Thermo-Mechanical Degradation Mechanisms Relevant for Field Failures and Solar Lifetimes

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(OPV, Perovskite and multi-junction active layers and electrodes)

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(ultra barrier films)

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Degradation and Reliability of PV Devices and Modules

operating environments:

- thermal cycling, stress, moisture, chemically active environmental species, solar UV, …
- coupled and often uncertain degradation kinetics and reliability models.
Outline
• Inherent Solar Thermo-Mechanical Reliability
  • adhesion and cohesion characterization and properties
  • silicon, OPV, CIGS and perovskite devices and modules
• Module Components: Backsheets, Frontsheets, Encapsulation
  • adhesion metrologies and challenges
  • debonding kinetics and lifetime predictions
• Reliability and Operational Lifetimes for CPV Technologies
  • coupled mechanical and photo-chemical mechanisms
  • correlation of in-door and out-door exposures
• Challenges for Emerging OPV and Perovskites
  • fundamental challenge for mechanically fragile systems
  • prospects for improvements

Device Reliability and Evolution of Defects

damage propagates if mechanical stresses are large enough so that

\[
G \geq G_c \left[ \frac{J}{m^2} \right]
\]

mechanical “driving force”

presence of chemical species and photons, damage propagates even if

\[
G < G_c \left[ \frac{J}{m^2} \right]
\]

environment and stress accelerates defect evolution

Role of coupled “stress” parameters:
• mechanical stress
• temperature
• environmental species
• photons (photochemical reactions)
Limitations of Thin-Film Adhesion Tests

- **Indentation/Scratch Test**
  - complex stress and deformation fields
  - principally qualitative results
  - (nano) scratch test even less quantitative

- **Peel/m-ELT Test**
  - difficult to apply loads
  - plastic deformation of film
  - temperature complications in m-ELT

- **Blister Test**
  - compliant loading system
  - environmental effects
  - etching/machining of cavity difficult

Major limitations: need detailed film properties, film stress relaxation and film plasticity

⇒ principally qualitative results for all above methods!

Quantitative Adhesion/Cohesion and Debond Kinetics

- **Debond Energy, G_c (J/m^2)**
  - Aging Treatment Temperature (°C)
  - 0% RH blisters
  - 80% RH 1000 hrs
  - Unaged

- **Debond-Kinetics**
  - Increasing temperature
  - Polyvinyl fluoride
  - Polyester

RH = 40%

Increasing temperature

Polyvinyl fluoride
Polyester

Unaged
Fracture Properties of Device Materials

- Silicon PV
- Polymers for Packaging Encapsulation
- Protective Coatings
- Dense SiO₂
- TEOS SiO₂
- ULK dielectrics
- CIGS
- OPV
- Perovskites

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Mechanical Reliability of Module Components

- Backsheets
  - multilayered TPE
  - full-size modules

- Frontsheets
  - dyad barrier films
  - polysiloxane films

- Encapsulation
  - EVA and PVB
  - ionomers and polyolefins

Mechanics-Based Adhesion Metrologies

Square and tapered specimens have simpler data analysis…

Debond Experiment

\[ P_c \approx \frac{P_c^2}{4B} \]

Data Analysis
Method Insensitive to Glass Fracture

Load, $P$ (N)

Displacement, $\Delta$ (mm)

$G_c \approx \frac{P_c^2}{4B'}$

Debond Length (mm)

Mechanical Compliance, $C$ ($\mu$m/N)

Test Temperature, $T$ (°C)

Debond Energy, $G_c$ (kJ/m$^2$)

Effective Temperature on Debond Energy

Debond Energy, $G_c$ (kJ/m$^2$)

Test Temperature, $T$ (°C)
Effect of Substrate Treatment on Debond Energy

![Graph showing the effect of various treatments on Debond Energy.](image)

- acetone + IPA + UV Ozone
- trichloroethylene
- ionomers

Encapsulation Thickness (mm)

Debond Energy (J/m²)

30 Year Historic Module Encapsulant Adhesion

![Graph showing energy release rate and load-displacement.](image)

- Adhesion of EVA after 30 years in service (exposed) and storage (unexposed).

Delamination of EVA/glass – EVA brown discoloration.

Debond of EVA from cell - localized EVA deformation between grid lines.
Mechanical Reliability of Module Components

- Backsheets
  - multilayered TPE
  - full-size modules

- Frontsheets
  - dyad barrier films
  - polysiloxane films

- Encapsulation
  - EVA and PVB
  - ionomers and polyolefins

Effect of Aging T and RH on Backsheet Adhesion

- Blisters in fielded PV modules

- PVF/PET
- EVA seed
- EVA encapsulant
- Glass

Adhesive PVF/PET

80% RH

0% RH

1000 hrs

Unaged

[Graph showing debond energy, Gc, as a function of aging treatment temperature (°C)]

Stanford ENGINEERING
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30 Year Historic Module Backsheet Adhesion

Adhesion degrades over an order of magnitude after 30 yrs in field.

Higher adhesion at PVF-PET interface in discolored region at junction of four silicon cells.

New Portable Full Panel Adhesion

Debond energy decreased by 97% after 10 years in Florida sun.

G_c = 2.8 J/m^2
Temperature-Activated Backsheet Debond Growth

**Debond Relaxation Model**

\[
\frac{da}{dt} = \frac{\pi}{8} \varepsilon_c \left( \varepsilon_c \varepsilon_p \right)^{\gamma/\eta} \left( \frac{G}{E_0(RH)} \right)^{\eta/\gamma} e^{-\frac{E_h}{RT}} 
\]

- **Arrhenius**
- **Williams-Landel-Ferry** (1955)

\[
\frac{da}{dt} = \frac{\pi}{8} \varepsilon_c \left( \varepsilon_c \varepsilon_p \right)^{\gamma/\eta} \left( \frac{G}{E_0(RH)} \right)^{\eta/\gamma} \frac{C_0(T-T_p)}{10^5(T-T_p)}
\]

**Polyvinyl fluoride**

**Viscoelastic relaxation**

**Polyester**

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Defect-Tolerant Lifetime Estimation

*Blister formation in PV modules*

\[
G = \frac{3}{32} \left(1 - \nu^2\right)pd^4 
\]
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CPV is ideal PV test vehicle with elevated “stress” parameters for reliability studies
- elevated thermal, moisture, light intensities, mechanical stresses

Dauskardt / Stanford; Miller and Kurtz / NREL; Hebert and Ermer / Spectrolab
PREDICTS Program

DOE Geoffrey Kinsey (Program Manager), Inna Kozinsky (Senior Technical Advisor)
Survey of Materials and Interfaces Relevant to CPV Industry

- Survey of 11 module and 2 optics manufacturers
- Materials/interfaces most relevant to degradation and reliability
- Sample questions posed to CPV industry:
  - What are the most important interfaces within a CPV module to be studied?
  - What interfaces would you recommend we study?

Role of Time and Temperature during In-Door UVB Exposure

80°C/10% RH, 50°C/10% RH, 110 °C/10% RH at 4.5 mW/cm² from 200 nm to 400 nm wavelength UV
Role of Out-Dooor Concentrated Solar Exposure

- Sylgard adhesive aged in outdoor concentrator at 1100x solar flux

UV Mediated Chemical Degradation at Interface

- XPS characterization of sapphire surface after mechanical testing
- Thickness of residual silicone layer on sapphire grows with increase in aging time
- Suggests formation of bonds at interface between sapphire and silicone adhesive
UV Mediated Chemical Degradation in Bulk

- transmission FT-IR shows increase in Si-O-Si peak with increased UV exposure
- suggests formation of oxygen bridges and crosslinking between chains, leading to embrittlement

Increase in Adhesion as a Result of Crosslinking

\[ G_{\text{adhesion}} = k N_{\text{crosslinks}} + G_0 \]

adhesion energy dependent on number of bonds between silicone and sapphire substrate

\[ N_{\text{crosslink}} = k_w W_{\text{tot}} e^{-\frac{E_a}{k_B T}} \]

linear relation between number of crosslinks and UV dosage

\[ G_{\text{adhesion}} = k_1 W_{\text{tot}} e^{-\frac{E_a}{k_B T}} + G_0 \]
Decrease in Cohesion as a Result of Crosslinking

\[ G_{\text{cohesion}} = k \left( \frac{3}{M_w^2} \right) \]
\[ = \frac{k_2}{(k_3 + N_{\text{crosslink}})^{3/2}} \]

adhesion energy dependent on molecular weight between crosslinks

\[ N_{\text{crosslink}} = k_{uv} W_{\text{tot}} e^{E_a/k_BT} \]

linear relation between number of crosslinks and UV dosage

\[ G_{\text{cohesion}} = \frac{k_2}{(k_3 + W_{\text{tot}} e^{-E_a/k_BT})^{3/2}} \]

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Factors Effecting Cohesion of BHJ Layers

- Heterojunction layer thickness
  - is cohesion in organic layers sensitive to layer thickness?

- Composition of the heterojunction layer
  - limited bonding to fullerene
  - polymer/PCBM ratio makes stronger layer

- Molecular intercalation
  - manipulating the types of intermolecular interactions

- Annealing
  - morphology of the BHJ layer changes with annealing

Stanford Engineering
Effect of Molecular Intercalation on Cohesion

Fracture Energy, $G_c (J/m^2)$

1:1 polymer to fullerene mass ratio

Post-Annealing to Control Interdiffusion and Adhesion

Adhesion Energy, $G_c (J/m^2)$

Annealing Time, $t$ (h)

Annealing time and temperature increases the debonding resistance

REFERENCE

PEDOT:PSS

P3HT:PC60BM

P3HT:PC71BM

Efficiency vs. Cohesion


Increasing BHJ layer thickness

Thin BHJ layer - low efficiency due to lower photon harvesting

Thicker BHJ layer - greater degree of charge carrier recombination

\[ \varepsilon = \frac{V_{OC}J_{SC}FF}{P_{in}} \]

Perovskite: Not Just Your Average Salt

\[ CH_3NH_3PbI_3 \quad NaCl \]

<table>
<thead>
<tr>
<th>Material</th>
<th>CH$_3$NH$_3$PbI$_3$</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>4.29 g/cm$^3$</td>
<td>2.16 g/cm$^3$</td>
</tr>
<tr>
<td>Fracture Energy, $G_c$</td>
<td>???: J/m$^2$</td>
<td>0.6-1.8 J/m$^2$</td>
</tr>
<tr>
<td>Solar Cell Efficiency</td>
<td>~20%</td>
<td>0%</td>
</tr>
</tbody>
</table>
Factors Influencing Perovskite Films

• Morphology/Processing
  - Grain size
  - Mesoporous vs. planar
  - Substrate temperature
  - Precursor ratio

• Deposition method
  - Roll to roll vs. blade coating

• Exposure conditions
  - Humidity
  - Temperature

• Molecular Additives

How do these factors affect perovskite film cohesion?

C60-S Increases Device Cohesion

Fracture Energy, $G_c$ (J/m$^2$)

Efficiency, PCE (%)
Effect of Morphology/Process Conditions

**Grain Size**
- Decreased MACl / PbI$_2$ ratio
- Decreased substrate temperature

**Cohesion Energy, $G_c$ (J/m$^2$)**

- Planar, Large-Grain
- Acetate
- Mesoporous

**Effect of Molecular Additives**

- Increasing concentration of diaminopropane
- Goal: Strengthen grain boundaries