

Degradation of Back-Surface Acrylic Mirrors for Low Concentration and Mirror-Augmented Photovoltaics

Myles P Murray¹, Laura S. Bruckman¹,
Devin Gordon¹, Samuel Richardson¹, Greg Reinbolt², Mark Schuetz², Roger H. French¹

¹Case Western Reserve University, 10900 Euclid Ave. Cleveland OH 44106

²Replex Plastics, 11 Mount Vernon Ave., Mt. Vernon OH 43050

ABSTRACT

Back-surface acrylic mirrors can be used in low concentration and mirror augmented photovoltaics (LCPV, MAPV) to increase the irradiance on a module. Back-surface mirrors can spectrally filter incoming solar radiation reducing the ultraviolet (UV) and infrared (IR) load on the module, while useful radiation is coupled into a module or photovoltaic cell. Degradation of these mirrors can occur from UV induced photodegradative processes and metallization corrosion. Environmental stresses such as humidity, thermal cycling and exposure to corrosive substances can cause an increase in scattering, reducing mirror performance. In order to increase the lifetime and durability of back-surface acrylic mirrors a better understanding of the degradation modes is necessary.

In a study of acrylic back-surface mirrors for LCPV and MAPV applications, optical properties and bidirectional scattering distribution functions (BSDF) were investigated and correlated to simulated exposure protocols. Formulations of Poly(methyl methacrylate) (PMMA) with differing concentration of UV absorbers were used for the aluminum back-surface acrylic mirrors.

The formulations of aluminum back-surface acrylic mirrors were exposed in a QUV accelerated weathering tester (Q-Labs) to ASTM G154 Cycle 4. Total and diffuse reflectance spectra were measured for each mirror under exposure using a diffuse reflectance accessory (DRA) from 180-1800 nm on a Varian Cary 6000i at defined dose intervals. The total reflectance losses in the 250-400 nm region were greater and diffuse-only reflectance increased for formulations of acrylic mirrors that contained the least amount of UV stabilizer after each dose of QUV exposure.

Acrylic back-surface mirrors were exposed to salt fog corrosion and QUV and were analyzed using BSDF. There was an increase in scattering from roughening of the mirror surface after exposure to the corrosive environment.

Keywords: Mirror Augmentation, Acrylic Mirror, Degradation, Scattering, Photovoltaics, Stress and Response

1. INTRODUCTION

1.1 Back-Surface Acrylic Mirrors

While many candidate reflectors have been studied for renewable energy generation, most mirrors for photovoltaics are first surface reflectors, meaning that a thin metal film is deposited on a substrate, usually glass or anodized aluminum. Candidate reflectors have been studied and their durability in outdoor and simulated environmental test conditions has been reported. In typical High Concentration Photovoltaic (HCPV) modules, where cell level irradiance is greater than 500x higher than 1-sun conditions, first surface mirrors are highly reflective across the useful solar spectrum enabling use of expensive multijunction cells that can harness most of the reflected light. For Low Concentration Photovoltaics (LCPV), where cell level irradiance is 1-7x higher than 1-sun conditions, low material costs are paired with inexpensive absorber materials for boosted performance. Since crystalline silicon absorbers do not convert UV light efficiently into electricity, and UV light can damage modules spectrally filtering back-surface mirrors are under consideration for LCPV systems.

Acrylic back-surface mirrors use a high optical quality, UV durable acrylic as the first surface, a deposited film of aluminum as the reflector and a polymeric protective coating behind. Acrylic is used instead of glass because it is an easily formable, low cost substrate suitable for outdoor use[1].

1.2 Motivations for Lifetime and Degradation Science (L&DS)

At the 2010 Department of Energy Science for Energy Technology workshop[2], photovoltaic device lifetime and degradation science (L&DS) was prioritized. While PV qualification standards have proved to be useful for investigating initial performance, quality of manufacture and assuring safety of modules[3], they are not indicative of lifetime performance. In order to determine the performance of materials, components and systems used for energy generation, new accelerated weathering protocols are needed that can be correlated to real world conditions providing insights into lifetime performance.

One motivation of L&DS is the story of Carizzo Planes, the first grid-scale PV power plant[4][5][6]. This plant utilized first surface mirrors to increase irradiance on PV modules. Because power output increases nearly linearly with concentration factor, it was expected that modules with mirror augmentation would provide increased power at reduced cost. Instead of exhibiting a 1% power degradation rate, the system suffered 10% degradation per year and was scrapped before year 10. While non-augmented solar panels suffered similar degradation, augmented irradiance was implicated as the culprit for the induced degradation. While mirror augmentation may have accelerated EVA browning, the chief culprit in power degradation was interconnect failure. Although most of the module failures at Carizzo Planes can be attributed to deviations from prescribed manufacturing practices, module suppliers still will not honor warranties claims on modules that were used in mirror augmented systems.

Carizzo Planes was a black-eye for a fledgling industry attempting to compete with traditional energy technologies, and highlights the need for L&DS. Poor material substitutions and experimental component substitution led to difficult questions about the viability of MAPV and PV in general.

Back-surface acrylic mirrors offer spectral selectivity, the intent being that usable light can be coupled into the PV device, while harmful radiation is filtered out. Only by determining the lifetime performance of the mirror system, and by determining the lifetime penalty to the module will MAPV systems be adopted by PV plant installers and manufactures. By determining the dominant degradation modes and their rates, performing accelerated environmental exposures and linking them to fielded materials and components with similar composition, L&DS provides a path towards adoption of new materials, components and systems without unknown lifetime penalties[7].

1.3 Optical Transfer Functions

Acrylic lenses and front surface mirrors exposed in real world conditions sometimes exhibit surface roughening leading to increased scattering[8]. Acrylic is also known to undergo photodarkening and haze formation after outdoor weathering[9]. The mirror surface can degrade in several ways due to causes such as photooxidization or hydrolysis. These can lead to surface roughening and surface darkening which tends to increase scattering and parasitic absorption of light respectively. Delamination of the protective coating can lead to increased transmission through mirrors, and increases environmental-susceptibility of mirror metallization.

Optical transfer functions can be used to quantify optical characteristics of optical elements such as reflectors[10][11]. When using a ray-transfer matrix, or multiple matrices integrated into a system matrix, to describe an optical system, a vector from the output plane (at the source) is propagated by matrices representing each interface or optical element in the system onto an output plane, which for photovoltaics is the incident plane of the PV absorber. An example matrix is:

$$\begin{pmatrix} x_2 \\ \theta_2 \end{pmatrix} = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} x_1 \\ \theta_1 \end{pmatrix} \quad (1)$$

Where x_1 and x_2 are the input and output location markers respectively, θ_1 and θ_2 are the direction vectors and $\begin{pmatrix} A & B \\ C & D \end{pmatrix}$ is the ray-transfer matrix. While traditionally, ray-transfer matrix analysis assumes coherence and direct transmission and reflectance, progress towards including textured surfaces and gratings has been made by augmenting the ray-transfer or the generalized optical transfer matrix with a redistribution matrix describing the effect of the surface[12]. This redistribution matrix accounts for source and non-source illuminated and confined orders. It is therefore expected that scattered light analysis can also be incorporated into ray-transfer matrix analysis and that both bulk and interfacial scattering can be accounted for using this method.

Light incident on a surface can be reflected in the specular direction (R), directly transmitted through the sample (T), absorbed by the mirror system in the bulk acrylic or parasitically at the interface (A), and, scattered (B_{b+i}) by the bulk or surface properties in the acrylic and at the metallization interface. Equations used for each of the two primary methods of accounting for optical transfer functions are listed in Table 1 below.

The main difference between the two methodologies is that the equations on the left of table 1 show scattered (some times referred to as diffuse) light terms separately, while in the equations on the right scattered light is integrated into the reflectance and transmittance values. There are benefits to each, but we have chosen to use the optical transfer functions listed on the left as Optical Transfer Functions with interfacial and bulk material properties. Using this system it is

possible to look at the rates of change of these properties with respect to their stress exposure level in order to quantify damage and determine degradation rates.

Table 1: Optical Transfer Functions	
OTFs with interfacial and bulk material properties	OTFs for optical systems
$R_{specular} + T_{direct} + A_{total} + B_{b+i} = 1$	$R_{hemispherical} + T_{total} + A_{total} = 1$
$R_{specular} = R_{hemispherical} + R_{diffuse}$	$R_{hemispherical} = R_{specular} + R_{diffuse}$
$T_{direct} = T_{total} - T_{Diffuse}$	$T_{total} = T_{Diffuse} + T_{direct}$
$A_{total} = A_{bulk} + A_{intefacial}$	$A_{total} = A_{bulk} + A_{intefacial}$
$B_{b+i} = \sum B_{bulk} + \sum B_{interface}$	
$B_{b+i} = \int BSDF = \int BRDF + \int BTDF$	

1.4 Stress and Response (R(S)) Framework

An approach for studying L&DS is the stress and response (R(S)) framework[13][14][15][16][17]. The lifetime stress profile for long lived systems must quantify all of the damaging environmental conditions, including but not limited to UV light, humidity and temperature. A single environmental stressor is characterized by:

$$S = \int \sigma dt \quad (2)$$

Where σ is the instantaneous stress intensity at any given time, and S is the integration of that stress over time or the net stress. Therefore, the total of a particular measurable stress seen by a system over its lifetime can be determined. However, since many environmental stressors may have synergistic or antagonistic effects, the net stress that a system sees over its lifetime will be a function of the convolution of stressor intensities integrated over time:

$$\sum S = \int (\sigma_i \otimes \sigma_j \dots \otimes \sigma_n) dt \quad (3)$$

A material's response (R) to both instantaneous stress level and integrated stress may correspond to a change in the optical properties of a material, a loss of mechanical strength, or any measurable change in properties arising due to stressors applied over time. The general relationship between stress and response is a function of both the stress and the stress intensity (Equation 3).

$$R = f(\sigma S) = \int f(\sigma) \sigma dt \quad (4)$$

Single factor accelerated testing is often performed on materials to determine their durability to a particular environmental stress. By varying the stress intensity it is possible to show the range of conditions that do not activate new degradation pathways. An expansion of this methodology to multiple stresses gives

$$R(S_i, S_j, \dots, S_n) = \int f(\sigma_i, \sigma_j, \dots, \sigma_n) (\sigma_i \otimes \sigma_j \dots \otimes \sigma_n) \quad (5)$$

where S_i, S_j, \dots, S_n are different stresses that cause responses.

2. R(S) FRAMEWORK FOR BACK-SURFACE ALUMINUM MIRRORS

2.1 Optical Transfer Functions in Back-Surface mirrors

Absorption in back-surface mirrors is due both to bulk absorption in acrylic and interfacial absorptance at the metallization and acrylic surface. Acrylic PMMA typically has high optical clarity, and only one formulation of mirrors have shown significant photodarkening in the bulk acrylic. Interfacial absorptance can be attributed to trapped light due to microscopic surface geometries and absorption by impurities or oxidation products.

Specular, diffuse-only and total hemispherical reflectance measurements of mirror samples were performed. Since the exclusion zone for determining diffuse-only reflectance is nominally the same as the exclusion zone for determining the scattering function, diffuse-only reflectance measurements serve as a useful reference value of the integrated scattering. Some scattered light in short-throw non-imaging optics can be acceptable, but changes in the scattering function of a mirror can indicate degradation of the metallization, the acrylic surface or indicate haze formation in bulk materials. Scattered light analysis also provides a platform on which to develop metrics for quantifying damage and eventually for predicting lifetime performance of mirrors.

In order to parameterize BSDFs so that they can be studied through time and used to model real optical systems, the Harvey-Shack method is used [18]:

$$BSDF(|\vec{B} - \vec{B}_0|) = \frac{A}{B + |\vec{B} - \vec{B}_0|^g} \quad (6)$$

In equation 5, the β vector represents the projection of the unit vector of the scattering direction onto the tangent plane and the β_0 vector represents the projection of the unit vector in the specular direction onto the tangent plane. A, B and g are fitting parameters that allow the model to accurately portray the scattering data. A determines the height of the fitting curve, B determines the inflection point where the curve transitions from flat to sloped and g determines the slope of the roll-off. If $g=0$ the model is equivalent to a Lambertian distribution. For polished surfaces, values of g generally range from 1.5 to 3.5, with 2 to 3 being the most common and the value of B is very small with a range of $1e-6$ to $1e-10$.

3. METHODS: EXPOSURE AND ANALYSIS

3.1 Component selection

Three grades of acrylic were used as substrates for metallization for the manufacture of back-surface mirrors (Figure 1). These grades are all extruded PMMA compositions from the same manufacturer with nominally identical thickness, but vary in their composition, primarily in the UV absorber package used. UV reflecting (UVR) mirrors utilize an acrylic with no UV absorbers, Multipurpose (MP) mirrors utilize a standard formulation of acrylic with a 10 year warranty. UVA mirrors are spectrally filtering mirrors that utilize an acrylic that has a very high concentration of UV absorber, such that all of the UV light is absorbed in the acrylic layer, and none of it is reflected off the back aluminum surface.

3.2 “Hot QUV” or UV-only Exposure

Hot QUV exposure, or UV-only degradation of back-surface

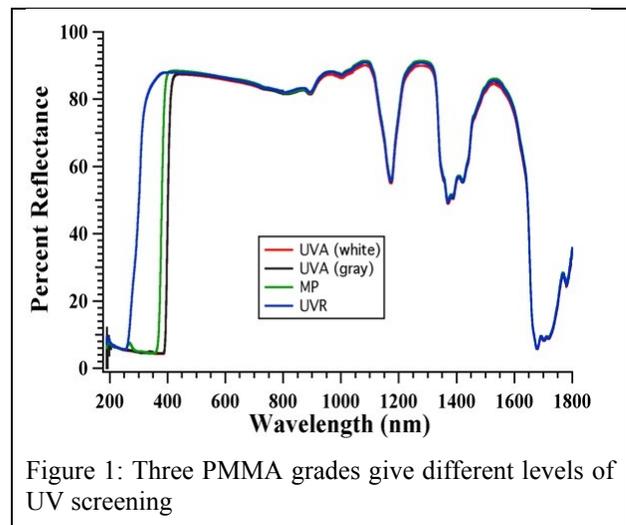


Figure 1: Three PMMA grades give different levels of UV screening

acrylic mirrors was performed with a Q-Labs QUV accelerated weathering tester, using UVA340 fluorescent lamps, that closely match the high energy UV spectral range of the solar spectrum [19]. This exposure was conducted in accordance with ASTM G154 Cycle 14 without the condensing humidity step²⁰. Test conditions were 1.55 W/m²/nm at 340 nm and chamber temperature was controlled at 70° C.

3.3 UV exposure with damp heat

Exposure of back-surface acrylic mirrors with UV and dark humidity was also performed with a Q-Labs QUV accelerated weathering tester. This exposure was conducted in accordance with ASTM G154 Cycle 4 with the condensing humidity step. Maximum irradiance, at 340 nm, was set at 1.55 W/m²/nm and chamber temperature was controlled at 70° C, condensing humidity was obtained at 50° C.

3.4 Salt-fog corrosion exposure

Salt-fog corrosion exposures were performed in a Q-Labs cyclic corrosion cabinet. The salt-fog solution was 5% NaCl and the cabinet temperature was 35° C as prescribed in ASTM B117²¹.

3.5 Optical analysis

Optical analysis of these mirrors was performed with a CARY 6000i spectrophotometer with a diffuse reflectance accessory (DRA-1800) which can give measurements of specular, diffuse-only ($\pm 4^\circ$) and total hemispherical reflectance²². In order to measure the Bidirectional scatter distribution functions were analyzed the ScatterScope 3D™ produced by ScatterMaster and distributed by Lambda Research [4]. Scattered light analysis was performed with the ScatterMaster™ suite of software and parametric fitting of the BSDF into the Harvey-Shack (ABg) model for scattered light was performed in Lambda Research's TracePro® BSDF converter utility²³.

4. RESULTS AND DISCUSSION

4.1 UV Only

Total hemispherical reflectance spectra for Hot QUV exposure exhibit little change for UVA and MP mirrors, however, photodarkening in the acrylic front surface is observed leading to a significant reduction in performance. Changes in yellowness index for the mirrors indicate that photodegradation in the acrylic is inhibited by the presence of UV absorbers, and that UVA grade shows no significant reduction in performance to date. Trends were not observed in integrated BSDF or in diffuse-only reflectance.

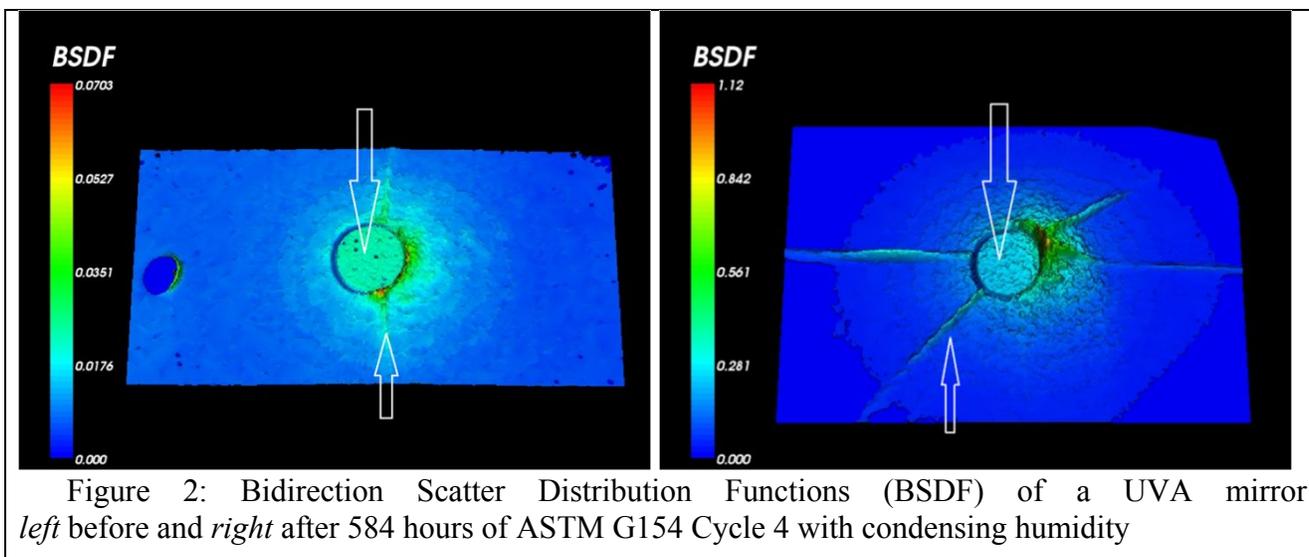
4.2 UV with condensing humidity

QUV exposure with dark humidity conditions also shows similar photodegradation, and indicate that photodegradation in the acrylic first surface is not greatly impacted by the dark humidity cycle. Scattered light analysis showed a decrease in *g* value of the ABg fit and an increase in integrated BSDF with stress exposure, confirmed as an increase in diffuse only reflectance.

4.3 Salt Fog Exposure

Visual inspection of samples subjected to corrosion testing showed several cases of browning in the back protective coating. Hemispherical reflectance of samples exposed to corrosion testing show no significant change. Though there are not large changes in the total hemispherical reflectance, changes in the diffuse-only component were observed in all samples. Initially a drop in the diffuse reflectance was seen, followed by gradual rise in subsequent dose steps.

The BSDF of samples showed increased scattering after exposure, with both intensity and scattering angle increasing. This corresponds to an increase in both integrated BSDF and a decrease in the *g*-parameter for the ABg fitted data. Imputed absorptance values of the mirrors were calculated from known values of reflectance, the BSDF, and by assuming transmittance is zero.



5. CONCLUSIONS

High stress intensity studies of acrylic back-surface mirrors for PV applications were conducted, optical properties and were investigated and correlated to simulated exposure protocols. PMMA photodegradation has been shown to be slowed by addition of UV absorbers.

The mirrors were exposed in a QUV accelerated weathering tester to ASTM G154 Cycle 4, with and without humidity, to salt fog corrosion and QUV and were analyzed using reflectance measurements and BSDFs. There was an increase in scattering from roughening of the mirror surface after exposure to the both the humid and corrosive environment. An increase in scattering was observed through the exposures and was quantified using the integrated BSDF and characterized using the Harvey-Shack scattering model. A decrease in g-values was seen through exposures, correlating to higher angles of scattering.

Total hemispherical reflectance was not greatly reduced for UVA or MP mirrors in these exposures. UVR however had a significant decrease in reflectance due to photodegradation of the acrylic.

Delamination seen in field aged specimens has not yet been observed during indoor exposure, but edge effects were seen in samples exposed to the corrosive environment. The architecture developed to account for incident light on the mirror allows for calculation of the mirror's absorptance, and this technique will be used to determine degradation rates. Future work will focus on extending exposure lengths, performing real time and accelerated outdoor exposures, correlating outdoor exposure results to indoor accelerated testing conditions and using data from accelerated weathering for modeling of full scale reflective PV systems.

6. ACKNOWLEDGEMENTS

This research was performed in the Solar Durability and Lifetime Extension (SDLE) Center at CWRU with funding support from Ohio Third Frontier under Tech 11-060 & Tech 12-004. The authors gratefully acknowledge the contributions of research members in VUV-Lab and Replex Plastics for their work. The authors also acknowledge Clinical and Translational Science Award - 1 UL1 RR024989 from NCCR/NI for the REDCap sample management database.

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