WATER-MODULE INTERACTION STUDIES *

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ABSTRACT

This paper reports on mechanisms by which moisture enters photovoltaic modules and on techniques for reducing such interactions. Results from a study of the effectiveness of various module sealants are reported. Techniques of measuring the rate and quantity of moisture ingress are discussed. It is shown that scribe lines and porous frit bridging conductors provide preferential paths for moisture ingress and that moisture diffusion by surface/interfacial paths is a considerably more rapid process than by bulk paths, which implies that thin-film substrate and superstrate modules are much more vulnerable to moist environments than are bulk-encapsulated crystalline-silicon modules. Design approaches to reduce moisture entry are discussed.

INTRODUCTION

In this paper we report the findings of ongoing investigations of the interaction of moisture with photovoltaic (PV) devices, and thin-film amorphous-silicon (a-Si) modules in particular. Preliminary test data obtained from field-degraded glass/glass modules suggest a high moisture content level in the module interior. This is not unlike reported moisture problems within hermetically sealed micro-circuits [1,2]. The interior moisture may result from exterior moisture diffusing along material interfaces and through the encapsulation or, less likely, from the outgassing of water entrapped in the encapsulant during lamination. We consider the problem of moisture ingress and diffusion into a module and subsequent moisture interaction with module components. We conclude with a discussion of design strategies to minimize the effects of moisture on active thin-film PV elements.

MOISTURE INGRESS

Sealant Studies

For moisture to diffuse into the interior of a glass/glass module, it must first diffuse either through or under the edge sealant material. An ideal edge sealant material will have a very high bulk resistivity and will bond "water-tight" to the module and to the frame. Tests to determine the effectiveness of edge seals for the above application involve measurement of bulk and interfacial resistivities and of the propensity of moisture to permeate through or around the sealant.

Certain polyurethane caulking compounds have been considered as sealants for field module repair. The measured bulk resistivities are reported in Table 1, together with those of the familiar polymers polyvinyl butyral (PVB) and ethylene vinyl acetate (EVA) [3].

It would seem that none of the tested polyurethane compounds will be even as effective as PVB, regarded as a relatively poor performer, in providing moisture protection to module circuitry.

In another study of module sealants, Humidial cobaltous chloride relative humidity sensors were employed to give a semi-quantitative estimate of how much moisture actually reaches a volume sealed within a glass/glass sandwich, Fig. 1. Each sensor is a 9-square strip of blotter paper, each square being differently treated to respond (by turning color) to differing amounts of sorbed moisture. If the relative humidity is less than 10%, the entire strip is blue; if the relative humidity is 100%, the entire strip is pink. For intermediate relative humidities, the strip is correspondingly partially blue and partially pink.

Sensors in dried air were embedded in glass/glass coupons and edge-sealed with various sealant compounds (epoxies, butyls, and vinyl acetates). The 18 samples were exposed to an 85°C/100%RH environment for 300 hours. The indicated relative humidities were read at 0, 100, 233, and 300 hours; values determined at 100 and 300 hours are shown in Fig. 2. Only two epoxy sealants, those labelled "O" and "P", survived the test.

MOISTURE DIFFUSION

It is a general observation that thin-film glass/glass modules suffer moisture-induced corrosion in high humidity environments. Ostensibly,

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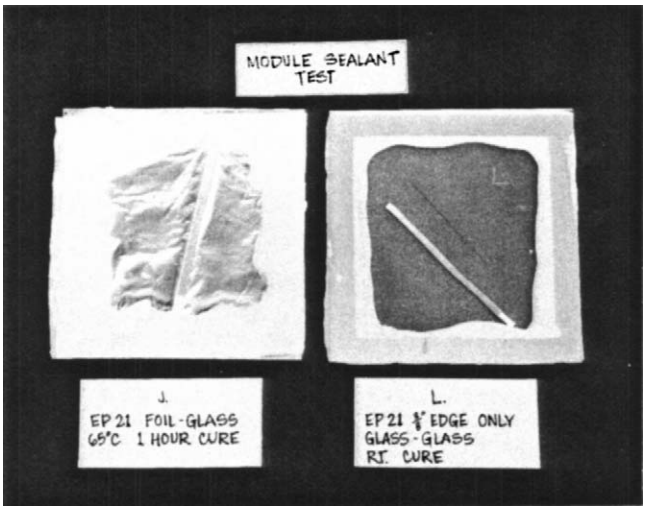

Fig. 1. Sealant Study Sample with Embedded Humidial Cobaltous Chloride Humidity Sensor

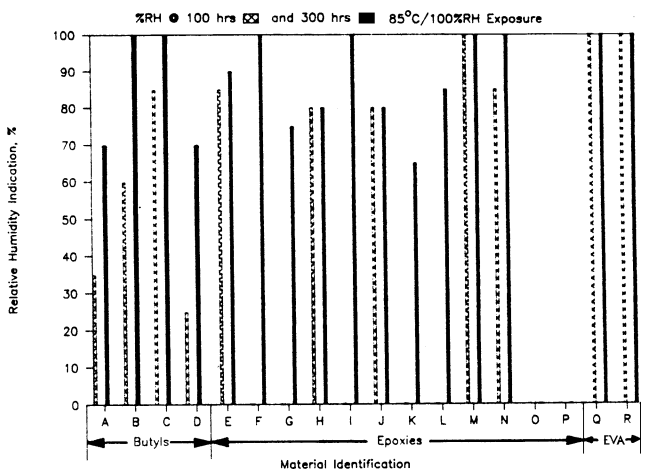

Fig. 2. Indicated RH-Values within the Interiors of Sealant Study Samples

the glass/EVA/glass sandwich should provide excellent humidity resistance. However, chamber and field testing have heretofore indicated otherwise.

In a module-level test to clarify the problem, a special a-Si glass/glass module was subjected to an 85°C/85%RH environment for 2000 hours. As graphically demonstrated in Fig. 3, moisture ingress results in substantial corrosion that slowly moves inward with the advancing moisture diffusion front. Obviously, the edge cells corrode more quickly and extensively than the center cells--they are exposed to a greater concentration of moisture for a longer period of time. Only the extreme ends of the center cells are exposed to excessive moisture concentrations.

In similar tests on two other glass/glass modules with leads attached to each cell, the resistance of

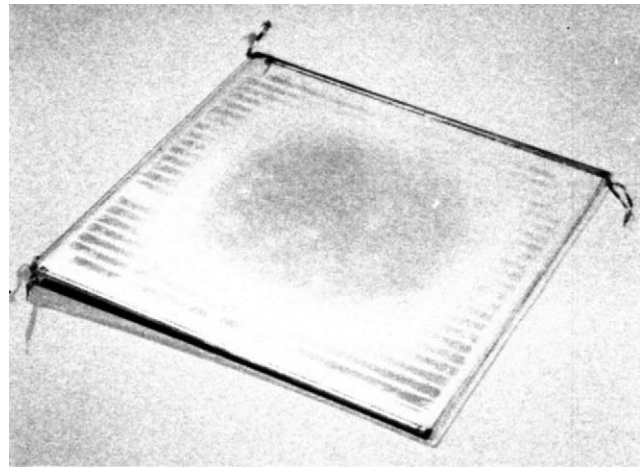

Fig. 3. Moisture Ingress, Module "Picture Framing"

each cell-to-cell interconnect was periodically measured. The data reveal that, after about 500 hours of 85°C/85%RH exposure, all the interconnect resistances increased by factors ranging from 3 to 7, the higher values generally being associated with the edge cells.

Moisture Diffusion in Glass/EVA/Glass Laminates.

Via what pathways does moisture enter PV modules? In crystalline-silicon (C-Si) modules, the cell string is completely surrounded by a polymer encapsulating matrix such as EVA; thus to reach and react with the cells, moisture must diffuse through the bulk of the encapsulant. In a-Si modules, the cells are monolithically deposited on a solid substrate, usually glass or stainless steel. Unless this cell-substrate lamina is completely surrounded by encapsulant prior to framing (which in present commercial module designs, for technical and economic considerations, it is not), there will be direct (surface and interfacial) paths from the environment to the cells.

Interfacial and Intercell Diffusion

Just as grain boundaries provide preferential paths for electromigration in conductor metallization [4], so it is expected that intercell zones--i.e., laser scribe lines through the transparent conductive oxide (TCO) and a-Si thin-film layers, porous frit bridging conductors (if any), and the aluminum metallization etch regions, and even unintentional scratches--may provide opportune pathways for entry of moisture into a-Si PV modules. To study the relative rates of moisture penetration via interfacial and intercell paths, two 15 cm x 15 cm laminated glass/EVA/glass samples were fabricated, each featuring two parallel vapor-deposited

aluminum stripes serving as an electrode system. The samples differed only in that one bore an edge-to-edge scratch running between and parallel to the electrodes (to model an intercell path). Thus by exposing both of these samples to the same humid (or liquid) environment and by monitoring sample current histories, we could observe differences in response of the two samples to the imposed environment and thereby make conclusions about the relative rates of moisture diffusion along interfacial and intercell paths. The samples were first exposed to an 85°C/85%RH environment for 175 hours and then their edges were dipped in 81°C water for an additional 100 hours. The data (monitored interelectrode current histories) for the two samples were similar--in both samples the current levels were approximately the same and increased by a factor of two during the 175-hr 85°C/85%RH exposure. After partial submersion in 81°C water, a greater (but not significant) divergence in current level was noted between the samples, with the scratched sample exhibiting the higher current levels. All-in-all, however, the results suggest that there may be little difference in moisture ingress rates between interfacial and intercell pathways.

Another means by which moisture may enter a module is by "wicking" up the porous bridging conductor, usually a paste or ink consisting of particles of silver and glass frit, together with a binding agent, which some manufacturers use to provide more intimate contact between the front TCO layer and the back thin-film aluminum metallization layer of adjacent a-Si cells. Water entering the module edge soon contacts the bridging conductor material; it is hypothesized that the porous nature of the conductor allows moisture to wick along it (toward the center of the module) via capillary action.

To test this hypothesis non-encapsulated manufacturer-supplied glass/TCO coupons with silver frit stripes were partially submerged for up to 20 hours in an organic dye penetrant (ARDROX BIO PEN P6F4), a material that fluoresces when irradiated with UV. Fluorescent analysis indicated that, for the unencapsulated specimens, the penetrant entered and wicked up the porous silver frit material to a level well above that of the dye in the beaker, Fig. 4. Thus it has been established that moisture which opportunely comes into contact with the silver frit near or at the module edge will, presumably by capillary action, "wick up" the silver frit stitch lines to the module interior.

A similar experiment on PVB-encapsulated coupons of the same type gave inconclusive results--penetrant entered and diffused upward (away from the dye surface) within the polymer and also at the polymer/substrate interface and along the stitch lines, but the optical scatter was too great to clearly differentiate effects.

Interfacial vs Bulk Paths

Does moisture enter and diffuse into modules more readily via interfacial and intercell pathways, or via pathways through the encapsulant bulk? We have attempted to directly measure the interface and

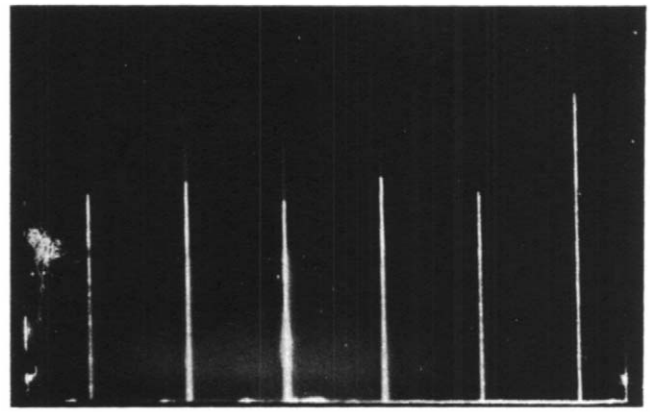

Fig. 4. Dye Penetrant Wicking Up Silver/Frit Bridging Conductor

bulk moisture diffusion rates for glass/EVA/glass and glass/EVA laminates, respectively.

Problems such as moisture entry along lead wires, difficulties associated with the fabrication and use of samples featuring vapor deposited electrode systems, and the semi-quantitative nature of the data obtained from the use of humidity sensors, have lead us to consider the use of an embedded micro-capacitor to monitor moisture content within an encapsulated coupon exposed to a humid environment. A Panametrics Mini-Mod-HT moisture sensor was mounted on a glass substrate, Fig. 5.

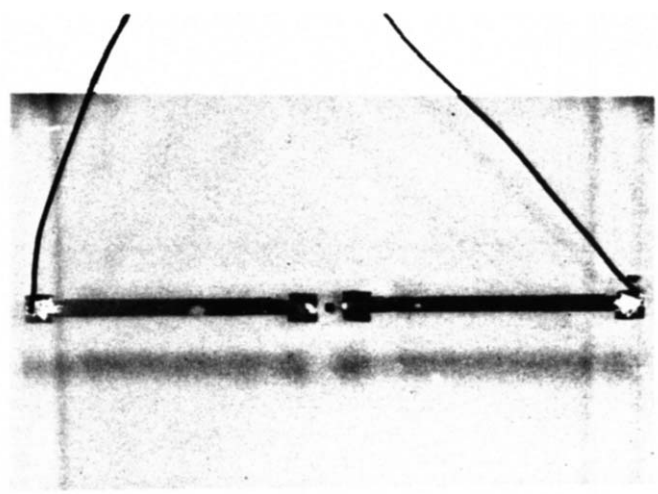

Fig. 5. Panametrics Micro-Capacitor Chip for Measuring Moisture Content.

Aluminum lead wires 0.0025-cm in diameter electrically joined the sensor to aluminum stripes vapor deposited on the substrate. Leads from these to a GenRad 1658 RLC Digibridge allowed measurement of the chip capacitance, which strongly varies with the moisture content in the chip, a specially

designed Au/Al_2O_3 capacitor. The device was then calibrated at several equilibrium T/RH set points varying from 22°C to 90°C and from 0%RH to 100%RH, yielding an equation relating moisture content (PPM_V) to measured capacitance (nF):

$$PPM_V = 24547.1 * C^{1.08}$$

The quantity PPMV was determined as follows:

$$PPM_V = 10^6 * \left(\frac{PPM_W}{621546.9 + PPM_W} \right)$$

$$PPM_W = 10^6 * W$$

$$W = 0.6215496 * \left(\frac{p}{p_A - p} \right)$$

$$p = p^W_{SAT} - \frac{(p_A - p^W_{SAT}) * (T_D - T_W)}{1546 - 1.44 * T_W}$$

$$p^W_{SAT} = 8.75 \times 10^7 * \exp\left(- \frac{10400}{R(T_W + 273.16)} \right)$$

$$p^D_{SAT} = 8.75 \times 10^7 * \exp\left(- \frac{10400}{R(T_D + 273.16)} \right)$$

$$RH = 100 * \frac{p}{p^D_{SAT}}$$

where

RH = relative humidity, %

T_D, T_W = dry, wet bulb temperatures, respectively, °C

p = water vapor pressure, cm Hg

p^D_{SAT} = saturated vapor pressure at T_D, cm Hg

p^W_{SAT} = saturated vapor pressure at T_W, cm Hg

p_A = atmospheric pressure, cm Hg

W = absolute humidity

PPM_W, PPM_V = parts per million by weight and by volume, respectively

Measurement of Diffusion

Sensors mounted on glass substrates and calibrated as discussed above, were then vacuum laminated to form glass/EVA laminate for bulk diffusion measurements, and glass/EVA/glass laminae for interfacial diffusion measurements. One of the latter was placed in a 65°C/88%RH environment for almost 2000 hours. The centrally located moisture sensor recorded that after almost 2000 hours of exposure only about 60% of the final equilibrium moisture content has been achieved. The edgewise moisture ingress and subsequent interfacial diffusion of moisture is a slow process.

But how slow? Regarding the moisture ingress as a Fickian diffusion process, both rectangular and cylindrical models indicate that the measured data fall on the analytical curve corresponding to a diffusion coefficient of $D = 2.4 \times 10^{-6}$ cm^2/sec, Fig. 6. The bulk diffusion of moisture in EVA is

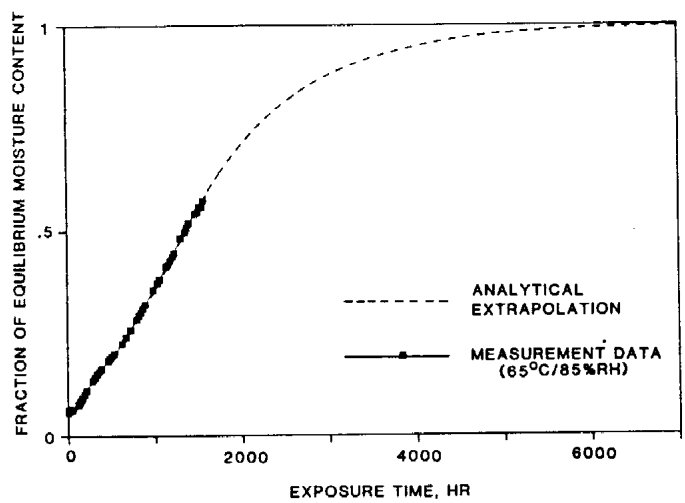

Fig. 6. Interfacial Diffusion of Moisture in Glass/EVA Laminates

$D = 1.5 \times 10^{-8}$ cm^2/sec [5]. This implies that, although slow, ingress and diffusion of moisture along a glass/EVA interface occurs 100 times more rapidly than diffusion of moisture through the bulk of EVA.

MOISTURE DAMAGE - DISCUSSION

We have observed two fundamental types of moisture damage in thin-film PV modules--material delaminations and electrochemical corrosion.

Material Delamination

Water molecules, being polar in nature, are generally quite effective in breaking interfacial material bonds via electrostatic forces. Means of reducing moisture-induced delaminations include (1) reducing the number of water molecules that reach material interfaces, and (2) neutralizing the effect of water molecules that do reach the interfaces. Drying and hermetic sealing is the state-of-the-art technique for minimizing moisture,

although the technique is not completely effective [1,2] and is very costly. Complete encapsulation of the PV elements will provide only bulk paths, thus reducing the rate of moisture ingress to the active PV elements. But encapsulation, complete or otherwise, is only partially effective--it will retard the rate of moisture ingress and reduce the number of water molecules that reach an interface, but it will not prevent eventual moisture-induced delamination.

The effect of moisture at material interfaces may perhaps be reduced by infusing the bulk of the mating materials with water-sorbing compounds in an effort to bar access of moisture to the interface or by developing new materials whose interfacial binding energies exceed that of their bonding with moisture.

Electrochemical Corrosion

Electrochemical corrosion requires an aqueous electrolyte to support ionic current between anodic and cathodic sites. It is characterized by the formation of reaction product, differing from the original interfacial materials, that can open- or short-circuit a module or cause delamination. This topic is covered extensively in a companion paper in this journal [6]; an example from that paper will suffice to illustrate the concepts presented here.

Moisture attacks the bonds between glass and TCO in anodic glass/TCO submodule components, an example of moisture-induced material delamination, but as cathodes, the moisture attacks the TCO (SnO_2) surface, producing various chemical compounds that undermine PV action, an example of electrochemical corrosion.

CONCLUDING REMARKS

What in general can be done to minimize moisture damage in a-Si and thin film PV modules? An expensive but technically sound option is to hermetically seal the modules. A less expensive, and correspondingly less effective, alternative is to employ various encapsulation strategies with effective edge seals. Novel concepts may include the use of effective interfacial bonding agents, moisture-sorbing fillers, a sacrificial electrode surrounding the active thin-film PV elements, or even a "dead space" around the edge of the active PV elements.

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TABLE 1

BULK RESISTIVITY OF MODULE SEALANTS

(ohm-cm @ 20 volts, 22°C/50%RH)

Material	Bulk Resistivity, ohm-cm
Sikaflex 240	$3.0 - 9.0 \times 10^{10}$
Dynatrol 1	1.6×10^{10}
PRC Caulk	$3.0 - 5.0 \times 10^{9}$
PVB	$4.0 \times 10^{10} - 1.0 \times 10^{11}$
EVA	3.0×10^{13}