Impacts of Humidity and Temperature on the Performance of Transparent Conducting Zinc Oxide

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ABSTRACT

The impact of humidity and temperature on a zinc oxide based transparent conducting oxide (TCO) was assessed under accelerated aging conditions. An *in situ* electroanalytical method was used to monitor the electrical properties for a conducting zinc oxide under controlled atmospheric (humidity, temperature and irradiation) conditions. A review of thin film photovoltaic (PV) literature has shown one major failure mode of cells/modules is associated with the ingress of water into modules in the field. Water contamination has been shown to degrade the performance of the TCO in addition to corroding interconnects and other conductive metals/materials associated with the module. Water ingress is particularly problematic in flexible thin film PV modules since traditional encapsulates such as poly(ethyl vinyl acetate) (EVA) have high water vapor transmission rates. The accelerated aging studies of the zinc oxide based TCOs will allow acceleration factors and kinetic parameters to be determined for reliability purposes.

INTRODUCTION

Knowledge of long term durability and reliability will play an important role in the successful emergence of thin film photovoltaic systems as a viable, cost effective alternative to traditional silicon based systems currently in the marketplace. Sandia National Laboratories is currently developing predictive models for PV system reliability with the goal of increasing consumer/investor confidence and aid in directing research and development efforts for more reliable PV systems. The model in its final form will integrate data ranging from operations and maintenance of large PV systems[1] to accelerated lifetime testing of individual PV system components[2]. As part of this overall reliability effort, accelerated life tests were performed on aluminum doped zinc oxide (AZO) transparent conducting oxides (TCO) to determine the effects of humidity, temperature and irradiation on sheet resistance over time. Aluminum doped zinc oxide is used heavily by thin film PV manufacturers for its high conductivity, optical transparency, manufacturing compatibility and cost. However the conductivity of AZO is known to degrade rapidly upon exposure to water at higher temperatures.[3-6] Research is continuing to improve the stability of AZO through different deposition techniques and conditions.[7-12] However, most degradation and performance studies of AZO and its variants have been performed under damp heat conditions (85 ^{o}C and 85% relative humidity (RH) for 1000 h) as related to International Electrotechnical Commission (IEC) test 61646. The aggressive conditions used in IEC 61646 may not adequately describe or be representative of TCO performance at lower temperatures and humidities. This research goes beyond damp heat conditions to examine AZO performance under other temperature/humidity/irradiation conditions and define kinetic parameters of degradation. The data shown in this report is part of a continuing effort to determine degradation rates and kinetic parameters for the prepared AZO. Table 1 shows the test matrix that is being worked through to fully describe AZO performance under a large number of operating conditions.

Table 1. Test matrix to study environmental effects on AZO.

Humidity (% RH)	Temperature (^{o}C)	Irradiation (Suns)	TCO Type
0	30, 50, 80	0, 1	AZO[1], *i*-ZO/AZO[2]
25	30, 50, 80	0, 1	AZO, *i*-ZO/AZO
50	30, 50, 80	0, 1	AZO, *i*-ZO/AZO
85	30, 50, 80	0, 1	AZO, *i*-ZO/AZO

[1] 2 wt% Alumina doped zinc oxide
[2] 2 wt% Alumina doped zinc oxide on top of intrinsic zinc oxide

MATERIALS & METHODS

Accelerated life tests were performed using a custom built environmental chamber (Figure 1) capable of controlling temperature, humidity and irradiation. The stainless steel chamber has internal dimensions of 33 × 33 × 15 cm and a 20 × 20 cm fused silica viewport for irradiation. A stream of water-saturated air is combined with a stream of dry air to produce desired humidity. Wet and dry flows are adjusted automatically using a custom Labview program based on humidity measurements (Vaisala HMT337). Total flow of humidified air through the chamber is 2 L/min. A thermocouple inside the chamber provides feedback for temperature control (Omega Technologies CSi8D Series) using externally mounted silicone rubber heaters (Omega Technologies). A Xe arc lamp (Oriel 66021) is used for irradiation experiments. The TCO sample is mounted on a custom polysulfone stage and contacted with a probe assembly (Accuprobe radius pogo, Lucas Signatone S2-S-1-CB). The environmental chamber was built with BNC pass-throughs

Figure 1. Picture of accelerated aging instrument.

for performing *in situ* four point resistance measurements using a digital multimeter (Keithly 2700).

The optical properties of the AZO films pre- and post-aging were evaluated using UV-Vis spectrophotometry (Shimadzu UV 3600).

Zinc oxide thin films doped with 2% alumina were prepared by magnetron sputtering (Thinfilms, Inc, Hillsborough, NJ) on sputter etched cleaned glass substrates (Corning 1737, 50 × 25 × 1 mm). The AZO thin films were 200 nm thick and had initial sheet resistances of 69 Ω/sq. Samples were exposed to temperature, humidity and irradiation conditions until the resistance of the sample doubled or upon reaching 400 h under test.

RESULTS & DISCUSSION

The initial series of aging studies examined the effects of humidity on the sheet resistance of AZO at 79 °C. Figure 2 shows increases in sheet resistance over time for all AZO samples held isothermally at various humidities. The resistance changes for the first 5 hours and are attributed to effects associated with the stabilization of temperature and humidity in the environmental chamber. For the first 24 h of accelerated aging, samples show a nonlinear increase in resistance over time, with higher humidity exposures amplifying non-linear effects. This could be attributed to water reacting with easily accessible

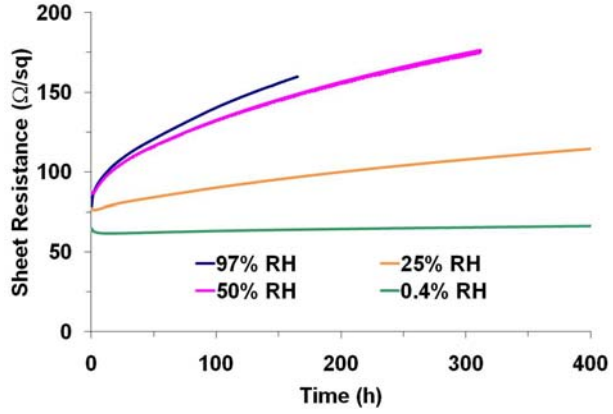

Figure 2. Time versus sheet resistance of AZO films under varied humidity conditions at 79 °C.

Table 2. Impact of humidity on AZO at 79 °C without irradiation.

Sample	% RH	Slope after 24 h (Ω/sq/h)
1	0.4	0.01
2	25	0.10
3	50	0.24
4	97	0.38

oxygen vacancies at the surface of the AZO film followed by a slowdown in reactivity due to less reactive (inaccessible) oxygen vacancies in the AZO film or another mechanism of degradation is at play. Further investigation is warranted. After 24 h, resistances increase linearly over time with coefficients of determination (R^2) greater the 0.99. Sheet resistances increased at a higher rate when samples were exposed to higher humidities (Table 2). Rates of increase in resistances after 24 h were 0.38 Ω/sq/h for an AZO film held at 79 °C and 97% RH compared to 0.01 Ω/sq/h held at a similar temperature, but 0.4% RH.

Table 3. Impact of temperature on AZO at 85% RH without irradiation.

Sample	Temperature (°C)	Slope after 24 h (Ω/sq/h)
5	30	0.002
6	44	0.011
7	85	0.372

In another set of aging experiments, the effect of temperature on sheet resistance at a constant relative humidity was examined. Table 3 shows the impact degradation rate on the sheet resistance of AZO over time at different temperatures under a constant 85% RH. As expected, an increase in temperature increased the rate of degradation (Figure 3). Samples held at 30 °C and 44 °C did not show any nonlinear degradation of sheet resistance upon exposure. However, the sample held at 85 °C and 85% RH showed a nonlinear rate of degradation during the first 24 h of exposure characteristic to that discussed earlier (Figure 1, 97% RH and 50% RH lines). This indicates a combination of high humidity and high temperature are required to promote the nonlinear degradation phenomena.

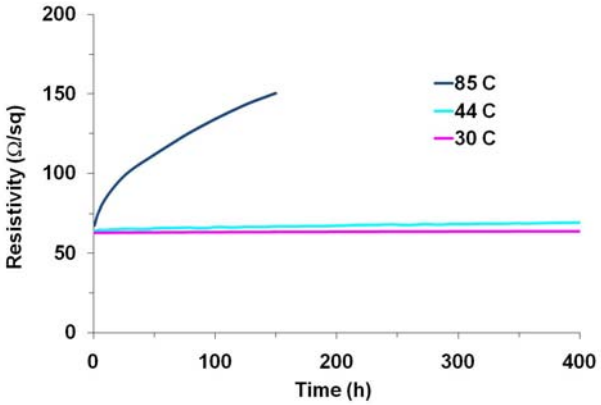

Figure 3. Time versus sheet resistance of AZO films under varied temperature conditions at 85% RH.

$$R_d = Ae^{\left(\frac{E_a}{kT}\right)} \quad (1)$$

The linear portion of the degradation for AZO at 85% RH can be related to temperature by the Arrhenius equation (1). Figure 4 shows a plot of 1/T versus the natural log of the sheet resistance degradation rate (R_d). The slope and intercept of the line suggest an activation energy (E_a) of 0.91 eV and pre-exponential factor (A) of 2.34×10^{12}. The Arrhenius values are only valid at the lower temperatures where degradation occurs at a constant rate throughout the temperature exposure at 85% RH.

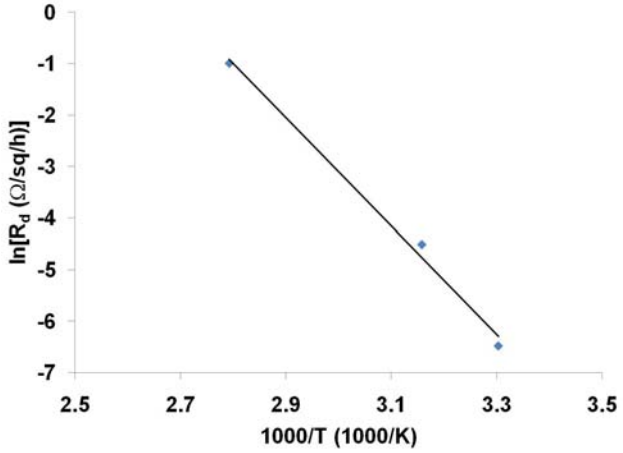

Figure 4. Arrhenius plot of 1000/T versus the natural log of the sheet resistance degradation rate for AZO exposed at 85% RH.

The optical properties of the AZO films were evaluated using UV-Vis spectrophotometry before and after exposure to accelerated aging conditions. Figure 5 shows the transmittance of an AZO film subjected to 79 ^{o}C and 97% RH for 165 h. As observed previously[4], the transmittance increased slightly after environmental aging. The amount of increase in transmittance after aging was dependent on the wavelength and ranged from 0 to 3.5% suggesting optical properties for the AZO used in this study are not significantly affected by high humidity and temperature. This plot is representative of samples subjected to lower humidity and temperature conditions.

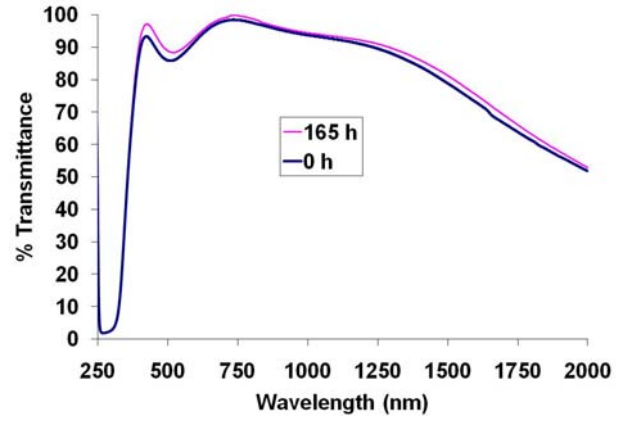

Figure 5. Transmittance of AZO film before and after exposure to 79 ^{o}C and 97% RH.

CONCLUSION

The performance of an AZO film was evaluated under varied humidity and temperature. High humidity increased the degradation of sheet resistance up to 38× relative to low humidity exposure at the same temperature. In addition a nonlinear increase in sheet resistance was noted during the initial exposure of AZO to environmental conditions; the nonlinearity was more pronounced at higher humidities and higher temperatures. Completion of the test matrix will allow a determination of acceleration factors and kinetic parameters of this critical component in the thin film PV cell/module.

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