Influence of the atmospheric species water, oxygen, nitrogen and carbon dioxide on the degradation of aluminum doped zinc oxide layers

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ABSTRACT

Aluminum doped zinc oxide (ZnO:Al) layers were exposed to the atmospheric gases carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2) and air as well as liquid H_2O purged with these gases, in order to investigate the chemical degradation behavior of these layers. The samples were analyzed by electrical, compositional and optical measurements before, during and after exposure to these conditions in order to follow the degradation behavior of these layers in time.

We have shown that ZnO:Al layers degraded in the presence of a mixture of H_2O and CO_2. Individually, CO_2 does not impact the degradation at all during the tested period, while the individual impact of H_2O is small. However, when CO_2 is also present, the concentration of OH increases greatly in the bulk and even more at the air/ZnO:Al and in the ZnO:Al/glass interfaces. Carbon based species are then also present, indicating that $Zn_5(OH)_6(CO_3)_2$ is also formed at the grain boundaries. The impact of gaseous O_2 as well as water purged with N_2 and O_2 on ZnO:Al degradation is very small.

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1. Introduction

Zinc oxide (ZnO) has been investigated extensively because of the increasing number of commercial applications. Being a wide band gap semiconductor ($E_g = 3.4$ eV), doped ZnO is emerging as a prospective material for among other gas sensors, electronics and thin film solar cells, such as Cu(In,Ga)Se$_2$. For the latter, aluminum doped ZnO (ZnO:Al) is often used as the front contact. It is known that the ingression of H_2O in this material leads to decreased device performance [1]. This effect is normally minimized by the use of encapsulated products which are often optimized to function as a barrier for water [2].

In order to choose the best required barrier product, based on costs and product performance, it is necessary to understand and limit the degradation behavior of ZnO:Al. This is often obtained according to certification standard IEC 61646, which contains among others the 'damp heat' test. This test (1000 h exposure to 85 °C and 85% Relative Humidity (RH)) can help in the identification of reliability problems in the material and can give an indication of its field performance. Several studies [3–9] have used damp heat testing, which has led to an increased insight of the changes in the optical and electrical properties during degradation. However, the degradation mechanisms as well as the chemical reactions leading to the change in properties are still largely unknown.

Furthermore, it is expected that other atmospheric species like O_2 or CO_2 might also play a role in the degradation, but this has not been studied thoroughly. The exact nature of the environmental molecules that are playing a role in the relevant degradation processes in ZnO:Al is proposed in literature, but has not been studied thoroughly. A suggestion for the main degrading species includes oxygen and water molecules [7] and water and CO_2 [9].

Knowledge about the species playing a role in ZnO:Al degradation is very important, because it can be used to optimize the product design for ZnO:Al containing products. This can for example be useful in the design of encapsulation materials in which the water and oxygen barrier properties (water vapor transmission rate and oxygen transmission rate respectively) are optimized, while the penetration of other atmospheric species is not defined at all.

In this study, we studied the impact of the exposure of thin film ZnO:Al to these atmospheric species (N_2, O_2, CO_2, H_2O), in order to learn more about the influence of these species and their combination on the degradation.

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2. Experimental

2.1. Sample preparation

ZnO:Al layers were deposited by radio frequency (rf) magnetron sputtering using a MRC 643 vertical batch sputtering tool. The layers were sputtered on a 10×10 cm^2 0.7 mm thick Eagle 2000 Corning glass substrate from a rectangular 5″ × 17″ high purity ZnO ceramic target with 2% Al$_2$O$_3$. The flow of pure Ar gas was set to 15 standard cubic cm^2 per minute. The chamber pressure was 0.42 Pa, while the rf power was 800 W, which corresponds to a power density of 1.46 W/cm^2. The deposition time was 35 min and was executed in 14 passes. The deposition was executed at room temperature.

2.2. Sample degradation

All samples in this study were obtained from one 10×10 cm^2 substrate with a ZnO:Al coating, which was cut into smaller samples. The initial thickness and sheet resistance measured over the complete sample had standard deviation of 5%. The water samples were placed in closed vessels, which were filled with 150 mL ultrapure water (demineralized water further treated by a Synergy Millipore tool). One vessel only contained water in an open connection to the atmosphere, while the other vessels were purged with the gases O$_2$ (purity: 99.995%), N$_2$ (purity: 99.99995%), CO$_2$ and compressed air (Fig. 1). It is expected that purging the water with the gases will lead to the presence of only water and gas, while no additional species are present, except for species that might have dissolved from the glass or the ZnO:Al layer. For water without purging, it is expected that all species present in the atmosphere are dissolved in water in small quantities.

The gas samples were placed in CO$_2$ and O$_2$ atm, while reference samples were kept in an argon glovebox (MBraun glovebox Unilab). All the samples were removed from the vessels at set times and analyzed. For the samples in the water vessels, these degradation periods took 4/4/4/4/4/6/6/6/6/6/17/17/17/17/17/17/17/17/17/20/20/20/20 h, which counted up to 310 h. The pH of the water in the vessels was checked before the removal of the samples, to observe whether the pH has changed. The samples in the gaseous O$_2$ and CO$_2$ were kept up to 1000 h under these conditions.

In Table 1, names used in this article to refer to the ZnO:Al samples and the conditions of the degradation experiments of the samples are summarized.
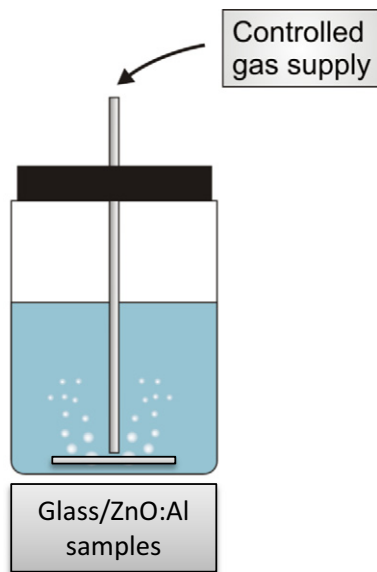

Fig. 1. Schematic picture of the degradation setup.

Table 1
Degradation conditions for the ZnO:Al samples and the name they are referred to in this article.

Conditions	Name
H$_2$O	H$_2$O
H$_2$O purged with CO$_2$	H$_2$O/CO$_2$
H$_2$O purged with O$_2$	H$_2$O/O$_2$
H$_2$O purged with N$_2$	H$_2$O/N$_2$
H$_2$O purged with compressed air	H$_2$O/air
CO$_2$ gas	CO$_2$
O$_2$ gas	O$_2$
Argon gas (glovebox)	Argon

2.3. Characterization of film properties

The optical, structural and electrical properties were determined by a number of techniques before, during and after degradation.

A PhysTech RH2010 Hall effect measurement tool was used to determine the electrical properties of the layers. The optical properties were determined by a Shimadzu UV-3600 UV-VIS-NIR, which allowed analysis of the transmittance and reflectance of the ZnO:Al samples including glass. From these data, the absorption is calculated. A Leica Wild M400 macroscope and a digital camera were used to determine the visual changes.

The morphological and structural properties of the layers were determined by a FEI Quanta 600 Scanning Electron Microscope (SEM) combined with Energy Dispersion X-ray (EDX) EDAX Genesis 4000, and a Zeiss Orion plus Helium Ion Microscope (HIM) with an Everhart–Thornley detector. The He ions have a voltage of 25 kV with a current of 0.5 to 2 pA. A Philips X'pert 5068 powder diffractometer, equipped with a CuK$_\alpha$ ($\lambda = 0.154$ nm) source in the 5° to 95° 2θ range with a step size of 0.02° was also used to determine the structural properties.

Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) depth profiling was performed using an Ion-Tof TOF-SIMS IV instrument, operated in negative mode, using high current 25 keV Bi$^+$ beam of ~3 μm diameter for analysis and 2 keV Cs$^+$ ions for sputtering.

3. Results

3.1. Structural properties

From cross section HIM and SEM pictures, it was concluded that the non-degraded ZnO:Al layer has a columnar structure and a thickness of 480–520 nm It was observed that the structure of the columns was not completely straight, but showed a wavy structure. This wavy structure can be caused by the movement of the substrate during deposition on the semi-industrial tool, which slowly moves the substrate back and forth during the deposition.

During degradation, the most striking observation was complete dissolution of the sample that was placed in H$_2$O purged with CO$_2$, which occurred within hours. No further results of this sample are therefore given in this article. The other samples did not dissolve and their compositional, optical and electrical properties were followed for 310 h.

After exposure to most treatments, no differences in structural properties could be observed. The structure of the H$_2$O/N$_2$ sample is shown in Fig. 2 as an example. However, an unexpected change in morphology was observed for the H$_2$O/air sample, in which gaps occurred in the ZnO:Al layer at the glass interface (Fig. 2), indicating local dissolution of the ZnO:Al. It was observed that only the bottom 200 nm was affected, while the top part of the ZnO:Al still looked intact. This was not expected, since the water and other reactive species are initially only present at the top of the ZnO:Al layer. This effect was not unambiguously shown for the non-purged H$_2$O, but probably also occurred.