CORROSION OF a-SI CELLS AND MODULES*

G.R. Mon**
L. Wen**
R.G. Ross, Jr.***

JPL, Pasadena, CA

ABSTRACT

This paper reports on corrosion/erosion phonemena observed in exposing a-Si cells, modules, and specially designed test structures to natural and accelerated test environments. Relevant cell and module I-V curve data, monitoring degradation, are presented. The causes of observed degradations, methods of mitigation, and consequences for fielded modules are discussed.

BACKGROUND

In a previous paper (1) two of the current authors presented data and observations on the degradations experienced by a-Si cells and modules upon exposure to various steady temperature/humidity environments. In summary, it was observed that unencapsulated modules exposed to an 85°C/100-%RH environment developed pinholes that enlarged with time of exposure. In the intercell zone (Region A-A in Fig.1) of the a-Si module, the pinholes tend to aggregate and interfuse, particularly along the a-Si layer laser scribe line boundaries (Regions D-E and D-C, Fig. 1) along which the thin-film layers are highly directionally stressed, to form a metallization-free line tending to open-circuit the module. The SEM micrographs in Fig. 2 quite emphatically depict this form of intercell corrosion. Another observed form of degradation is filiform corrosion, the loss of back surface (aluminum) metallization in worm-like patterns. Both of the above phenomena are manifestations of stress corrosion cracking in the thin-film module layers.

Energy dispersive X-ray analysis of modules exposed for long periods of time to an 85°C/100%RH environment confirmed the loss of aluminum along the a-Si laser scribe boundaries.

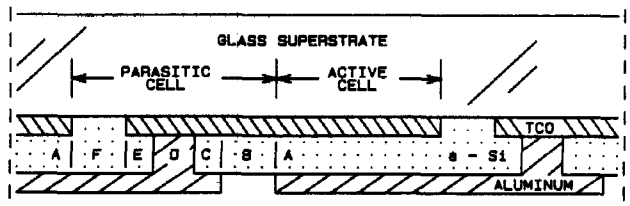

Fig. 1. Schematic of a-Si Module Intercell Zone.

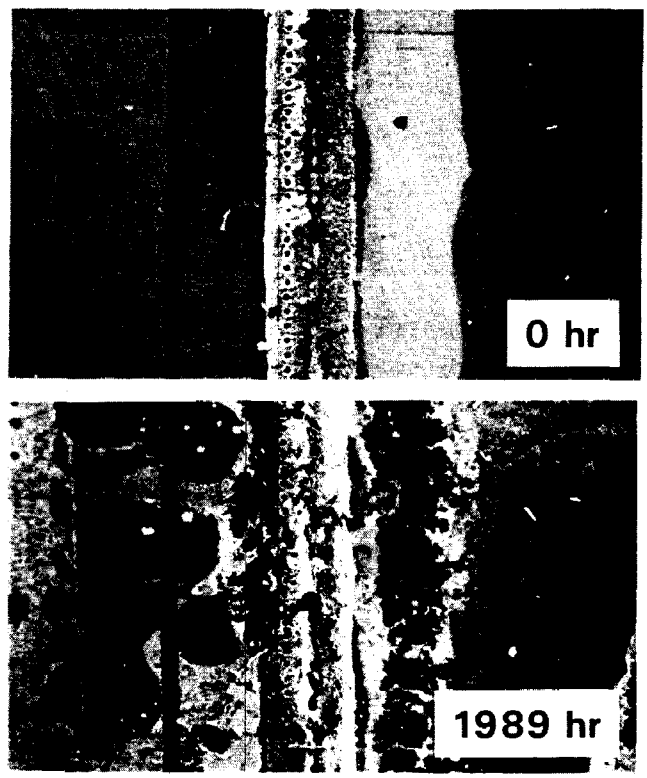

Fig. 2. SEM Micrographs of Intercell Zone -- Bare Module Exposure to 85°C/100%RH.

---

* This paper presents the results of one phase of research conducted at the Jet Propulsion Laboratory, California Institute of Technology, for the U.S. Department of Energy, through an agreement with the National Aeronautics and Space Administration.

** Member of the Technical Staff, Photovoltaic Engineering Group, System Integration Section.

*** Supervisor, Photovoltaic Engineering Group, System Integration Section.

Proceedings of the 19th IEEE Photovoltaic Specialists Conference
New Orleans, Louisiana, May 4-8, 1987

In Figs. 3 and 4 are presented additional data collected during these tests. Note in Fig. 3 how the dark I-V curves "fan out", exhibiting ever increasing series resistance. Figs. 4 and 5 exhibit the effects of exposure on series resistance and on power output for two modules of different manufacture. The module of Mfgr. A featured a polymeric substrate design and exhibited little post-test degradation. The module of Mfgr. B featured a polymer/glass substrate design. It exhibited "picture framing", i.e., fogging of the metallization around the module edges, where moisture enters and slowly diffuses inward, Fig. 6. The module design differences are crucial to the observation--moisture penetrated both modules, to be sure, but the aluminum metallization of Module A was thicker and purer, hence more corrosion resistant, than that of Module B.

This paper will describe the results of additional tests to determine the nature of moisture/module interaction, will confront the many questions raised by these studies, and will attempt to provide an integrated explanation of results to date, together with consequences for fielded modules and suggestions for design and performance improvement.

DESIGN CONSIDERATIONS

Just what are the moisture-induced degradation processes in a-Si modules that the design engineer must address? Laboratory evidence, based upon unencapsulated modules exposed to humid 85°C environments, suggests that it is intercell corrosion/erosion of aluminum metallization along the a-Si scribe line boundaries in the intercell region, as previously described, involving the erosive processes of pinhole formation and coalescence by stress corrosion cracking, and the corrosive processes of aluminum oxide and hydroxide formation. However, observations on encapsulated modules suggest other possibilities. Encapsulated modules were observed to suffer a much reduced metallization corrosion/erosion process that occurred more uniformly thoughout both the active and intercell regions of the module. Some modules in the field exhibited severe degradation of the active cell region but very little degradation of

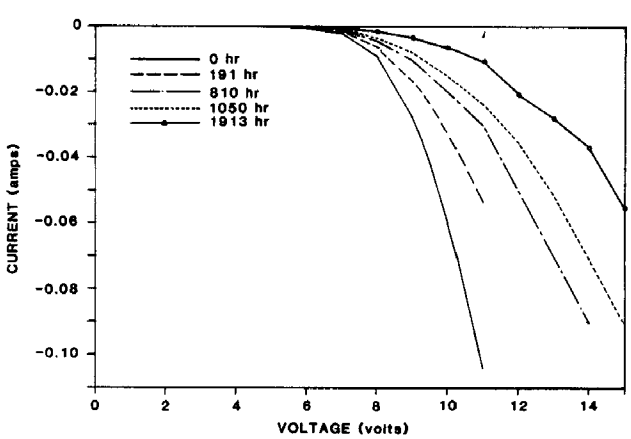

Fig. 3. Dark I-V Curves of 4"x4" a-Si Modules.

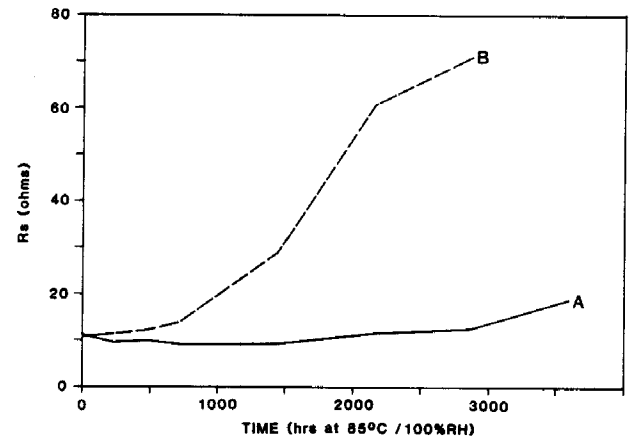

Fig. 4. Series Resistance vs. 85°C/100%RH Exposure Time for Two 1'x1' a-Si Modules of Different Manufacture.

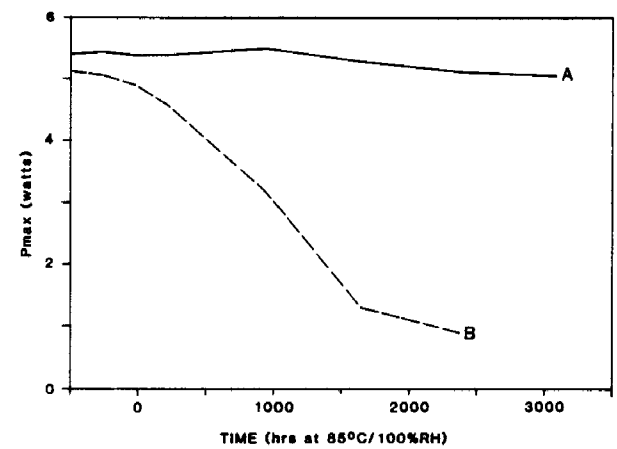

Fig. 5. Maximum Power Output vs. 85°C/100%RH Exposure Time for Two 1'x1' a-Si Modules of Different Manufacture.

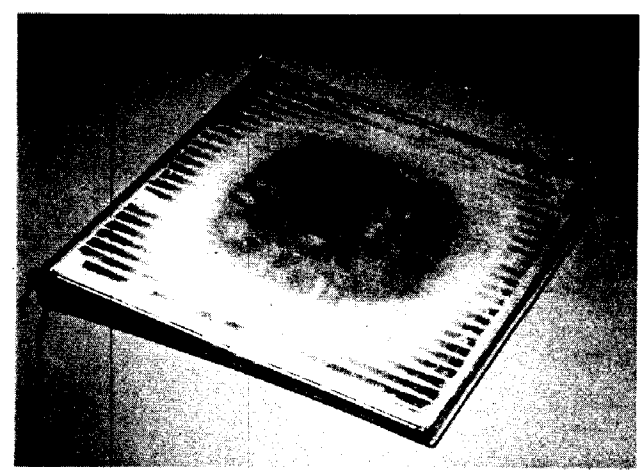

Fig. 6. "Picture Framing" of Glass Superstrate a-Si Module Resulting from Moisture Ingress.

the intercell zone. The glass substrate module shown in Fig. 6 suffered degradation due to moisture creeping inwardly from its edges--in both regions, but apparently more severely in the active cell region than in the intercell zone.

The two basic design strategies for inhibiting moisture-induced degradation of a-Si modules are to use corrosion-resistant metallization and moisture-resistant encapsulation.

Metallization.

Concerning metallization, experimental evidence suggests that purer and thicker aluminum metallization layers quite effectively retard corrosion. Sputtered metallization adheres better than vapor deposited metallization and may afford greater corrosion protection, but at significantly greater cost. Laser scribing is to be preferred to mechanical scribing, and masking is preferable to metallization etching.

The actual details of aluminum metallization corrosion involves the formation of aluminum oxides (Al_2O_3) and hydroxides ($AlO(OH)$). Aluminum dissociates anodically to form mono- and tri-valent aluminum ions, but the former react with water to form tri-valent aluminum ions and hydrogen gas. The process involves multiple reactions but can be summarized in two all-inclusive reactions. In the presence of oxygen:

$$6Al + 3H_2O + 4O_2 \rightarrow 4AlOOH + Al_2O_3 + H_2,$$

and in the absence of oxygen:

$$4Al + 7H_2O \rightarrow 2AlOOH + Al_2O_3 + 6H_2.$$

The evolution of hydrogen gas may be a source of bubble formation and material delamination in the fielded module.

Additional factors relating to aluminum metallization corrosion include the facts (2) that aluminum corrodes rapidly for pH < 4.5 and pH > 7 and that the Cu-Al and Cu-Ag couples are very galvanically active. Regarding the former fact, at temperatures below 25°C, the pH of water is greater than 7 and aluminum/moisture corrosion reaction rates accelerate. Regarding the latter fact, it is bad practice to couple copper (or silver) lead wire to aluminum metallization or interconnect strips anywhere within the module to where moisture is likely to penetrate.

Encapsulation.

Moisture accelerates corrosion; thus to reduce performance degradation of a-Si modules, moisture interaction with module materials must be retarded or eliminated. One approach to electronic packaging is hermetic sealing, which significantly retards the moisture ingress leakage rate and thus delays the onset of corrosion. A less expensive technique employs polymeric encapsulations. Although moisture penetrates most polymers in a short time, these materials generally have very low water sorption capacity and provide an environment with low ionic conductivity. They are weak electrolytes; hence through their use, an otherwise active electrochemical environment can be considerably passivated.

There are two basic encapsulation schemes: (1) a polymer substrate; and (2) a polymer/glass substrate addition to the monolithically fabricated a-Si module. Which design will best inhibit moisture-induced degradation? The answer is not yet conclusive.

Polymer Substrate.

In polymer-encapsulated modules, one function of the polymer is to hamper the transport of moisture to the metallization surface and to inactivate metallization surface adsorption sites (3). Nevertheless, moisture can more freely enter and exit such modules, there being much greater encapsulant surface area in contact with the ambient. Their greater interplay with moisture makes them more susceptible to corrosion phenomena but less susceptible to hydro-thermo-mechanical degradation than glass substrate modules. Encapsulant thickness may be a critical design parameter.

Polymer/glass Substrate.

In a glass substrate module, moisture that enters via interfacial paths originating at the module edge, slowly diffuses toward the center of the module. An effective design strategy, albeit somewhat compromising efficiency, may be to provide a cell-free zone around the module periphery and an effective edge sealant. Moisture that enters such a module usually cannot exit; this moisture buildup within the module can have adverse consequences for performance--chemical, leading to corrosion, and thermo-mechanical, resulting in delaminations.

MOISTURE INGRESS

The several corrosion and moisture/module interaction experiments performed to date raise many questions about these subjects--perhaps more than they answer. Not the least among these is: How does moisture enter an a-Si module? A key entry point is the lead-wire/module interface. Evidence suggests that, in addition, material interfaces and scribe lines provide opportune paths for moisture ingress and diffusion to the module interior. It appears (Fig. 6) that moisture diffusion along organosilane-primed glass/polymer interfaces is a relatively slow process, and that diffusion through the polymer bulk is even slower.

The glass substrate module shown in Fig. 6 suffered degradation due to moisture creeping inwardly from its edges--in both regions, but apparently more severely in the active cell region than in the intercell zone.

A series of experiments were performed to determine the nature of the moisture/module interaction mechanism. In all of these, glass/polymer or glass/polymer/glass test structures featuring different types of moisture sensors embedded in the polymer surface, or bulk, or at the polymer-glass interface, were exposed to humid environments and the rate or quantity or physical distribution of sorbed moisture was monitored. When the sensors used were ionic current detectors, rapid increases in measured currents in response to isothermal humidity increases were observed; this

observation was ultimately attributed to moisture entering via the lead wires. When the sensors were wireless chemical indicators, there was no evidence for rapid ingress of moisture. Moisture does enter, however, at cracks in the glass or along the edges of the module (Fig. 6) and proceeds to diffuse slowly along the primed interfacial paths.

DISCUSSION

Tests at 85°C/85%RH and 85°C/100%RH on encapsulated and unencapsulated fully aluminized back surface modules revealed that encapsulation effectively retards gross metallization loss in the active cell region (1). When the metallization is highly corrosion resistant, however, the addition of encapsulation does not seem to retard the rate of increase of measured sheet resistivity over that observed for unencapsulated specimens: see Figs. 7 and 8, Reference (1).

In two recent papers Ross (4,5) presented I-V curve results of aging modules in dark temperature/humidity environments and in accelerated and real-time outdoor environments. The results of dark oven aging, Fig. 7, in dry and moist environments demonstrate the important influence of moisture upon series resistance, a parameter generally regarded as being allied to corrosive degradation. A comparison of the responses of unbiased and forward biased modules demonstrates the light induced (Staebler-Wronski) effect--an immediate but modest short-circuit current loss, approaching a stable asymptote, accompanied by a shunt-like loss in fill factor (6).

The results of accelerated outdoor testing indicate that modules uniformly heated to 100°C degraded more severely, perhaps as expected, than modules uniformly heated to 85°C. These modules exhibited both series-like and shunt-like losses in fill factor. In general, modules exposed to the natural environment exhibited greater degradation than modules exposed to uniform temperature/humidity environments. The postulation is that the outdoor environment is considerably more severe, involving actual liquid water contact (dew, rain, snow) and stress-inducing temperature/humidity cycles. The moisture sorption and diffusion dynamics are such that moisture concentration within the module tends to increase over long periods of outdoor exposure--modules tend to retain sorbed moisture.

Water/module interaction physics are discussed in some detail in a companion paper in this journal (7). In it are presented material sorption and ionic conductivity data of PV module polymers and glass/polymer composites, and data comparing ionic leakage currents in laboratory and outdoor environments.

CONCLUDING REMARKS

Ongoing reseach is focussed upon continuing the study of the deleterious effects of moisture on a-Si modules. The aim is to optimize a-Si module design. The procedure is to assess the performance

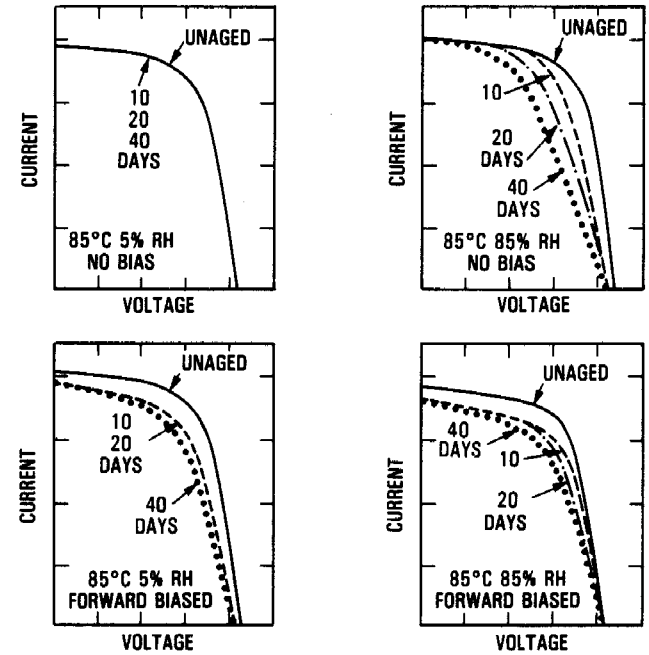

Fig. 7. Results of Dark Oven Aging of Modules in 85°C/85%RH.

of various module design types by measuring their degradation rates in a "standard" moist environment. Techniques for reducing moisture entry into substrate modules, such as edge sealing, and of mitigating the effects of moisture, such as by means of cell-free perimeters or sacrificial electrodes, are being tested.

In light of the extreme sensitivity of a-Si modules to interaction with moisture, however, it may ultimately prove more cost effective to develop a truly water-tight module than to attempt to mitigate the effects of moisture in water-interactive modules.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Senior Engineering Assistants Elizabeth Jetter and John Meyer, and technicians Scott Leland and Otto Witte for their services in the evolution of this investigation.

REFERENCES

1. G.R. Mon, R.G. Ross, Jr., "Amorphous-Silicon Module Intercell Corrosion", Proceedings of the American Institute of Physics Conference on Stability of Amorphous Silicon Alloy Materials and Devices, Palo Alto, Jan. 1987.

2. H.H. Uhlig, Corrosion and Corrosion Control (Wiley, New York, 1963).

3. H. Koelmans, "Metallization Corrosion in Silicon Devices by Moisture-Induced Electrolysis", IEEE 12th Annual Proceedings on Reliability Physics, pp. 168-171, 1974.

4. R.G. Ross, Jr., "Long-term Stability of Amorphous-Silicon Modules", in FSA Progress Report 26 and Proceedings of the 26th PIM, JPL Publication 86-23, pp. 497-503, 1986.

5. R.G. Ross, Jr., R.S. Sugimura, "Long-term Experimental Testing of a-Silicon Modules", Proceedings of the American Institute of Physics Conference on Stability of Amorphous Silicon Alloy Materials and Devices, Palo Alto, CA, January 1987.

6. D.L. Staebler, C.R. Wronski, Applied Physics Letters, v. 31, p. 292, 1977.

7. G.R. Mon, L.Wen, R.G. Ross, Jr., "Encapsulant Free-Surfaces and Interfaces: Critical Parameters in Controlling Cell Corrosion", this journal.