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# Positron Annihilation Studies on the Damp Heat Degradation of ZnO:Al Transparent Conductive Oxide Layers for CIGS Solar Cells

Wenqin Shi, Mirjam Theelen, Veronique Gevaerts , Andrea Illiberi, Nicolas Barreau, Maik Butterling, Henk Schut, Werner Egger, Marcel Dickmann, Christoph Hugenschmidt, Miro Zeman, Ekkes Brück, and Stephan W. H. Eijt 

**Abstract**—Positron annihilation depth-profiling is used as an innovative tool to monitor the evolution of vacancy defects in two series of ZnO:Al transparent conductive oxide (TCO) layers for Cu(In,Ga)Se<sub>2</sub> (CIGS) solar cells under accelerated degradation at 85 °C/85% relative humidity. The first series of ZnO:Al layers are deposited directly on flat glass substrates, leading to low densities of (extended) grain boundaries in the ZnO:Al. These ZnO:Al layers only show an increase in open volume upon degradation in the near-surface range. The second series of ZnO:Al layers are deposited on the more corrugated surface of CdS/CIGS/Mo solar cells, and show, on the other hand, a pronounced formation of open volume throughout the layer. Its depth-dependence is consistent with indiffusion of molecules such as H<sub>2</sub>O and CO<sub>2</sub> into the ZnO:Al layer via the grain boundaries, as primary driver for the degradation. The detected time-dependence of the growth of open volume at the grain boundaries in the ZnO:Al TCO layer matches the time scale of the observed reduction in solar cell efficiency and series

resistance, suggesting that the generated open volume induces a significant barrier against charge carrier transport.

**Index Terms**—Buffer layers, and back contacts, CIGS and CdTe thin film solar cells, degradation, grain boundaries, positrons, transparent conductors, ZnO:Al.

## I. INTRODUCTION

Cu(In,Ga)Se<sub>2</sub> (CIGS) solar cells have reached efficiencies as high as 22.9% [1]. Apart from such high efficiencies, large-scale commercial introduction of CIGS photovoltaics (PV) requires modules with low costs and long and predictable lifetimes. Unfortunately, the lifetime of bare CIGS modules in ambient environments is still limited. Therefore, considerable costs are made for reliable package materials, which are especially high for flexible modules. These costs can be reduced by the development of intrinsically more stable solar cells. Therefore, the identification of the degradation mechanisms of CIGS solar cells is a crucial aspect in their development.

Earlier solar cell lifetime studies have focused, amongst others, on the structural and compositional changes [2], but did not identify or quantify the presence and evolution of vacancy defects in the various layers in the stack, which can help to understand the material changes in more detail and can provide information on the mechanism of degradation. Positron annihilation spectroscopy analysis is an attractive technique for this goal, since by employing a low-energy positron beam, implanted positrons can reach the various individual layers in a CIGS solar cell depending on their implantation energy, and provide detailed insights into the defect properties of each individual layers separately [3], [4], including the ZnO:Al transparent conductive oxide (TCO) and CIGS absorber layer [5].

In this study, we compare and discuss the results of positron analysis on as-deposited and damp heat degraded ZnO:Al layers deposited either on bare (flat) soda lime glass substrates or on CdS/CIGS/Mo solar cells with corrugated surfaces. The comparison of the evolution of open volume with the time-dependence of key solar cell parameters [5] such as efficiency and series resistance provides important clues on the degradation mechanism.

## II. RESULTS AND DISCUSSION

The unpackaged CIGS solar cells consisted of a multi-layer stack of aluminum-doped zinc oxide (ZnO:Al)/intrinsic

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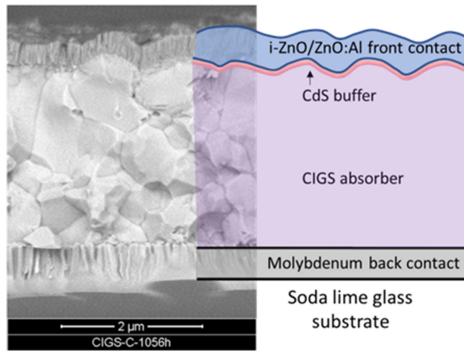


Fig. 1. Schematic representation of the ZnO:Al/i-ZnO/CdS/CIGS/Mo/SLG layer composition of CIGS solar cells merged with a representative SEM image.

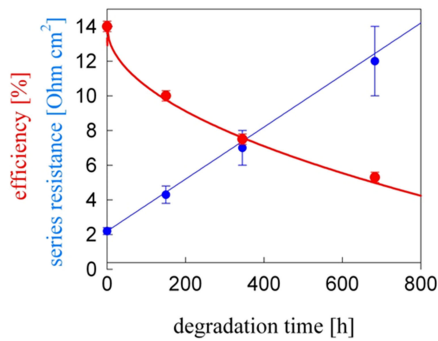


Fig. 2. CIGS solar cell efficiency and series resistance as a function of damp-heat degradation time. Full lines are guides-to-the-eye.

zinc oxide (i-ZnO)/cadmium sulfide (CdS)/coevaporated CIGS/molybdenum (Mo) on soda lime glass (SLG), with an additional Ag front contact and an additional Ag back contact on the Mo film for the devices used in the current–voltage ( $I$ – $V$ ) solar cell characterization. Fig. 1 provides a schematic overview of the layer composition of the first series of samples investigated in the positron annihilation studies, merged with a representative SEM image, indicating a  $\sim 250$  nm thickness of the ZnO:Al TCO, tailored to observe both the ZnO:Al and the CdS/CIGS/Mo layer underneath in the positron depth profiles. Furthermore, a second series of samples was studied, for which ZnO:Al TCO layers with a thickness of  $\sim 1$   $\mu\text{m}$ , that is more characteristic for use in actual solar cells, were deposited directly on bare SLG glass substrates.

Fig. 2 shows the time-dependence of solar cell efficiency and the series resistance, determined under AM1.5 illumination, of unpackaged CIGS solar cell devices as a function of accelerated degradation time of up to 683 h of exposure to temperature–moisture conditions of 85 °C/85% relative humidity (RH). The efficiency of the CIGS solar cells decreased substantially from 14.0% in the as-prepared state to 5.3% after a degradation time of 683 h, demonstrating that substantial degradation takes place on this time scale. Simultaneously, a large increase in series resistance ( $R_s$ ) occurs, that contributes to the decrease in solar cell efficiency. The increase in series resistance due to damp heat exposure of CIGS solar cells [6]–[12] can be caused by various reasons, including molybdenum oxidation, delamination, degradation or migration of the grid, and reduced conductivity of the front contact ZnO:Al [6]. Generally, the latter is known to play

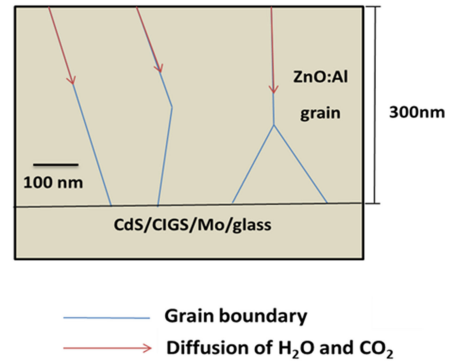


Fig. 3. Schematic of the in-diffusion process of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  molecules into the ZnO:Al TCO layer via the grain boundaries, where they react and create additional open volume, as an important factor to the environmental degradation of the CIGS solar cells.

a major role, due to its sensitivity to damp heat [7], combined with the fact that cell sizes are mostly optimized based on the conductivity of the ZnO:Al. If this material then degrades, this can quickly impact the  $R_s$ .

In previous studies [7], [8], the degradation of the ZnO:Al TCO was linked to the formation of  $\text{Zn}(\text{OH})_2$  and Zn-based carbonates including mixtures of these, i.e.,  $\text{Zn}_x(\text{OH})_y(\text{CO}_3)_z$ , at the grain boundaries due to the reaction with ZnO of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  molecules after diffusion into the layer via the grain boundaries (see Fig. 3). The formed Zn-based compounds will effectively disturb lateral charge carrier transport through the ZnO:Al TCO layer, by imposing increasingly large transport barriers and reducing charge carrier mobility due to enhanced scattering at the grain boundaries. Moreover, charge carriers could be more effectively trapped at grain boundaries, reducing the charge carrier density. These factors will lead to a strong increase in series resistance, as observed, and this will contribute in its turn to the large reduction in efficiency of the ZnO:Al/i-ZnO/CdS/CIGS/Mo solar cells.

#### A. Positron Doppler Depth Profiling

In order to examine which parts of the CIGS solar cell are degraded during the damp-heat treatment, we first used positron Doppler broadening depth-profiling to monitor the ZnO:Al/i-ZnO/CdS/CIGS/Mo samples as a function of depth and degradation time at 85 °C and 85% RH. Briefly, upon implantation of monoenergetic positrons with a kinetic energy in the range of  $\sim 0.1$ –25 keV into a solid, they will rapidly (typically within a few ps) thermalize by collisions with the ions and by excitation of abundant electrons in the material. Subsequently, the positron will diffuse in the crystal lattice, and either annihilate in the interstitial space of the bulk crystal lattice or trap at vacancies or larger open volume, e.g., vacancy clusters, and finally annihilate under emission of, mostly, two gamma photons with an energy of  $\sim 511$  keV (see Fig. 4). By varying the initial kinetic energy of incident positrons, a depth-profile of the multilayered system can be obtained (see Fig. 5).

In Doppler broadening studies, the measured Doppler-shift in the energy of the annihilation photon is proportional to the momentum component of the electron parallel to the emission direction. The positron Doppler  $S$  parameter, extracted from

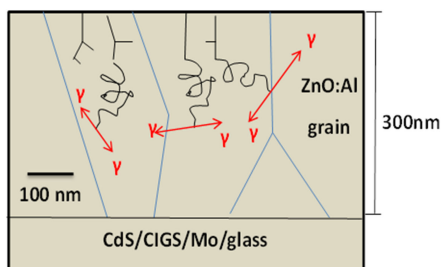


Fig. 4. Positrons implanted into a ZnO:Al TCO film thermalize and subsequently diffuse inside of the layer, before they trap at vacancies inside the grains or at open volume at the grain boundaries, and annihilate primarily upon emission of two 511 keV gamma photons.

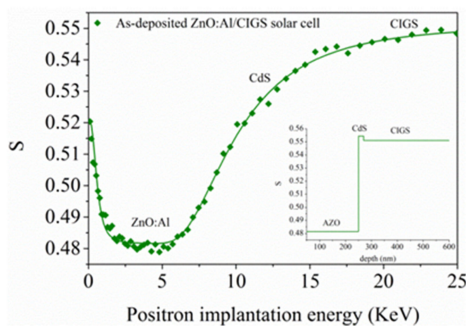


Fig. 5.  $S$  parameter as a function of positron implantation energy for the as-deposited ZnO:Al/CIGS solar cell. The layer structure used as model in the VEPFIT program is inserted in the figure. The curve through the data points represents a best-fit using VEPFIT [13].

the Doppler broadened 511 keV annihilation photopeak, is a measure of positron annihilation with valence electrons, which provides sensitivity to the presence of open volume defects such as vacancies or vacancy clusters [3]. The increase in concentration or size of vacancies or vacancy clusters in an otherwise identical material generally leads to an increase of the positron  $S$  parameter [3], [4]. Doppler broadening measurements [14] were performed using the monoenergetic Variable Energy Positron beam VEP. The implantation energy of positrons was varied from 0.1 to 25 keV. A liquid-nitrogen-cooled high-purity Ge detector with an energy resolution of 1.3 keV was used to determine the energy of the emitted annihilation  $\gamma$ -rays.

Turning first to the ZnO:Al TCO deposited on the CdS/CIGS/Mo solar cell, in Fig. 6, shows that the degradation leads to pronounced changes in the Doppler broadening  $S$  parameter at low positron implantation energies. The  $S$  parameter shows a strong increase already for a relatively short degradation time of 25 h in the low energy range up to 4 keV. The rise in  $S$  parameter continues for longer degradation times up to 683 h, extending toward increasingly higher positron implantation energies of up to at least 8 keV. This indicates that vacancies and open volume in the ZnO:Al layer is formed at increasingly large depths below the surface with prolonged degradation time. This suggests a relationship of the open volume formation with in-diffusion of atmospheric molecules, such as  $H_2O$  and  $CO_2$ , which were found to play a key role in the degradation mechanism [7], [8]. As shown in Fig. 6, there is no significant change in the CIGS absorber layer, since the Doppler depth profiles remain unchanged in the energy range beyond  $\sim 10$  keV, while

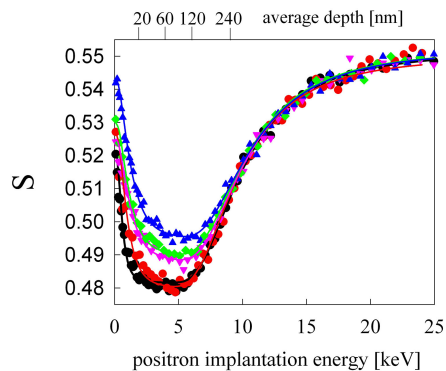


Fig. 6. Positron Doppler broadening  $S$  parameter as a function of positron implantation energy for ZnO:Al TCO layers deposited on CIGS solar cells at various degradation times ( $\bullet$  0 h,  $\bullet$  25 h,  $\blacktriangledown$  150 h,  $\blacklozenge$  347 h,  $\blacktriangle$  683 h) at 85 °C/85% RH. Symbols are experimental data; solid lines are fit curves obtained by VEPFIT analysis using a 4-layer model, including a  $\sim 20$  nm top and a  $\sim 260$  nm bottom ZnO-layer.

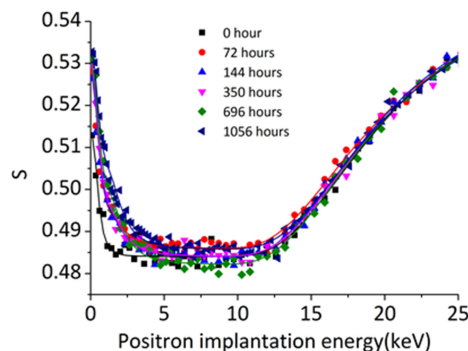


Fig. 7. Positron Doppler broadening  $S$  parameter as a function of positron implantation energy for ZnO:Al TCO layers deposited on bare glass substrates at various degradation times at 85 °C/85% RH. Symbols are experimental data and solid lines are fit curves obtained by VEPFIT analysis employing a four-layer model.

the accelerated degradation clearly affects the ZnO:Al layer substantially. In Fig. 6, we included estimates for the average implantation depth in the ZnO:Al layer at selected implantation energies, based on  $z_{\text{average}} = \alpha_p E^n / \rho$ , with  $\rho = 5.606 \text{ g/cm}^3$  the density of ZnO,  $E$  the positron implantation energy (in keV), and the empirical parameters  $\alpha_p = 4.0 \mu\text{g}/(\text{cm}^2 \text{keV}^{1.62})$  and  $n = 1.62$  were used [3].

It is instructive to compare these changes with the Doppler depth profiles obtained for the second series of samples consisting of ZnO:Al deposited on bare SLG substrates, as a function of damp heat degradation time (see Fig. 7). The Doppler depth-profile for the as-deposited sample resembles that of the first series; the much broader range of the  $S$ -parameter plateau of the ZnO:Al layer reflects its much larger thickness of  $\sim 1 \mu\text{m}$ . Also here, a strong increase in the  $S$  parameter at the surface and in the  $\sim 20$  nm top part of the ZnO:Al layer is observed upon degradation. However, hardly any change is visible in the range beyond  $\sim 5$  keV, indicating that the formation of open volume now occurs only at shallow depths.

The increase in  $S$  in both types of films suggests that the degradation of the ZnO:Al layer involves the formation of open volume defects. The size of the increase in  $S$  parameter indicates a pronounced formation of monovacancies and also



small vacancy clusters [4], [5]. The defect formation in the ZnO:Al layer occurs on a time scale that is very similar to the decay of the solar parameters such as solar cell efficiency and the series resistance that increased from an initial value of  $2.2 \pm 0.2$  to  $12 \pm 2 \Omega\text{cm}^2$  after 683 h of exposure to 85 °C/85% RH (see Fig. 2). This suggests a relationship between the solar cell degradation observed in the devices made for the ZnO:Al/ZnO/CdS/CIGS/Mo samples and the formation of additional open volume defects such as vacancies or vacancy clusters in the ZnO:Al layer for the samples made from the same batch, as a result of the damp-heat accelerated degradation treatment. Furthermore, the depth-dependence of open volume formation is consistent with the previously proposed mechanism involving the in-diffusion of environmental gas molecules via grain boundaries and their subsequent chemical reaction with ZnO, leading to solar cell degradation [7], [8].

The intriguing difference in the depth dependence between the two series of ZnO:Al samples studied indicates a difference in grain boundaries for these two series, that relates to the deposition of the ZnO:Al on rough (here: CdS/CIGS/Mo) and smooth (here: SLG glass) substrates [15], [16]. Previous studies [15] indicate that the growth of ZnO:Al on rough surfaces, such as CIGS, may lead to the formation of so-called extended grain boundaries at the position of the grain boundaries of CIGS. These extended grain boundaries appear to be more susceptible to degradation than the more numerous regular grain boundaries between the ZnO:Al grains [15]. Also the density of grain boundaries in the ZnO:Al layer could be different. The evolution of open volume at the grain boundaries in the ZnO:Al will be further examined in the following paragraphs, where we compare the positron annihilation lifetime spectroscopy (PALS) results for the two series.

### B. Defect Identification by Positron Lifetime Spectroscopy

In order to identify the size and concentration of vacancy-related defects, we employed PALS [3], [4], [17], [18]. The samples were examined using the pulsed low-energy positron lifetime spectrometer instrument [18] of the neutron induced positron source facility [19] at the Heinz Maier-Leibnitz Zentrum research reactor in Garching. The positron lifetime is a sensitive measure of the local electron density at the positron-electron annihilation site. The positron lifetime depends not only on the type of material (atomic composition, electronic structure), but also sensitively on the size of the local open volume available to the positron, that may be affected via the density of the material, and the presence of a vacancy or vacancy cluster. The positron lifetime can thus be used to quantitatively determine the size of the vacancy cluster, as the electron density at the center of the vacancy (cluster) gradually decreases with the size of the available open volume.

Positron lifetime spectra were therefore collected at selected positron implantation energies for the ZnO:Al TCO layers deposited on bare glass substrates and for the ZnO:Al-based CIGS solar cells at various stages of degradation in the range of 0–1200 h of accelerated degradation. Figs. 8 and 9 show the evolution as a function of degradation time of the mean positron lifetime of the PALS spectra collected at shallow depth (1–2 keV) and much deeper inside the ZnO:Al layer (4

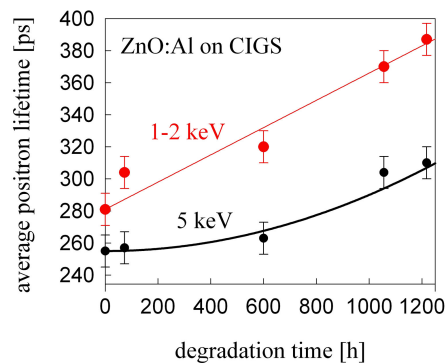


Fig. 8. Average positron lifetime collected at a positron implantation energy of 1 and 2 keV, averaged, (●) and 5 keV (●), respectively, as a function of damp-heat degradation time for the first series of ZnO:Al TCO layers deposited on CIGS solar cells. Full lines are guides-to-the-eye.

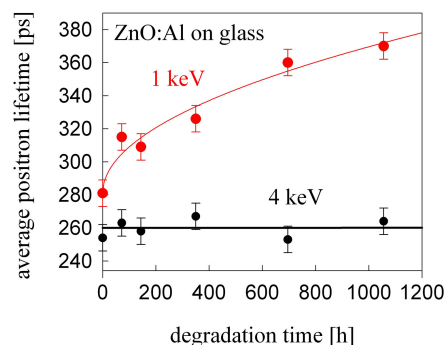


Fig. 9. Average positron lifetime collected at a positron implantation energy of 1 keV (●) and 4 keV (●), respectively, as a function of damp-heat degradation time for the second series of ZnO:Al TCO layers deposited on bare glass substrates. Full lines are guides-to-the-eye.

or 5 keV) for the two respective series of samples. While the mean positron lifetime shows a strong increase at 1–2 keV for both types of sample, indicating the formation of open volume at shallow depths below the surface of the ZnO:Al, it stays virtually constant for ZnO:Al deposited on bare glass substrates at a positron implantation energy of 4 keV for degradation times up to 1056 h (see Fig. 9). In contrast, the mean positron lifetime at 5 keV for ZnO:Al deposited on CdS/CIGS/Mo shows a clear increase for degradation times beyond  $\sim 600$  h, where it starts to follow the trend visible at shallow depth (1–2 keV) (see Fig. 8). This indicates that little open volume formation occurs well inside the ZnO:Al layer deposited on glass, while this is prominent for ZnO:Al deposited on CdS/CIGS/Mo, in line with the conclusions drawn from the Doppler depth profiling results.

It is instructive to take the decomposition of the PALS spectra, performed using the LT10 software package [17], into account. In the positron lifetime decomposition, in general, two main short lifetime components were extracted, with a positron lifetime for both the as-deposited ZnO:Al layer on glass and on CdS/CIGS/Mo of 1)  $\sim 224$  ps and 2) ranging from  $\sim 370$  to  $\sim 320$  ps depending on the depth in the ZnO:Al layer, respectively [5]. These two lifetimes, with depth-dependent intensities of around 70%  $\rightarrow$  90% and 30%  $\rightarrow$  10%, respectively, are characteristic for 1) the Zn monovacancy and 2) small vacancy clusters (six vacancies to four vacancies, depending on the depth below the surface). Upon degradation, the second, longer lifetime in-

creases substantially in the top layer of both types of ZnO:Al layers to a value of about 440–460 ps, demonstrating a pronounced increase in the size of the defects, reaching a size of the vacancy clusters similar to about six missing  $V_{\text{Zn}}-V_{\text{O}}$  pairs [5]. For the ZnO:Al deposited on CdS/CIGS/Mo, the lifetime of the second lifetime component is seen to increase also substantially in the bottom layer of the ZnO:Al to a value of about 410 ps, indicating the growth of the vacancy clusters toward a size of around 4 missing  $V_{\text{Zn}}-V_{\text{O}}$  pairs [5].

A model involving positron trapping and annihilation in the grain boundaries of the ZnO:Al layer and in vacancies inside the grains developed by Oberdorfer and Würschum *et al.* [20] was applied to simulate the positron annihilation lifetime spectroscopy results, based on the equations given in [20]. The simulations, the details of which will be presented elsewhere [5], provide support for positron trapping in Zn monovacancies inside the ZnO:Al grains and in larger vacancy clusters at their grain boundaries. The smaller formation of open volume inside the ZnO:Al layer that are deposited directly on flat glass substrates is in line with this observation, since the density of grain boundaries sensitive to degradation generally is smaller in the case of growth of ZnO:Al on a smooth substrate compared with a rough substrate, such as the CdS/CIGS/Mo used in this study (see Fig. 1).

Summarizing, our study demonstrates that the observed larger open volume defects at the grain boundaries for the ZnO:Al deposited on CdS/CIGS/Mo increase substantially in size upon degradation, with a time- and depth-dependence that suggest a match with the in-diffusion of molecules via the grain boundaries of the ZnO:Al TCO layer [7], [8]. Furthermore, the time-scale of open volume formation is very similar to the time-scale of key solar cell parameters. This provides further strong support for the previously proposed mechanism of in-diffusion of environmental molecules via the grain boundaries of the ZnO:Al TCO layer, that react with ZnO to form a variety of zinc-based carbonates and hydroxyls (see Fig. 3) [8]. Moreover, the created open volume at the grain boundaries may act as additional barriers to charge carrier transport, leading to increased series resistances and thus, substantially reduced solar cell efficiencies.

### III. CONCLUSION

Thin-film positron annihilation spectroscopies were employed to monitor the accelerated degradation of Al-doped ZnO films deposited as TCO on bare glass substrates and on CIGS-based solar cells, providing new insights into the mechanism of degradation of the latter upon damp-heat exposure. A pronounced growth of vacancy clusters at the grain boundaries was observed for the solar cells exposed to a combination of elevated temperature and humidity levels (85 °C/85% RH). Substantial smaller formation of open volume is seen for ZnO:Al deposited on smooth glass substrates, indicating that the roughness of the substrate is an important parameter for the resulting density and type of grain boundaries, which are a key element in the degradation mechanism of ZnO:Al layers exposed to environmental conditions. This study also provides further support that the in-diffusion (and local chemical reactions) of molecules such as H<sub>2</sub>O and CO<sub>2</sub> into ZnO:Al TCO films and the subsequent

creation of open volume at the grain boundaries play a key role in the degradation of the CIGS solar cells. The created open volume imposes additional transport barriers to charge carrier transport in the TCO, likely leading to a strong increase in series resistance and reduction in the efficiency of the solar cells.

### ACKNOWLEDGMENT

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Authors' photographs and biographies not available at the time of publication.