An Investigation of Stability Issues of ZnO and Mo on Glass Substrates for CIGS Solar Cells upon Accelerated Weathering and Damp Heat Exposures

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ABSTRACT

We conducted an exploratory study of the materials stability for the intrinsic/Al-doped ZnO bilayer and Mo sputtered on glass substrates used on NREL's high-efficiency $CuIn(Ga)Se_2$ (CIGS) solar cells. The ZnO and Mo samples were exposed in a weatherometer (WOM), damp-heat chamber, or oven with individually set conditions. Optical, electrical, structural, and imaging analyses were used to characterize the samples periodically before, during, and after the exposures. The present results show that the bilayer ZnO and Mo degraded faster in the damp heat at 85°C and 85% relative humidity (RH) than in the WOM at 60°C and 60% RH and 2.5 UV suns. Presence of acetic acid vapor in the 85°C and ~78% RH damp heat degraded the original conducting ZnO to insulating in 162 h. Severe corrosion of Mo on soda-lime glass under damp-heat condition resulted in blue-yellowish rust formations, pinholes, and extended microcracklines. Degradation of Mo exposed in the WOM was relatively mild and resulted in altered silver-gray products on the surfaces.

INTRODUCTION

Long-term performance reliability for the polycrystalline thin-film CIGS and CdTe PV modules is required for competing with crystalline Si-based PV to secure a wider market share. To achieve this end, reliable and stable materials and device structures, and appropriate encapsulation design, are needed. Therefore, we initiated an R&D activity that will study and address the stability issues of various constituent materials implemented in the CIGS devices. Another important objective for this work is the establishment of systematic experimental procedures and test designs that eventually will encompass all constituent materials, solar cell devices, and encapsulation schemes. We plan to identify the degradation mechanism, quantify degradation rates, seek chemical or physical mitigation methods, explore more stable new materials or device designs, and evaluate different encapsulation materials and schemes. All of these efforts will aim to enhance and achieve a highly reliable and durable performance of CIGS PV. This paper presents some of our initial results on the degradation of bilayer ZnO and Mo on glass substrates imposed by accelerated weathering and damp-heat (DH) exposures with and without acetic acid vapor. Preliminary investigation of a chemical method for mitigating ZnO degradation was also explored. Degradations of ZnO, Mo, and CIGS, especially with DH tests, were also reported previously by some groups [1-3].

EXPERIMENTAL

The bilayer ZnO composed of an intrinsic (~0.1 μm) layer and an 2% Al-doped (~0.1 μm) layer were sequentially deposited by magnetron sputtering on 5-cm x 5-cm x 0.5-mm 7059 glass plates as the "witness" along with CIGS solar cells. The Mo of bi-layer structure was also deposited by magnetron sputtering in two runs on 7.6-cm x 7.6-cm x 2.2-mm soda-lime glass (SLG) substrates. The square plates were cut into various sizes of specimens for exposure tests and convenience of measurements. Accelerated weathering was conducted in an Atlas Ci4000 WOM, with a water-cooled long Xe arc lamp and borosilicate inner and outer filters, operated at 2.5 UV suns (300-400 nm range), 60°C controlled chamber temperature, 60% RH, and 93°~103°C black panel temperature. DH exposure was conducted in a chamber operated at 85°C and 85% RH. Another DH exposure was done in an oven at 85° ± 3°C only for ZnO specimens placed in 250-mL wide-mouth glass jars with 5-mL saturated KCl using 17.3-MΩ deionized H_2O, which produced a ~78% RH, with or without 0.10 mL glacial acetic acid in a 5-mL vial. Whereas suitable, the ZnO and Mo specimens were characterized for transmittance, reflectance, resistivity, mobility, carrier concentration, X-ray diffraction, optical imaging, and scanning electron microscopy.

RESULTS AND DISCUSSION

1. Degradation of ZnO Bilayer on Glass

The initial ZnO bilayers showed an average transmittance of ~88% in the range of 400-1100 nm and a bandgap of 3.3–3.4 eV as derived from transmission spectra. In general, the ZnO bilayer samples showed changes in T% and R%, as seen in Fig. 1a for a DH-exposed sample, decrease of the (002) plane peak in XRD (not shown), and increase in sheet resistance (R_{sh}) measured by Hall and/or 4-probe method, as seen in Fig. 1b for three specimens from one ZnO bilayer sample exposed separately to the DH and in the WOM. The magnitude of R_{sh} increase varied on different samples. The specimens of a sample showed large changes from an initial 70-80 ohm/sq to 1680–2740 ohm/sq (not shown),

depending on the exposure length and whether the surface was treated briefly with a polydimethylsiloxane (PDMS) silane. The brief silane treatment offered certain protective effect for the ZnO in DH, as evidenced by the difference in R_{sh} = 1680 ohm/sq at 528 h vs. R_{sh} = 2160 and 2740 ohm/sq at 288 h without silane treatment. The DH-exposed ZnO also exhibited significant decreases in minority carrier mobility, but change in the bulk carrier concentration (N) was less apparent at 288 h; however, one of the five samples did show a large increase in the bulk N at 528 h (not shown). The effect of acetic acid was also investigated in a manner simulating the potential presence of acetic acid from EVA encapsulant for laminated PV modules tested in DH condition. The results were surprising and showed that the ZnO bilayer became white and insulating in as short as 162 h. The T%, R%, and XRD characteristics of the originally conducting ZnO were essentially totally lost, suggesting a likely transformation into $Zn(OH)_2$.

2. Degradation of Mo on SLG

The Mo on the SLG substrates degraded and corroded quickly and severely in DH with obvious rust formation, pinholes, increased sheet resistance, and substantially decreased (110) XRD peak height. The blue-yellowish appearance suggests the formation of MoO_3 and/or $Mo(OH)_3$ due to oxidation by the steam, which was soluble when rinsed with deionized H_2O. The SEM topographs in Fig. 2 illustrate the large structural and morphological changes with microcracks on a MoSLG sample after 288-h exposure in DH. Formation of silver-gray products was observed on the surfaces of MoSLG exposed in the WOM. The reflective gloss was also largely lost in both cases.

CONCLUSIONS

We have shown clear evidence of changes in the optical, electrical, and structural degradations of the intrinsic/Al-doped ZnO bilayer and Mo on glass substrates when exposed to damp heat without and with acetic acid and accelerated weathering. Details will be presented in a poster in the meeting. However, more systematic studies with thorough experiment designs close to actual device and module structures and encapsulation are required to better assess quantitatively the detrimental effects of the materials instability on the performance reliability of the CIGS solar cells.

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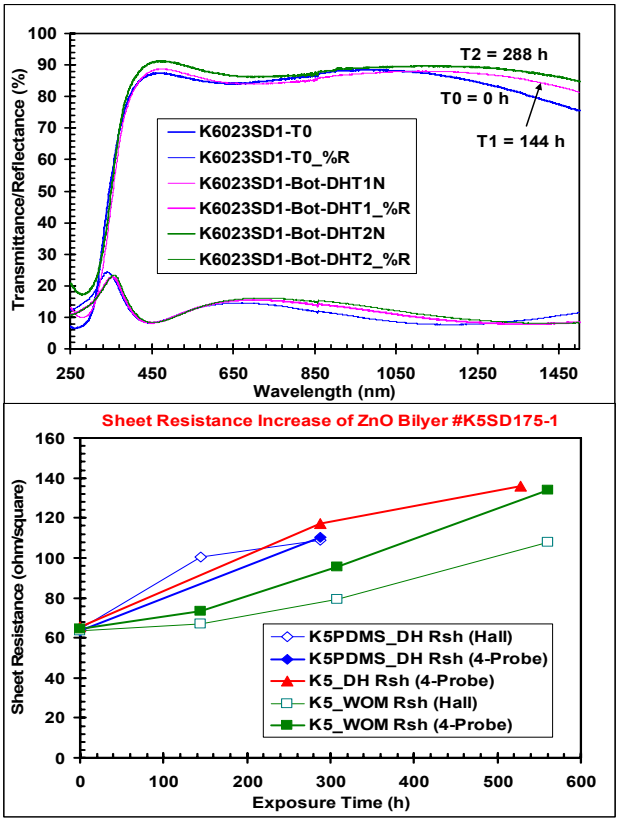

Fig. 1. (a) T% and R% spectral changes for a ZnO bilayer exposed in DH for 288 h. (b) Sheet resistance increase for specimens, with or without silane treatment, of ZnO bilayer samples exposed in DH and WOM.

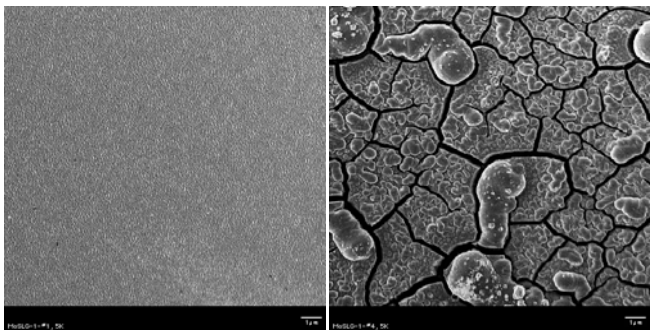

Fig. 2. SEM topographs at 5k X for a Mo-on-SLG sample before (left) and after (right) 288 h DH exposure. The white bar is 1 μm for both images.