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ADHESION and THIN-FILM MODULE RELIABILITY*

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ABSTRACT

Among the infrequently measured but essential properties for thin-film (T-F) module reliability are the interlayer adhesion and cohesion within a layer. These can be cell contact layers to glass, contact layers to the semiconductor, encapsulant to cell, glass, or backsheet, etc. We use an Instron mechanical testing unit to measure peel strengths at 90° or 180° and, in some cases, a scratch and tape pull test to evaluate inter-cell layer adhesion strengths.

We present peel strength data for test specimens laminated from the three T-F technologies, before and after damp heat, and in one instance at elevated temperatures. On laminated T-F cell samples, failure can occur uniformly at any one of the many interfaces, or non-uniformly across the peel area at more than one interface. Some peel strengths are $\ll 1$ N/mm. This is far below the normal ethylene vinyl acetate/glass interface values of >10 N/mm. We measure a wide range of adhesion strengths and suggest that adhesion measured under higher temperature and relative humidity conditions is more relevant for module reliability.

INTRODUCTION

Interlayer adhesion and cohesion within a layer can be a problem for thin-film (T-F) module reliability. To avoid delamination we must understand the many materials and interfaces that comprise a T-F module and how they respond to environmental stresses. A few years ago SnO₂-to-glass delamination caused significant problems; A recurring problem is the "bubble" type of delamination found in some double-glass-laminated T-F modules, both shown in Fig. 1 [1]. The SnO₂ delamination failures are caused by multiple stress factors that involve water vapor and ionic currents flowing through the soda-lime glass or on its surface. A solution was found, and screening tests were developed for SnO₂-coated glass [2,3]. The "bubble" type of delamination is caused by a reduction of the ethylene vinyl acetate's (EVA) viscosity and adhesion at higher field temperatures along with tensile stress due to glass warpage. Encapsulant to backsheets or cell layers, backsheets, scribeline vias, layers within the cell, etc. are all subject to delamination failure.

Sometimes solutions rely on reducing the internal stress in the T-F layer, for example, Mo on glass used for CIGS module construction [4]. As another example, we

found that for an oxide barrier coating on polyethylene terephthalate (PET) to survive lamination without cracking, the internal stress in the coating must be below 5×10^9 Ncm⁻² [5].

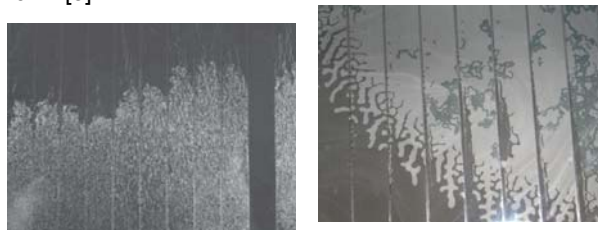


Fig. 1. "Bar-graph" delamination of SnO₂/a-Si cells, left; "bubble" delamination, right[1]

More recently, we have measured and tried to optimize the interfacial adhesion between soda-lime glass substrates and the most commonly used encapsulant material, EVA. Although initial adhesion values were important, we were looking for maximum adhesion after damp heat at 85°C/85% relative humidity (RH) exposure based on earlier work at the Jet Propulsion Laboratory [6]. At NREL, a similar effort to optimize the wet resistant strength of the interface between EVA and a smooth glass interface has recently been completed [7]. Specialized Technology Resources (STR) has reported on a recently developed EVA-based encapsulant to bond to Si cells that doesn't degrade with damp heat [8]. Adhesion to glass surfaces that have been mechanically abraded, for the purpose of electrical isolation, is extremely important to achieve high module reliability. In one study we found loss in adhesion after damp heat to be greater for mechanically abraded surfaces than for smooth glass [9].

One of the strategies for obtaining good adhesion to polymer surfaces as well as to back metal contacts is to deposit oxide barrier coatings before lamination. These polymers can be metal-impregnated back metal contacts, screen-printed grid-line contacts, back sheet materials such as PET, or possibly transparent front sheets of Tefzel. Barrier layers on PET can greatly reduce water vapor transmission and increase adhesion to EVA; peel strength values that were < 1 N/mm before coating increased to >10 N/mm after coating [4]. We use this oxide coating to facilitate our testing of one T-F cell interface. Oxide coatings can also enable us to produce a more durable module package.

Peel strengths depend on the length of the ambient dry-out period after removal from the 85° C/85%

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RH exposure. Because hydrolysis weakens interfacial Si-O bonds [6], peel strength values measured immediately after removal from damp heat can be half as great as values after a 3-h dry out. Values measured after several days can show complete healing of a coating/PET interface to the pre-damp-heat condition. Increasing the temperature during peel significantly reduces adhesion. We suggest that adhesion measured under higher temperature and RH conditions is more relevant for module reliability.

PEEL TESTS

Table 1. Peel strengths for many sample types and interfaces.

Device: Source	Failure Interface	Weathering		Peel Strength (N/mm)
		Time	Type	
a-Si: A	EVA / a-Si	0	none	3.8
	EVA / a-Si	92 h	85/85	3.1
SiO _x N _y / Ni paste/ Graphite/ CdTe: B	EVA / SiO _x N _y	0	none	5.6
	SiO _x N _y / Ni paste	256 h	85/85	4.5
SiO _x N _y / CdTe: B	EVA / SiO _x N _y	0	none	7.0
	SiO _x N _y / CdTe	0	none	2.0
	SiO _x N _y / CdTe	256 h	85/85	0.3
SiO _x N _y / CdTe: C	EVA / SiO _x N _y	0	none	6.4
	EVA / SiO _x N _y	256	85/85	4.9
CdTe: C	EVA / Metal-CdTe	0	none	1.1
	EVA / Metal-CdTe	256	85/85	0.6
CdTe: C (left) (middle) (right)	EVA / Metal-CdTe	0	none	1.0
	EVA / Metal-CdTe	0	none	0.7
	Metal / CdTe	0	none	0.06
CIGS:D1	CIGS / Mo	0	none	0.05
CIGS:D2 60°C 80°C	EVA / CIGS	0	none	7.0
	EVA / CIGS	0	none	1.1
	EVA cohesive	0	none	0.05
CIGS: E	EVA / CIGS	0	none	0.9
CIGS	CIGS / Mo	0	none	0.3
CIGS	EVA / CIGS	258 h	85/85	0.6
CIGS	Tefzel / EVA	258 h	85/85	0.02
CIGS	Stainless / EVA	258 h	85/85	0.5
CIGS	EVA / CIGS	7 mo	Cocoa, FL	0.8
CIGS	EVA / CIGS	16 mo	Golden, CO	0.9
CIGS	Stainless / EVA	16 mo	Golden, CO	0.8
		16 mo	Golden, CO	0.8
TPE/EVA/ Glass: F control	EVA / Glass	0	none	5.5
	EVA / Glass	16 h	85/85	3.8
TPE/EVA/ Glass: F exposed	EVA / Glass	7 yr equal	UV lamp	2.0
	EVA / Glass	+ 16 h	85/85	1.5
	EVA / Glass	0	none	3.2
Tedlar/EVA / Glass: G control	EVA / Glass	17 h	85/85	1.8
	EVA / Glass	7 yr equal	UV lamp	0.4
Tedlar/EVA / Glass: G exposed	EVA / Glass	+ 17 h	85/85	0.4
Scotch Tape/Glass	Tape / Glass	0	none	0.08
ASTM Tape/Glass	Tape / Glass	0	none	0.4

Table 1 shows peel strength adhesion values measured for a number of T-F module types from different sources (A thru E) and, for reference purposes, on other types of Si modules/samples (F, G, and 2-tape pulls), with and without 85° C/85% RH damp heat weathering. An example of such a T-F peel sample (CdTe:B) is shown in Fig. 2. The corresponding peel data from the right hand peel tab are shown in Fig. 3. The pull rate was 10 mm/min with data taken before and after 256 h of damp heat.

Tedlar/PET/EVA back sheet material from Madico is laminated to the module or mini-module with one sheet of STR's 15295 P-UF EVA. Typically, 25 mm-wide peel tab strips are defined with a razor blade and, in this case, mounted in the Instron for a 90° pull. Samples from B had low adhesion of the EVA to the back contact Ni-paste (< 1 N/mm), so we deposited a SiO_xN_y film to increase the EVA/SiO_xN_y/Ni-paste interface strength. Because this is still the weakest interface, now failing at 5.6 N/mm, we can say that all of the other cell adhesive and cohesive strengths are greater than 5.6 N/mm.

The Ni-paste contact area is shown on the right hand side of Fig. 2. After damp heat, the failure interface moves from the EVA/SiO_xN_y to the SiO_xN_y/Ni-paste with only small bits of the cell cracking from the SnO₂. On the left side of Fig. 2, the cell always remains in contact with the SnO₂: the dark areas are where the barrier coating remains on the CdTe, and the grey areas are where the coating comes off with the EVA.

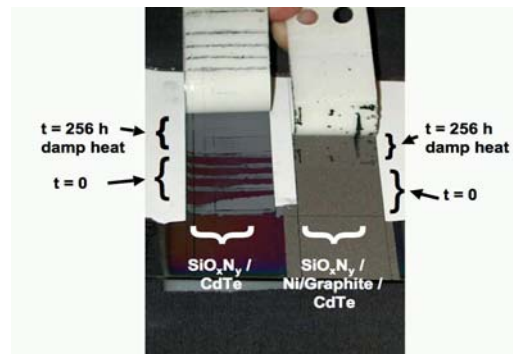


Fig. 2. Oxide-coated CdTe:B superstrate cell after 90°-peel testing. Left, without a back contact; right, with a graphite/Ni paste back contact.

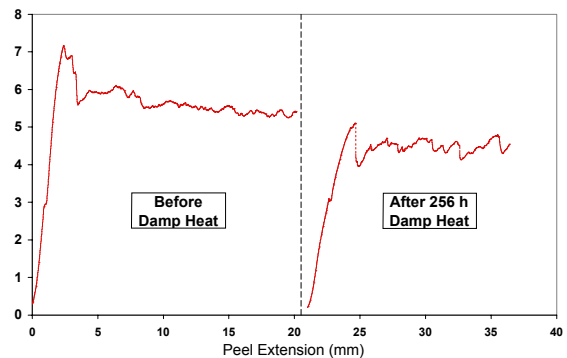


Fig. 3. Instron peel strength data in N/mm for the right hand side of the SiO_xN_y-coated CdTe:B pictured in Fig. 2.

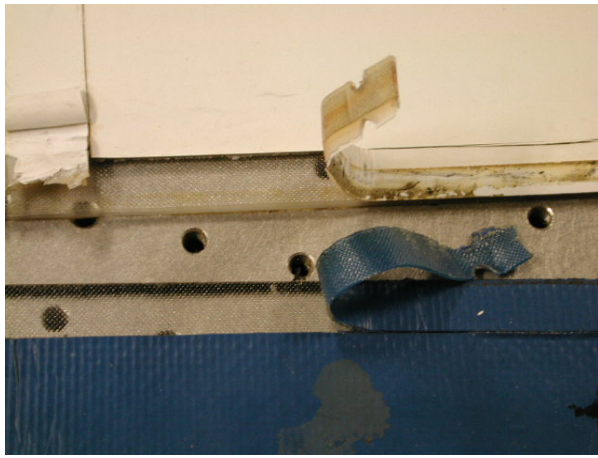


Fig. 4. Instron peels for the edge seal regions of the two Si-modules listed from sources F and G. The Al-channel frame is removed and never blocked much of this edge-seal area from UV exposure.

Similarly, for other T-F peel strengths where failure is not within the cell stack, e.g. a-Si:A, the lower limit of the cell adhesive and cohesive values is the value cited in the right hand column of Table 1, e.g. > 3.8 N/mm. The remaining T-F sample from source E was a flexible module package. Peel strengths for most of the interfaces in front of and behind the CIGS cell are shown in Table 1 before and after damp heat and field exposures as noted. This package was never intended for the rigorous requirements of the power market; the peel strength values are somewhat lower than found for other cells.

Fig. 4 shows the pull tabs on two of the four Si-modules measured for comparison purposes. Two sets of peel-strength values are entered in the table for each of the “F” and “G” module brands. Values measured for the two brands of aged (7-year UV equivalent) Si-modules at the EVA/glass interface near the edge are 2.0 and 0.4 N/mm. These are down more than 60% from 5.5 and 3 N/mm measured on the unexposed control modules; these are to be compared to typical EVA/glass values of > 10 N/mm. Results after additional damp heat exposure for each of the four modules are listed as well.

A final but important point to make is the effect that the measurement temperature has on adhesion. The values measured in the edge seal region of modules “F” and “G” after UV (2.0 and 0.4 N/mm) will decrease even further with increasing temperature. Anyone who has de-encapsulated a module with a heat-gun knows this. Because neither “F” or “G” would fit in the oven that is used with the Instron, we had to confine our temperature-dependent studies to the smaller CIGS:D2 sample. It had the room temperature value of 7.0 N/mm. As the table indicates, at T = 60°C the pull strength falls to 1.0 N/mm and at 80°C the EVA fails cohesively at 0.05 N/mm. This loss of adhesion and viscosity results in the bubble-type of failure shown in Fig. 1. Applying this train of thought to the modules shown in Fig. 4, any remaining strength left in the edge-seal region of “F” or especially “G” must be very small. We discuss this point later.

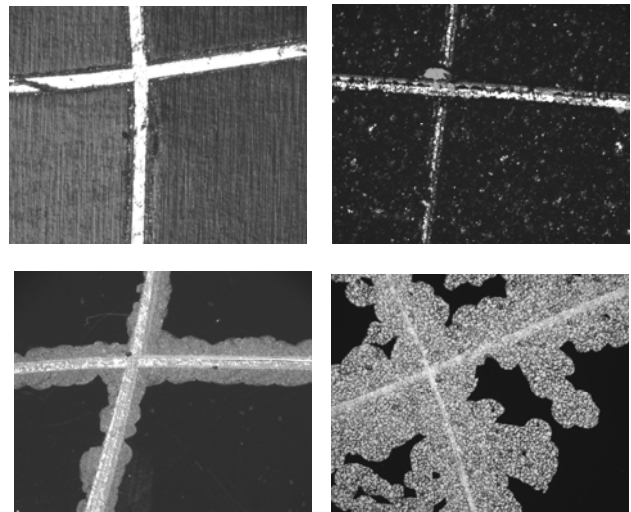


Fig. 5. ASTM scratch test images (1.4 mm wide) for four samples: top right, a-Si:A; top left, CdTe:B; bottom-left, CIGS:D2(>7 N/mm); bottom-right CIGS:D1(0.05 N/mm).

SCRATCH ADHESION TESTS

To measure cell layer adhesion properties only, without the complications of attaching pull-tabs and sometimes having to ascribe lower limit values as above, another, easier-to-do, adhesion scratch test can be performed. Initially developed for the paint industry, the ASTM D 3359-02 “Measuring Adhesion by Tape Test” was applied to all the cells tested. The test requires that a lattice pattern be scratched into the coated surface with six or seven lines in each direction. Any loose fragments are brushed away, the ASTM qualified tape is pressed firmly to that area, and, within 30 to 90 s, the tape is pulled back at a 180° angle. The last entry in Table 1 shows the ASTM-designated tape would exert a force of 0.4 N/mm on any cell material disturbed or loosened by the scratch tool. Some close-up after-test images of single, representative crossings, are shown in Fig. 5. We now correlate these images with results in Table 1.

The top-left image is of the a-Si:A that had a peel strength of 3.8 N/mm at the EVA/cell interface. It was the least affected by this test and, although we could only establish a lower limit value of 3.8 N/mm, it very likely has the highest overall adhesive and cohesive strength. The top-right image is of the CdTe:B that had a peel strength of 5.6 N/mm at the EVA/cell interface. These scratch-followed-by-tape-pull results show virtually no removal of cell material in the area adjacent to the actual scratch mark.

The bottom-left image, D2, is from a commercial product with a peel strength > 7 N/mm, and the bottom-right image, D1, is from a “reject” low adhesion test sample with only 0.05 N/mm. These side-by-side images reflect this difference, albeit in a non-quantifiable way. At the left, a fairly uniform but limited amount of cell material is fractured by the scratch mark. At the right, a large and non-uniform amount of cell material is fractured from the surface adjacent to the scratch marks. Referring to Table 1, the failure interface is between the CIGS/Mo-interface.

Adhesion at this interface was the focus of an earlier study that showed a sensitivity to the Se-processing [10].

Within a given technology, it could be useful to apply the ASTM D 3359-02 test procedure to screen for cell-layer adhesion strength. It is testing adhesion in a very different way from the pull-testing that we usually do in our laboratory. Depending on the types of stress in the field, one or the other may be more valid.

DISCUSSION

Many field failures can be attributed to packaging deficiencies as shown in Fig. 1 and discussed in [1]. When damage does occur, it usually happens at elevated stress levels. In this paper, we have shown how interfacial adhesion values can vary within the layers of a T-F module. Large differences are found that depend on the source, technology, amount of exposure to stress, and measurement conditions (temperature and RH). Therefore, when we screen encapsulant materials, we should measure relevant properties under those higher stress conditions to avoid packaging-related failure.

Specifying a minimum strength, which would insure a durable module, is problematic. It is unlikely that one value will be adequate for all technologies and for each interface therein. For example, modules like "F" and "G" have framed edges that mechanically hold the encapsulated module together at the edges so that when high temperature and RH occur in the field, the edge remains intact. The situation for a frameless or double-glass laminate will require more strength.

A minimal strength limit near the center of a module may not be adequate for the edge seal border region. Corrosion protection and reduction of interfacial water ingress may be more important considerations for requiring the highest possible adhesion strength[11].

Finally, when EVA is used as an encapsulant, as the softening temperature at 85°C is approached and exceeded, cohesive failure and viscous flow can occur if a tensile or shear stress is present. Mechanical stress in a double-glass laminated module can cause bubble-type delaminations or a compromised edge seal.

CONCLUSIONS

We presented peel strength values for the weakest interface of various T-F module technologies and measured how they are affected by environmental stress; some were quite low.

We showed that measurement at higher temperature and RH, and after extended UV and RH exposure reduce EVA's adhesion strength compared with measurement before exposure and under normal laboratory conditions. If minimal guidelines were to be set for adhesion, they ought to include the effects of higher temperature and RH. An added problem associated with EVA is a softening near 85 °C which can also lead to failure.

Our data show that measured inter-layer adhesion within the *T-F cell* can be quite small. Within a

technology the ASTM D 3359-02 "Measuring Adhesion by Tape Test" is useful as a screening test for cell adhesion.

While no minimum adhesion strength could be determined from mechanical considerations, others have shown that strong adhesion reduces both corrosion and interfacial water ingress, thus contributing to a durable module package in these additional ways.

ACKNOWLEDGEMENTS

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REFERENCES

- [1] T.J. McMahon, "Accelerated testing and failure of thin-film modules," Prog. Photovolt: Res. Appl. **12**(2004), p.234-248. And references therein.
- [2] K.W. Jansen and A.E. Delahoy, "A laboratory technique for the evaluation of electrochemical transparent conductive oxide delamination from glass substrates", Thin Solid Films 423 (2003) 153.
- [3] D.E. Carlson, R. Romero, Willing F, Meakin D, Gonzalez L, Murphy R, Moutinho HR, Al-Jassim M. Corrosion effects in thin-film photovoltaic modules. Progress in Photovoltaics 2003; 11: 377-386.
- [4] R. Wieting, R. Gay, H. Nguyen, J. Palm, C. Rischmiller, A. Seapan, D. Tarrant, and D. Willett, "CIS Thin-Film Manufacturing at Shell Solar: Practical Techniques in Volume Manufacturing," Proc of the 31st IEEE PVSC Jan 2005, Orlando, FL, p. 177.
- [5] G. Barber, G. Jorgensen, K. Terwilliger, J. Pern, S. Glick, and T.J. McMahon, "New barrier coating materials for PV module backsheets", Proc. of the 29th IEEE PV Spec. Conf., New Orleans, LA, p. 1541 (2002).
- [6] E.P. Pleuddmann, Silane Coupling Agents, Chap. 5, Plenum, New York, 1991.
- [7] F.J. Pern and G.J. Jorgensen, "Development of Damp-Heat Resistant Self-Primed EVA and Non-EVA Encapsulant Formulations at NREL," Solar Rev Mtg., Nov 2005, Denver, CO.
- [8] R. Tucker, Solar Rev Mtg., Nov 2005, Denver, CO.
- [9] T.J. McMahon and G.J. Jorgensen, "Electrical currents and adhesion of edge deleted regions of EVA-to-glass module packaging," Proc. of the 2001 NCPV Program Review Mtg., Lakewood, CO, Oct 2001; pp 137-138.
- [10] Tarrant, D. E.; Gay, R. R. (1995). Research on High-Efficiency, Large-Area CuInSe₂-Based Thin-Film Modules: Final Subcontract Report, 16 August 1993 - 30 June 1995. 99 pp.; NREL Report No. TP-413-8121. (83014.PDF)
- [11] J. Tonge, DOW Chemical Corporation.