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| **Project Title:** | Coupled Thermo-Mechanical and Photo-Chemical Degradation Mechanisms that determine the Reliability and Operational Lifetimes for CPV Technologies |
| **Project Period:** | 10/01/13 – 3/31/17 |
| **Project Budget:** | $1,500,000 |
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| **Recipient:** | Stanford University |
| **Working Partners:** | Spectrolab (Boeing) |
| | National Renewable Energy Laboratory (NREL) |
| **Award Number:** | DE-EE0006343 |
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## Executive Summary

This project sought to identify and characterize the coupled intrinsic photo-chemo-mechanical degradation mechanisms that determine the reliability and operational lifetimes for CPV technologies. Over a three year period, we have completed a highly successful program which has developed quantitative metrologies and detailed physics-based degradation models, providing new insight into the fundamental reliability physics necessary for improving materials, creating accelerated testing protocols, and producing more accurate lifetime predictions.

The tasks for the program were separated into two focus areas shown in the figure below. Focus Area 1, led by Reinhold Dauskardt and Warren Cai with a primary collaboration with David Miller of NREL, studied the degradation mechanisms present in encapsulant materials. Focus Area 2, led by Reinhold Dauskardt and Ryan Brock with a primary collaboration with James Ermer and Peter Hebert of Spectrolab, studied stress development and degradation within internal CPV device interfaces. Each focus area was productive, leading to several publications, including findings on the degradation of silicone encapsulant under terrestrial UV, a model for photodegradation of silicone encapsulant adhesion, quantification and process tuning of antireflective layers on CPV, and discovery of a thermal cycling degradation mechanism present in metal gridline structures.

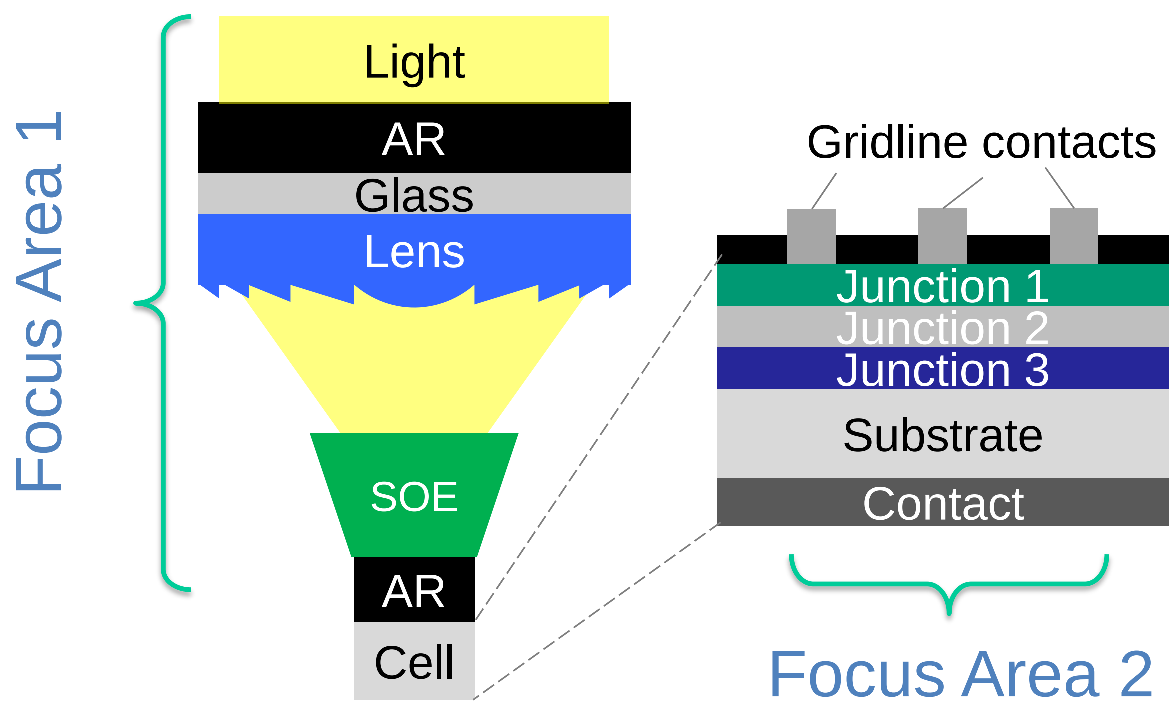


Figure showing the two focus areas of our program.

*Main findings of the study included:*

1. We studied and modelled the effects of terrestrial UV on silicone adhesives for CPV applications generally connecting the secondary optics to the AR coating of the device. The adhesion energy between the silicone to the adjacent interfaces increased by ~2 orders of magnitude with initial UV weathering, and subsequent exposure decreased the adhesion energy related to embrittlement of the bulk silicone. Specimens aged in the outdoor concentrator exhibited a similar increase in adhesion energy with initial exposure and subsequent decrease in adhesion to with prolonged exposure. A fracture mechanics model was developed to model the adhesion energy as a function of cumulative radiant UV exposure and temperature and can be used to predict the behavior of encapsulant materials with accelerated aging test.
2. We developed a science-based framework for predicting the photodegradation of adhesion of silicone encapsulants. Input to the modeling included adhesion results from specimens artificially weathered under three different UV bandpass filters to identify the wavelengths responsible for photodegradation. The threshold damaging wavelength was determined to be 350 nm based on a statistical analysis of samples weathered under the UV filters. The failure of the law of reciprocity was incorporated into the model with statistical analysis of degradation data from the filtered UV exposure. By using an effective temperature, UV irradiance, and UV dose during natural weathering in the solar concentrator, the model shows good agreement (despite the variation in intensity ranging over three orders of magnitude) with the experimentally observed data for specimens weathered with and without heatsinks.
3. The development of the new composite double cantilever adhesion test to probe the reliability of interfaces within multijunction PV devices on fragile germanium substrates. We were able to identify the best combination of processing and materials to produce a resilient, high adhesion antireflective layer. Exposure to the damp heat was confirmed to have a significant detrimental effect on adhesion, primarily due to oxidation within the window layer. This information, along with understanding of the stresses developed in the field, will allow for a much more robust design for reliability in multijunction cells, fostering wider adoption of CPV technologies in terrestrial applications.
4. We made a significant discovery underlying the mechanism of thermal cycling failures at the gridline-semiconductor interface in multijunction photovoltaics. We were able to dispel the previously held notion that this cracking was induced via either fatigue or accumulation of high residual stress within the cell. We showed that the cause of is a combined effect of the work hardening of gridline structures and the stress concentration at the sharp corner formed by the semiconductor cap layer. This information will allow for much more robust design for reliability in multijunction cells, fostering wider adoption of CPV technologies.

## Table of Contents

# Introduction

The statement of purpose and objectives (SOPO) for the program is included below, including all tasks, subtasks, milestones, and go/no-go points. The program was completed as-planned (no modifications to the plan during the 3 years with a 6 month no-cost extension).

## 1. Project Overview

### *a. Background*

Concentrating photovoltaics (CPV) is a leading candidate for large-scale ground-based PV installations. The high efficiency multijunction cell technology used in CPV systems was pioneered in the US and several new light collection strategies offer great potential for utility scale energy production and continued US leadership in the growing CPV market. The possibility of high-volume and cost-effective PV technologies depends critically on their reliability over extended operating lifetimes (> 25 yrs). Ironically, undiscovered degradation modes, the lack of testing metrologies, poor accelerated testing protocols, the almost complete lack of science-based kinetic degradation models, and uncertain lifetimes currently present significant barriers for adoption.

### *b. Objectives*

We sought to identify and characterize the *coupled* intrinsic thermo-mechanical and photochemical degradation mechanisms that determine the reliability and operational lifetimes for CPV technologies. We developed quantitative metrologies to characterize degradation processes during PV field exposures, developed detailed kinetic models of degradation mechanisms, performed the first reliability benchmarking of materials and interfaces in CPV devices and modules, and provided the fundamental materials science and reliability physics for improved materials, accelerated testing protocols, and accurate lifetime predictions. Our degradation models were validated with quantitative experimental results and field testing of representative samples and CPV structures.

### *c. Statement of Novelty*

The novelty of the proposed research is to leverage from our internationally recognized device reliability capabilities to provide the metrologies and scientific basis to characterize, model and predict coupled thermo-mechanical and photo-chemical degradation processes. In addition, we will use CPV systems as an ideal PV research vehicle, applying elevated levels of “stress” parameters (thermal, moisture and environmental species, light intensities, mechanical stresses, complex structures) to exacerbate degradation mechanisms that are likely to occur in PV technologies in general. By starting with CPV systems, we can more quickly leverage (adapt and create) methods developed for the thin film industries (semiconductors and microsystems) so that they may be applied to all PV technologies.

## 2. Technical Work Plan

Our detailed work plan was centered on developing repeatable/scalable metrologies to quantitatively characterize *coupled* thermo-mechanical and photo-chemical degradation of materials and interfaces in the two focus areas critical to CPV reliability. We benchmarked material formulations and representative test structures under a range of simulated and field exposed conditions. Finally, we developed mechanics, physics and chemical-reaction based kinetic degradation models that form the basis for lifetime predictions.

Focus Area 1 examined CPV optics and encapsulation materials and samples obtained from a number of manufactures. We designed and constructed the specimen coupons that were aged and examined. This included laminates containing glass/silicone, bulk PMMA, and glass/acrylic. The selection of specific material formulations (silicones and acrylics) benefitted from feedback from our contacts in the industry, including NuSil Technologies and other material and chemical manufactures. Details including the structure (laminate geometry), size, and materials were chosen for the coupons that will be used.

Focus Area 2 examined the multijunction cells, specifically the antireflection coatings and gridline metallization interconnects required to extract current from the devices. A series of cells designed to elucidate variations in salient compositions, interface chemistry and processing conditions were obtained from Spectrolab. This included adhesion of antireflection (AR) coating and metallization to the semiconductor layers and interactions between front metallization and semiconductor defects.

## 3. Tasks

Tasks and subtasks were *interrelated* and were not necessarily be executed sequentially. The anticipated timing of milestones is listed after the task descriptions.

### Task 1: Metrologies to Characterize Degradation Mechanisms

Research will be centered on metrology development using the coupon specimens to characterize degradation mechanisms in the presence of the synergistic effects of mechanical stress, environmental species, temperature, and UV exposure.

Relevant subtasks and milestones include (subtasks listed may be executed in subsequent years):

- Subtask 1.0: We will consult the PV industry to begin to develop a pareto of CPV thermomechanical failure modes that will help inform our specific degradation studies and the choice of materials and interfaces during the course of the first year of the program. For Focus Area 1 we will consult both module (*e.g*. Emcore, Amonix, Soitec), lens (e.g., Reflexite) and materials (e.g. Walker, DuPont, Dow-

Corning, NuSil, Evonik, Arkema) manufacturers on CPV failure processes for their optical elements and/or materials. In Focus Area 2 we will consult PV cell device manufacturers (e.g. Spectrolab, Solar Junction, Cyrium, Emcore, Azur, Soitec) for their input on the dominant thermomechanical failure processes in single and multijunction cells. This will include the reliability of interfaces with AR coatings and electrical conducting lines. Our information to date from the CPV industry for both focus areas is that delamination of interfaces and the evolution of defects are among the most frequently reported failure modes. This includes defect evolution in optical elements, delamination of encapsulants, and degradation of front metal adhesion in cells, which will be used as the basis for initial sample materials selection and layered test sample design.

- **Milestone (Subtask 1.0):** Present the pareto of CPV failure modes to the industry CPV conferences in 2014.
- Subtask 1.1: Identify optics and encapsulation coupon geometry and materials for Focus Area 1. We plan to select typical materials from monolithic Fresnel lens-based systems including PMMA, silicone-on-glass (SoG) and acrylic-on-glass (AoG) structures that will allow us to simulate field exposure. Materials will be procured from a number of different materials and chemical manufacturers.
- Subtask 1.2: Identify multijunction device structures containing selected metallized grid arrays and AR coating systems for Focus Area 2. Initial structures will include interfaces between front metal and underlying semiconductor device structures and the adhesion of AR coatings on top of device structures.
- **Milestone (Subtasks 1 and 2)**: The partners will agree to the sample design (materials and geometry), and have the components on order or in fabrication. We will include a minimum of two industry partners.
- Subtask 1.3: Demonstrate the successful quantification of the adhesion and thermomechanical characteristics for the test specimens and coupons. The weakest failure path in the structures will be characterized including the adhesion of weak interfaces or the cohesion of weak layers. For Focus Area 1, we anticipate defect evolution in lens materials, delamination of lens attachment, and delamination of encapsulants to be important failure processes. For Focus Area 2, metal adhesion to semiconductor, AR adhesion to cell and evolution of epitaxial defects are expected to be dominant thermomechanical failure modes. Fracture properties will be quantified in accordance with strict fracture mechanics principles involving critical values of the strain energy release rate, $G_c$. Other salient mechanical properties may include the elastic modulus and residual stresses as they related to the degradation or failure process. Baseline optical properties (e.g., transmittance) will also be characterized.
- **Milestone (Subtask 1.3)**: Demonstrate adhesion and thermomechanical measurements using the baseline measurement of unaged (reference) specimens. Adhesion and cohesion studies will involve propagation of delaminations or cracks over at least 100 $mm^2$ and generally represent high levels of statistical significance. Depending on the level of scatter observed, from 2 – 6

samples will be tested for each condition to achieve better than 95% confidence in the results.

- **Go/No-Go Decision Point 1:** The specimen coupons must demonstrate capability to examine the adhesion and thermomechanical characteristics of the material systems used. The coupons may be redesigned, if they do not function properly. This Go/No-Go decision will be based on the ability to generate statistically significant results using the minimum number of tests and meeting the confidence interval mentioned in Milestone (Subtask 1.3). Sample or coupon redesign will be undertaken to isolate interfaces or material layers in order to achieve the requirements of the milestone above.

- Subtask 1.4: Develop capability to perform adhesion and kinetic defect evolution rate measurements subject to aging factors in real-time.

  Selected UV in-situ radiation (UVA and UVB fluorescent lamp together with other UV narrow band spectrum lamps), controlled temperature (-20 to 200C), moisture (inert to 80% RH) and variable mechanical stress. The capability allows the factors to be individually applied, so that their relative significance and synergistic effects on the kinetics of interface separation or defect evolution may be quantified in real time. The rate of crack advancement (bond rupture) in the present Stanford test system may be measured to defect evolution rates as low as ~$10^{-12}$ m/s, allowing the kinetics to be assessed for accurate prediction. We will target a defect evolution rate range for characterization of three orders of magnitude in growth rates, and a minimum defect evolution rate of $10^{-8}$ m/s.

- **Milestone (Subtask 1.4)**: Quantified material and degradation properties for specimens from Focus Area 1 and 2 including salient thermomechanical properties (adhesion, cohesion, film stresses and elastic properties) together with kinetic defect evolution rates under controlled conditions will be characterized and available as input for degradation modeling. Adhesion and cohesion will be characterized using fracture mechanics based testing techniques, film stresses using substrate curvature methods, and elastic properties using conventional indentation, micro-tension or acoustic wave propagation methods as appropriate for the materials and interfaces and in accordance with Subtasks 1.1 through 1.3 and the minimum tests and statistical relevance defined in Milestone (Subtask 1.3).

- Subtask 1.5: Develop initial screening techniques to identify cell structures with latent defects.

  All epitaxial layers contain defects and the evolution of these defects during service represents a significant failure mode. Front metallization deposited on top of semiconductor defects does not always cause immediate failure, leaving latent defects that may fail in the field. This subtask attempts to define a fast, inexpensive method to screen for metal defect interactions.

- **Milestone (Subtask 1.5)**: Initial screening method identified.

- Subtask 1.6: Perform reliability testing on cells that fail the initial electrical screening test to determine if they perform worse than cells that pass the initial electrical screening test. Reliability testing will include thermal cycling, power cycling and steady state electrical bias. Samples stresses electrically in combinations of reverse bias and forward bias to identify conditions that detect metal– defect interactions. Perform reliability tests to verify that the electrical stress does not damage cells that pass the screen test.

- **Go/No-Go Decision Point 2**: Evaluate salient results from experimental studies in Task 1 to ensure required input for models of failure mechanisms are defined and quantified. Material properties include adhesion and cohesion of interfaces and layers quantified in terms of Gc values, defect and crack evolution rates as a

  function of applied G, stress in as deposited films, mechanical strength of deposited films and contacting layers, along with elastic properties as needed to conduct mechanical modeling. Errors in the measurement of less than 20% will be targeted.

- **Milestone (Task 1)**: Salient inputs required to model failure mechanisms are defined and quantified. Material properties include adhesion and cohesion of interfaces and layers quantified in terms of Gc values, defect and crack evolution rates as a function of applied G, stress in as deposited films, mechanical strength of deposited films and contacting layers, along with elastic properties as needed to conduct mechanical modeling. Errors in the measurement of less than 20% will be targeted.

**Task 2: Accelerated Ageing and Longer-Term Field Exposures**

Accelerated ageing and longer-term field exposures of representative test coupons and specimens will be initiated.

Relevant subtasks and milestones include (subtasks listed may be executed in subsequent years):

- Subtask 2.1: Fabrication of field CPV test fixture for samples and coupons in Focus Areas 1 and 2. Reconfigure the existing CPV fixture. The design of the modified CPV fixture will be agreed upon by the partners, the drawings for custom parts submitted for manufacture, and purchased components placed on order. Deploy the CPV fixture in the field (dual axis tracker at NREL), including: mounting; aligning; and specimen incorporation, to achieve prescribed field exposure.

  NREL has a modified CPV module product ("CPV fixture") that may be used (mounted on a tracker at the NREL campus) for the field exposure of Focus Area 1 and Focus Area 2 specimens. The CPV fixture operates by focusing the sun onto a 1cm x 1cm region at nominally 1100x geometric concentration at 15 sites. Specimens will be exposed in the field for prescribed durations, then removed and examined at Stanford, NREL, and Spectrolab to assess the effects of field exposure. The CPV fixture has been used at NREL previously to study the fatigue of the solder die attachment of the multijunction cell, but could be easily reconfigured to accommodate encapsulation and/or cell (metallization, AR) specimens.

- **Milestone (Task 2.1)**: The partners will agree to finalize the fixture design; complete construction of modified CPV module test fixture, including assembly of fixture; placement and alignment on CPV tracker.
- Subtask 2.2: Completion of initial 6 month field CPV fixture aging period. Field CPV fixture will be modified to incorporate subsequent design features and capabilities.
- **Go/No-Go Decision Point 3:** Field exposures must involve sufficient (but not excessive) concentration and elevation of “stress” parameters to produce identifiable degradation, including delamination or change in mechanical characteristics (modulus or yield strength). Characterization will include optical transmittance, the adhesion/cohesion test, XPS and/or ATR-FTIR chemical characterization of the delaminated surfaces, and a combination of optical, SEM and AFM fractography of the test region of at least 1 specimen of each type selected for study (e.g., glass/silicone #1, glass/silicone #2, glass/silicone #3). Routine screening that may involve, for example, optical transmittance or visual examination for degradation, will be undertaken on all field exposed samples. Redesign fixtures and concentration to either increase or decrease exposure conditions as needed.
- **Milestone (Subtask 2.2)**: 15 specimens removed from field CPV fixture after initial 6 month aging period, examined and any required modifications completed. At least one specimen of each type will be subject to the battery of tests described above (e.g., transmittance, adhesion/cohesion, XPS, ATR-FTIR SEM, AFM).
- Subtask 2.3: Field exposures of test structures and coupons to occur in 6 month periods for remaining duration of the program. At least one specimen of each type will be subject to the battery of tests described above (e.g., adhesion/cohesion, XPS, ATR-FTIR SEM, AFM).
- **Milestone (Subtask 2.3**): Extensive set of field exposed specimens harvested and examined for damage and defect evolution processes quantified and available for model verification.
- Subtask 2.4: Indoor weathering of specimens from Focus Areas 1 and 2.

The optics coupons will be aged using a Weather-ometer (where the nominal dose occurs at roughly 10x based on the intensity and continuous 24-hour duration of exposure). Initial temperatures that will be examined are 50, 70, and 90 °C (with the humidity and UV intensity settings maintained the same) so that the activation energy for degradation may be assessed. With robust degradation data, three exposure temperatures are sufficient to produce activation energy values with errors less than 15% of the measured values. A 6-month maximum duration at each temperature is consistent with the duration and budget of the project. Separate batches of coupons may be removed for examination at 1, 2, 3, 4, 5, 6 months cumulative exposure. The completion of each 6 month aging period is significant based on the number of specimens processed (aged) for testing and the time involved. Insight from subtask 1.4 may be applied (humidity setting) to make the best use of the Weather-ometer ageing.

- **Milestone (Subtask 2.4)**: Specimens (9 replicates of silicone/glass, silicone/acrylic, acrylic) removed from Weather-ometer after initial 6 month aging period and examined. Characterization will include optical transmittance, the adhesion/cohesion tests, XPS and ATR-FTIR chemical characterization of the delaminated (or fractured) surfaces, SEM and AFM fractography of at least 1 specimen of each type.
- **Go/No-Go Decision Point 3:** Indoor exposures must involve sufficient (but not excessive) concentration and elevation of “stress” parameters to produce identifiable degradation. A threshold for identifiable degradation will be considered to be > 5% change in the thermomechanical property or defect distribution of interest. Conditions may need to be increased or decreased as needed.
- Subtask 2.5: Completion of second and third 6 month weather-ometer aging period.
- **Milestone (Subtask 2.5)**: Specimens removed from weather-ometer after second and third 6 month aging period and examined. At least one specimen of each type will be subject to the battery of tests (transmittance, adhesion/cohesion, XPS, ATR-FTIR, SEM and AFM).
- Subtask 2.6: Measure intrinsic material property degradation for Focus Area 1 (optics and encapsulation) and Focus Area 2 (multijunction device, anti-reflective coatings, and metallization grid) including adhesion/cohesion, mechanical stresses, thickness, optical characteristics, defect distributions, and failure/ damage sites.
- **Milestone (Subtask 2.6)**: Identify principal failure mechanisms and their dependence on ageing conditions to provide validation data for degradation model development.

**Task 3: Physics-Based Degradation Model Development**

An important aspect of the research is to develop physics-based mechanistic models to describe the kinetics of degradation and defect evolution under service conditions. We will use physics- and chemical-reaction rate models involving a range of kinetic parameters (degradation rate, activation energy, $G_c$ for adhesion and/or cohesion, rate of crack growth) to rationalize the effects of materials chemistry, environmental species, mechanical stress, and UV photon energy and flux on the kinetics of defect evolution and degradation. The models are intended to capture the essential physics and mechanics of the degradation process, and provide a predictive capability as a function of salient variables like the applied mechanical loads or layer stresses, temperature, moisture content of the environment, on the loss of adhesion, rate of defect evolution, and change in other material properties such as the elastic properties of the material layers.

Relevant subtasks and milestones include (subtasks listed may be executed in subsequent years):

- Subtask 3.1: Formulation of mechanics model to describe loss of interfacial adhesion and fracture resistance for results obtained from Subtask 1.4. Models will account for the changes in inherent viscoelastic and mechanical deformation properties of the materials.

- **Milestone (Subtask 3.1)**: Initial formulation of mechanics models capable of describing the degradation of inherent adhesive and cohesive properties of pristine and aged structures from focus areas 1 and 2. Typical inputs to the models may include thermomechanical properties like the adhesion of interfaces, the cohesive fracture resistance of layers, the dependence of these properties on interface chemistry and adjacent layer composition, and their dependence on testing or exposure conditions that include temperature and relative humidity. Model outputs may include predictions of the time dependent loss of adhesion of interfaces, the rate of defect evolution in terms of salient exposure or ageing conditions.

- Subtask 3.2: Development of physics and chemical reaction rate models capable of describing the time-dependent kinetics of defect evolution measured under simulated and field solar exposure conditions. Experimental data to be obtained from Task 1 and include the effects of in-situ mechanical stress, temperature, moisture, and UV exposure. Validation of the models will be undertaken to a high level of statistical significance and models should be predictive to within the scatter inherent in the data. For example, comparison of the measured delamination growth rate of interfaces in solar back sheet structures as a function of mechanical loads, temperature and RH as shown in Fig 5 of the technical proposal, reveals that the accompanying models we have developed can predict growth rates to better than 5%, within the scatter of the measured data. It is not possible to predict if such fidelity in model predictions and resulting behavior will be possible for all degradation processes anticipated to be studied, but where ever possible, we will attempt to construct models of the fundamental failure mechanisms that provide predictive capabilities that are accurate to at least 10% of the measured data.

- **Milestone (Subtask 3.2)**: Experimentally validated degradation models capable of describing the time-dependent change in salient materials and fracture properties along with the kinetic evolution of defects that are accurate to at least 10% of the measured data. Specific parameters as noted in the subtasks above will include applied mechanical loads or layer stresses, temperature, moisture content of the environment and UV exposure conditions.

- Subtask 3.3: Incorporation of multi-scale models including finite element analysis to account for large scale deformation in test structures along with molecular dynamics simulations of defect tip regions to account for local molecular relaxation.

- **Milestone (Subtask 3.3)**: Multi-scale physics and mechanics models in place to fully describe degradation processes and experimental results from Task 1.

### Task 4: Model Verification and Lifetime Predictions

Our degradation models will have been validated using experimentally measured data obtained in Task 1 under both pre-aged and in-situ ageing conditions. This task will be to validate the degradation models using data collected from samples after accelerated ageing and field exposure in Task 2, and to employ the models to make life-time predictions for components and structures critical for the reliability of CPV technologies.

Relevant subtasks and milestones include:

- Subtask 4.1: Using the degradation results obtained after accelerated ageing of samples in Subtask 2.4, 2.5, and 2.6 employ degradation models to predict the extent of damage and defect evolution observed.
- Subtask 4.2: Based on the predictive capabilities of the models and their application to the specific degradation observed in the accelerated ageing in subtask 2.4, 2.5, and 2.6, the models may need to be adapted to account for unforeseen or unknown synergistic interactions.
- **Milestone (Task 4.2)**: Validation of degradation models and their predictive capabilities for specimens exposed to accelerated ageing conditions. Validation of the models will involve assessing their ability to model trends in the adhesion and thermomechanical properties with ageing or field exposures. For example, we will validate defect evolution rate models by demonstrating that they provide consistent predictions of the defect evolution rates as a function of applied loads, temperature and relative humidity of the environment. Yet other validation may involve the ability to predict the decrease in the adhesion energy of interfaces with ageing or exposure.
- Subtask 4.3: Using the degradation results obtained after field exposures of samples in Subtask 2.3, employ degradation models to predict the extent of damage and the defect evolution observed.
- Subtask 4.4: Based on the predictive capabilities of the models and their application to the specific degradation observed after field exposures in subtask 2.3, the models may need to be adapted to account for unforeseen or unknown synergistic interactions.
- **Milestone (Task 4.4)**: Validation of degradation models and their predictive capabilities for specimens exposed to field exposures.
- Subtask 4.5: Application of the degradation models to make lifetime predictions for CPV components and structures critical for CPV reliability. Specific interfaces and materials are noted in the subtask 1.0 and our studies will seek to include additional materials and interfaces as they are identified in the development of the pareto of CPV thermomechanical failure modes along with our own ageing and field exposure studies. Provide estimated statistical significance of the model predictions using analysis of the statistical variance of the degradation models.
- **Final Goal:** Our final goal is to validate the physics- and chemical-reaction based kinetic degradation models and their predictive capabilities for specimens exposed to accelerated ageing and field exposures. They are intended to form the basis for lifetime predictions for CPV technologies.

**Task 5: Knowledge Transfer**

Knowledge transfer from the program will be ensured through a number of mechanisms. The information gained in the program will be disseminated by presentations at a wide range of conferences and workshops attended by the team investigators. Information will be disseminated directly to collaborators in a range of new and existing interactions with industry, research lab and academic researchers in the PV area broadly and through the BAPVC. Finally, publications will be prepared and submitted to peer-reviewed journals through the course of the program describing metrology, experimental results, models, and predictions.

- **Milestone 5.1:** Present the pareto that includes a refined understanding based on the results of tasks 1-4 concerning CPV failure modes to the CPV industry standard meetings, including the IEC WG7 (semi-annual) and International Quality Assurance Task-Group 9.
- **Milestone 5.2:** Preparation of international conference abstracts for presentation in Years 2 and 3 of the program of degradation studies in Focus Areas 1 and 2.
- **Milestone 5.3:** Preparation and submission of peer reviewed journal publications describing degradation process characterization and modeling for Focus Areas 1 and 2.

## Milestones

The anticipated timing of the milestones is as follows:

Year 1(Q1):

- **Milestone (Subtasks 1 and 2)**: The partners will agree to the sample design (materials and geometry), and have the components on order or in fabrication. We will include a minimum of two industry partners.

Year 1(Q2):

- **Milestone (Subtask 1.5)**: Initial screening

method identified. Year 1(Q3):

- **Milestone (Subtask 1.0):** Present the pareto of CPV failure modes to the industry CPV conferences in 2014.
- **Milestone (Task 2.1)**: The partners will agree to finalize the fixture design; complete construction of modified CPV module test fixture, including assembly of fixture; placement and alignment on CPV tracker.

Budget Period 1 Year 1(Q4):

- **Go/No-Go Decision Point 1:** The specimen coupons must demonstrate capability to examine the adhesion and thermomechanical characteristics of the material systems used. The coupons may be redesigned, if they do not function properly. This Go/No-Go decision will be based on the ability to generate statistically significant results using the minimum number of tests and meeting the confidence interval mentioned in Milestone (Subtask 1.3). Sample or coupon redesign will be undertaken to isolate interfaces or material layers in order to achieve the requirements of the milestone above.

Year 2(Q1):

- **Milestone (Subtask 1.3)**: Demonstrate adhesion and thermomechanical measurements using the baseline measurement of unaged (reference) specimens. Adhesion and cohesion studies will involve propagation of delaminations or cracks over at least 100 $mm^2$ and generally represent high levels of statistical significance. Depending on the level of scatter observed, from 2 – 6 samples will be tested for each condition to achieve better than 95% confidence in the results.
- **Milestone (Subtask 2.4)**: Specimens (9 replicates of silicone/glass, silicone/acrylic, acrylic) removed from Weather-ometer after initial 6 month aging period and examination initiated. Characterization will include optical transmittance, the adhesion/cohesion tests, XPS and ATR-FTIR chemical characterization of the delaminated (or fractured) surfaces, SEM and AFM fractography of at least 1 specimen of each type.

Year 2(Q2):

- **Milestone (Subtask 2.2)**: 15 specimens removed from field CPV fixture after initial 6 month aging period, examined and any required modifications completed. At least one specimen of each type will be subject to the battery of tests described above (e.g., transmittance, adhesion/cohesion, XPS, ATR-FTIR SEM, AFM).

Year 2(Q3):

- **Milestone (Subtask 3.1)**: Initial formulation of mechanics models capable of describing the degradation of inherent adhesive and cohesive properties of pristine and aged structures from focus areas 1 and 2. Typical inputs to the models may include thermomechanical properties like the adhesion of interfaces, the cohesive fracture resistance of layers, the dependence of these properties on interface chemistry and adjacent layer composition, and their dependence on testing or exposure conditions that include temperature and relative humidity. Model outputs may include predictions of the time dependent loss of adhesion of interfaces, the rate of defect evolution in terms of salient exposure or ageing conditions.

Budget Period 2 Year 2(Q3)

- **Go/No-Go Decision Point 2**: Evaluate salient results from experimental studies in Task 1 to ensure required input for models of failure mechanisms are defined and quantified. Material properties include adhesion and cohesion of interfaces and layers quantified in terms of Gc values, defect and crack evolution rates as a function of applied G, stress in as deposited films, mechanical strength of deposited films and contacting layers, along with elastic properties as needed to conduct mechanical modeling. Errors in the measurement of less than 20% will be targeted.

Year 2(Q4):

- **Milestone (Subtask 2.3**): Second set of field exposed specimens harvested and examined for damage and defect evolution processes quantified and available for model verification.

- **Milestone 5.1:** Present the pareto that includes a refined understanding based on the results of tasks 1-4 concerning CPV failure modes to the CPV industry standard meetings, including the IEC WG7 (semi-annual) and International Quality Assurance Task-Group 9.

- **Milestone 5.2:** Preparation of international conference abstracts for presentation in Years 2 and 3 of the program of degradation studies in Focus Areas 1 and 2.

Budget Period 2 Year 2(Q4)

- **Go/No-Go Decision Point 3:** Field exposures must involve sufficient (but not excessive) concentration and elevation of “stress” parameters to produce identifiable degradation, including delamination or change in mechanical characteristics (modulus or yield strength). Characterization will include optical transmittance, the adhesion/cohesion test, XPS and/or ATR-FTIR chemical characterization of the delaminated surfaces, and a combination of optical, SEM and AFM fractography of the test region of at least 1 specimen of each type selected for study (e.g., glass/silicone #1, glass/silicone #2, glass/silicone #3). Routine screening that may involve, for example, optical transmittance or visual examination for degradation, will be undertaken on all field exposed samples. Redesign fixtures and concentration to either increase or decrease exposure conditions as needed.

Year 3(Q1):

- **Milestone (Subtask 1.4)**: Quantified material and degradation properties for specimens from Focus Area 1 and 2 including salient thermomechanical properties (adhesion, cohesion, film stresses and elastic properties) together with kinetic defect evolution rates under controlled conditions will be characterized and available as input for degradation modeling. Adhesion and cohesion will be characterized using fracture mechanics based testing techniques, film stresses using substrate curvature methods, and elastic properties using conventional indentation, micro-tension or acoustic wave propagation methods as appropriate for the materials and interfaces and in accordance with Subtasks 1.1 through 1.3 and the minimum tests and statistical relevance defined in Milestone (Subtask 1.3).

Year 3(Q2):

- **Milestone (Task 1)**: Salient inputs required to model failure mechanisms are defined and quantified. Material properties include adhesion and cohesion of interfaces and layers quantified in terms of Gc values, defect and crack evolution rates as a function of applied G, stress in as deposited films, mechanical strength of deposited films and contacting layers, along with elastic properties as needed to conduct mechanical modeling. Errors in the measurement of less than 20% will be targeted.
- **Milestone (Subtask 3.2)**: Experimentally validated degradation models capable of describing the time-dependent change in salient materials and fracture properties along with the kinetic evolution of defects that are accurate to at least 10% of the measured data. Specific parameters as noted in the subtasks above will include applied mechanical loads or layer stresses, temperature, moisture content of the environment and UV exposure conditions.

Year 3(Q3):

- **Milestone (Subtask 2.5)**: Specimens removed from weather-ometer after second and third 6 month aging period and examined. At least one specimen of each type will be subject to the battery of tests (transmittance, adhesion/ cohesion, XPS, ATR-FTIR, SEM and AFM).
- **Milestone (Subtask 2.6):** Identify principal failure mechanisms and their dependence on ageing conditions to provide validation data for degradation model development.
- **Milestone (Subtask 3.3)**: Multi-scale physics and mechanics models in place to fully describe degradation processes and experimental results from Task 1.

Year 3(Q4):

- **Milestone (Task 4.2)**: Validation of degradation models and their predictive capabilities for specimens exposed to accelerated ageing conditions. Validation of the models will involve assessing their ability to model trends in the adhesion and thermomechanical properties with ageing or field exposures. For example, we will validate defect evolution rate models by demonstrating that they provide consistent predictions of the defect evolution rates as a function of applied loads, temperature and relative humidity of the environment. Yet other validation may involve the ability to predict the decrease in the adhesion energy of interfaces with ageing or exposure.
- **Milestone (Task 4.4)**: Validation of degradation models and their predictive capabilities for specimens exposed to field exposures.
- **Milestone 5.3:** Preparation and submission of peer reviewed journal publications describing degradation process characterization and modeling for Focus Areas 1 and 2.
- **Final Goal:** Our final goal is to validate the physics- and chemical-reaction based kinetic degradation models and their predictive capabilities for specimens exposed to accelerated ageing and field exposures. They are intended to form the basis for lifetime predictions for CPV technologies.

**List of Acronyms Used**

AFM – Atomic Force

Microscopy AR – Anti

Reflection

ATR-FTIR – Attenuated Total Internal Reflectance Fourier Transmission

Infrared Spectroscopy BAPVC – Bay Area Photovoltaic Consortium

SEM – Scanning Electron

Microscopy UV – Ultraviolet

CPV – Concentrated Photovoltaics

XPS – X-Ray Photo-Spectroscopy

## Project Background, Results and Discussion

Included below is an abstract and selected sections (with figures and **Background** references) from each of our four published works produced from this program. Each of these represents a comprehensive write-up of the completed work (**Results and Discussion**), including experimental methods, literature background, and future work (**Path Forward**).

# Degradation of Thermally-Cured Silicone Encapsulant under Terrestrial UV

Can Cai, David C. Miller, Ian A. Tappan, Reinhold H. Dauskardt

Concentrator photovoltaic (CPV) modules operate in extreme conditions, including enhanced solar flux, elevated operating temperature, and frequent thermal cycling. Coupled with active environmental species such as oxygen and moisture, the operating conditions pose a unique materials challenge for guaranteeing operational lifetimes of greater than 25 years. Specifically, the coatings and encapsulants used in the optical elements are susceptible to environmental degradation during operation. For example, the interfaces must remain in contact to prevent optical attenuation and thermal runaway. We developed fracture mechanics based metrologies to characterize the adhesion of the silicone encapsulant and its adjacent surfaces, as well as the cohesion of the encapsulant. Further, we studied the effects of weathering on adhesion using an outdoor concentrator operating in excess of 1100 times the AM1.5 direct irradiance and in indoor environmental chambers with broadband ultraviolet (UV) irradiation combined with controlled temperature and humidity. We observed a sharp initial increase in adhesion energy followed by a gradual decrease in adhesion as a result of both outdoor concentrator exposure and indoor UV weathering. We characterized changes in mechanical properties and chemical structures using XPS, FTIR, and DMA to understand the fundamental connection between mechanical strength and the degradation of the silicone encapsulant. We developed physics based models to explain the change in adhesion and to predict operational lifetimes of the materials and their interfaces.

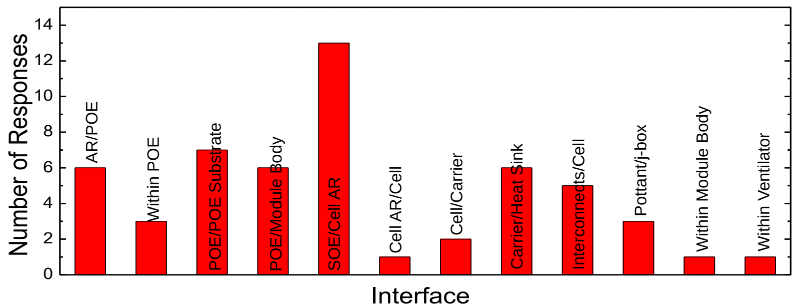


Figure 1. Pareto of critical adhesive interfaces for study in CPV modules. 13 CPV module or optics manufacturers were surveyed to identify the most critical interfaces. The attachment of the secondary optical element to the anti-reflective coating of the multi-junction cell was determined to be the most critical for CPV reliability.

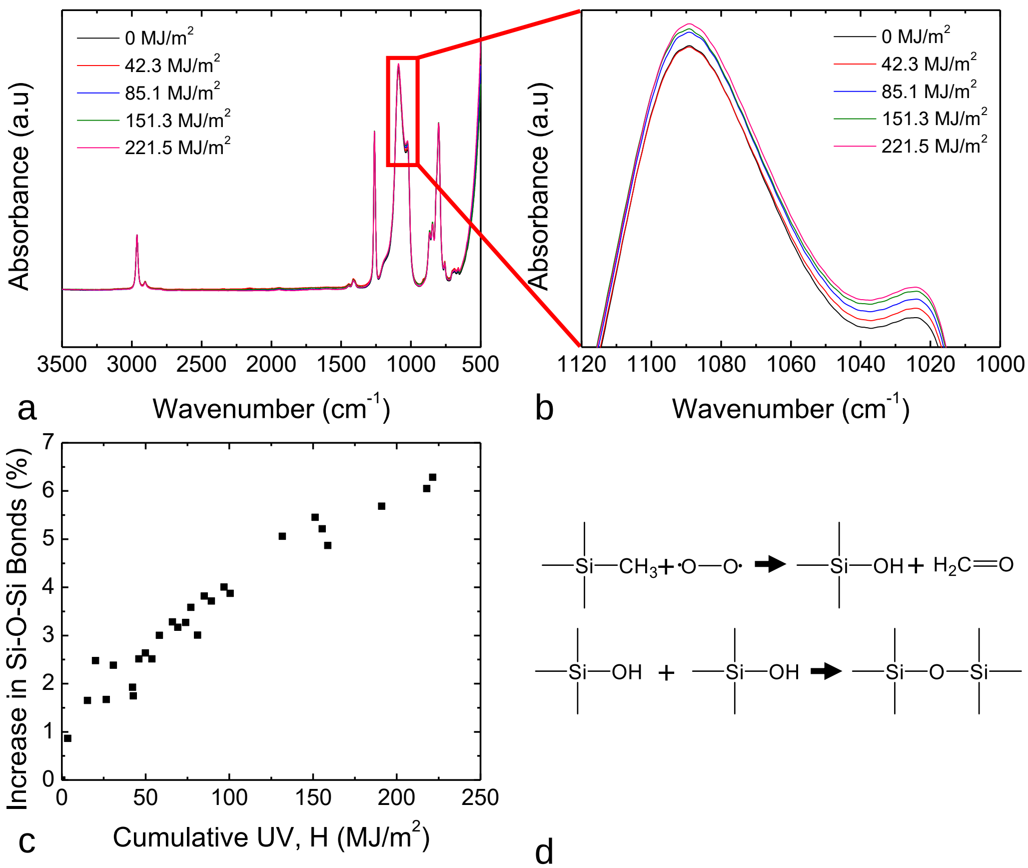


Figure 2. Transmission FT-IR characterization of silicone after UV exposure (a) (b) showed an increase in intensity for the Si-O stretching mode peak with increased cumulative radiant UV exposure. The percentage increase in Si-O bonds (c) can be calculated using the relative peak intensity at different cumulative radiant UV exposure. A possible reaction scheme (d) for the oxidation of the silicone involves the formation of crosslinks following from UV mediated scission methyl sidegroups.

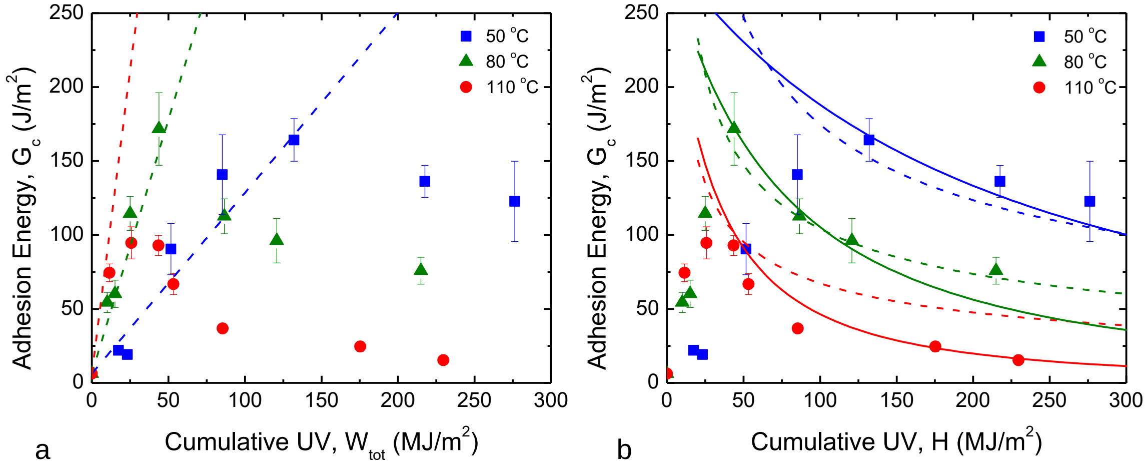


Figure 3. Overlay of the experimental and modeled behavior for UV aged silicone encapsulant. The linear fit (a) from Eq. 4 characterizes the initial increase in adhesion. The power function (b) from Eq. 6 characterizes the decrease in cohesion with the dotted line representing the ideal $M_c^{1/2}$ scaling for a planar crack and the solid line representing the fitted $M_c^{1.66}$ scaling for a meandering crack.

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# Framework for predicting the photodegradation of adhesion of silicone encapsulants

Can Cai, David C. Miller, Ian A. Tappan, Reinhold H. Dauskardt

We developed a framework to predict and model the photodegradation of adhesion and cohesion of a silicone encapsulant for concentrator photovoltaic applications. Silicone encapsulant specimens were artificially weathered under narrow band UV filters to determine the effects of individual wavelengths within the UV spectrum on the photodegradation of the cohesion of encapsulant material and its adhesion with adjacent interfaces. The threshold wavelength, signifying the upper bound of the damaging action spectrum for the silicone, was identified from the results. In addition, specimens were artificially weathered with different relative humidities to understand the effects of moisture on the rate of photodegradation. The adhesion energy was measured using a fracture mechanics approach. The complementary delaminated surfaces were characterized to determine the failure pathway and chemistry changes resulting from photodegradation. A previously developed model was modified to account for the effects of damaging wavelengths in the terrestrial solar spectrum and reciprocity law failure due to varying UV intensity during weathering. With these modifications, the model showed good agreement with the behavior of the silicone encapsulant exposed in an outdoor solar concentrator simulating concentrator photovoltaics operating conditions. Similar studies can be adopted to develop models that can have high predictive accuracies based on accelerated aging studies.

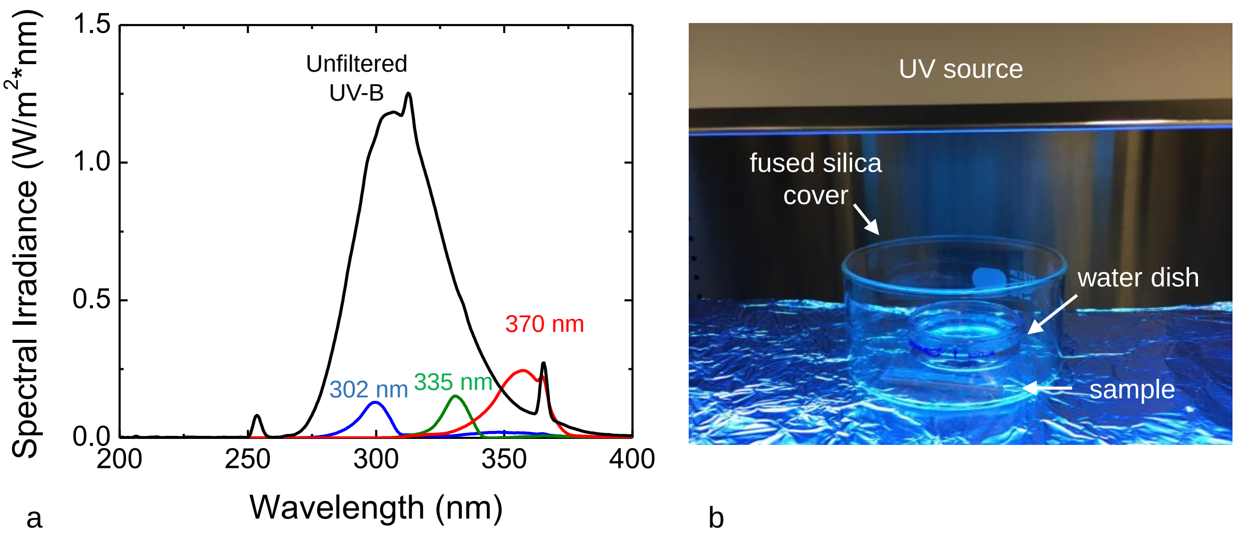


Figure 1. (a) Spectral irradiance of the unfiltered UV-B source superimposed with the spectra for the 302 nm, 335 nm, and 370 nm UV filters used for artificial UV weathering in environmental chambers and (b) experimental set up for samples weathered in 100% relative humidity.

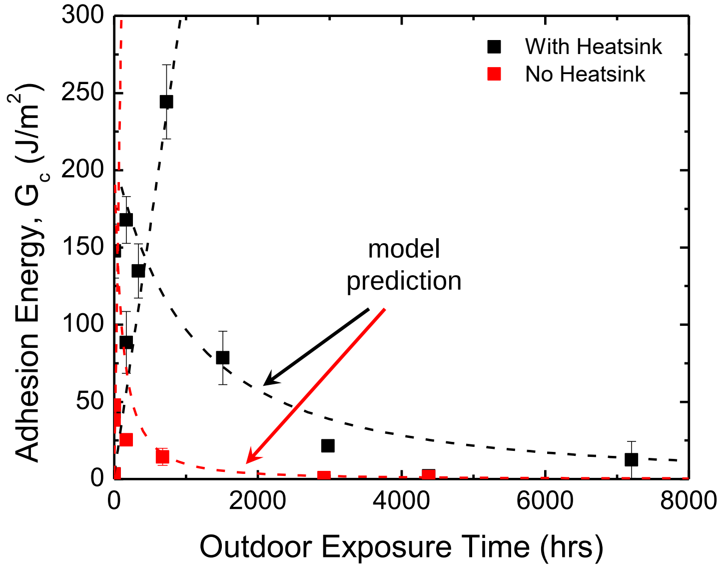


Figure 6. The data from samples weathered in the outdoor concentrator both with and without heatsinks are plotted with the predicted adhesion energy from the model.

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# Quantitative Adhesion Characterization of Antireflective Coatings in Multijunction Photovoltaics

Ryan Brock, Raunaq Rewari, Fernando D. Novoa, Peter Hebert, James Ermer, David C. Miller, Reinhold H. Dauskardt

We discuss the development of a new composite dual cantilever beam (cDCB) thin-film adhesion testing method, which enables the quantitative measurement of adhesion on the thin and fragile substrates used in multijunction photovoltaics. In particular, we address the adhesion of several 2- and 3-layer antireflective coating systems on multijunction cells. By varying interface chemistry and morphology through processing, we demonstrate the marked effects on adhesion and help to develop an understanding of how high adhesion can be achieved, as adhesion values ranging from 0.5 J/m$^2$ to 10 J/m$^2$ were measured. Damp heat (85 °C/85% RH) was used to invoke degradation of interfacial adhesion. We demonstrate that even with germanium substrates that fracture relatively easily, quantitative measurements of adhesion can be made at high test yield. The cDCB test is discussed as an important new methodology, which can be broadly applied to any system that makes use of thin, brittle, or otherwise fragile substrates.

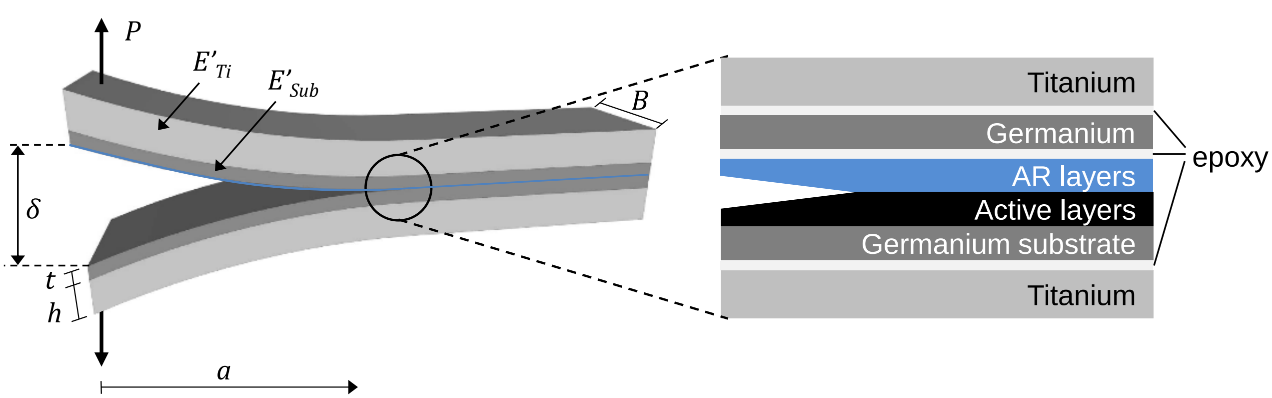


**Figure 2.** The composite dual cantilever beam (cDCB) specimens consist of a blank germanium beam adhered to the as-deposited multijunction structures, and then further adhered to two titanium beams. These tough outer beams allow for testing to continue beyond fracture events in the fragile germanium beams.

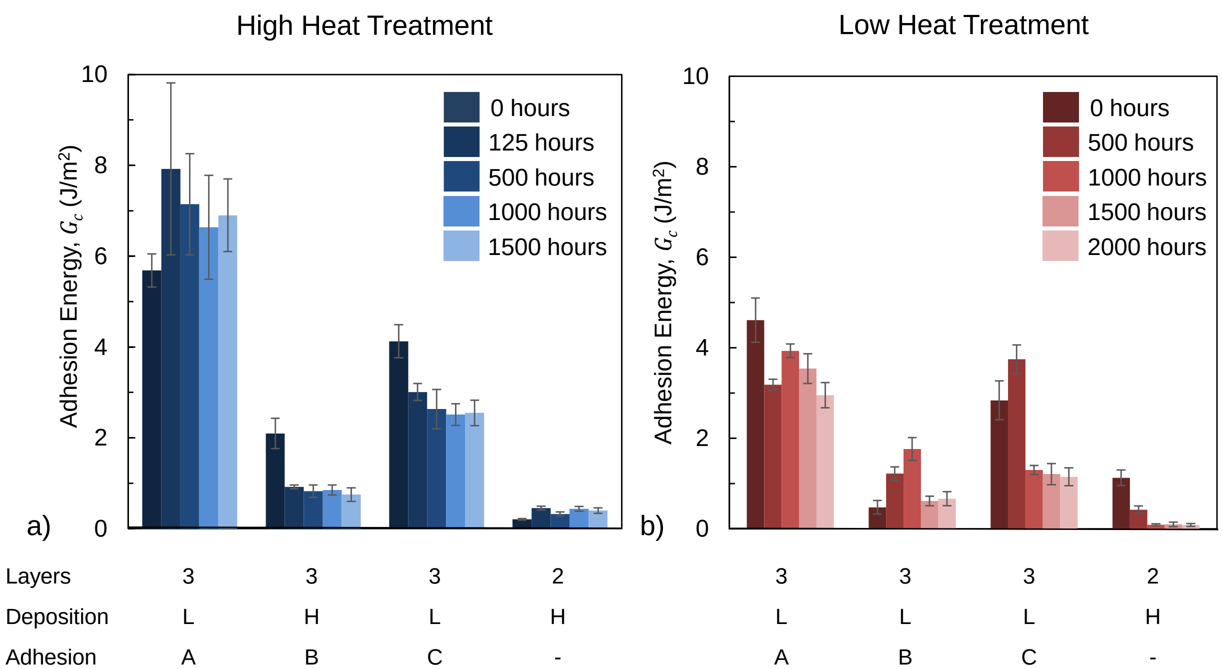


**Figure 5.** Adhesion energy for antireflective layers aged in the 85ºC/85% RH Damp Heat condition for up to 2000 hours for coatings treated under (a) high heat and (b) low heat. Each bar corresponds to multiple $G_c$ measurements across each sample and at least three samples.

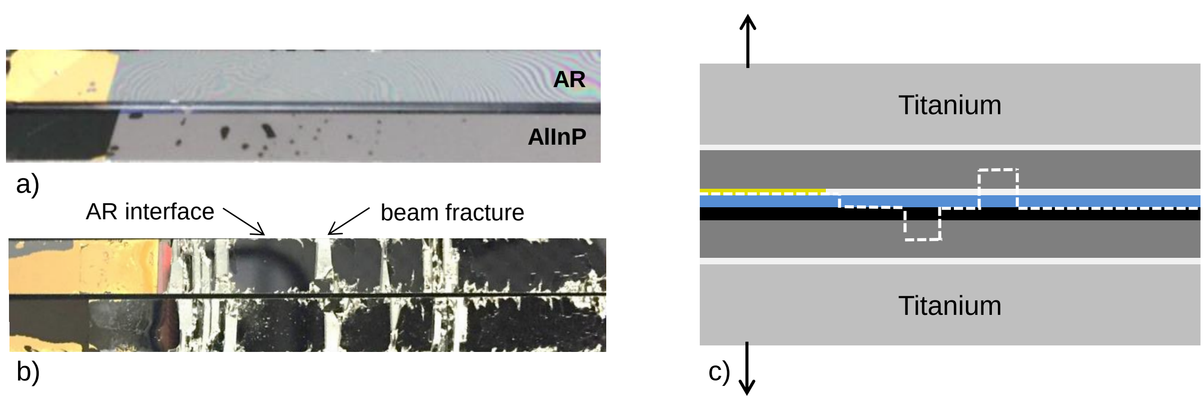


**Figure 7.** In cases of (a) weak adhesion, germanium beams remain perfectly intact, but for (b) stronger adhesion, the germanium fractures and the crack path can meander before returning to the antireflective layer interface, (c) as schematically represented within the cDCB structure, where the white dotted line illustrates a representative local crack path. Note initial crack initiation is achieved using a gold release layer, as seen at the left in images (a) and (b).

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# Degradation of Multijunction Photovoltaic Gridlines Induced via Thermal Cycling

Ryan E. Brock, Peter Hebert, James Ermer, Reinhold H. Dauskardt

We systematically explore the potential evolution of stress, grain size, roughness, and hardness of metal gridlines during thermal cycling as it pertains to top cell cracking behavior. As is fairly typical in multijunction PV systems, gridline metals composed primarily of silver are used. For a variety of deposition rates and thermal cycling conditions, we discover that although top cells are found to crack after many cycles, this is not due to an accumulation of damage, but rather an accumulation of stress within the metal gridlines due to cyclic plastic deformations. It is likely that the development of cracks is specifically enabled by the relatively low fracture toughness of the top cell material (InGaP), but the methodologies employed herein can be broadly applied to any photovoltaic with similar geometries and design constraints. Ultimately this suite of characterization techniques not only reveals the underlying behavior leading to gridline-induced top cell cracking failures in multijunction photovoltaics, but also suggests a route forward for the development of improved gridline materials.

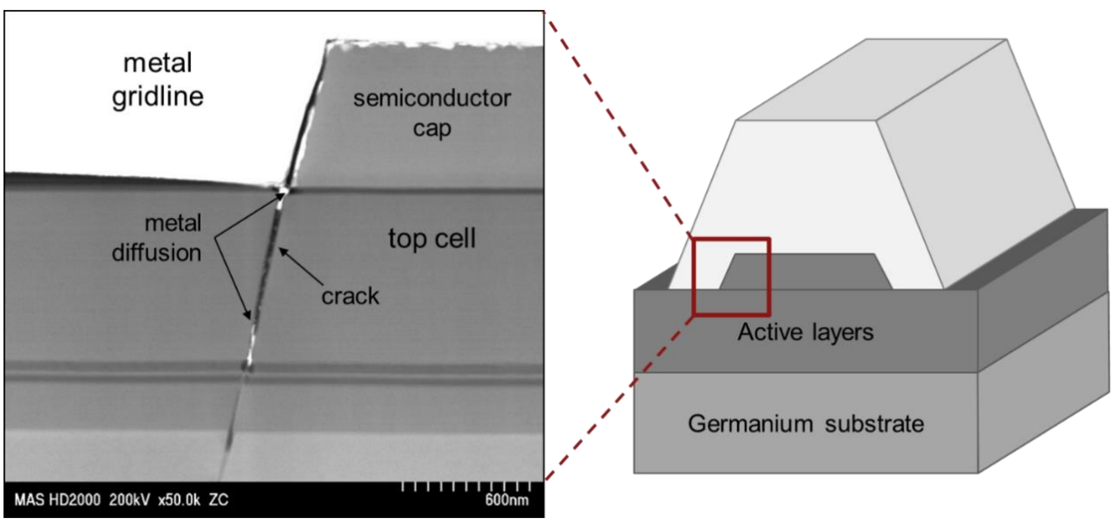


**Figure 1:** A cross-sectional area of a gridline structure atop a multijunction cell imaged via SEM. This cell has been thermally cycled, causing the top cell to develop a crack originating from the corner of the semiconductor cap, which serves as a catastrophic failure mechanism as metal subsequently diffuses into the cell and shorts it.

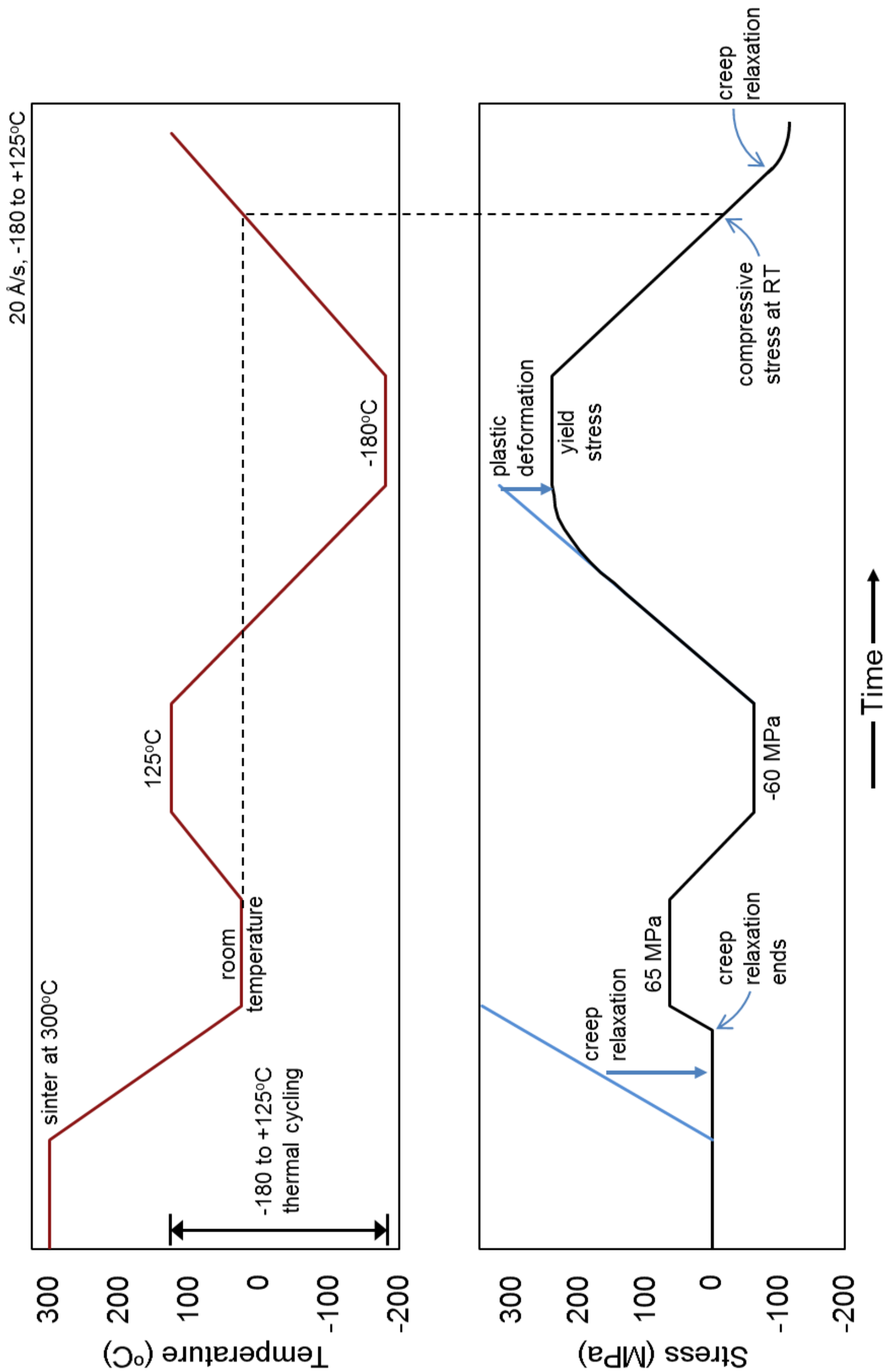


**Figure 5:** Step-by-step analysis of the predicted stress evolution within a blanket metal film during thermal cycling. Thermal mismatch would predict a very high tensile stress to develop during initial cooling from sintering (indicated in blue), but creep relaxation prevents this until the temperature falls below the creep relaxation temperature. From the initial tensile stress at room temperature, an increase in temperature leads to compressive stress in the film, but a nonlinearity occurs when cycling down to negative temperatures, as the expected thermal mismatch stress (again in blue) exceeds the yield stress.

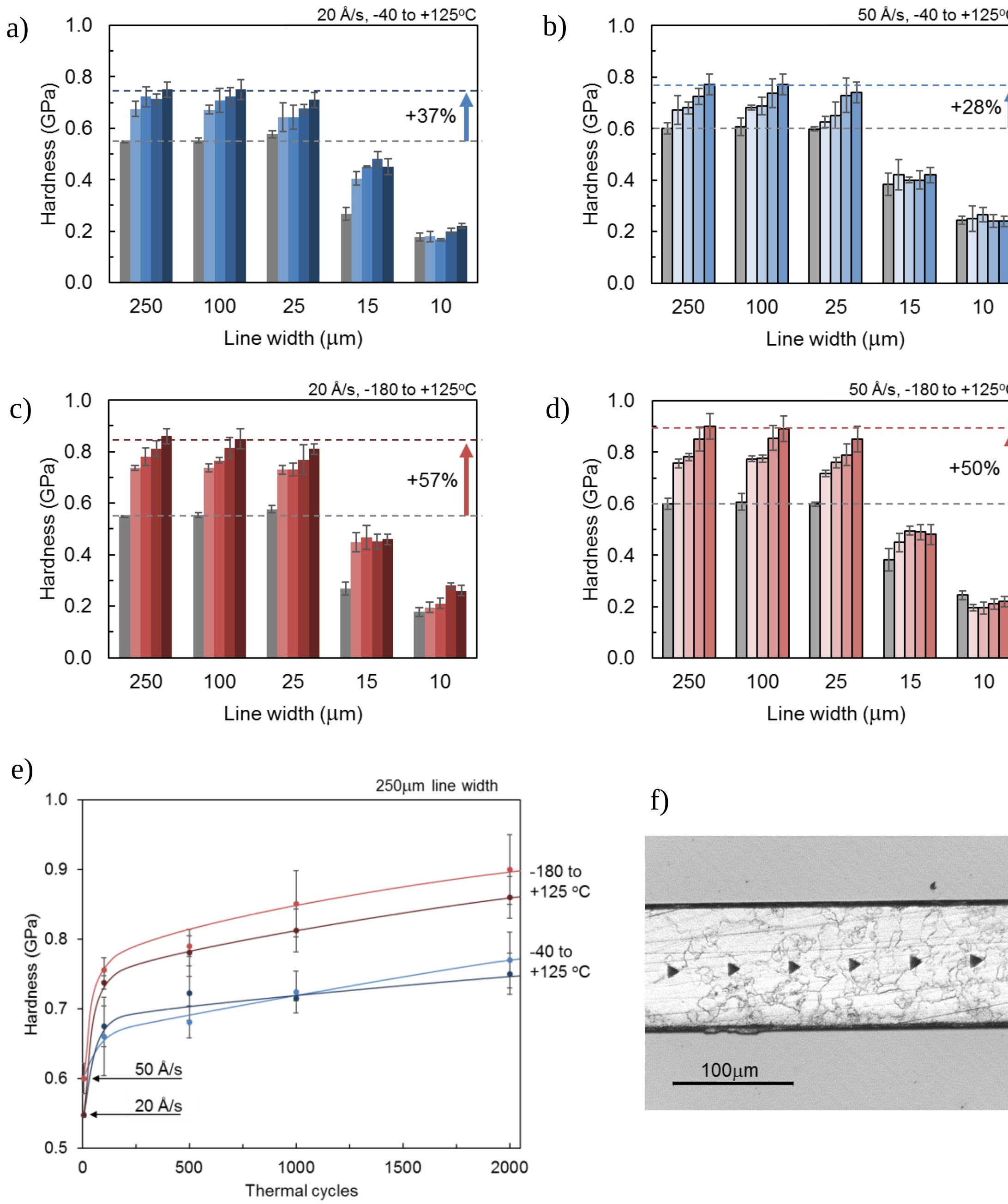


**Figure 9:** (a)-(d) Hardness measurements for each of the gridline structures considered in this study (two deposition conditions, two temperature cycling conditions, five gridline widths). In each plot, the gray bar represents the baseline hardness (no cycling), and each subsequent darker colored bar is hardness measured at each time break (breaks at 250, 500, 1000, and 2000 cycles). Each bar represents between three and nine nanoindentation measurements of hardness. (e) Characteristic hardness vs. thermal cycles behavior is demonstrated for the 250μm wide lines. (f) Optical image of representative indents produced in the surface of a 100μm wide line shows relative scale of indents vs. line width.

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## Path Forward

The results of our program have been fully shared in journal publications, at conferences and workshops. The test methods developed and validated in both focus areas are available for use in industry and research and development groups. The findings have allowed materials manufactures to rethink their recommended curing procedures for high-performance silicon adhesives, and the underlying role of metal gridline failures has been elucidated so that more robust line structures can be designed.

## Publications Resulting from This Work

1. David C. Miller, Michael D. Kempe, Matthew T. Muller, Matthew H. Gray, Kenji Araki, and Sarah R. Kurtz. "Durability of Polymeric Encapsulation Materials in a PMMA/glass Concentrator Photovoltaic System" 10th International Conference on Concentrator Photovoltaic Systems. April 7-9,2014, Albuquerque, NM.
2. R. H. Dauskardt, "Reliability and Operational Lifetimes for BAPVC Technologies." BAPVC Bi-Annual Meeting 2014. May 12-13, 2014 Stanford.
3. C. Cai, R.E. Brock, R.H. Dauskardt, D. Miller, I.A. Tappan, S. Kurtz, P. Herbert, J. Emer. "Coupled Thermo-Mechanical and Photo-Chemical Degradation Mechanisms that Determine the Reliability and Operational Lifetimes for CPV Technologies." SunShot Grand Challenge Summit. May 19-22, 2014, Anaheim, CA.
4. Chris Bruner, Stéphanie Dupont, Ryan Brock, Nick Rolston, Fernando Novoa, Warren Cai, Scott Isaacson, and R.H. Dauskardt "Thermomechanical Reliability in PV Devices and Structures," Reliability of PV & Renewables Workshop during IEEE RSAMD, Golden CO.
5. R. H. Dauskardt, "Reliability and Operational Lifetimes for BAPVC Technologies." BAPVC Bi-Annual Meeting 2014. Oct 6-7, 2014 Berkeley CA.
6. R.E. Brock, P. Hebert, H. Cotal, J. Ermer, R.H. Dauskardt, "Adhesion and Reliability of Complex Multijunction Photovoltaic Structures." Materials Research Society Spring 2015 Meeting. April 6-10, 2015 San Francisco, CA.
7. November 2015, "Thermo-Mechanical Degradation Mechanisms and Field Failures for Solar Reliability and Lifetimes," KAUST Solar 2015 Future Symposium, Jeddah, Saudi Arabia.
8. C. Cai, D. Miller, R.H. Dauskardt, "Reliability and Degradation of Optical Interfaces in Concentrator Photovoltaic Modules." Materials Research Society Spring 2015 Meeting. April 6-10, 2015 San Francisco, CA.
9. December 2015, "Thermo-Mechanical Degradation Mechanisms Relevant for Field Failures and Solar Lifetimes," 3rd Atlas/NIST Workshop on Photovoltiac Materials Durability, Gaithersburg, MD.
10. R. H. Dauskardt, "Reliability and Operational Lifetimes for BAPVC Technologies." BAPVC Bi-Annual Meeting 2016. May 16-17, 2016 Stanford.
11. R. Brock, R. Rewari, F.D. Novoa, P. Hebert, J. Ermer, D.C. Miller, R.H. Dauskardt, "Quantitative Adhesion Characterization of Antireflective Coatings in

Multijunction Photovoltaics", Solar Energy Materials and Solar Cells, 153, 2016, 78-83.

12. R. Brock, D.C. Miller, R.H. Dauskardt. "Adhesion of Antireflective Coatings in Multijunction Photovoltaics", IEEE PVSC. June 7, 2016 Portland OR.
13. Can Cai, David C. Miller, Ian A. Tappan, Reinhold H. Dauskardt. "Degradation of Silicone Encapsulants in CPV Optics." IEEE PVSC, June 6, 2016. Portland, OR.
14. C. Cai, D. Miler, R.H. Dauskardt. "Degradation of Thermally-Cured Silicone Encapsulant under Terrestrial UV," Solar Energy Materials and Solar Cells, 157, 2016, 346-353.
15. C. Cai, D.C. Miller, I.A. Tappan, R.H. Dauskardt. "Framework for predicting the photodegradation of adhesion of silicone encapsulant." Progress in Photovoltaics: Research and Applications, 2017. In press.
16. R. Brock, P. Hebert, J. Ermer, R.H. Dauskardt, "Degradation of Multijunction Photovoltaic Gridlines Induced via Thermal Cycling," Solar Energy Materials and Solar Cells , 2017. In press.

## Conclusions

The program successfully passed each go/no-go milestone and each of the major milestones in our initial SOPO have been completed. Summary of key points are as follows.

**Degradation of Thermally-Cured Silicone Encapsulant under Terrestrial UV**

We studied the effects of terrestrial UV on silicone adhesives for CPV applications. Representative coupon specimens systems were used to simulate critical interfaces (silicone/glass or silicone/$Al_2O_3$) and allow for weathering in an outdoor concentrator and under UV in an environmental chamber. The adhesion energy between the silicone to the adjacent interfaces increased by ~2 orders of magnitude, from 6.3 J/m$^2$ to ~200 J/m$^2$ with initial UV weathering. The initial increase in adhesion was attributed an increase in the population of bonds between the silicone and the underlying superstrate. Subsequent exposure decrease the adhesion energy to ~20 J/m$^2$, which, is caused by the embrittlement of the bulk silicone as a result of UV-photochemical crosslinking. The rate of change in adhesion energy as a result of UV exposure varied significantly with temperature. Specimens aged in the outdoor concentrator exhibited a similar increase in adhesion energy to ~200 J/m$^2$ with initial exposure and subsequent decrease in adhesion to ~2 J/m$^2$ with prolonged exposure. The crack path changed from the interface of the silicone and the superstrate for short exposure times to within the silicone for long exposure times. A fracture mechanics model was developed to model the adhesion energy as a function of cumulative radiant UV exposure and temperature and can be used to predict the behavior of encapsulant materials with accelerated aging test. We find that UV crosslinking could limit the life of silicone encapsulation used in CPV modules through reduced adhesion or embrittlement and subsequent cracking of the bulk material. The durability of materials under high UV flux must be considered to ensure the reliability of CPV modules.

**Framework for predicting the photodegradation of adhesion of silicone encapsulants**

The effects of photodegradation on a silicone encapsulant for concentrator photovoltaics applications was investigated. Specimens were weathered in an outdoor solar concentrator, both with and without heatsinks to simulate representative and worst case operating conditions, respectively.The adhesion energy between the silicone encapsulant and the adjacent interfaces increased with initial exposure and decreased with prolonged exposure. In addition, the failure pathway changed from adhesive failure at the interface to cohesive failure in the encapsulant with increasing radiant exposure. Sample specimens were artificially weathered under three different UV bandpass filters to identify the wavelengths responsible for photodegradation. The threshold damaging wavelength was determined to be 350 nm based on a statistical analysis of samples weathered under the UV filters. The failure of the law of reciprocity was incorporated into the model with statistical analysis of degradation data from the filtered UV exposure. By using an effective temperature, UV irradiance, and UV dose during natural weathering in the solar concentrator, the model shows good agreement (despite the variation in intensity ranging over three orders of magnitude) with the experimentally observed data for specimens weathered with and without heatsinks. Similar predictive models can be developed to predict the lifetime behavior of polymeric encapsulant materials with accelerated aging tests to aid in materials selection.

**Quantitative Adhesion Characterization of Antireflective Coatings in Multijunction Photovoltaics**

The development of the cDCB adhesion test represents a fundamental change in the ability to quantify the reliability of interfaces within multijunction PV devices. Within the set of parameters considered, we were able to identify the best combination of processing and materials to produce a resilient, high adhesion antireflective layer. Adhesion values ranging from 0.5 to 10 $J/m^2$ were measured and serve as a baseline for future studies of adhesion on similar devices. Exposure to the Damp Heat test condition was confirmed to have a significant detrimental effect on adhesion, primarily due to oxidation within the window layer. This information, along with understanding of the stresses developed in the field, will allow for a much more robust design for reliability in multijunction cells, fostering wider adoption of CPV technologies in terrestrial applications. Paired with the existing suite of electrical and optical characterization methods available, new materials can be easily tested and qualified for both performance and reliability.

**Degradation of Multijunction Photovoltaic Gridlines Induced via Thermal Cycling**

The discovery of the underlying mechanism behind thermal cycling failures at the gridline-semiconductor interface in multijunction photovoltaics is yet another step towards the goal of extended operating lifetimes for terrestrially deployed MJPV systems. We were able to dispel the previously held notion that this cracking was induced via either some fatigue mechanism or via accumulation of high residual stress within the cell, and found that the cause of fracture is likely a combined effect of the work hardening of gridline structures and the stress concentration at the sharp corner formed by the semiconductor cap layer. Hardness increases of over 50% were measured in the most extreme cases examined. Exposure to larger temperature ranges accelerates this increase in hardness, lending credence to the ability to perform accelerated full-lifetime tests using elevated stressing parameters. This information will allow for much more robust design for reliability in multijunction cells, fostering wider adoption of CPV technologies.

## Budget and Schedule

As reported in previous RPPR2 reports, program budget was spent as scheduled, with minor adjustments. The final period of the program was extended (no-cost extension) to allow completion of the work.