

US DOE, Office of Basic
Energy Sciences



Center for Advanced Molecular Photovoltaics
STANFORD UNIVERSITY

Adhesion and Thermomechanical Reliability for PV Devices and Modules

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Solar Outlook

Then...

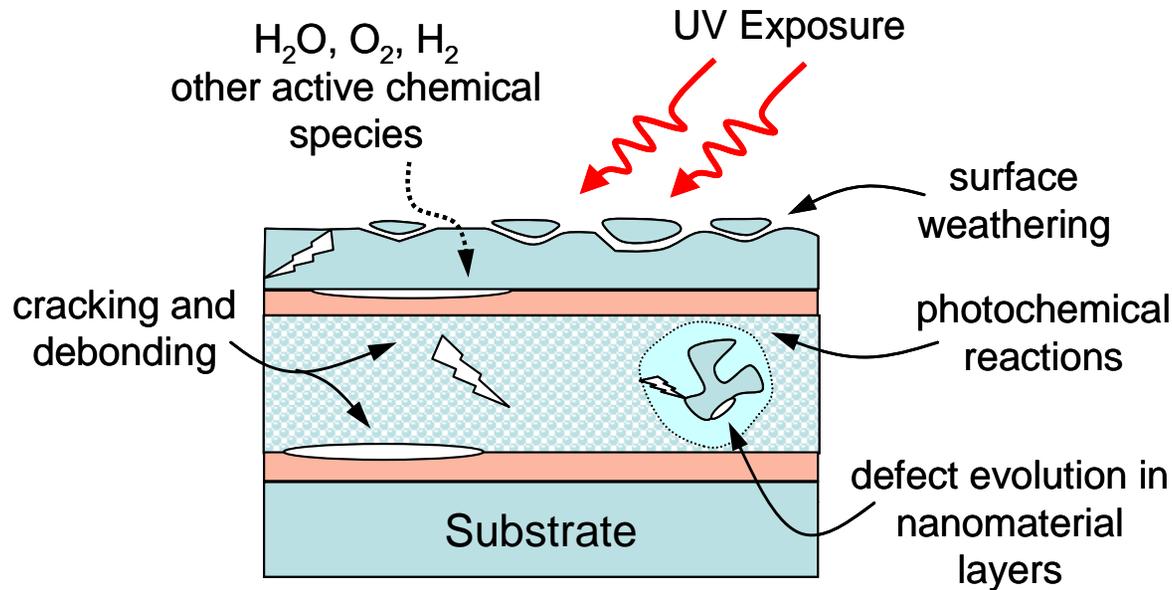
1. Efficiency
2. Reliability
3. Cost

To make a difference...

1. Cost
2. Reliability
3. Efficiency

- Engineer durable solar technologies with robust and predictable lifetimes. Start early in development – avoid roadblocks.
- Leverage from reliability physics in microelectronics – thin-film metrologies, kinetic models, accelerated tests, life prediction.
- Are degradation processes coupled and how?
- Kinetic models for damage evolution - basis for life prediction and accelerated testing (T, environment, stress, solar flux, etc.)
- Effective defensive strategies – e.g. transparent barriers with anti-reflective properties.

Degradation and Reliability of PV Devices and Modules



Severe operating environments.

Exposure to thermal cycling, stress, moisture, chemically active environmental species, and UV.

Uncertain degradation kinetics and reliability models.

Activation Energies for Bond Rupture:

VDW ~ 0.001 - .4 eV/bond

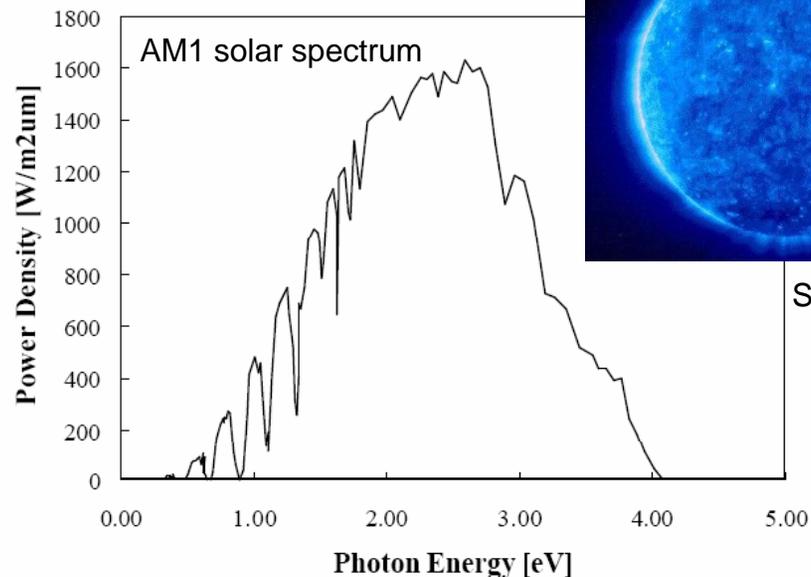
H-bonds ~ .1 - .4 eV/bond

Ester Hydrolysis (100% RH)

$E^* \sim .81$ eV/bond

SiO₂ cracking in water

$E^* \sim 1.39$ eV/bond



Solar spectrum from B. Van Zeghbroeck, U. Colorado

Evolution of Defects and Device Reliability

absence of chemically active environmental species, damage propagates if

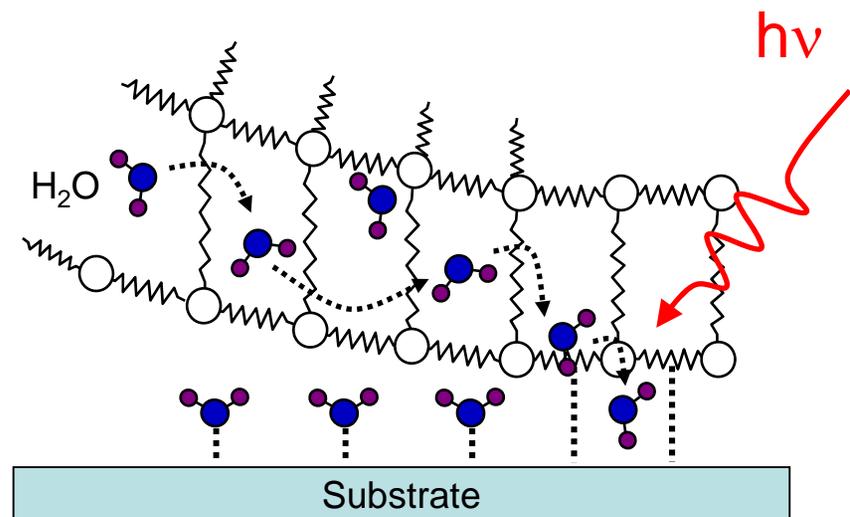
$$G \geq G_c \left[J / m^2 \right]$$

presence of chemical species and photons, damage propagates even if

$$G < G_c \left[J / m^2 \right] \quad \text{environment and stress accelerates defect evolution}$$

Role of coupled kinetic parameters:

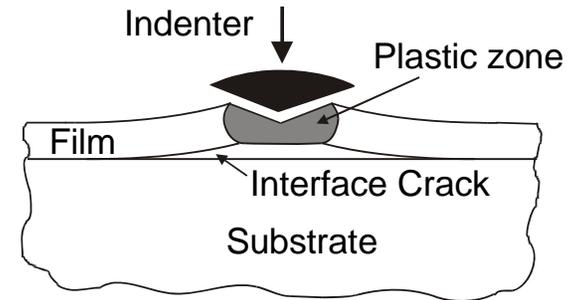
- *mechanical stress*
- *temperature*
- *environmental species*
- *photons*
(*photochemical reactions*)



Typical Film Adhesion Tests that Don't Work Well

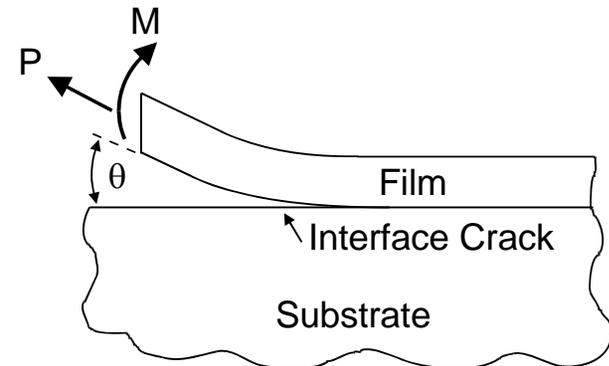
- Indentation/Scratch Test

- complex stress and deformation fields
- principally qualitative results
- (nano) scratch test even less quantitative



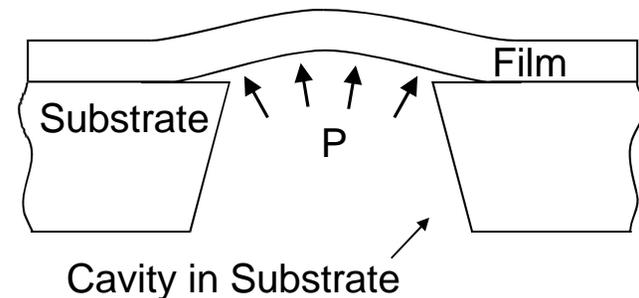
- Peel/m-ELT Test

- difficult to apply loads
- plastic deformation of film
- temperature complications in m-ELT



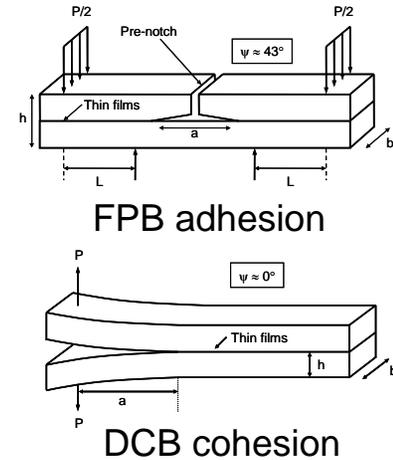
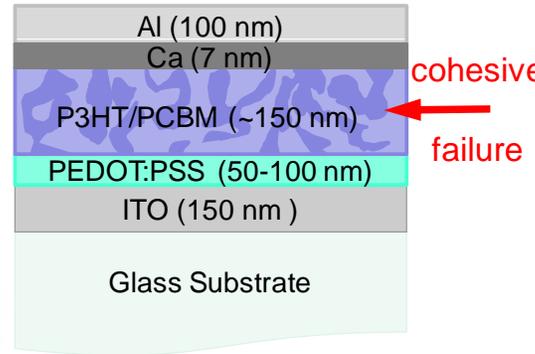
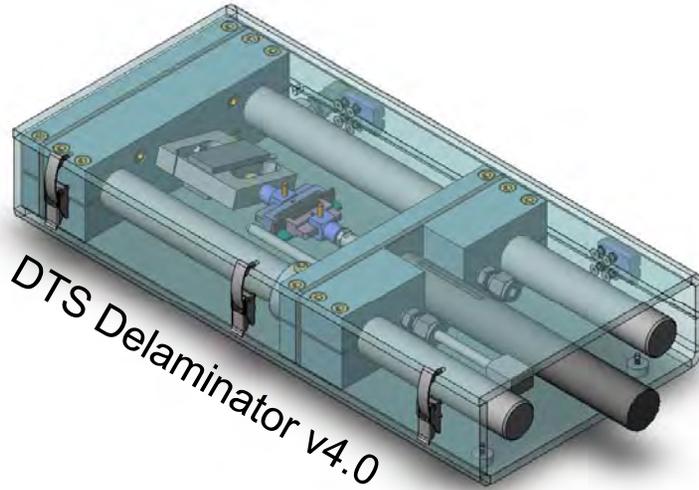
- Blister Test

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

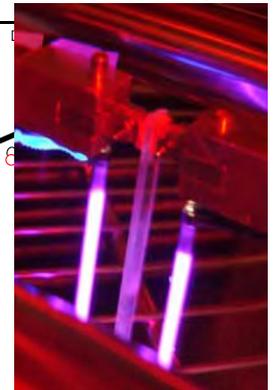
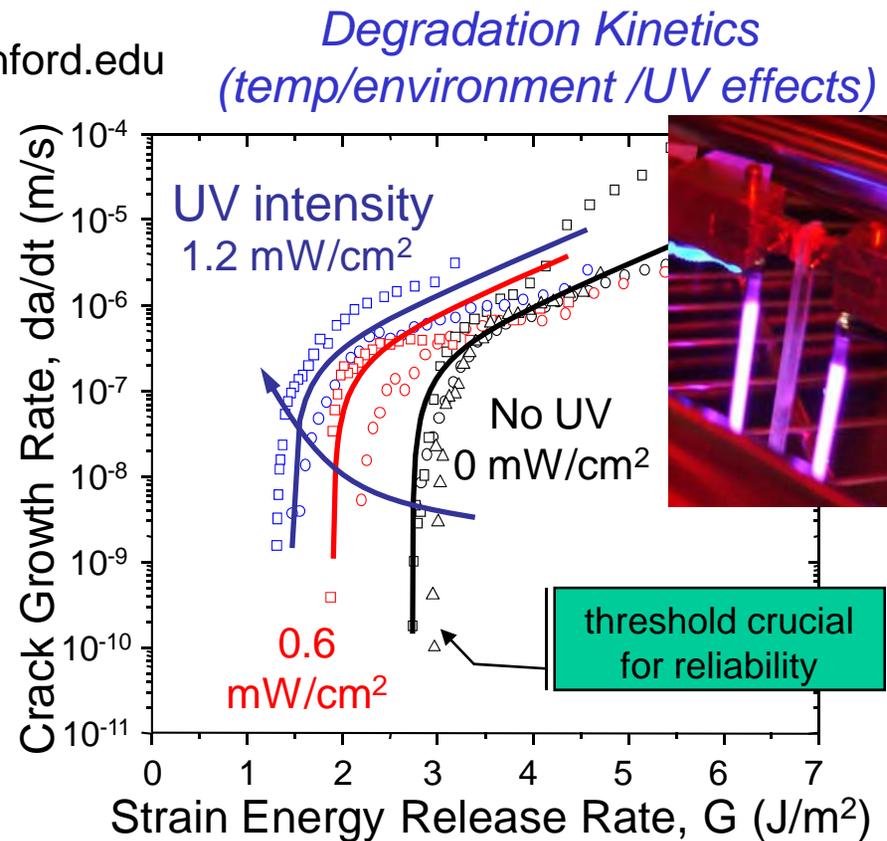
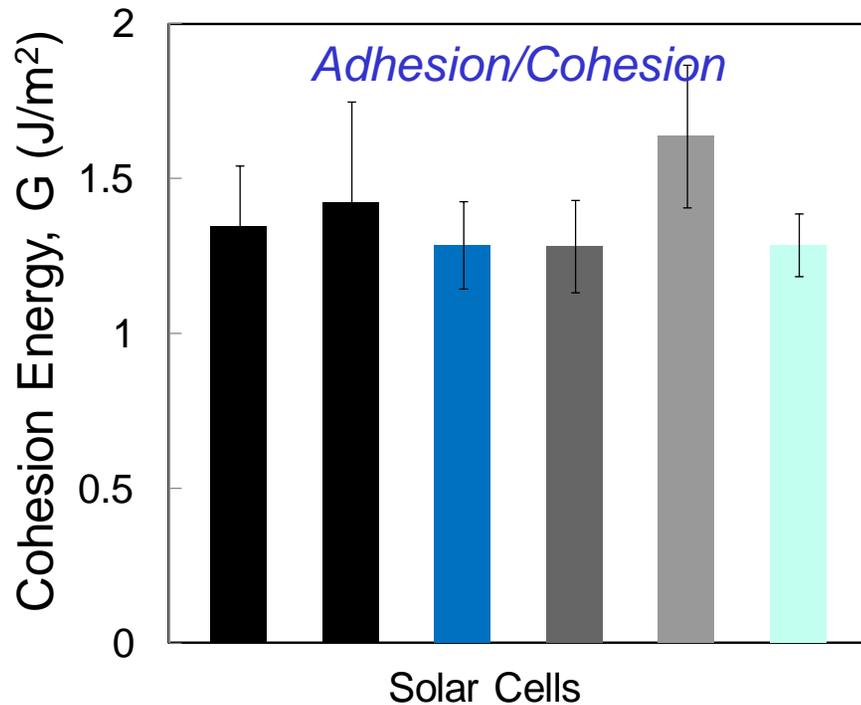


Major limitations: need detailed film properties, film stress relaxation and film plasticity
⇒ principally qualitative results for all above methods!

Quantitative Adhesion/Cohesion and Debond Kinetics



DTS system and support contact dauskardt@stanford.edu

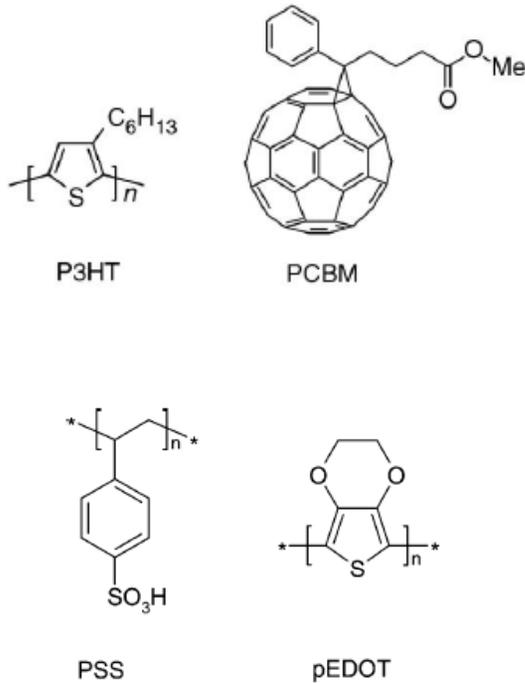


Inherent Solar Cell Thermomechanical Reliability, G_c

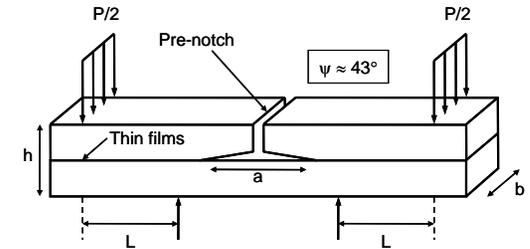
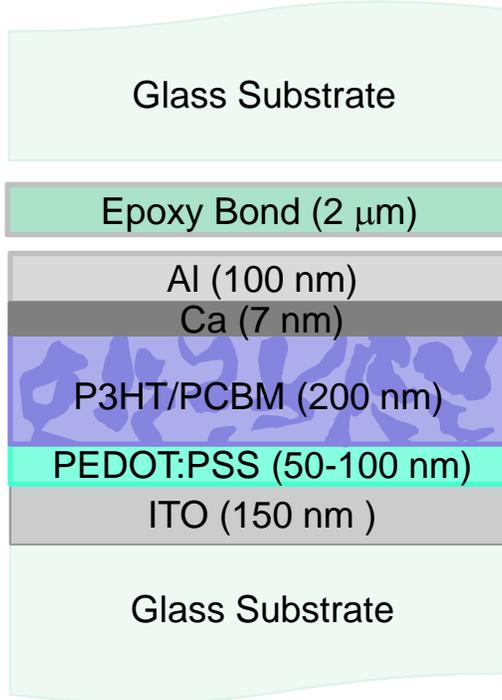
Grad students: Vitali Brand, Jeff Yang and Chris Bruner

Adhesion/Cohesion Sample Preparation

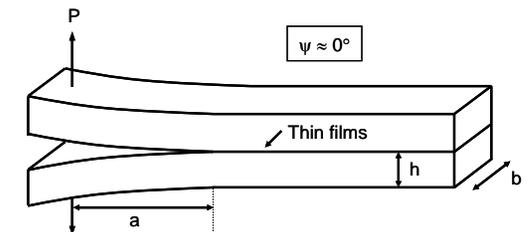
Thin films sandwiched between elastic substrates



Gunes, et. Al. *Chem. Rev.* 2007.



FPB adhesion

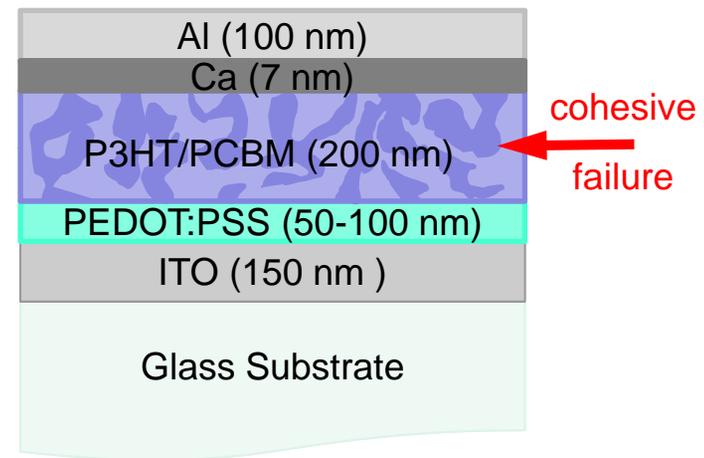
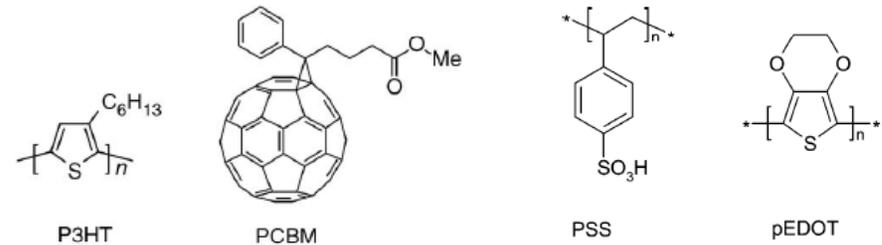
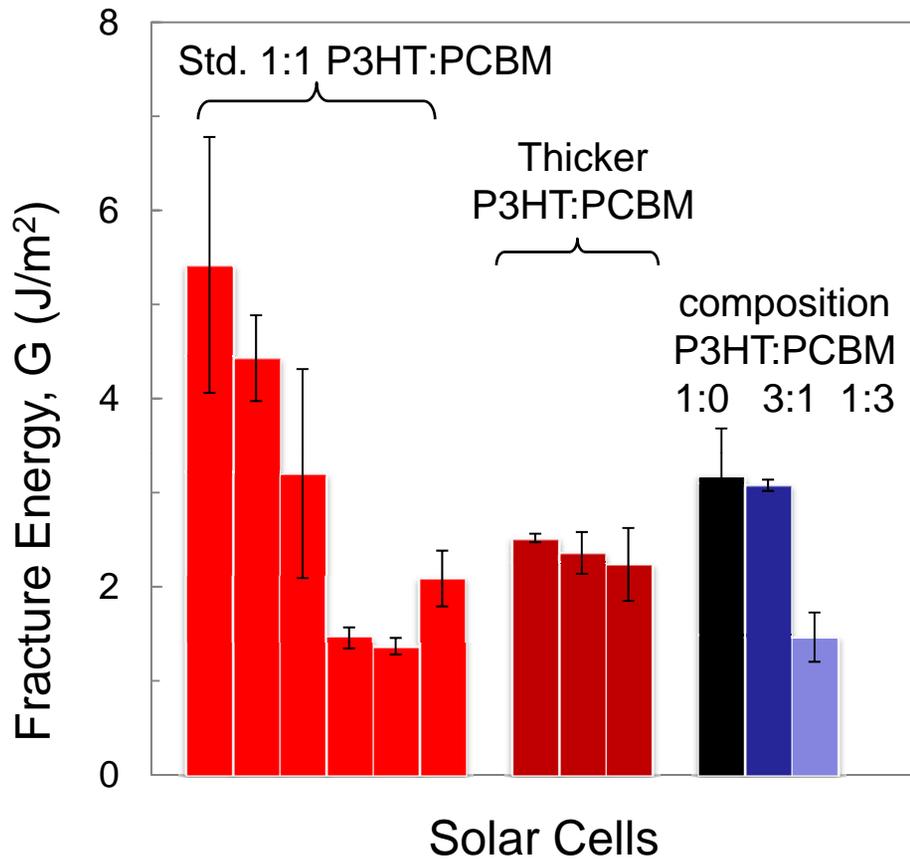


DCB cohesion

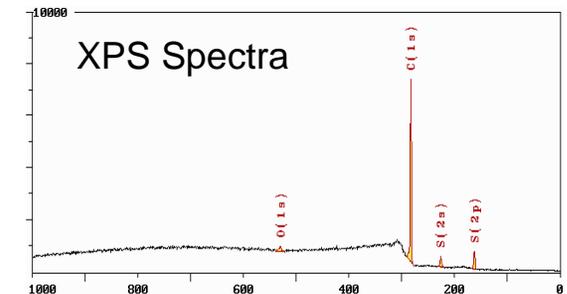
Fabricated 4-point bend adhesion and DCB cohesion test structures using standard epoxy bonding techniques.

Similar transparent glass substrates on each side.

Adhesion/Cohesion of P3HT/PCBM Structures

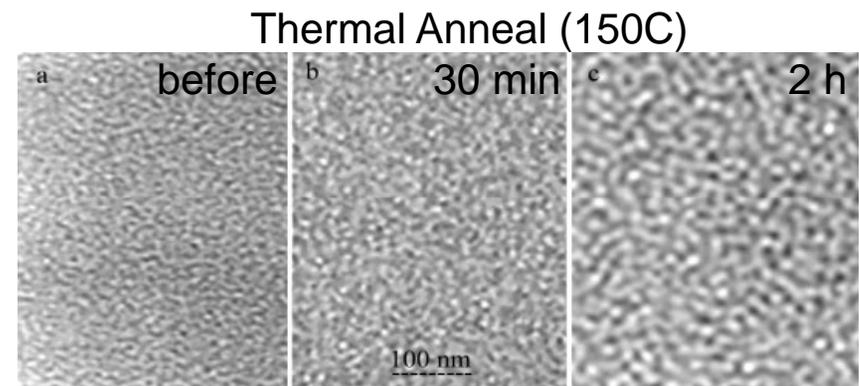
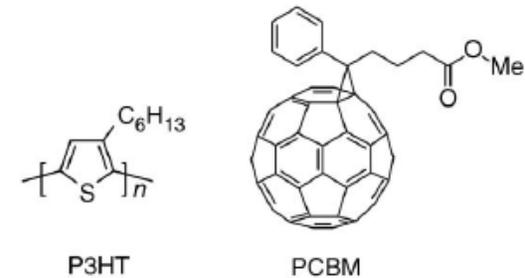
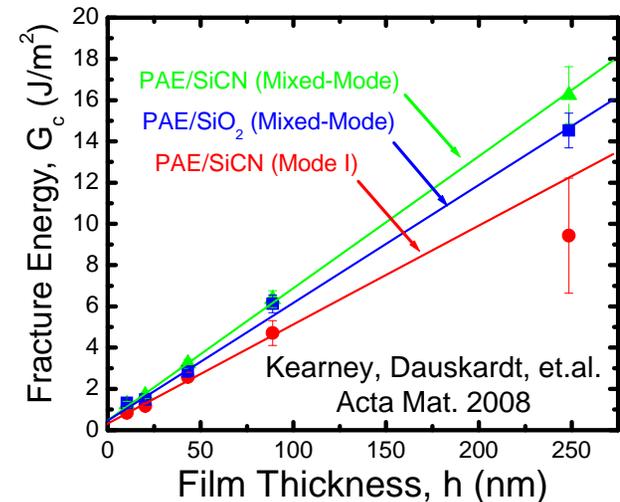


- XPS reveals similar debond path for DCB and 4-pt bend samples
- C ~ 92%, S ~ 6%, O ~ 2%
- Suggests cohesive failure in PCBM:P3HT layer

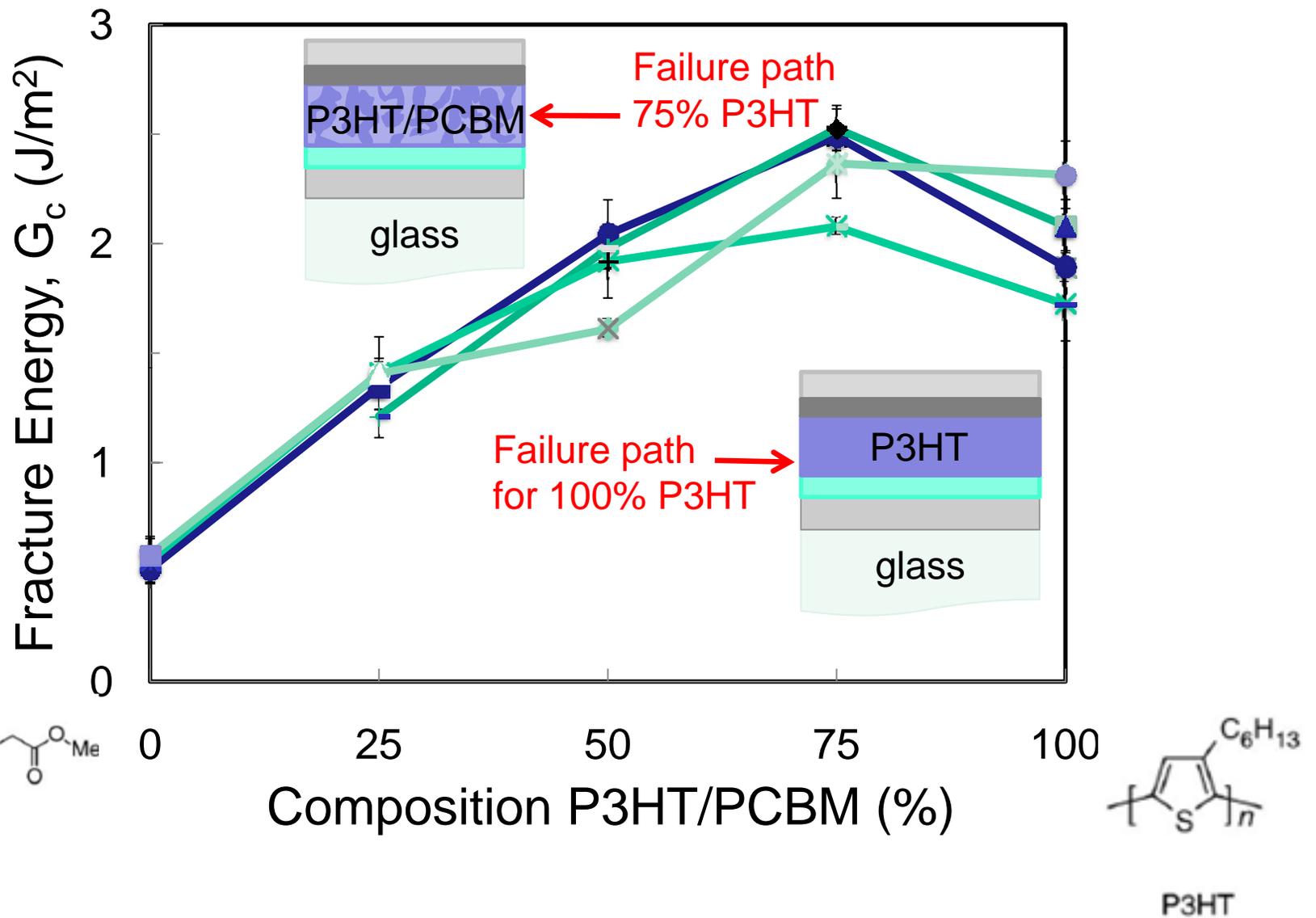


Factors Effecting Cohesion of P3HT/PCBM Layers

- Heterojunction layer thickness
 - cohesion in polymer layers is sensitive to layer thickness
 - plastic energy dissipation in organic layers
- Composition of the heterojunction layer
 - limited bonding to fullerene – expect low cohesion
 - preliminary measurements indicate higher ratios of P3HT to PCBM make stronger active layer
- Annealing
 - morphology of the P3HT:PCBM film changes with annealing, expect effect morphology on cohesion



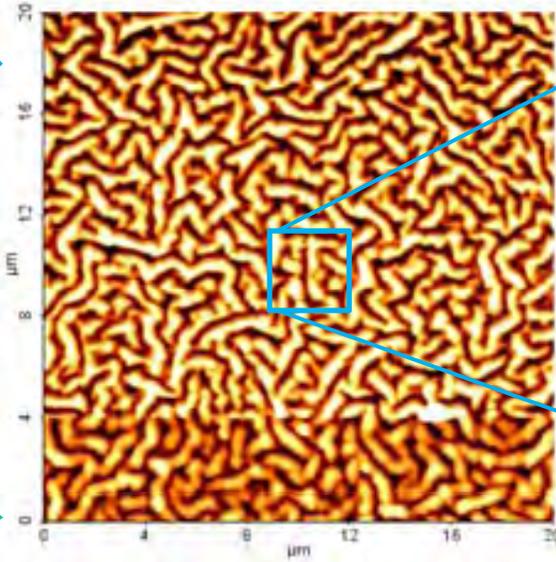
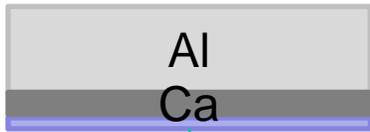
Effect of Composition of BHJ on Cohesion



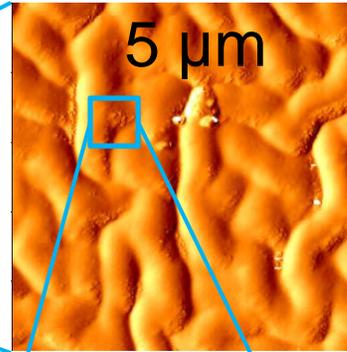
AFM of Failure Path Near Ca Interface

Topography →

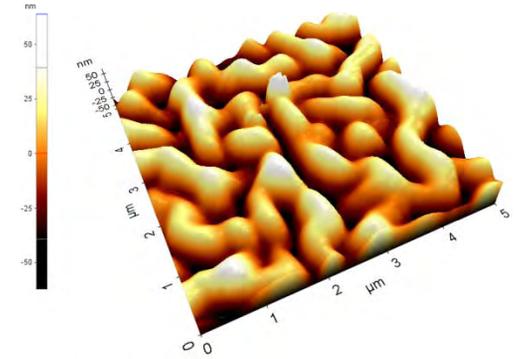
$R_a = 20 \text{ nm}$
 $R_q = 24 \text{ nm}$



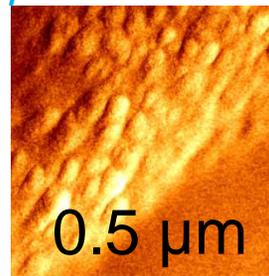
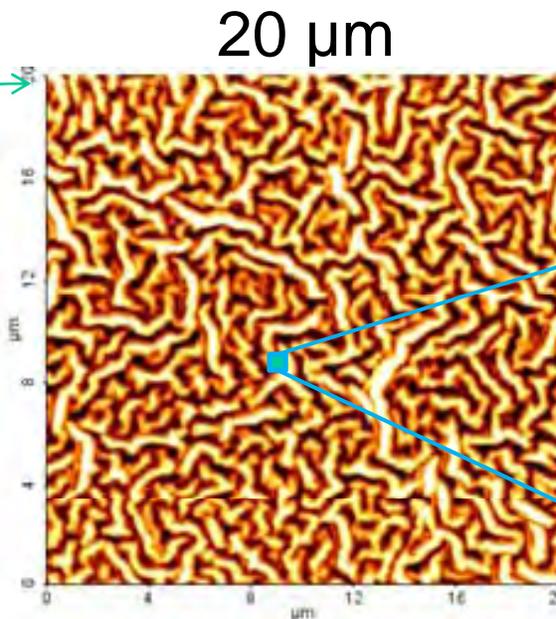
Phase



Topography

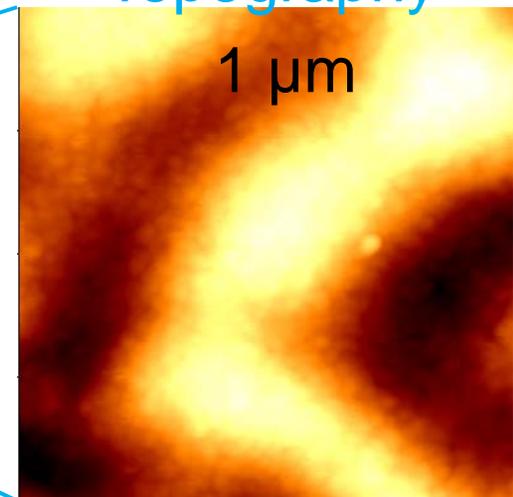


cohesive surfaces



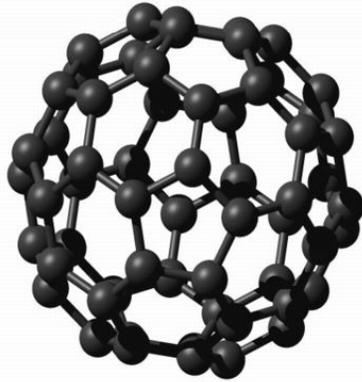
Annealing effects during Al vapor deposition is a possibility

Topography

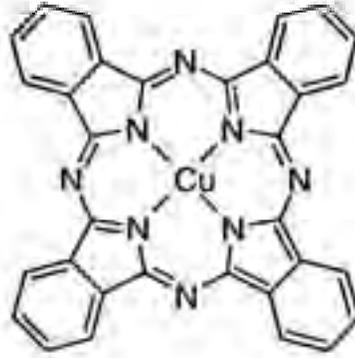


$R_a = 25 \text{ nm}$
 $R_q = 30 \text{ nm}$

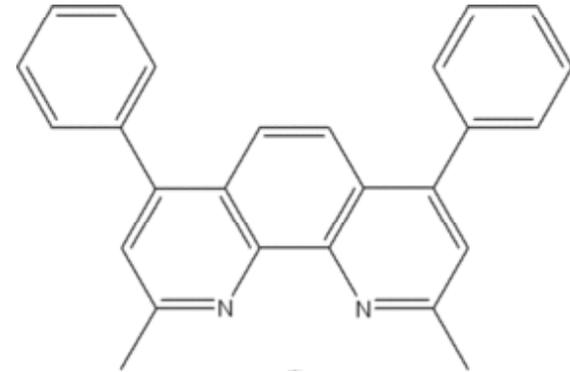
Small Molecule Solar Cell Thin Films



C60

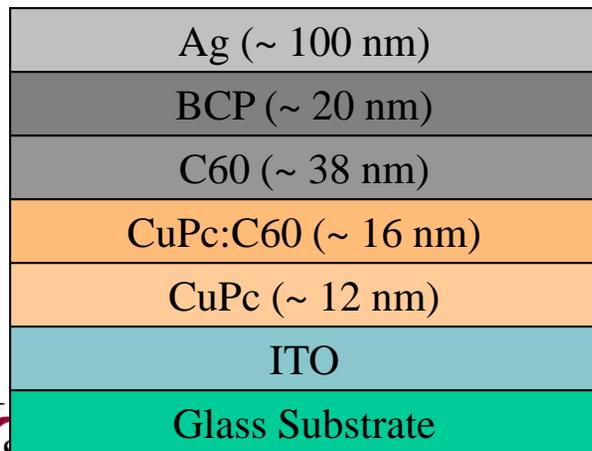


CuPc

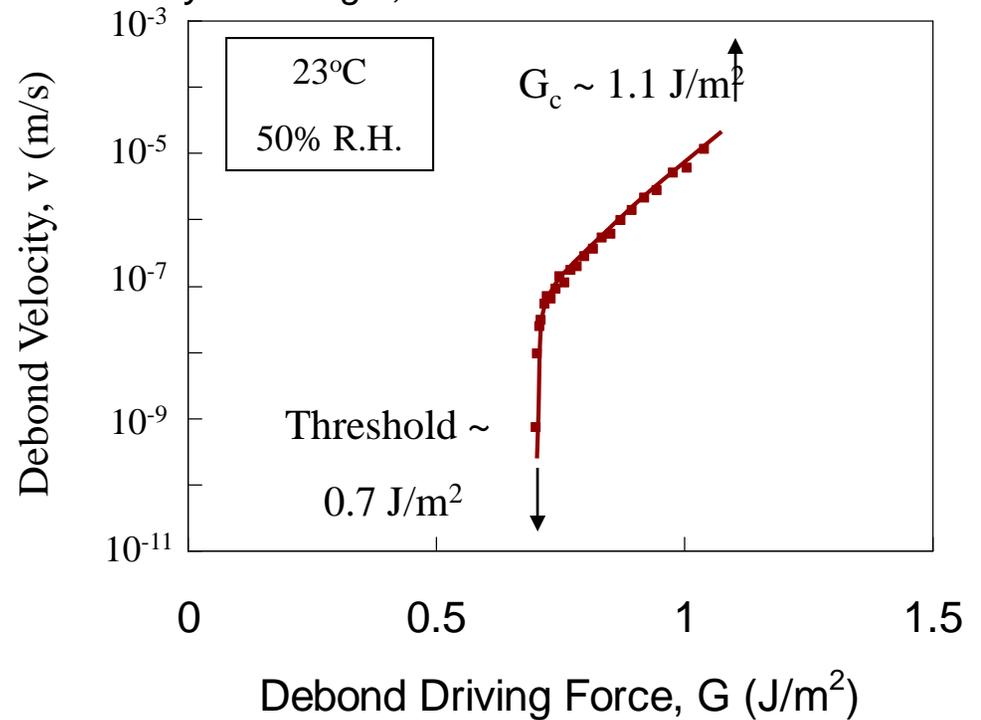


BCP

$$G_c = 1.1 \pm 0.4 \text{ J/m}^2$$



Ryan Birringer, Uraib Aboudi and Peter Peumans



Molecular Bond Rupture Kinetics (Barrier Films)

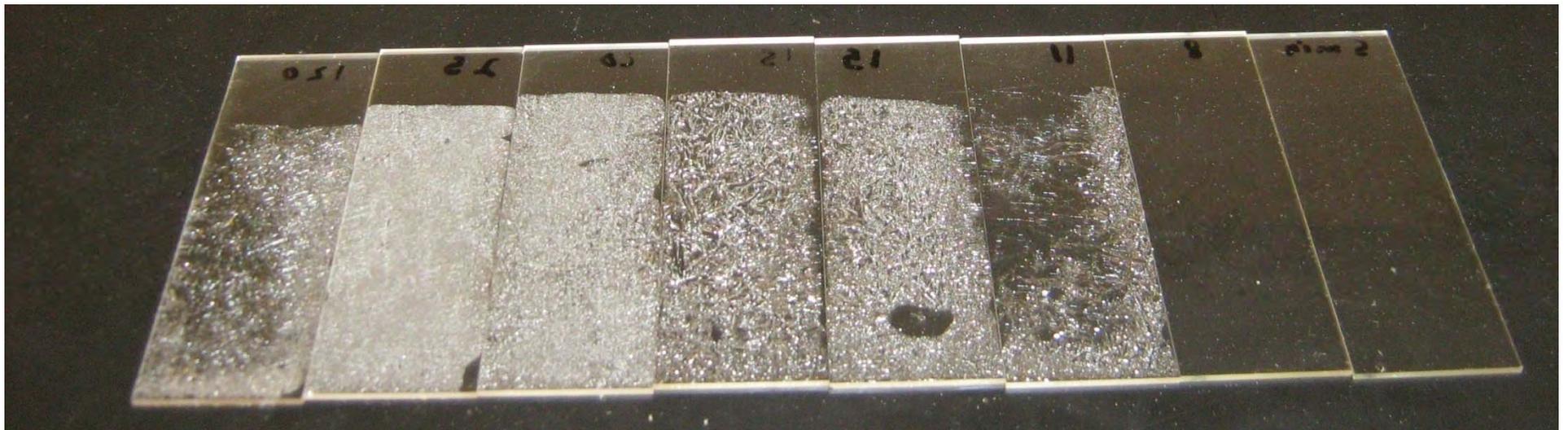
Grad student: Fernando Novoa and Monika Kummel

$$G < G_c \left[J / m^2 \right] \quad \textit{environment and stress accelerates defect evolution}$$

Weathering Test of Polysiloxane Barrier

UV exposure: 28 mW/cm² at 6 mm UV-257nm

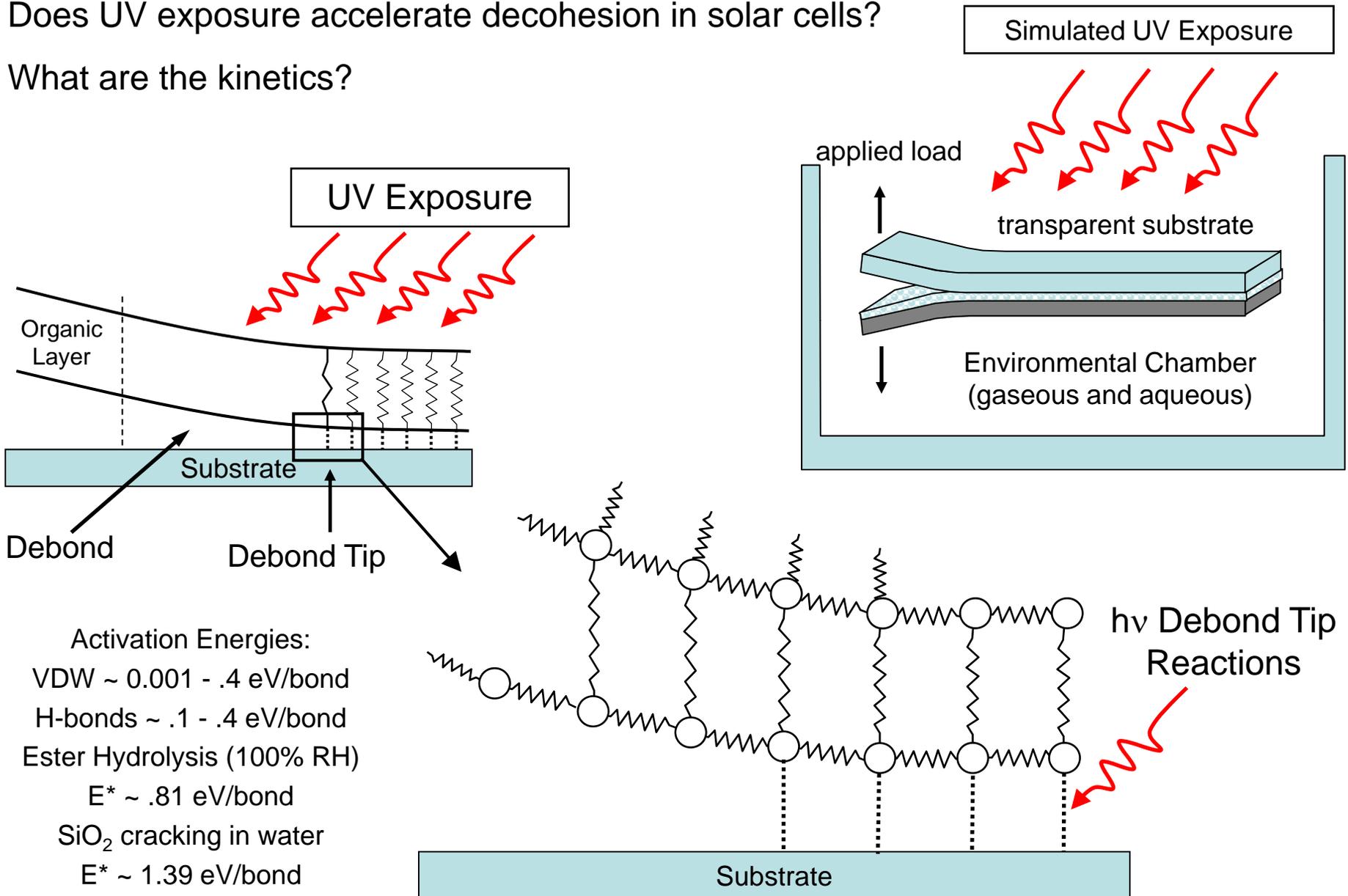
120 min.....15 min.....5 min



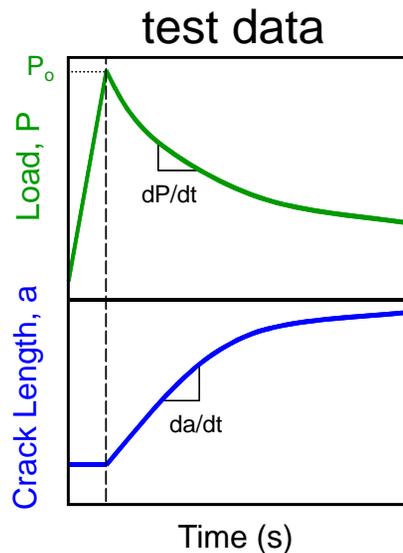
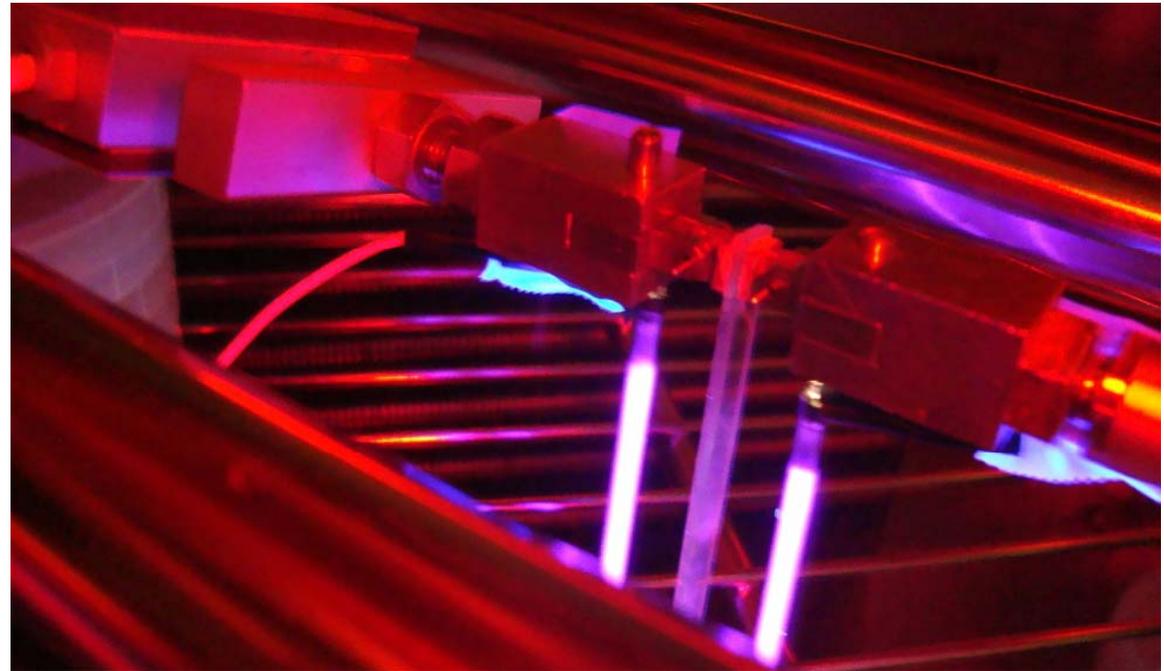
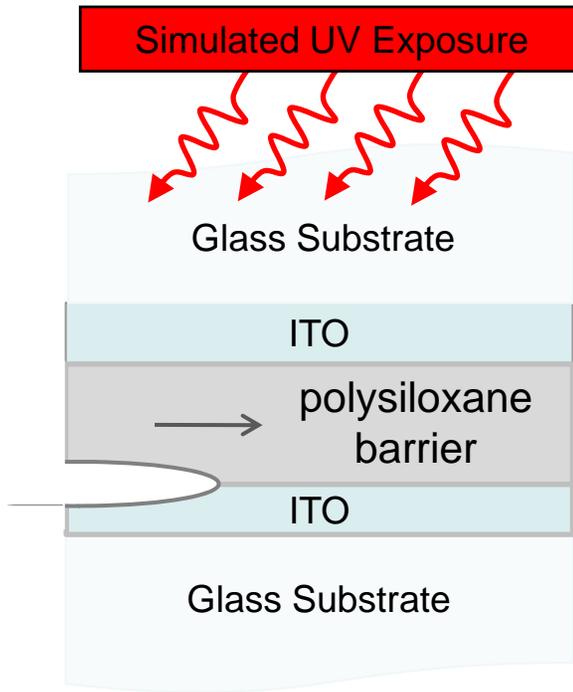
Environment and Stress Accelerates Damage

Does UV exposure accelerate decohesion in solar cells?

What are the kinetics?



Assessing UV and Environment on Debonding Kinetics



DTS Delaminator v4.0
*automated load
relaxation debond
growth analysis*

compliance analysis

sensitivity to $< 10^{-10}$ m/s

DTS system and support contact dauskardt@stanford.edu

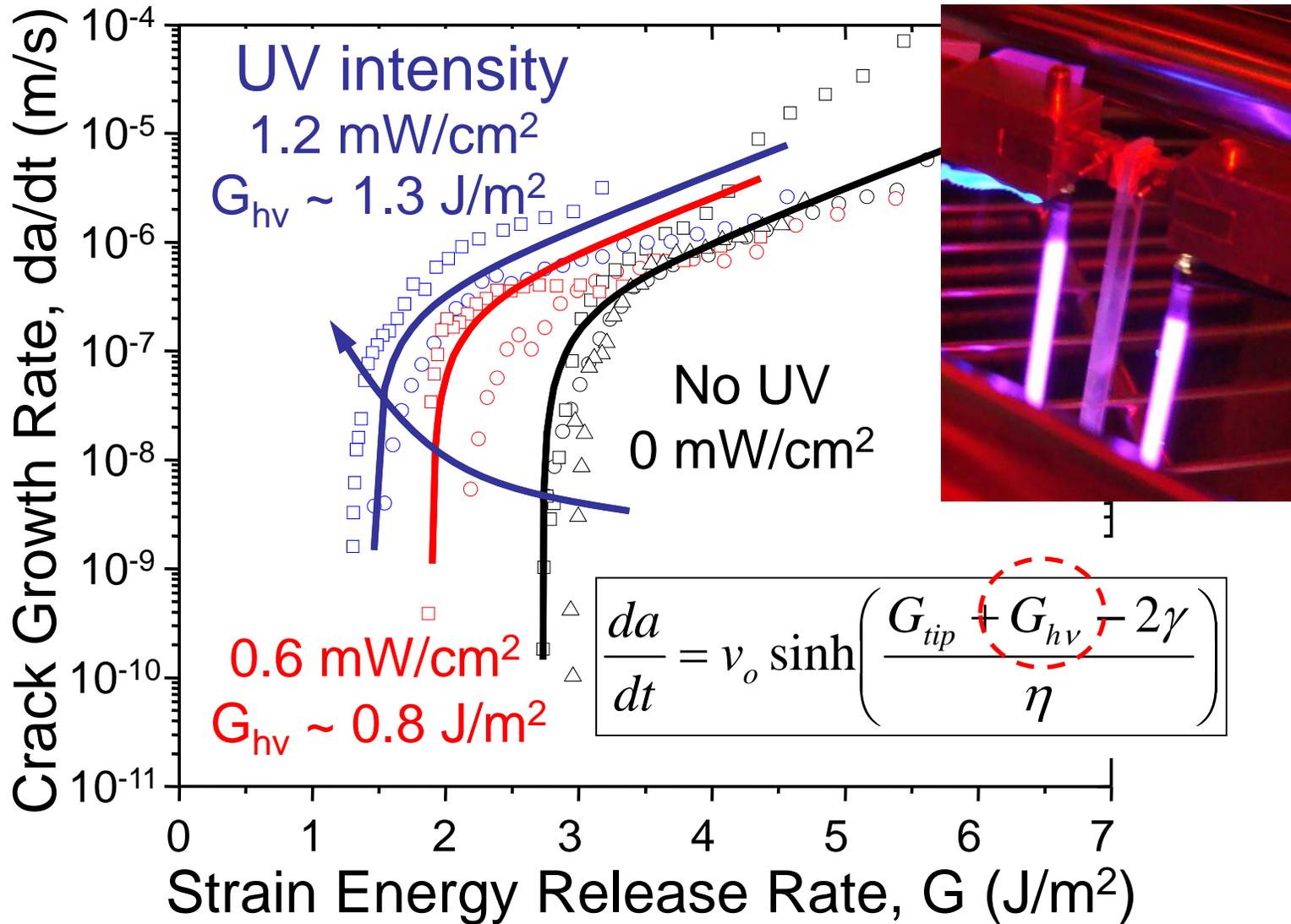
Debonding Kinetics

explore role of:

- UV flux
- humidity, O_2 , OH, ...
- temperature
- mechanical loading

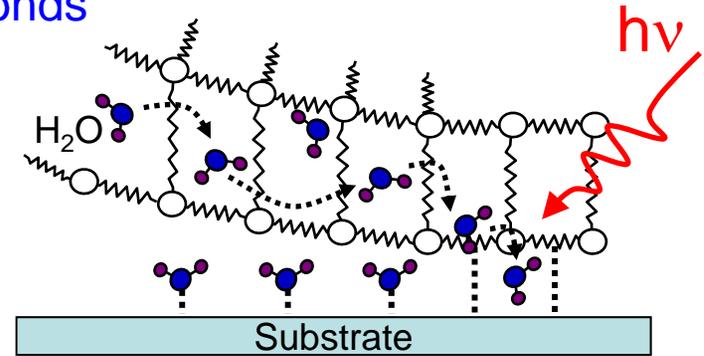
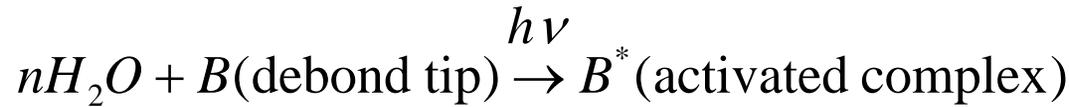
UV Effects on Molecular Bond Rupture

UV Exposure (3.4 eV)



Modeling Bond Rupture Kinetics

- Interaction of moisture with strained debond tip bonds



- Atomistic bond rupture models:

$$\text{rate} = f_o \left[\exp \left(\frac{-U_+^*}{kT} \right) - \exp \left(\frac{-U_-^*}{kT} \right) \right]$$

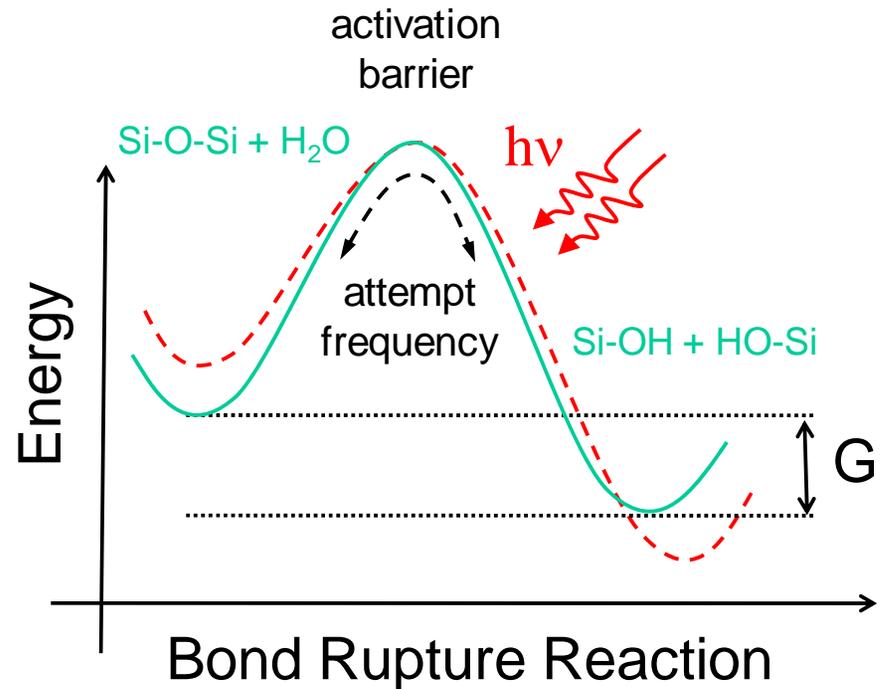
- Damage growth rate:

$$\frac{da}{dt} = v_o \sinh \left(\frac{G_{tip} + G_{hv} + 2\gamma}{\eta} \right)$$

$$v_o = \frac{2 f_o}{Nw} \exp \left(\frac{-u_1}{kT} \right)$$

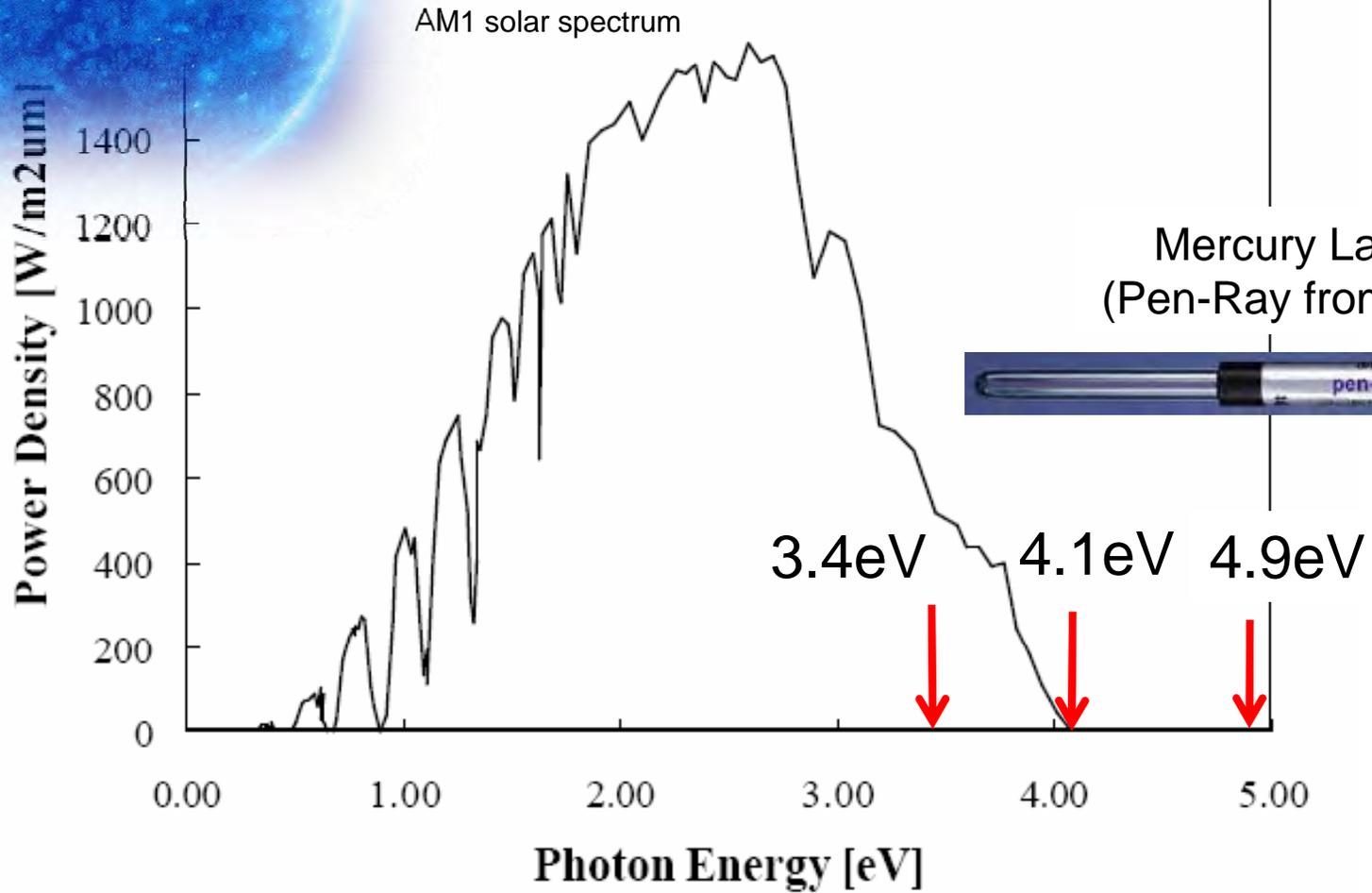
Bond Rupture Parameters

N - bonds per unit area f_o - attempt frequency
 u_o - work of rupture u_1 - energy barrier
 2γ - $N u_o$ η - $2NkT$
 w - crack width



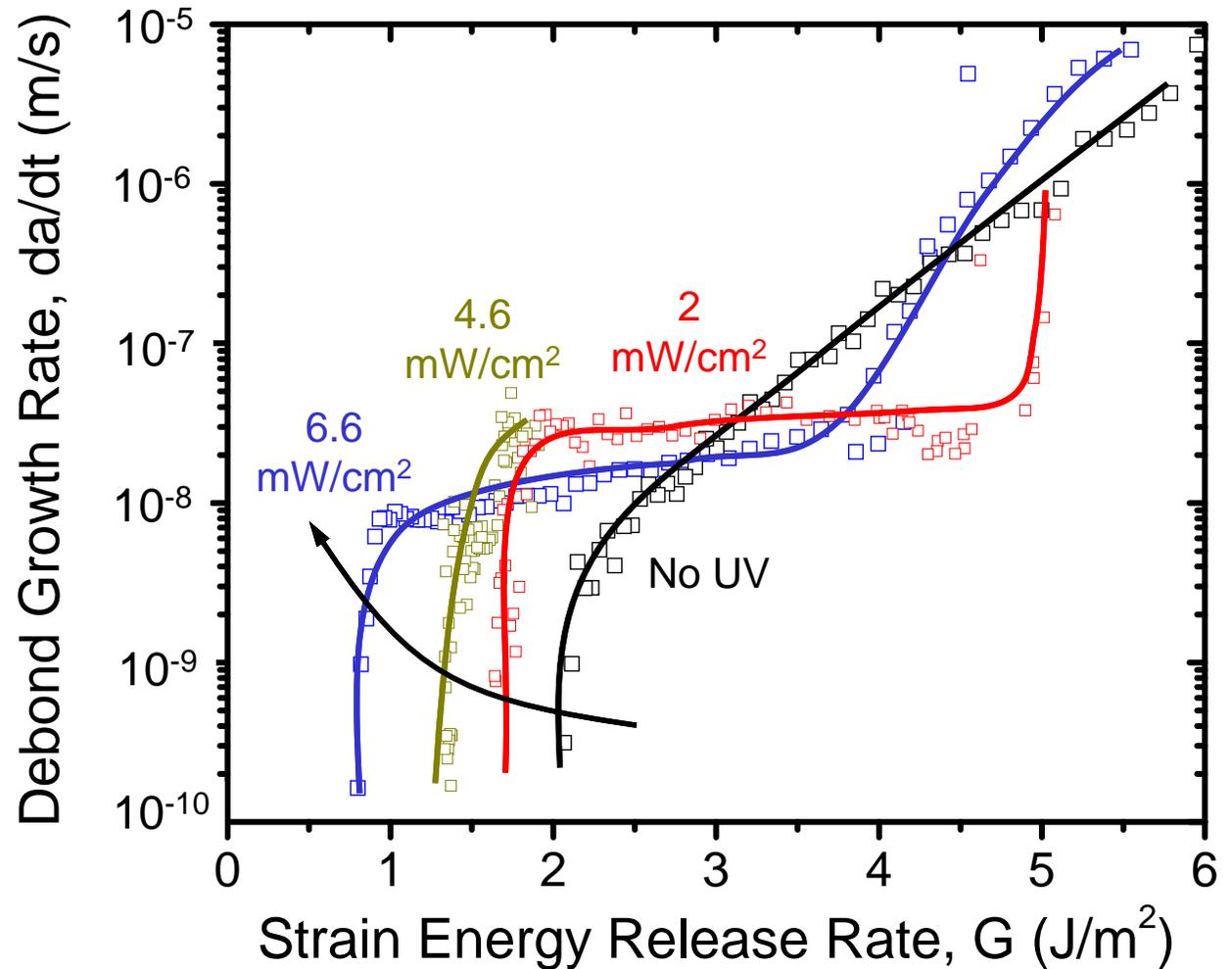
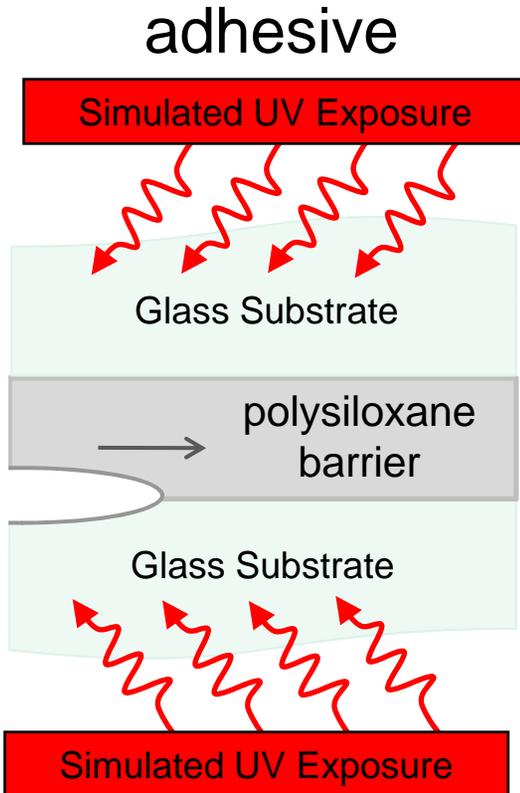
UV Sources

Fluorescent Lamp



UV Effects on Molecular Bond Rupture

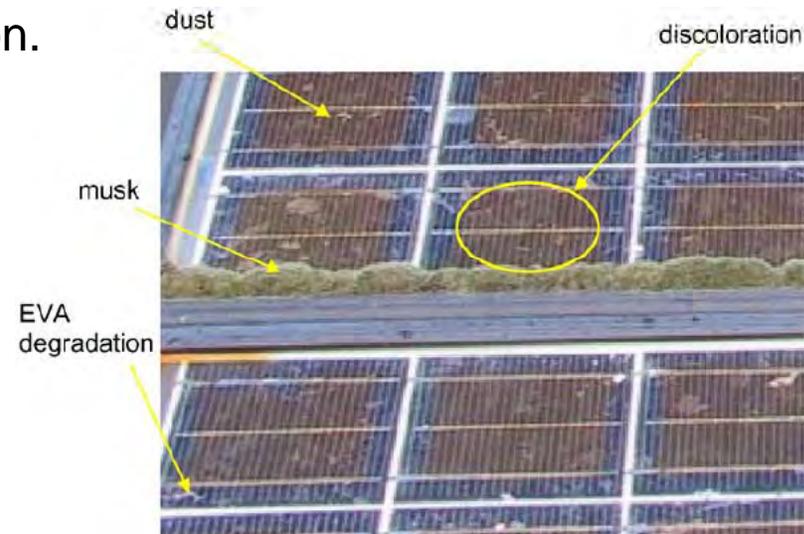
UV exposure 4.9 eV
adhesive failure at 20°C 40%RH



Delamination of EVA-TPE Lamination

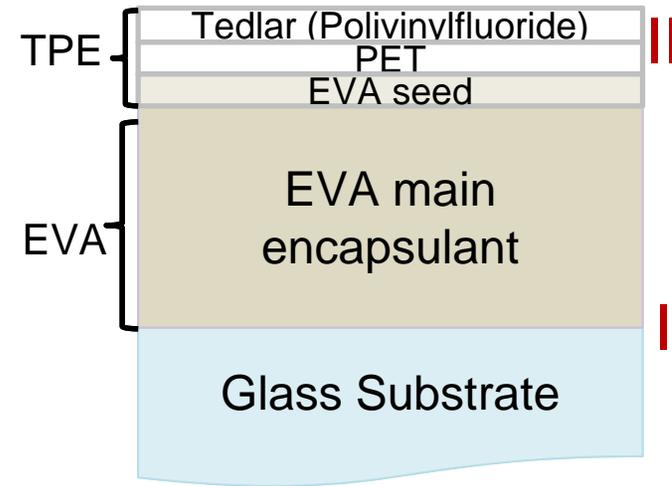
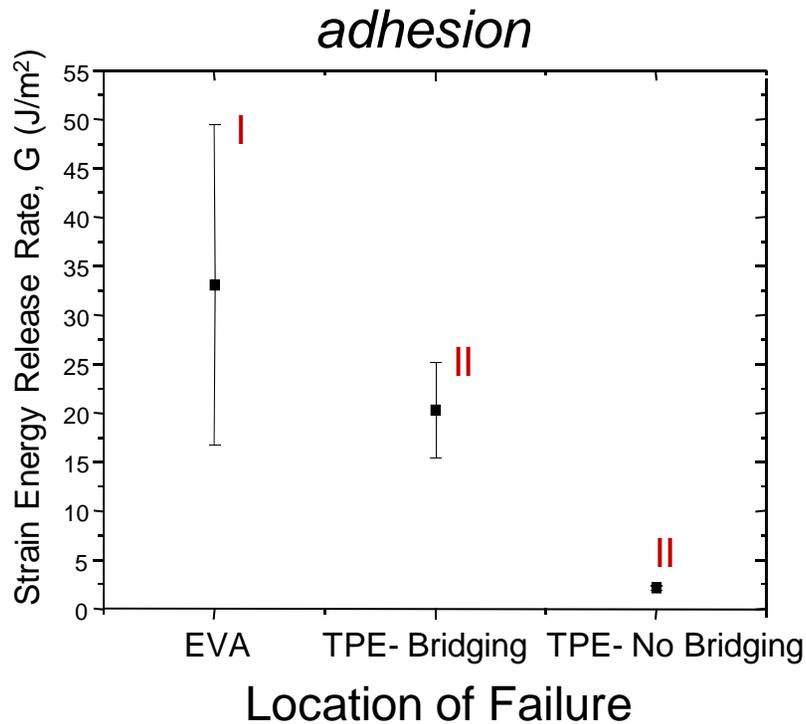
- Poly-ethylene vinyl acetate (EVA) copolymer extensively used by solar module manufacturers, particularly for laminating c-Si photovoltaic modules.
- Good optical properties and high adhesive contact with glass cover and Si cells.
- Inexpensive and relatively easy fabrication.

Parreta Antonio, et al., Solar Energy Materials & Solar Cells, 2005

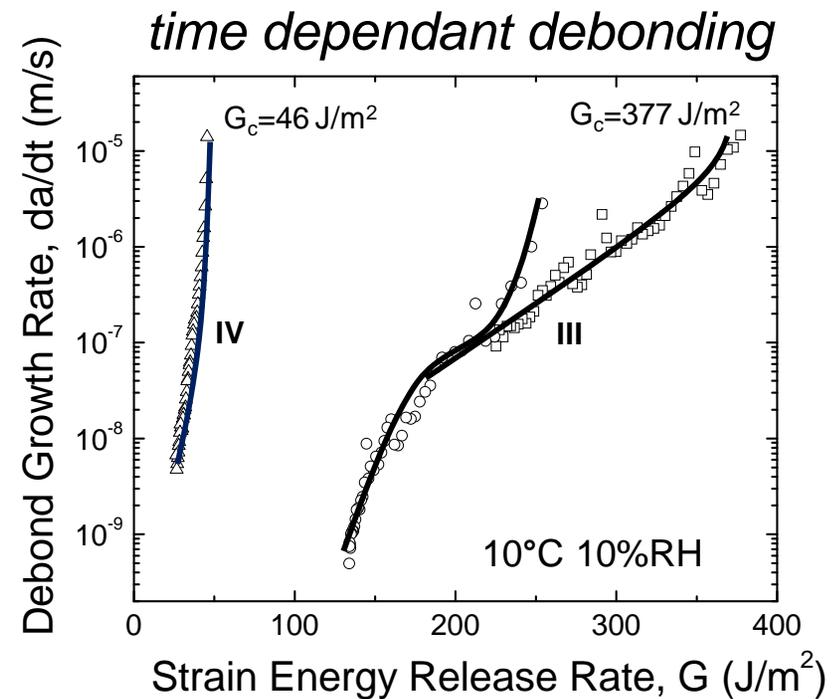


- Delamination can occur between EVA and the front surface of the solar cells.
- More frequent and in hot and humid climates.
- Exposure to atmospheric water and/or ultraviolet radiation leads to EVA decomposition to produce acetic acid, lowering the pH and increasing corrosion.
- EVA $T_g \sim -15^\circ\text{C}$ so lower temperatures may result in “ductile-to-brittle” transition in adhesive/cohesive properties.

Delamination of EVA-TPE Lamination



Interface "I" located between EVA and Glass
 Interface "II" inside the TPE multilayer



Summary for PV Durability and Reliability

We want to engineer durable PV devices and modules with robust and predictable lifetimes.

- Leverage from reliability physics in microelectronics – mechanisms, kinetic models, accelerated tests and life prediction
- Develop metrologies to quantitatively characterize thermo-mechanical properties (e.g. adhesion, cohesion), photochemical and environmental degradation processes
- Are degradation processes coupled and how?
- Kinetic models of damage evolution - basis for life prediction and accelerated testing (effect of operating temperature, environment, mechanical stress, solar flux, etc.)
- Effective transparent barriers with anti-reflective properties and low cost.