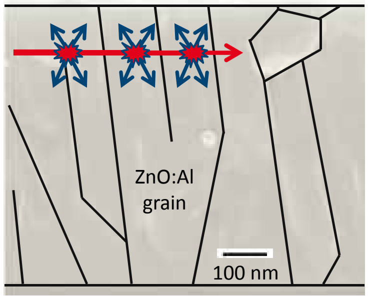
On the basis of the stable carrier concentration and the decreasing mobility, it can be expected that the formation of detrimental compounds in ZnO:Al occurs at the grain boundaries and not in the bulk material. Since the grain size for the RT sample is smaller than that for the 200°C sample, more grain boundaries are present in the former: degradation therefore occurs more quickly in the RT samples.

Changes in optical properties

The optical properties were studied by ultraviolet-visible (UV-VIS) spectroscopy and are shown in Fig. 5 for the RT sample (the 200°C shows a similar behaviour). Initially, the samples including glass transmitted 81% and 84% of the light for the RT and the 200°C samples respectively. During degradation, in the measured wavelength region (240–2400nm) the average transmission barely changed



Increased potential at the grain boundaries



Ionized impurity scattering

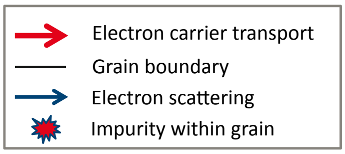


Figure 4. Possible scattering mechanisms in ZnO samples (based on Steinhauser et al. [10]).

with time. The constant plasma frequency and transmission in both the near-infrared and ultraviolet regions implies that the carrier concentration is constant in the bulk of the film, as was also concluded from the Hall measurements [11].

The only changes observed were a small drop in reflection and a small increase in absorption in the near-infrared region. These changes might be explained by the white spots, which might absorb some of the near-infrared light.

Within the highly transparent region, the measured spectra demonstrate an oscillatory behaviour, which is caused by interference effects due to multiple internal reflections of the incoming light in the ZnO:Al layer. Since the degradation did not influence this behaviour, no texturing or reduction of ZnO to Zn has occurred.

Changes in composition

The composition as a function of depth was measured by negative mode time-of-flight secondary ion mass spectroscopy (ToF-SIMS) through the layer before and after degradation. The depth profiles of the RT sample are shown in Fig. 6: these graphs show the difference in concentration of various important ions within the depth of the layers, as well as the impact of degradation. It should be noted that the concentrations depend on the ionization probability of the atoms and molecules, which varies per species and per background material. Therefore, no absolute concentrations are obtained in this study.

The ToF-SIMS depth profiling showed that the damp heat exposure introduced hydroxides, chlorine, sulphur and carbon into the film. The hydroxyl profile decayed by about one order of magnitude in the depth range 300–500nm, and it was higher everywhere than before degradation. When the RT sample was compared with the 200°C sample, it was observed that the hydroxyl profile for the RT film had a slightly higher maximum value, which indicated that more water had diffused into this sample. This can be explained by the higher number of grain boundaries.

Looking now at the bottom 300nm of the layer, the OH$^-$ and H$^-$ concentrations were found to be lower than in the top layer, indicating that the diffusion and thus the degradation can develop still further. In addition, there was a large amount of Cl$^-$ in the films after degradation, which decreased by one order of magnitude in the depth range 100–200nm. In the region near the surface, the concentration of Cl$^-$ is probably comparable with the hydroxide concentration, assuming that the ionization probabilities of OH$^-$ and Cl$^-$ in ZnO:Al are similar. Degradation thus induces a relatively high concentration of Cl$^-$ in the top layers of the samples. Similarly, there was a slightly increased sulphur signal in the top 200nm after degradation, which was visible in the cross-section mappings as a very thin surface layer; the sulphur is probably present as sulphite or sulphate (SO_3^{2-} or SO_4^{2-}). Since ToF-SIMS does not provide absolute concentration, and chlorine and sulphur were barely detected by EDX, the total amount of these species in ZnO:Al is most likely very low. The treatment thus only induces these species near the surface of degraded ZnO:Al.

The C$^-$ signal is only significantly raised in the top 100nm of the film as a result of damp heat exposure. The carbon concentration is difficult to estimate, because the C$^-$ ionization probability is usually much lower than that of OH$^-$ and Cl$^-$, but the

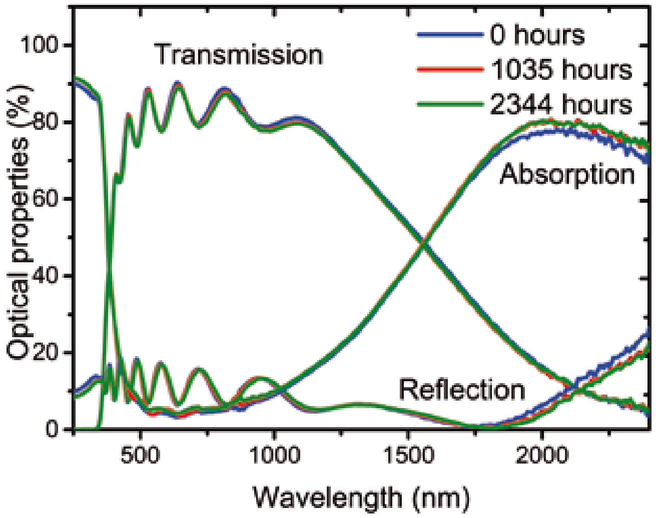


Figure 5. Evolution of the optical properties of the RT sample before and after exposure to 85°C/85% RH.

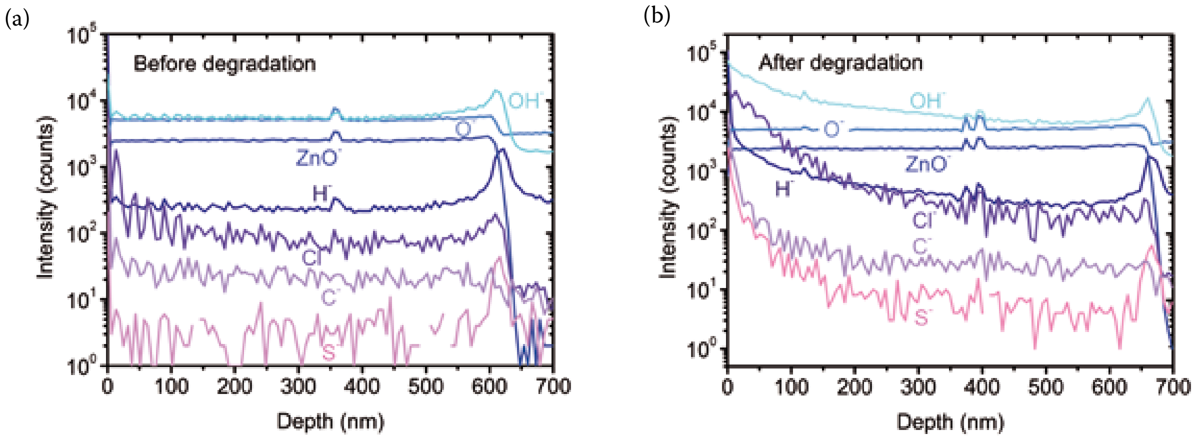


Figure 6. SIMS depth profiles of the RT sample before (a) and after (b) exposure to 85°C/85% RH. The depth profiles show the composition from the air–ZnO:Al interface (left of graph) to the ZnO:Al–glass interface (right of graph).

concentrations in the bulk are quite likely low. The chemical state of the carbon cannot be easily determined from a depth profile in an oxide film, but it might be (bi-)carbonate.

The O^- concentration did not change because of degradation and is completely stable as a function of depth, so it is unlikely that adsorption of O_2 is the main reason for ZnO:Al deterioration.

Since the complete thickness of the ZnO:Al layer is used for lateral transport of the electrons, it can be assumed that the impact of the surface element on the electrical properties is small. The main cause of the decrease in conductivity can therefore be found in the presence of $ZnOH^-$ and OH^-, which is present in the entire layer.

Degradation reactions

When considering the observed results, the following conclusions on physical and chemical changes in ZnO:Al due to damp heat treatment can be drawn:

- The three-dimensional structure of the samples stayed intact. The grain size and the thickness of the layers did not change with damp heat treatment.
- The main visual change was the appearance of white spots containing elements – such as calcium and silicon – which had migrated from the glass and reacted with elements, including oxygen and carbon, from the environment. These spots had a small influence on the absorption of light in the near-infrared region, but did not have an impact on the electrical properties or the overall transmission. The optical properties were also constant.
- The resistivity increased, mainly driven by a large drop in the Hall mobility, whereas the carrier concentration stayed constant. This implies the formation of a potential barrier in the grain boundaries.
- Chlorine, sulphur and carbon are present near the surface of degraded ZnO:Al, whereas OH^- is present in the bulk of the entire samples.

> "The grain size and the thickness of the layers did not change with damp heat treatment."

Reactions in the grain boundaries

On the basis of these observations, it is concluded that the diffusion of species into the grain boundaries is the main cause of degradation. Water plays a significant role in the degradation; however, on the basis of the constant oxygen concentration in the ToF-SIMS depth profiling and of preliminary experiments on the impact of atmospheric species, a large role for oxygen is not suggested. On the other hand, a role for carbon dioxide is suggested. The impact of oxygen and carbon dioxide was found in a study by Theelen et al. [12]: ZnO:Al samples were exposed to water that was purged with air (mainly consisting of oxygen, nitrogen and carbon dioxide), which led to fast degradation. Purging with pure nitrogen and oxygen, on the other hand, only induced very slow degradation. It is therefore concluded that the reactivity of carbon dioxide in combination with water is much larger than the impact of oxygen. The impact of carbon dioxide, which is omnipresent in the atmosphere, should thus not be underestimated [12]. Since chlorine and sulphur were also encountered in the degraded ZnO, a role for these materials is also proposed.

When the nature of the reactions occurring in the grain boundaries is considered, the diffusion of the degrading species can influence the resistivity in two ways, which are not easily distinguishable:

1. Molecular adsorption (physical reaction)

2. Chemical reaction

A combination of molecular adsorption and chemical reaction is the most likely scenario. This can also be inferred from the reversibility experiments in Tohsophon et al. [13], where both a change in resistivity when annealing at 150°C and an effusion of water, CO_2 and H_2 at higher temperatures (around 500°C) was reported. This indicates the involvement of two different phenomena.

Molecular adsorption

When the molecules are adsorbed at the grain boundaries or at the surface, electron traps can be formed. ZnO is known to have excellent H_2, CO and CO_2 absorptivity after being cleaned of absorbed H_2O and CO_2 by vacuum heating [14]. It is proposed that H_2O can be adsorbed at the grain boundaries, on the basis of the fact that OH^- and H^- were encountered.

Chemical reactions

Chemical degradation begins with the presence of unbound zinc, oxygen or aluminium species. These species can be present either because of dangling bonds or defects, or because of the dissolution of ZnO:Al in the thin water film present at the surface and possibly in the grain boundaries. Both chemical and electrochemical dissolution of ZnO can result in the formation of a Zn^{2+} cation. Electrochemical reactions depend on the electrode potential, which regulates the absorption of protons at the surface. This situation is not expected in these experiments, but might occur in solar cells, which are electrically active.

Whether ZnO dissolves in an aqueous solution is mainly a function of the acidity. It is thermodynamically

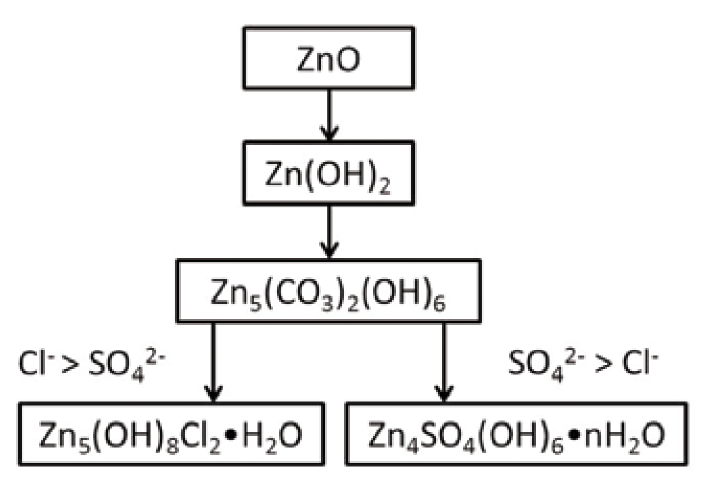


Figure 7. General reaction scheme for the degradation of ZnO (based on Odnevall & Leygraf [15]).

stable in the pH range of 6 to 12, but can dissolve in solutions with a higher or lower pH [14]:

$$\mathrm{ZnO(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2O(l)} \quad \text{(chemical dissolution)} \qquad (2)$$

ZnO can also dissolve under certain conditions as a result of illumination. After Zn^{2+} formation, this ion can either wash away with the water or react with other species. In this study, the layers kept the same structural characteristics, so it is unlikely that Zn^{2+} had disappeared from the samples.

More information about the nature of the species formed in the grain boundaries is available in the literature and by calculations. The first hint of possibly stable reaction products of ZnO degradation can be found in nature: in exposed deposits, most of the mined zinc compounds are sulphides, carbonates and hydrocarbonates.

The reaction products of zinc compounds in nature have already been described in the literature [14]; it has been shown that there are large amounts of reaction products occurring in nature, and that there is the possibility of multiple corrosion products being present in the same place. Although ZnO:Al is naturally a different material to pure Zn, it can be assumed that several of its reaction products should be similar.

Odnevall & Leygraf [15] propose the formation of the major corrosion products of zinc under sheltered conditions and show a reaction sequence from zinc hydroxide, via hydroxycarbonates, to chlorides and sulphates, as shown in Fig. 7.

Goux et al. [16] showed experimentally that $Zn(OH)_2$ is kinetically favoured at low temperatures (under 34°C) and can thus also be formed according to:

$$\mathrm{Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2} \qquad (3)$$

This species can react further in the presence of CO_2 to hydrozincite:

$$\mathrm{Zn(OH)_2\,(s) + 4Zn^{2+}\,(aq) + 4OH^{-}\,(aq) + 2CO_3^{2-}\,(aq) \rightarrow Zn_5(CO_3)_2(OH)_6\,(s)} \qquad (4)$$

In the presence of Cl^- and SO_4^{2-} ions, the hydrozincite can be replaced. Subsequent steps might lead to the formation of compounds containing sodium and of products containing both sulphate and chlorine. The species as shown in Fig. 7 have most likely formed in the grain boundaries, where they function as a potential barrier.

Since carbon and sulphur are mainly found at the top of the samples in the ToF-SIMS measurements, it is expected that the hydroxycarbonate – e.g. $Zn_5(CO_3)_2(OH)_6$ – and the hydroxysulphate – $Zn_4SO_4(OH)_6{\bullet}nH_2O$ – are surface compounds. However, the chloride compounds – e.g. $Zn_5(OH)_8Cl_2{\bullet}H_2O$ – and the hydroxide-containing species will be present in a larger portion of the sample and will therefore have a greater impact on the change in the electrical parameters.

> "Species from the glass as well as from the environment migrate through the ZnO:Al."

Degradation mechanism based on the migration of species

The results have demonstrated that species from the glass as well as from the environment migrate through the ZnO:Al. It is therefore proposed that migration occurs in two directions (Fig. 8): the downward diffusion (blue arrow) leads to an increased resistivity, while the upward migration (green arrow) does not seem to influence the electronic properties. However, the impact of this migration on the optical properties is minor.

We propose that the degradation in ZnO:Al occurs in the following steps:

1. (a) Small molecules – such as water, carbon dioxide, sulphur species and chloride species – diffuse from the environment into the grain boundaries.

   (b) Small elements – such as calcium, silicon and aluminium – leach from the glass and enter the grain boundaries.

2. (a) The small molecules react with or adsorb to the grain boundaries, which results in an increase in potential barriers and thus a decrease in mobility. The rate of this reaction is determined by diffusion and differs by species. The hydroxide-based elements have the highest diffusion rate.

   (b) Calcium, silicon and aluminium reach the ZnO surface.

3. (a) Once the grain boundaries are saturated with hydroxides, the decrease in mobility slows down.

   (b) Spots and stains form as a result of the reactions of calcium, silicon and aluminium with carbon and oxygen from the environment. When the samples are removed from the climate chamber, drying stains are formed because of the evaporation of residual moisture at the surface.

Acknowledgements

The authors would like to thank T. Boumans, F. Stegeman, F. Colberts, J. van Berkum, A. Eijk and E. van Veldhoven for their help with the measurements and analysis. The authors also acknowledge P. Poodt and A. Illiberi for the fruitful discussions. This research was carried out under Project No. M71.9.10401 in the framework of the research programme of the 'Materials innovation institute' M2i (www.m2i.nl).

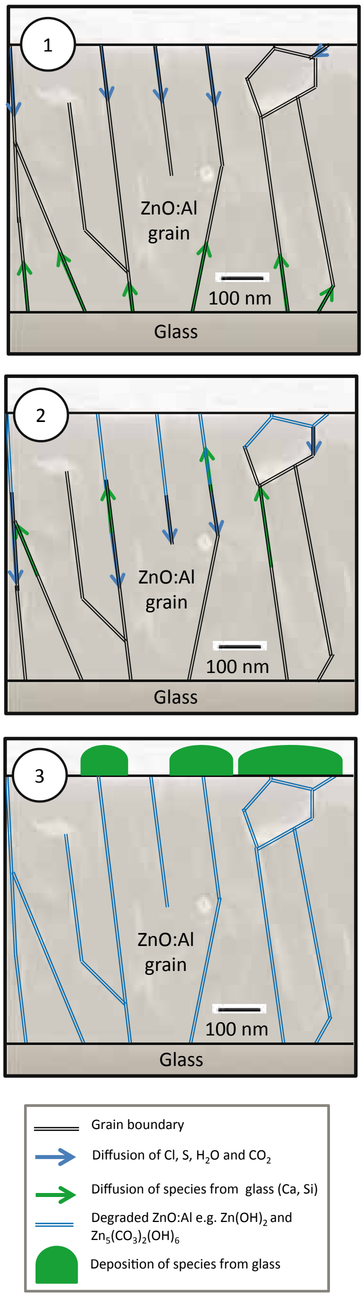


Figure 8. Proposed degradation mechanism for ZnO:Al layers.

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Miro Zeman has been a full professor at Delft University of Technology in the field of photovoltaic materials and devices since 2009. He is a leading expert on light management, modelling, and novel materials and nanostructures in thin solar cells. He has authored and co-authored 200 articles and contributed to five scientific books.

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