

Damp-Heat Induced Degradation of Transparent Conducting Oxides for Thin-Film Solar Cells

Preprint

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*Presented at the 33rd IEEE Photovoltaic Specialists Conference
San Diego, California
May 11–16, 2008*

Conference Paper
NREL/CP-520-42525
May 2008

NREL is operated by Midwest Research Institute • Battelle Contract No. DE-AC36-99-GO10337



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ABSTRACT

The stability of intrinsic and Al-doped single- and bi-layer ZnO for thin-film CuInGaSe₂ solar cells, along with Al-doped Zn_{1-x}Mg_xO alloy and Sn-doped In₂O₃ (ITO) and F-doped SnO₂, was evaluated by direct exposure to damp heat (DH) at 85°C and 85% relative humidity. The results show that the DH-induced degradation rates followed the order of Al-doped ZnO and Zn_{1-x}Mg_xO >> ITO > F:SnO₂. The degradation rates of Al:ZnO were slower for films of higher thickness, higher substrate temperature in sputter-deposition, and with dry-out intervals. As inferred from the optical micro-imaging showing the initiation and propagation of degrading patterns and regions, the degradation behavior appears similar for all TCOs, despite the obvious difference in the degradation rate. A degradation mechanism is proposed to explain the temporal process involving thermal hydrolysis.

INTRODUCTION

Long-term performance reliability is required for all photovoltaic (PV) modules ranging from crystalline-Si based to thin films including CuInGaSe₂ (CIGS), CdTe, amorphous Si, dye-sensitized, and organic PV that employ transparent conducting oxides (TCOs) as electrical contacts or electrodes. Achieving this goal requires not only reliable constituent component materials and device structure of the solar cells, but also reliable electrical interconnects and packaging. To assess the quality of a PV module, one of the qualification tests in the IEC61215 or IEC61464 specifies a 1000-h exposure in damp heat (DH) at 85°C and 85% relative humidity (RH). Most CIGS solar cells use a combination of intrinsic and Al-doped ZnO as the conducting buffer layer. Reliability of the bi-layer i-/Al:ZnO (BZO), along with the Mo base electrode, can be the determining factor for durable long-term performance of a CIGS-based device/module. Similar reliability requirements of TCO-based contacts or electrodes are also applicable to other thin-film PVs.

In a previous paper, we reported some results from an exploratory study that demonstrated the instability of Mo and BZO when exposed to DH or to a 2.5 UV-sun at 60°C and 60% RH in a weatherometer (WOM) chamber [1]. The Mo was sputtered on 2.2-mm-thick soda lime glass. We found that Mo was rapidly corroded by the hot steam in DH condition, but was significantly less sensitive to the exposure in WOM and even less to the heating at

85°C in ambient relative humidity typically in the 11%~15% RH range in our laboratory. The BZO samples in that study were old “witness” films deposited along with CIGS solar cells on thin 0.5-mm 7059 glass slides with some variations in film quality. Nonetheless, when exposed to the DH, the “witness” BZO films were all degraded by the hot steam, but more rapidly in the presence of acetic acid vapor [1]. The acetic acid was intentionally introduced to simulate the possible presence of the acid from thermal processing and photothermal degradation of the ethylene-vinyl acetate (EVA) encapsulant commonly used in PV module encapsulation [2]. There are also some other studies on the stability issues of Al:ZnO by DH exposure reported in the literature [3-5].

In the present work, we used 1.1-mm-thick 7059 glass slides with single-layer intrinsic and Al-doped ZnO and bilayer i-/Al:ZnO that were specifically prepared with greater consistency in quality and property according to the “standard” conditions well established in our laboratory. The investigation was also extended to include Al-doped Zn_{1-x}Mg_xO alloy, Sn-doped In₂O₃ (ITO), and F-doped SnO₂ that can be employed as electrodes for various thin film solar cells. The Al-doped Zn_{1-x}Mg_xO alloy, fabricated in house, was tested to evaluate its potential to replace the conventional Al:ZnO. The present study focused only on the DH exposure-induced degradations. It should be emphasized that the direct exposure of the TCO coatings on the glass substrates to the DH conditions represents a fairly extreme situation that normally may not be experienced by a well-encapsulated and packaged PV module. This study, therefore, represents primarily our efforts to evaluate and compare the stability of various TCO materials for thin-film PV applications.

EXPERIMENTAL

To differentiate the differences among the three, 0.1- μ m single-layer intrinsic ZnO and Al-doped ZnO, and 0.2- μ m bi-layer ZnO were prepared separately by magnetron sputtering on 7.6-cm x 7.6-cm x 1.1-mm 7059 glass plates using a Semicore system, in which the *in-situ* substrate temperatures were determined to not exceed 60°C with a temperature indicator strip. Another set of single-layer Al-doped ZnO with or without MgO (Al:Zn_{1-x}Mg_xO, x= 0 to 0.1) at a thickness of 0.3~0.6 μ m was made in an ATC 2200-V sputtering system from AJA International, Inc. The ambient substrate temperature inside the ATC system has

not yet been definitely determined. The ITO glass plates were previously provided by Applied Film Laboratory (AFL). One of the F-doped SnO₂ samples was made in house (ID# L6A3) and the other two were from glass manufacturers, one is a commercial product noted as P-TCE and the other is an experimental product noted as P-TCO. Specimens of ~2.0-cm x 2.8-cm were cut from the TCO-coated plates for exposures in a chamber operated at 85°C and 85% RH. After baseline measurements, the TCOs were characterized periodically during the course of DH exposure by transmittance and reflectance measurements for optical properties, Hall measurements for sheet resistance, majority carrier mobility and concentration, x-ray diffraction (XRD) analysis for structural changes, and interference optical micro-imaging for morphological changes. Upon completion of the experiments, the exposed samples were examined with scanning electron microscopy (SEM). The systems used were a Cary 5G UV-Vis-NIR spectrophotometer with an integration sphere, an Ascent Hall550 Advance system, an X1 Advanced Diffraction System from Scintag Inc., a WYKO Optical Profiler Model 1100 system from Veeco, and a Nova Nano SEM 630 system from FEI, respectively.

RESULTS AND DISCUSSION

The single-layer intrinsic and Al-doped ZnO showed apparent difference from their combined bi-layer i/Al:ZnO in transmittance and reflectance spectra as seen in Fig. 1a. The Al:Zn_{1-x}Mg_xO also showed variation in T% and R% spectra, being influenced by the content concentration (x = 0, 0.01, or 0.1) of MgO in the alloy, as seen in Fig. 1b. More detailed material information of the tested specimens is given in the upper half of Table 1, which includes type of TCO, MgO content, substrate temperatures during deposition, and film thickness if available. The initial and subsequent changes of sheet resistance (R_{sh}) from Hall measurements as a function of DH exposure time are given in the lower half. For the purpose of convenience to compare the degradation rate, as given in the bottom row, a linear degrading relationship was assumed. After 480 h DH exposure, all Al-doped ZnO films, including Al:Zn_{1-x}Mg_xO, became either insulating or highly resistive (> 1

MΩ/square) and turned from initial clear to white hazy with visible delamination on some specimens. The calculations for the degradation rates in R_{sh} are therefore only up to 242 h for Al-doped ZnO, and 886 h for ITO and F-doped SnO₂. From the calculated degradation rates, it is clear that the ITO and F:SnO₂ were about two to four orders of magnitude more stable than ZnO-based films. For the

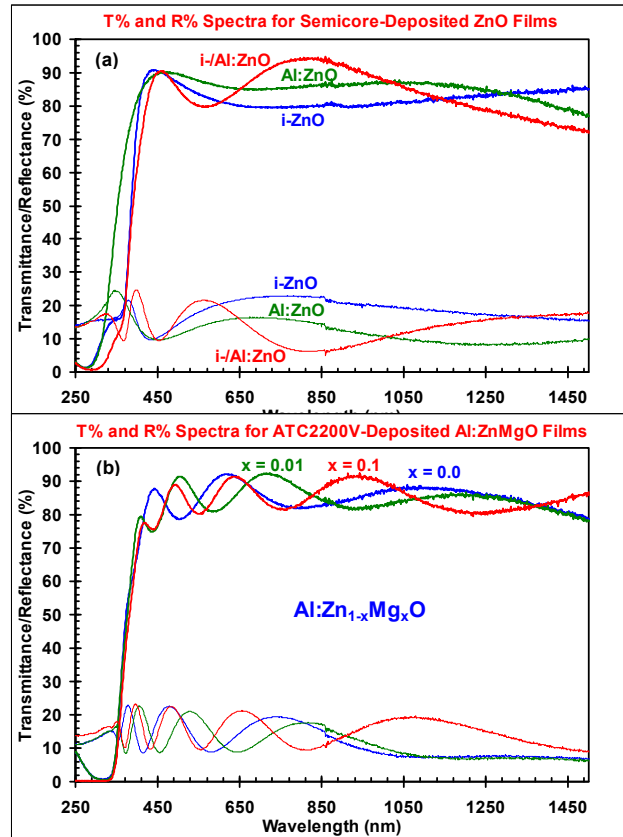


Fig. 1. Transmittance and reflectance spectra for (a) single-layer intrinsic, Al-doped, and intrinsic/Al-doped ZnO (i-ZnO, Al:ZnO, and i-/Al:ZnO), and (b) Al-doped Zn_{1-x}Mg_xO films sputter-deposited on 1-mm-thick 7059 glass plates.

Table 1. Sample Data and Sheet Resistance Changes upon Damp Heat Exposure

Sample ID	IZO-11	AZO-21	BZO-31	AZO-383	AZO-471	AZO-501	AZO-681	AFL-1	L6A3-1	P-TCO1	P-TEC3
Composition	int.-ZnO	Al:ZnO	i-/Al:ZnO	Al:ZnO	Al:ZnO	Al:ZnO	Al:ZnO	Sn:In2O3	F:SnO2	F:SnO2	F:SnO2
MgO added	0%	0%	0%	0%	1%	10%	0%				
Dep. T _{sub} (°C)	Ambient	Ambient	Ambient	Ambient	100	100	100	N/A	N/A	N/A	N/A
Thickness (μm)	0.1	0.1	0.2	0.3	0.5	0.5	0.6	N/A	0.5-0.6	0.26	N/A
DH Time (h)	Rsh (ohm/sq)										
0	HR*	85.71	64.03	68.19	73.30	HR*	29.34	83.00	8.30	17.92	12.53
120		967.00	107.70	155.60	165.50		39.11	77.87	7.98	17.15	12.82
242		15110.00	510.50	236.10	272.50		50.10	82.05	7.80	17.42	12.66
480		HR*	HR*	HR*	HR*		HR*	83.20	8.00	17.82	12.77
886		HR*: Highly resistive						84.34	8.24	17.38	12.69
Deg. Rate [(ohm/sq)/h]		6.21E+1	1.84E+0	6.94E-1	8.23E-1		8.58E-2	1.51E-3	-6.99E-5	-6.09E-4	1.80E-4

initially insulating intrinsic ZnO (ID# IZO-11) and 10%-MgO Al:Zn_{0.9}Mg_{0.1}O (ID# AZO-501), degradations were determined by measuring changes in optical properties, XRD, and micro-imaging. The results show that DH-induced R_{sh} degradation rates of single-layer Al:ZnO films are faster for thinner films (e.g., AZO-21 vs. AZO-383). Also, Al:ZnO films deposited at ambient substrate temperature in the ATC system degraded faster than those deposited at 100°C substrate temperature (e.g., AZO-383 vs. AZO-681).

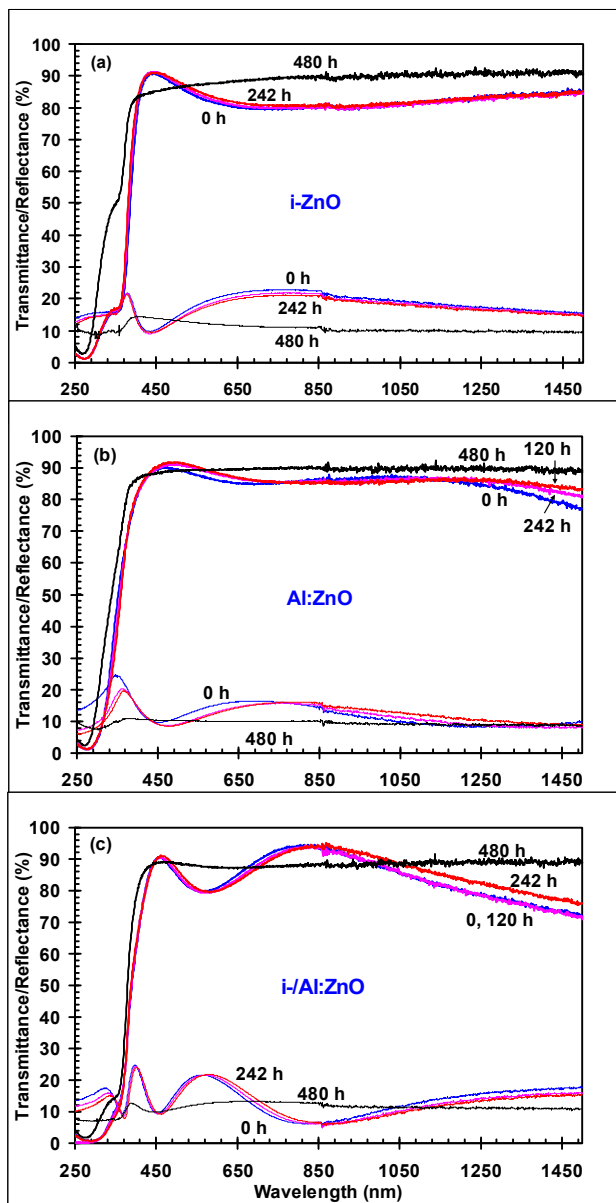


Fig. 2. Transmittance and reflectance spectra for (a) single-layer intrinsic ZnO (IZO-11), (b) single-layer Al-doped ZnO (AZO-21), and (c) bi-layer i/Al:ZnO (BZO-31) before (T₀ = 0h) and after accumulating 120 h, 242 h, and 480 h DH exposure.

The single-layer i-ZnO, Al:ZnO, and their combined bi-layer i-/Al:ZnO did not show substantial changes in transmittance and reflectance spectra until after 480 h DH exposure, whereas the hazy films exhibited essentially the same flat curves losing the characteristic features of Al-doped conducting ZnO as shown in Fig. 2. This is also evidenced by the corresponding decrease in the mobility, determined by Hall measurements, as seen in Fig. 3a. One notable observation is that the degradation rate would be greater if the Al:ZnO specimens (not given in Table 1) were exposed in the DH chamber continuously for 240 h.

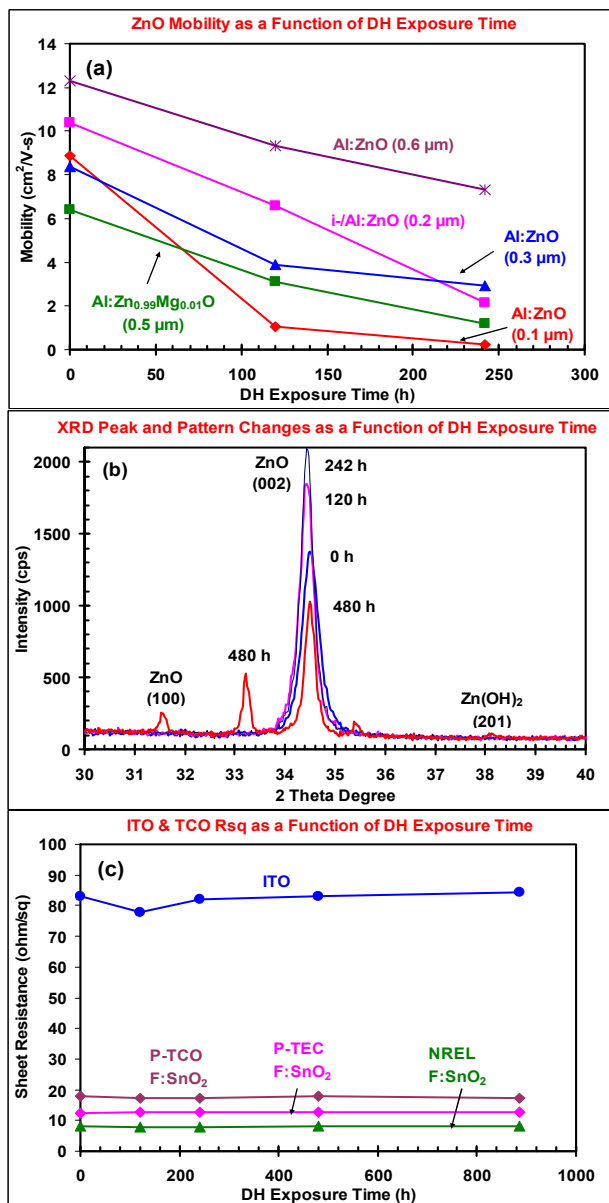


Fig. 3. (a) Decrease in mobility of mono- and bi-layer Al-doped ZnO films as a function of DH exposure time, (b) change in XRD feature for IZO-11 DH-exposed upto 480 h, and (c) sheet resistance of ITO and F:SnO₂ DH-exposed to 886 h.

The sample set would become insulating with a white hazy appearance, the same as those in Table 1 for 480 h with periodic removal from the DH chamber for measurements. This suggests that the films removed from the DH chamber were capable of recovering their physical properties to some extent, as also indicated by the gradual change to a somewhat less cloudy appearance after ~2 days in the air. One likely reason is the loss of water molecules from the hydrated or hydrolyzed film bulk and film/glass interface. Another interesting observation is that a bi-layer i-/Al:ZnO sample was highly resistive when it was still moist just after being taken out from a bottle filled with moisture in the DH chamber, and then became conducting as expected for a film with DH=94 h exposure after drying naturally in the air for some minutes. In comparison to the ZnO-based films, the optical property of the ITO and F:SnO₂ films were essentially unchanged in transmittance and reflectance spectra after 886 h DH exposure.

The structural changes by DH exposure are also reflected in the XRD patterns, per the example shown in Fig. 3b for the sample of intrinsic ZnO (IZO-11). Except for the bi-layer BZO-31, all single-layer ZnO films show an increase in (002) peak intensity at 34.50° (2 theta) up to DH 242 h, possibly a result of morphological changes (see below), before exhibiting a moderate to large decrease at DH 480 h due to structural disintegration. For the Al:Zn_{0.9}Mg_{0.1}O (AZO-501) alloy, a main peak appeared at 34.12° with a long tail. The main peak shifted to ~33.95° upon DH exposure up to 242 h and then back to 34.12° at 480 h. IZO-11 and AZO-471 were the two samples that produced four new peaks at DH 480 h (Fig. 3b), possibly a consequence of structural degeneration effected by the hot moisture-induced degradation. The peaks at 31.38°, 33.22°, and 35.38° are assigned, using PDF#89-0510, 65-2880, and 75-1533 index references for ZnO, to be hexagonal (100), cubic (111), and hexagonal (101),

respectively. The peak at 38.12° may be from cubic (200) or Zn(OH)₂ (201), as referred to PDF #65-2880 and 89-0138. Additionally, the peak width at half height for some samples showed notable narrowing at DH 480 h (e.g., Fig. 3b), but its cause is not yet clearly understood. These results suggest the ZnO might have undergone structural degeneration from original highly (002) preferential orientation to a more disordered state with some transformation from original hexagonal to cubic, in addition to the formation of insulating ZnO and Zn(OH)₂. Meanwhile, it is not clear yet on the fate of the Al dopant upon DH exposure, although it is possible that the Al was also readily transformed into Al(OH)₃.

The surface morphology of the various TCO films was also examined periodically for the initiation and propagation of the defecting patterns and regions as a function of DH exposure time by using the WYKO interference optical microscope. More than 1000 micro-images were taken. A few of the images are illustrated in Fig. 4 for the IZO-11 sample at four stages, showing the progressive morphological degradation as the DH exposure time increased to 480 h. The initially grainy but fairly smooth surface started to show some small spikes that appeared in a random manner upon exposure to DH in the first ~100 h. The number of spikes increased along with the appearance of full or partial ring-like features that showed ditch-like cutting into the depth of the film as the DH time increased (e.g., 240 h). The ring features are suspected to arise from the finite water droplets condensed from the moisture, which was the case observed when the cool films were just loaded into the hot steamy DH chamber. As the degradation progressed further, the film disintegrated greatly into fabrics-like features at DH 480 h and was difficult to be micro-photographed because of large loss of light reflection from the rough surface. This morphological degradation process and pattern development was essentially the

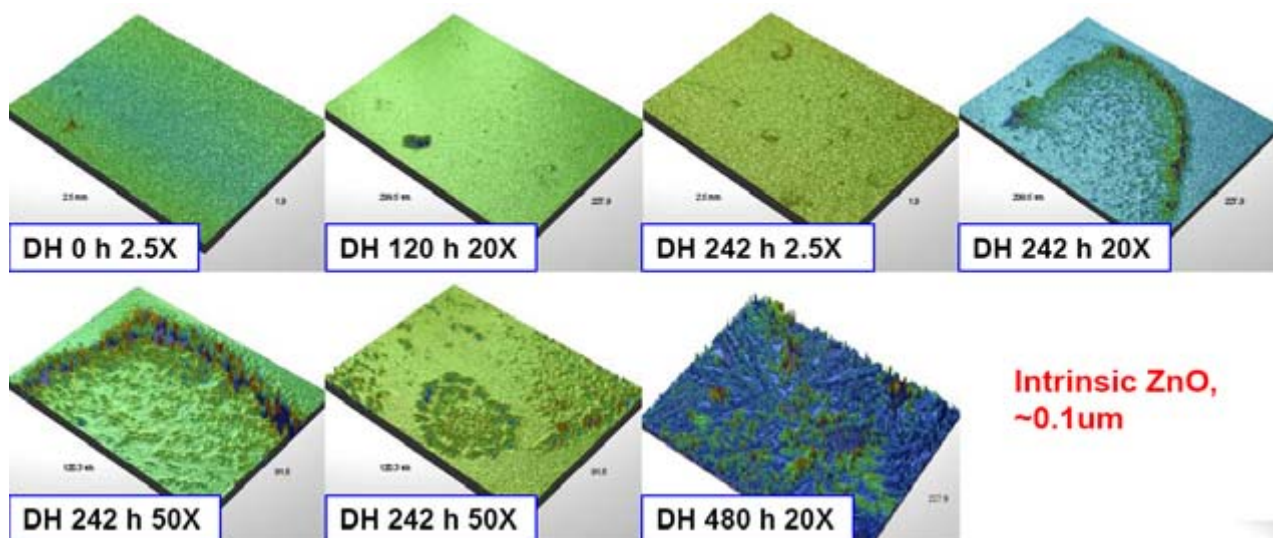


Fig. 4. Optical micro-images for the sample of intrinsic ZnO (IZO-11), showing the progressive morphological degradation as the DH exposure time increased to 480 h. The magnification factors are also indicated.

same for all ZnO-based films as observed in this study. While starting with grainy surfaces for the Semicore-deposited Al:ZnO, the DH exposure at 480 h resulted in obvious morphological differences for the single-layer i-ZnO and Al:ZnO, and bi-layer i-/Al:ZnO, as shown by SEM topographs in Fig. 5. Similar surface morphological degradations for the two samples of Al:Zn_{1-x}Mg_xO alloy (top row), ITO and the experimental P-TCO F:SnO₂ (bottom row) at DH 242 h are illustrated in Fig. 6. The T-PEC F:SnO₂ also exhibited a similar pattern of changes as ITO and P-TCO (not shown). At 10% of MgO, the Al:Zn_{0.9}Mg_{0.1}O (AZO-501) was originally insulating and, upon DH exposure, exhibited localized spot-wise material loss (see the third image on the top row of Fig. 6), suggesting the MgO-ZnO was not fully alloyed during co-sputtered process.

In comparison with Al-doped ZnO and Zn_{1-x}Mg_xO alloy, the ITO and F:SnO₂ were more stable with little or no changes in the overall optical and structural properties upon 886 h DH exposure (figures not shown), although optical micro-images revealed finite corrosions occurring at DH 242 h (Fig. 6, bottom row). All three F:SnO₂ samples tested were definitely more stable than the ITO at 886-h DH exposure. Although the low degradation rates and relatively flat curves for sheet resistance, R_{sh}, of ITO and F:SnO₂, as seen in Table 1 and Fig. 3c, up to DH 886 h may suggest their high stability against the damp heat, the truth is that the R_{sh} values at DH 480 h and 886 h were obtained by moving the four contact probes in the Hall measurements around the film surfaces to avoid the highly resistive regions or spots as illustrated in Fig. 6 (bottom row). This was especially required for the ITO sample (AFL-1) at DH 886 h having a number of large and small highly resistive regions or spots. The measured R_{sh} values

are therefore for the surface areas that still possessed continuous conducting paths. Overall, when compared with ZnO and ITO, F:SnO₂ films were more stable, as could be expected also from the literature [6]. Among all three, the NREL F:SnO₂ (L6A3-1) showed the highest stability in all aspects against damp heat even with very little change in optical morphological micro-imaging observations.

Regardless of the film composition and the obvious difference in the degradation rate, the degradation behavior appears similar for all TCO films studied, as

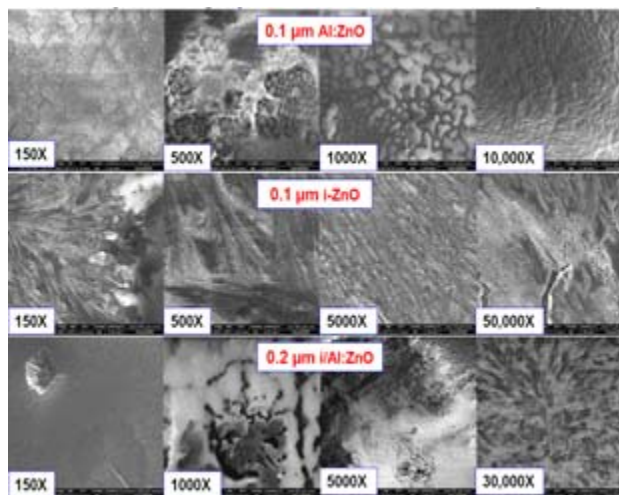


Fig. 5. SEM topographical microimages for the samples of Al:ZnO (AZO-21), i-ZnO (IZO-11), and bilayer i-/Al:ZnO (BZO-31) at DH exposure of 480 h. The magnification factors are also indicated.

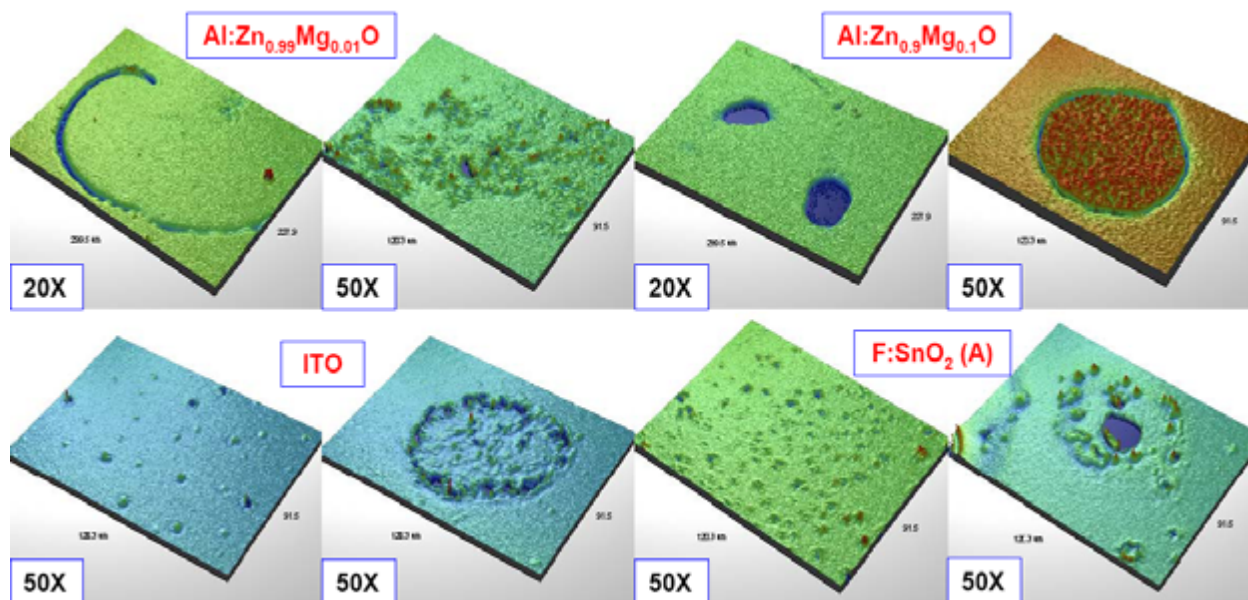


Fig. 6. Optical micro-images for the samples of (top row) Al:Zn_{1-x}Mg_xO ($x = 0.01$ and 0.1); and (bottom row) ITO, and P-TCO F:SnO₂, showing morphological degradations at DH 242 h exposure. The magnification factors are also indicated.

inferred from optical micro-imaging observations. In general, the first sign of degradation started at a few small spots or areas with appearance of irregular circles and spikes (e.g., Figs. 4 and 6 at 120~242 h); as the DH exposure increased, the hydrolysis-induced corrosion circles, spikes, and pop-ups increased and became more widely spread (e.g., Figs. 4 and 6 at DH 242 h), and finally, especially for ZnO-based films, severe disintegration resulted (e.g., Fig. 4 at DH 480 h). This thermal hydrolytic process might have started from the surface of the film as well as at the grain boundary and progressed downward and inward. If this was the case, then it would take longer exposure time to allow the “ditches” (e.g., Fig. 4, leftmost figure at the bottom row) to grow deeper to break up the electrical conducting path on a thicker ZnO film, and to break up the better grain crystallites on a ZnO film made at higher temperature. In addition, visible delaminations were seen on some ZnO films after 480 h DH exposure, suggesting the destruction of the bonding at the interface between the ZnO layer and glass substrate. On the other hand, with extended DH exposure to 886 h, the ITO (AFL-1) film showed two large and some small insulating regions, while F:SnO₂ films remained *visibly* intact. Accordingly, based on all the optical, electrical, structural and morphological observations, the temporal process of DH-induced degradation is proposed to involve first hydrolysis of the oxides at some sporadic “weak” spots, swelling and popping of the hydrolyzed spots due to volume increase, “segregation” of hydrolyzed regions causing discontinuity of electrical path, hydrolysis of the oxide-glass interface, and finally formation of insulating M(OH)₂ along with visible delamination over larger areas.

CONCLUSIONS

We have shown the relative stability of a number of TCOs, including intrinsic and Al-doped ZnO, Al-doped Zn_{1-x}Mg_xO, ITO, and F-doped SnO₂, on glass substrates when exposed to damp heat at 85°C and 85% RH. From the electrical, optical, structural, and morphological analysis, the order of degradation rate is determined to be ZnO >> ITO > F:SnO₂. With only one conducting Al-doped Zn_{1-x}Mg_xO alloy at x = 1% that failed in the DH test in the same way as other Al:ZnO samples, it is too premature to conclude whether the alloy has the potential with appreciable stability to replace Al:ZnO. New experiments will be conducted to examine the stability of single-layer i-ZnO and Al:ZnO, bilayer i-/Al:ZnO, and interconnect contact resistance of bilayer i-/Al:ZnO on Mo as a function of temperature and relative humidity in order to determine the activation energy of degradation. The protective effectiveness of moisture-blocking SiO_xN_y barrier coating deposited by PECVD process coupled with surface chemical treatment using PDMS silane [1] and DH-resistant SnO₂ on bi-layer i-/Al:ZnO will be also investigated.

ACKNOWLEDGEMENTS

We thank NCPV staff D. Albin for useful discussions, and S. Glick, Jie Zhou, and J. Pankow for preliminary work on barrier oxide coatings, some XRD measurements, and XPS analysis, respectively. This work was performed at the National Center for Photovoltaics under DOE contract number DE-AC36-99-GO10337 with the National Renewable Energy Laboratory.

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1. REPORT DATE (DD-MM-YYYY) May 2008		2. REPORT TYPE Conference Paper		3. DATES COVERED (From - To) 11-16 May 2008	
4. TITLE AND SUBTITLE Damp-Heat Induced Degradation of Transparent Conducting Oxides for Thin-Film Solar Cells: Preprint			5a. CONTRACT NUMBER DE-AC36-99-GO10337		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) J. Pern, R. Noufi, X. Li, C. DeHart, and B. To			5d. PROJECT NUMBER NREL/CP-520-42525		
			5e. TASK NUMBER PVB76701		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393				8. PERFORMING ORGANIZATION REPORT NUMBER NREL/CP-520-42525	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S) NREL	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER	
12. DISTRIBUTION AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT (Maximum 200 Words) The stability of intrinsic and Al-doped single- and bi-layer ZnO for thin-film CuInGaSe ₂ solar cells, along with Al-doped Zn _{1-x} Mg _x O alloy and Sn-doped In ₂ O ₃ (ITO) and F-doped SnO ₂ , was evaluated by direct exposure to damp heat (DH) at 85°C and 85% relative humidity. The results show that the DH-induced degradation rates followed the order of Al-doped ZnO and Zn _{1-x} Mg _x O >> ITO > F:SnO ₂ . The degradation rates of Al:ZnO were slower for films of higher thickness, higher substrate temperature in sputter-deposition, and with dry-out intervals. As inferred from the optical micro-imaging showing the initiation and propagation of degrading patterns and regions, the degradation behavior appears similar for all TCOs, despite the obvious difference in the degradation rate. A degradation mechanism is proposed to explain the temporal process involving thermal hydrolysis.					
15. SUBJECT TERMS CIGS; PV; transparent conducting oxide; damp- heat induced degradation; sputter deposition; thin film; optical micro-imaging; thermal hydrolysis;					
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