DEGRADATION OF TRANSPARENT CONDUCTIVE OXIDES: MECHANISTIC INSIGHTS AND INTERFACIAL ENGINEERING

by

HEATHER MARIE LEMIRE

Submitted in partial fulfillment of the requirements
For the degree of Master of Science

Department of Materials Science and Engineering
CASE WESTERN RESERVE UNIVERSITY

January, 2014
Degradation of Transparent Conductive Oxides: Mechanistic insights and Interfacial engineering

Case Western Reserve University
Case School of Graduate Studies

We hereby approve the thesis\(^1\) of

HEATHER MARIE LEMIRE

for the degree of

Master of Science

---

Dr. Roger H. French

Committee Chair, Adviser
Department of Materials Science and Engineering
11/21/13

Dr. Ina T. Martin

Committee Member
Department of Materials Science and Engineering
11/21/13

Dr. Alp Sehirlioglu

Committee Member
Department of Materials Science and Engineering
11/21/13

\(^1\)We certify that written approval has been obtained for any proprietary material contained therein.
Dedicated to the science and engineering of photovoltaics, in an effort to make a better world.
# Table of Contents

List of Tables vii

List of Figures viii

Acknowledgements xiv

Abstract xv

Chapter 1. Introduction 1

Transparent Conductive Oxides 1

PEDOT:PSS 2

Silanes 2

This Work 2

Chapter 2. Literature Review 5

Transparent Conductive Oxide Material Standards 5

Transparent Conductive Oxide Degradation in PV context 7

Interfacial Layers or Coatings for TCOs 10

Data Science Methodology Background 12

Chapter 3. Experimental Methods 13

Exposure Study Map and Protocol 13

Measurements of TCO Properties 13

Exposure Parameters 15

Cleaning Procedure 16

Encapsulation Process 18

PEDOT:PSS 19
## List of Tables

3.1 Baseline properties of the TCOs. 15

3.2 Exposure parameters used in this study. 17

5.1 T-test p-values of yellowness index comparison. Note, p-values < 0.055 are considered statistically significant. 62

7.1 Baseline Surface energies and contact angles of APTES on ITO and AZO 89

C.1 Laminator Recipe: Setpoints 135

E.1 T-test p-values of water contact angles in open-faced accelerated exposures comparison. 137

E.2 T-test p-values of resistivities in open-faced accelerated exposures comparison. 137

E.3 T-test p-values of water contact angles in open-faced accelerated exposures comparison. 138
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Study Protocol Sample Diagram</td>
<td>14</td>
</tr>
<tr>
<td>3.2</td>
<td>Transmission Spectra of AZO, ITO, FTO</td>
<td>16</td>
</tr>
<tr>
<td>4.1</td>
<td>AZO in damp heat: pairs plot</td>
<td>22</td>
</tr>
<tr>
<td>4.2</td>
<td>AZO in damp heat: correlation coefficient chart</td>
<td>23</td>
</tr>
<tr>
<td>4.3</td>
<td>AZO in damp heat: pairs and correlation plot</td>
<td>24</td>
</tr>
<tr>
<td>4.4</td>
<td>AZO in 5 suns UV: Water contact angle</td>
<td>26</td>
</tr>
<tr>
<td>4.5</td>
<td>AZO in damp: water contact angle</td>
<td>27</td>
</tr>
<tr>
<td>4.6</td>
<td>AZO in damp: center resistivity</td>
<td>28</td>
</tr>
<tr>
<td>4.7</td>
<td>AZO in damp with APTES: water contact angle</td>
<td>28</td>
</tr>
<tr>
<td>4.8</td>
<td>AZO in damp with APTES: center resistivity</td>
<td>29</td>
</tr>
<tr>
<td>4.9</td>
<td>AZO in cyclic: yellowness index and % haze</td>
<td>30</td>
</tr>
<tr>
<td>4.10</td>
<td>AZO in cyclic: total surface free energy</td>
<td>31</td>
</tr>
<tr>
<td>4.11</td>
<td>AZO in cyclic: center resistivity</td>
<td>31</td>
</tr>
<tr>
<td>4.12</td>
<td>AZO encapsulated in damp heat: water contact angle</td>
<td>32</td>
</tr>
<tr>
<td>4.13</td>
<td>AZO encapsulated in damp heat with PEDOT:PSS: yellowness index</td>
<td>33</td>
</tr>
<tr>
<td>4.14</td>
<td>AZO encapsulated in damp heat with PEDOT:PSS: water contact angle</td>
<td>34</td>
</tr>
<tr>
<td>4.15</td>
<td>AZO encapsulated in damp heat with PEDOT:PSS: center resistivity</td>
<td>34</td>
</tr>
<tr>
<td>4.16</td>
<td>AZO encapsulated in 1x outdoor: water contact angle</td>
<td>35</td>
</tr>
<tr>
<td>4.17</td>
<td>AZO encapsulated in 1x outdoor: center resistivity</td>
<td>36</td>
</tr>
</tbody>
</table>
4.18 AZO encapsulated with PEDOT:PSS in 1x outdoor: haze 37
4.19 AZO encapsulated with PEDOT:PSS in 1x outdoor: diiodomethane contact angle 37
4.20 AZO encapsulated with PEDOT:PSS in 1x outdoor: center resistivity 38
4.21 AZO encapsulated in 5x outdoor: water contact angle 39
4.22 AZO encapsulated with PEDOT:PSS in 5x outdoor:yellowness index and % haze 40
4.23 AZO encapsulated with PEDOT:PSS in 5x outdoor:diiodomethane contact angle 40
4.24 AZO encapsulated with PEDOT:PSS in 5x outdoor:center resistivity 41
4.25 ITO open-faced in 5 suns UV: water and diiodomethane contact angles 42
4.26 ITO open-faced in damp heat: diiodomethane contact angle 43
4.27 ITO open-faced in damp heat: center resistivity 44
4.28 ITO open-faced with APTES in damp heat: silane water contact angle 44
4.29 ITO open-faced with APTES in damp heat: silane diiodomethane contact angle 45
4.30 ITO open-faced with APTES in damp heat: center resistivity 45
4.31 ITO open-faced in cyclic: yellowness index and % haze 46
4.32 ITO encapsulated in damp heat: L* 47
4.33 ITO encapsulated in damp heat: Diiodomethane contact angle 48
4.34 ITO encapsulated in damp heat: center resistivity 49
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.35</td>
<td>ITO encapsulated with PEDOT:PSS in damp heat: $L^*$</td>
</tr>
<tr>
<td>4.36</td>
<td>ITO encapsulated with PEDOT:PSS in damp heat: Diiodomethane contact angle</td>
</tr>
<tr>
<td>4.37</td>
<td>ITO encapsulated with PEDOT:PSS in damp heat: resistivity</td>
</tr>
<tr>
<td>4.38</td>
<td>ITO encapsulated in 1x outdoor with PEDOT:PSS: center resistivity</td>
</tr>
<tr>
<td>4.39</td>
<td>ITO encapsulated in 5x outdoor: water contact angle</td>
</tr>
<tr>
<td>4.40</td>
<td>ITO encapsulated in 5x outdoor: center resistivity</td>
</tr>
<tr>
<td>4.41</td>
<td>ITO encapsulated with PEDOT:PSS in 5x outdoor: center resistivity</td>
</tr>
<tr>
<td>4.42</td>
<td>FTO open-faced in 5 suns UV: yellowness index</td>
</tr>
<tr>
<td>4.43</td>
<td>FTO open-faced in 5 suns UV: haze</td>
</tr>
<tr>
<td>4.44</td>
<td>FTO open-faced in damp heat: haze</td>
</tr>
<tr>
<td>4.45</td>
<td>FTO open-faced in damp heat: diiodomethane contact angle</td>
</tr>
<tr>
<td>4.46</td>
<td>FTO open-faced in cyclic: haze</td>
</tr>
<tr>
<td>5.1</td>
<td>AZO in accelerated exposures: yellowness index</td>
</tr>
<tr>
<td>5.2</td>
<td>AZO in accelerated exposures: haze</td>
</tr>
<tr>
<td>5.3</td>
<td>AZO in damp heat: Transmission spectra</td>
</tr>
<tr>
<td>5.4</td>
<td>AZO in cyclic: Transmission spectra</td>
</tr>
<tr>
<td>5.5</td>
<td>AZO in accelerated exposures: water contact angle</td>
</tr>
<tr>
<td>5.6</td>
<td>AZO in accelerated exposures: edge effects micrographs</td>
</tr>
<tr>
<td>5.7</td>
<td>AZO in damp heat and cyclic: Resistivity</td>
</tr>
<tr>
<td>5.8</td>
<td>AZO Outdoor vs. Accelerated Exposure: Optical Properties</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>5.9</td>
<td>AZO Outdoor vs. Accelerated Exposure: Water contact angle</td>
</tr>
<tr>
<td>5.10</td>
<td>AZO Outdoor vs. Accelerated Exposure: Resistivity</td>
</tr>
<tr>
<td>5.11</td>
<td>ITO Outdoor vs. Accelerated Exposure: Optical Properties</td>
</tr>
<tr>
<td>5.12</td>
<td>ITO Outdoor vs. Accelerated Exposure: Water contact angle</td>
</tr>
<tr>
<td>5.13</td>
<td>ITO Outdoor vs. Accelerated Exposure: Resistivity</td>
</tr>
<tr>
<td>5.14</td>
<td>ITO Outdoor vs. Accelerated Exposure: Water contact angle</td>
</tr>
<tr>
<td>5.15</td>
<td>ITO Outdoor vs. Accelerated Exposure: Resistivity</td>
</tr>
<tr>
<td>5.16</td>
<td>FTO Accelerated Exposure: Haze</td>
</tr>
<tr>
<td>6.1</td>
<td>PEDOT:PSS on AZO in Damp Heat: YI</td>
</tr>
<tr>
<td>6.2</td>
<td>PEDOT:PSS on AZO in Damp Heat: haze and water contact angle</td>
</tr>
<tr>
<td>6.3</td>
<td>AZO in damp heat with PEDOT:PSS: Transmission spectra</td>
</tr>
<tr>
<td>6.4</td>
<td>PEDOT:PSS on AZO in Damp Heat and Outdoor: haze and water contact angle</td>
</tr>
<tr>
<td>6.5</td>
<td>AZO with PEDOT:PSS in 5x outdoor exposure: Transmission spectra</td>
</tr>
<tr>
<td>6.6</td>
<td>PEDOT:PSS on AZO in Damp Heat and Outdoor: Resistivity</td>
</tr>
<tr>
<td>6.7</td>
<td>PEDOT:PSS on ITO: Interfacial Properties</td>
</tr>
<tr>
<td>6.8</td>
<td>Hydrophobic PEDOT:PSS on 5x outdoor exposed ITO</td>
</tr>
<tr>
<td>6.9</td>
<td>PEDOT:PSS on ITO: Resistivity</td>
</tr>
<tr>
<td>6.10</td>
<td>PEDOT:PSS on AZO: Hazing images</td>
</tr>
<tr>
<td>7.1</td>
<td>APTES Chemical Structure</td>
</tr>
<tr>
<td>7.2</td>
<td>ITO with APTES in Damp heat: optics</td>
</tr>
</tbody>
</table>

xi
<table>
<thead>
<tr>
<th></th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.16</td>
<td>ITO in damp heat encapsulated with PEDOT:PSS: pairs plot</td>
<td>125</td>
</tr>
<tr>
<td>A.17</td>
<td>ITO in 1x outdoor encapsulated: pairs plot</td>
<td>126</td>
</tr>
<tr>
<td>A.18</td>
<td>ITO in 1x outdoor encapsulated with PEDOT:PSS: pairs plot</td>
<td>127</td>
</tr>
<tr>
<td>A.19</td>
<td>ITO in 5x outdoor encapsulated: pairs plot</td>
<td>128</td>
</tr>
<tr>
<td>A.20</td>
<td>ITO in 5x outdoor encapsulated with PEDOT:PSS: pairs plot</td>
<td>129</td>
</tr>
<tr>
<td>A.21</td>
<td>FTO in 5 suns irradiance: pairs plot</td>
<td>130</td>
</tr>
<tr>
<td>A.22</td>
<td>FTO in Damp Heat: pairs plot</td>
<td>131</td>
</tr>
<tr>
<td>A.23</td>
<td>FTO in Cyclic: pairs plot</td>
<td>132</td>
</tr>
<tr>
<td>B.1</td>
<td>Diagram of resistivity measurements</td>
<td>133</td>
</tr>
<tr>
<td>D.1</td>
<td>Shelf stable resistivity</td>
<td>136</td>
</tr>
</tbody>
</table>
Acknowledgements

Ms. Lemire would first like to acknowledge the funding for this work. The open-faced study was supported by Underwriters Laboratories. The encapsulated study was supported by the Bay Area Photovoltaic Consortium Prime Award No. DE-EE0004946, Subaward Agreement No. 60220829-51077-T. Research was performed at the SDLE Center, which was established through funding through the Ohio Third Frontier, Wright Project Program Award tech 12-004, and at the MORE Center at Case Western Reserve University.

Ms. Lemire would like to thank her mentors and committee members, Professor Roger H. French, Dr. Ina T. Martin, and Dr. Alp Sehirlioglu. Their support, advice, and guidance throughout the research and writing process have been invaluable. An extra thanks is extended to Professor Roger H. French for patiently cultivating professional confidence and pride, and never saying no. A special thanks is extended to Dr. Ina T. Martin for taking an eager undergraduate under her wing, teaching her how to work in a lab and conduct research, and always being supportive.

Many thanks are extended to the other members of the SDLE Center. Thanks to Dr. Tim Peshek and Dr. Laura Bruckman for their technical support and conversation of data and analysis. Thanks to Yang Hu and Daniel Dryden for their comradery and support. Ms. Lemire would like to extend a special thanks to Kelly Peterson for providing extra focus, organization and exceptionally capable hands and eyes to the research process, and always asking the right questions.

Finally, Ms. Lemire would like to thank her family, Penny and Dave Lemire, for their love and encouragement throughout her education, and her fiance, Brian Tietz, for his love, patience, and emotional support.
Degradation of Transparent Conductive Oxides: Mechanistic insights and Interfacial engineering

Abstract

by

HEATHER MARIE LEMIRE

0.1 Abstract

Understanding transparent conductive oxide (TCO) degradation is critical to improving lifetimes of thin film photovoltaics, which utilize TCOs like aluminum-doped zinc oxide (AZO), indium tin oxide (ITO), and fluorine-doped tin oxide (FTO). Commercial AZO, ITO, and FTO were exposed in accelerated and outdoor exposures in several configurations, utilizing environmental stressors such as irradiance, heat and humidity. Electrical and optical properties and surface energies were measured. yellowness, haze, water contact angle and resistivity of different materials trended differently with exposure time and type, indicating different degradation mechanisms.

Interfacial layers for photovoltaic applications were also studied for AZO and ITO. OPVs PEDOT:PSS degrades TCO optics only, suggesting decoupled optical and electrical degradation mechanisms. Hazing of AZO by PEDOT:PSS appears photo-sensitive; 5x outdoor exposures demonstrated higher haze than exposures with no light. 3-aminopropyltriethoxysilane was applied to improve TCO stability and exposed to damp heat. 3-aminopropyltriethoxysilane reduces AZO's resistivity increase and edge effects.
1 Introduction

1.1 Transparent Conductive Oxides

Photovoltaics (PVs), display and touch screens, organic light emitting diodes (OLEDs) and other opto-electronic devices utilize transparent conductive oxides (TCOs). Attaining a high conductivity while maintaining optical transparency makes them ideal electrical contacts in these systems. However, when deployed in the field for long lifetime applications, durability concerns arise. The cost and reliability of solar power are often cited as primary limiting factors for its widespread adoption.\textsuperscript{1–4} These aspects of PV power systems are linked; increasing the lifetime of an installation can reduce the levelized cost of energy (LCOE, the total cost of the installation levelized over its lifetime). Many components in PV systems require lifetime extension; in particular, TCOs are a critical failure mode in many PV technologies that hold the potential to be cost-effective.\textsuperscript{1,5–7} Delamination at the TCO-absorber and TCO-glass interfaces have been reported in thin film silicon solar modules\textsuperscript{8–10}, CIGS modules\textsuperscript{6,11,12} and OPV technologies.\textsuperscript{13–16} An increase in resistivity and structural changes are observed in the TCO bulk.\textsuperscript{6,17–19} Corrosion is known to occur across a number of optoelectronic devices.\textsuperscript{8,9,20} In significantly degraded CIGS cells, replacing the TCO restores its electrical activity to near peak performance\textsuperscript{11}.


1.2 PEDOT:PSS

PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)) is a polymer commonly used as an electron blocking layer in OLEDs and standard architecture OPV devices, which improves device efficiency, and adhesion between the ITO and polymer absorber layer\textsuperscript{16}. Unfortunately, PEDOT:PSS is highly acidic and hygroscopic, causing corrosion of the TCO layer (via dissolution of the indium from the In\textsubscript{2}O\textsubscript{3} matrix).\textsuperscript{14–16,21} and water related damage to the entire device\textsuperscript{7,22}

1.3 Silanes

The chemically sensitive TCO surfaces can be modified by a variety of techniques, including thin polymer layers, silanization (resulting in covalent bond formation), and the chemisorption of small molecules, among other methods.\textsuperscript{10,16,23} Silanes are an excellent candidate due to their dipole like structure, their customizability, and their established use in commercial processes.\textsuperscript{23–25} Wong et al. demonstrated that the detrimental interaction between the PEDOT:PSS and the TCO can be blocked on a short time scale in OLEDs by inserting a monolayer of silane between the two layers.\textsuperscript{13}

1.4 This Work

In this study, three commercially available TCO materials on glass were exposed to three types of accelerated environmental exposures and two outdoor exposures in one of four configurations. Degradation was characterized by monitoring changes in their optical and electrical properties and surface free energies. Additionally, APTES (3-aminopropyltriethoxysilane) was applied to ITO and AZO samples and exposed in
open-faced configuration to damp heat, and the degradation characterized in the same fashion.

The accelerated exposures used here are industry qualification testing standards. The ideal outcome of an accelerated exposure is to provide rapid, straight-forward insights into the lifetime performance of a material or device. However, recent studies and colloquial knowledge have called into question the reasonableness of some of these exposures and their relationship to degradation mechanisms of the real world.\textsuperscript{1,2} Many of these tests were developed as qualification standards for marketability, not designed for lifetime prediction.\textsuperscript{1} For example, a single stressor exposure is straight-forward to conduct and may cause degradation. When environmental stressors are combined, a more difficult exposure to conduct, different degradation mechanisms may appear whose interactions are not necessarily a simple linear function. Thus, a reasonable accelerated exposure is defined as one which induces the same degradation mechanisms as seen in outdoor exposures.

To address the above in this study, a variety of accelerated and outdoor exposures were conducted, and the properties of the TCOs’ were monitored. Insights into a variety of mechanisms of TCO degradation were gathered from these exposures, and the comparisons between accelerated and outdoor exposures.

Moving forward, Chapter 2 provides an overview of the literature, touching on TCOs properties and degradation mechanisms, as a material as well as in the context of various thin film PV technologies. Silanes as interfacial layers are then discussed, followed by a brief point on data science.
Chapter 3 provides an explanation of the study protocol, including TCO measurements and baselines, exposure parameters, procedures for cleaning, silanization, PEDOT:PSS deposition, and encapsulation.

Chapter 4 introduces the data through an exploratory data analysis methodology, utilizing pairs plots, correlation coefficients, and extracting variables with significant responses. The error analysis procedure is then explained, with reference to the analysis R code.

The first discussion of the data concerns TCO degradation in various exposures, expounded upon in chapter 5.

Next, chapter 6 discusses the degradation of AZO and ITO when encapsulated with PEDOT:PSS, followed by their degradation with APTES in chapter 7.

Finally, in chapter 8 mechanistic insights are gleaned from the previous chapters, broken down by the three primary material attributes, with final thoughts on accelerated testing.

Everything is summarized and wrapped together in chapter 9, with some suggestions for the continuation of this work in chapter 10.

Note that the correlation coefficient colored pairs plots for each data subset are in appendix A, the explanation of resistivity measurements is in appendix B, the shelf stability of the TCOs is shown in appendix D, and any p-values from t-tests not mentioned in the discourse are in appendix E.
2 Literature Review

2.1 Transparent Conductive Oxide Material Standards

TCOs are used in optoelectronic devices from displays, to photovoltaics, to sensor applications. They were first developed for energy efficient window coatings to reduce solar heating and radiative cooling, and therefore the load on heating/cooling systems.\textsuperscript{26,27} In this text, we are primarily concerned with their use in PV (photovoltaics), although from the perspective of lifetime and degradation, which is important to numerous other technologies. Thin film PV includes a-Si, CdTe, Copper Indium Gallium Selenide (CIGS) and their newest relatives (ex:Copper Zinc Tin Sulfide (CZTS)), and polymer/organic photovoltaics (OPV). Our discussion of interfacial properties will be primarily concerned with OPV, but many observations will be cross technology applicable.

For PV applications, a TCO needs to be\textsuperscript{10,27,28}:

- transparent over the solar spectrum
- highly conductive
- easily patterned/engineered for optical scattering and trapping
- made of low cost, non-toxic, abundant materials
- chemically and environmentally stable, both in the bulk and at the interfaces
- work-function matched, with compatible electrical properties
- deposition compatible with other layers and process conditions

This is a steep set of criteria for any material to attain; however, there are a broad variety of materials that can accomplish a significant portion of this list. The most well established of these materials are the doped metal oxides, typically based on In$_2$O$_3$, SnO$_2$, and ZnO, which are all n-type with a direct optical band gap.\textsuperscript{28,29} These can be doped with a wide variety of metals including Al, Ga, F, Sb, Sn, or In.\textsuperscript{28} Sputter and chemical vapor deposition (CVD) processes dominate the deposition techniques of TCOs, producing the highest quality films, although everything from sol-gel methodology and spray pyrolysis, to pulsed laser deposition has been used to varying success.\textsuperscript{26,29} Fluorine-doped tin oxide (FTO) is currently the most commonly used for thin film PV devices, while indium-tin oxide (ITO) is currently preferred for OPV, as well as high performance display applications.\textsuperscript{8,10,12,28} Aluminum-doped zinc oxide (AZO) is a hopeful material, made of earth-abundant elements; it has a lower cost and is a better electronic match for CIGS devices.\textsuperscript{5,11,28} These are the primary materials that are considered in the work because they are the most commercially relevant and represent a broad range of TCOs; however, the reader should note that there are many more combinations and permutations of doped-metal oxides. The baseline properties of the specific AZO, ITO and FTO studied here are presented in Chapter 3.

AZO can attain resistivities as low as $3 \times 10^{-4} \Omega \cdot \text{cm}$, with average optical transmittance over 85%. Films can be either amorphous or wurtzite crystalline, typically sputtered, though atmospheric solution processing has been explored.\textsuperscript{28–30}

ITO is the high performance TCO, with resistivities as low as $1 \times 10^{-4} \Omega \cdot \text{cm}$ paired with transmission above 95% for much of the solar spectrum, and is used heavily in display applications. The crystalline structure is bixbyite, with up to 10% Sn. Highest
conductivity is obtained with an optimized oxygen partial pressure in dc/rf magnetron sputter deposition process. The major drawback of ITO is the indium cost, which has been increasing recently with the increasing number of touch screen devices.\textsuperscript{28,29}

Finally, the robust FTO is typically very lightly doped, with resistivities as low as $5 \times 10^{-4} \Omega \cdot \text{cm}$, although these require very high process temperatures and the percent transmission is not as high as other TCOs. FTO can be amorphous or rutile crystalline, and can be deposited by atmospheric pressure CVD or spray pyrolysis.\textsuperscript{28,29}

There are a number of alternatives to "our favorite doped-metal oxide(s) that we love to hate", and some promising options are emerging. Graphene is an excellent candidate for flexible PV and has the reputation of being corrosion resistant.\textsuperscript{31} Along the same lines, carbon nanotube arrays are being studied for transparent conductors, given their high conductivity along the length of the tube.\textsuperscript{32} Metal nanowires, most commonly silver, are also coming under greater scrutiny to replace doped-metal oxides.\textsuperscript{27,33} The primary drawback to most of these new technologies is the difficulties of processing.

The wide variety of TCOs and TCO alternatives is driven by the need to bring down the cost and better suit individual technologies. Currently, the TCO is the dominating cost of thin film PV, and with each new absorber material or cell design, the demands on the TCO will change.\textsuperscript{3,29} This emphasizes the need for understanding the interfaces within a device, for both initial and lifetime performance.

### 2.2 Transparent Conductive Oxide Degradation in PV context

TCOs are known to degrade in real world environments. FTO is generally acknowledged to be the most stable, AZO the least, with ITO somewhere in the middle.\textsuperscript{10,17,29} Stability of the films is of course dependent on the film properties, like grain size, thickness,
composition and a multitude of other factors.\textsuperscript{10,11,18,29} The stability not only depends on film properties, but also on the device context, where observed problems range from delamination, to corrosion, to work function mismatch.\textsuperscript{4}

For example, Beyer et al. observe that different deposition temperatures affect the grain size of ZnO and the diffusion of environmental gases through those grain boundaries.\textsuperscript{10} Greiner et al. proposed a 1D model for the electrical conductivity differences between the AZO bulk and the grain boundaries, demonstrating that much of the loss of conductivity in damp heat comes from grain boundary mobility losses.\textsuperscript{18} The formation and permeation of gases through the film has lent insight into these grain boundary problems.\textsuperscript{34} Similarly, both Greiner and Delahoy observe that there is a relationship between the "texture" of AZO films and resistivity, as a result of the anisotropic intra-grain mobility of ZnO.\textsuperscript{18,29,35} The ZnO of AZO is known to be highly sensitive to water, causing structural break down and resistivity increase.\textsuperscript{12,17} An excellent study of AZO film degradation in damp heat was conducted by Tohsophon et al., demonstrating that water adsorption into grain boundaries of the film caused resistivity increase, as a result of carrier concentration decreasing.\textsuperscript{19,35} Sundaramoorthy et al. relate the increase in transparency in the infrared region to a reduction in free carriers, which relates to the increase in resistivity.\textsuperscript{11} They also characterize the structural degradation of a variety of AZO films in damp heat.\textsuperscript{11,34}

The primary way in which FTO has been known to degrade is to delaminate from the front glass, a corrosion type mechanism that occurs under a humid environment when the TCO is at a negative bias with respect to the glass.\textsuperscript{8,9}

Like FTO, ITO is primarily damaged by corrosion in the presence of water and an electric field, converting to its two metallic compounds.\textsuperscript{20} Additionally, if there are other
species present, such as mild acids or other metal ions, ITO will react with them and etch away. While this work does not consider the wide variety of substrates used in various TCO applications, it should be noted that ITO is a brittle material, and its use in flexible optoelectronics creates a plethora of additional problems, which cause decreased performance. Not only are TCO materials unstable under environmental stressors, but they will also react with the neighbor layers in a device context. Each thin film technology has different reactions, which are summarized here.

2.2.1 a-Si

According to one set of arguments, the primary stability issues of TCOs that concern the a-Si thin film industry are stability during exposure to hydrogen plasma, exposure to environmental stressors, and interface stability. In this work, hydrogen plasma stability is not considered, but it is noted in the literature that SnO is not stable in hydrogen plasma, whereas ZnO is more stable. Additionally, at the interface with a-Si, the TCO is liable to react and form a layer of SiO$_2$, which is detrimental to the performance of the cell and in some cases has been known to react with the entirety of the TCO contact. Lastly, as noted earlier, FTO will delaminate from the front glass of a-Si devices under biased corrosion conditions.

2.2.2 CIGS and CdTe

CIGS devices utilize AZO as their primary TCO based on energy level matching for more ideal band structure through the device. This PV technology has proven to be fairly stable in dry environments, however, when placed in humid environment, severe to catastrophic degradation is observed. With water exposure, voids and large scale
physical degradation occur in the AZO film.\textsuperscript{6,17,38} Demonstrating that the AZO contact is a significantly weak link, Sundaramoorthy et al. performed photoluminescence imaging of CIGS before and after damp heat exposure. Post exposure, little activity was present in the devices; however, when the cells were disassembled, and the AZO replaced, the device functionality was restored to nearly as-deposited levels.\textsuperscript{37}

In a high temperature test, CdTe devices were observed to delaminate from the CdS/TCO layer.\textsuperscript{39} FTO is the primary TCO utilized for CdTe cells, and as noted previously, it is also known to delaminate from the front glass, especially in the presence of a biased frame.\textsuperscript{1,8}

### 2.2.3 OPV

While OPV has the potential to be the cheap, rapid production flexible solar technology, it has serious degradation problems to overcome.\textsuperscript{7,16,22} PEDOT:PSS is a good candidate as buffer layer between the active polymer and the ITO in many ways; it can smooth the rough ITO, it improves adhesion and increases efficiency as an electron-blocking layer.\textsuperscript{16} However, PEDOT:PSS is well known in the literature to decrease the stability of ITO.\textsuperscript{7,14,15,40} PEDOT:PSS etches the ITO surface in the presence of water, primarily during deposition and exposure to air, allowing diffusion of Indium ions through the rest of the device.\textsuperscript{7,14} It is noted in several sources that the water involved in this mechanism is absorbed by the hygroscopic PEDOT:PSS, and this water adsorbtion causes a significant amount of the OPV degradation.\textsuperscript{7,13,16,41}

### 2.3 Interfacial Layers or Coatings for TCOs

Engineering of the interfaces of TCOs is important to every technology that utilizes these materials.\textsuperscript{10,16,40,42} While TCOs are ideal front electrode materials in many ways, for
technologies like OLEDs and OPV, the very polar TCO surface does not promote good adhesion to the polymeric functional layers.\textsuperscript{16,43} Using small molecules to modify these highly reactive surfaces is a fairly simple method of stabilizing the TCO, increasing or customizing compatibility with other device layers, and tuning interfacial electrical properties.\textsuperscript{13,23,42}

Silanes are a common industry method of changing surface energies, resulting in increased adhesion and water repelling in technologies like composites, encapsulants, thin film transistors, and fiber optics.\textsuperscript{24,25,42} Their use on TCO materials is established; they have been applied in a number of studies to change the work function, increase adhesion, and block interfacial reactions.\textsuperscript{13,21,42,43} Specifically, silanes have been used to successfully block the reaction between ITO and PEDOT:PSS in OLED devices on a short time scale.\textsuperscript{13} However, these silanes have not been studied as an environmental buffer layer in PV for lifetime extension applications, which is the perspective presented here.

Apart from their ability to bridge polar to non-polar surfaces, silanes are also ideal for modifying the TCO surface because of the large library of available molecules. These include a selection of organofunctional groups, as well as a range of type and number of hydrolyzable groups, which create mono- or multi-layers.\textsuperscript{23} The dipole structure bridges nicely from the very polar TCO to the next non-polar device layer. The surface coverage and thickness is highly tunable by changing the deposition parameters and selecting the hydrolyzable group(s), which react(s) with the TCO surface.\textsuperscript{23}
2.4 Data Science Methodology Background

This work has aimed to conform to the ideals of big data science methodology.\textsuperscript{44} The intent is to allow the data to tell its story without projecting domain-knowledge restrictions onto the collection process. As such, analysis is conducted in R studio, and all data is presented in pairs plots, allowing the comparison of all variables at the same time, each finding even ground from which to stand out if they have a story to tell. Additionally, the data and R code used to analyze the data is provided publicly, in keeping with the attitude of free and open source techniques. While the data here is no where near as immense as those typically handled in "big data", we apply the same type of methodology to all experimental data in the Solar Durability and Lifetime Extension Center.
3 Experimental Methods

3.1 Exposure Study Map and Protocol

AZO (Zhuhai Kaivo Electronic Components Co., Ltd.), ITO (Colorado Concept Coatings LLC), and FTO (Hartford Glass Company Inc.) on soda lime glass (5 cm by 5cm) were purchased commercially. Samples were subjected to exposures in 168 or 336 hour (1 or 2 week) increments for a total of 1000 to 2526 hours of exposure. After each exposure step, 2-3 samples were removed, cleaned, characterized and stored. The three TCOs were found to be fairly shelf stable; the resistivities of shelf stored samples is presented in appendix D, demonstrating no degradation over 4 months. Samples were exposed in one of 4 configurations; open-faced, open-faced with silane, edge seal encapsulated, or edge seal encapsulated with PEDOT:PSS. A total of 258 samples were exposed whose data is presented here, distributed as shown in Figure 3.1.

3.2 Measurements of TCO Properties

To quantify the properties of the TCO, optical, electrical and surface measurement techniques were used. The surface free energy (SFE) was calculated from contact angles with water and diiodomethane using the Kruss EasyDrop, DSA4 system, circular and tangent 1 fitting, and the Wu method. Contact angle values are the average and standard
\textbf{Experimental Methods}

Figure 3.1. Chart of number of samples in exposure type and configuration. 'X' represents an attempted subset whose data is not shown here.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
 & \textbf{AO} & \textbf{ITO} & \textbf{FTO} & \textbf{AO} & \textbf{ITO} & \textbf{FTO} \\
\hline
\textbf{Hot QUV} & 12 & 12 & 12 & 12 & 12 & 12 \\
\textbf{Damp Heat} & 12 & 12 & 12 & & & \\
\textbf{Cyclic} & 18 & 18 & 18 & & & \\
\hline
\textbf{Damp Heat} & 6 & 6 & 12 & 12 & & \\
\textbf{Cyclic} & X & X & X & X & & \\
\textbf{1x Outdoor} & 6 & 6 & 12 & 12 & & \\
\textbf{5x Outdoor} & 6 & 6 & 12 & 12 & 12 & 12 \\
\hline
\end{tabular}
\caption{Number of samples in study (spread across 6 exposure steps*)}
\end{table}

*encapsulated TCOs without PEDOT:PSS were removed from exposure in pairs at exposure steps 1, 3, and 6.

deviation of five 50 frame video measurements on 1-2 samples; SFEs are calculated from these contact angles. Transmission spectra were obtained using a Varian Cary 6000i, in-line transmission, equipped with an integrating sphere. Percent haze, yellowness index, L*, a*, and b* values were obtained using a Hunterlab UltraScan Pro Colorimeter, where a* and b* are the axes of the color plane, and L* is the perpendicular axis, tracking white to black. L*, a*, and b* are used to calculate yellowness index and percent haze (see HunterLab Colorimeter Pro documentation for more details). Changes in L*, a*, and b* are not necessarily detrimental, but increases in yellowness and % haze are generally taken to be negative. The resistivity of the ITO films was measured using an EDTM R-chek four point probe (which is prone to edge effects deviating up to 20%), and the
resistivity of the AZO and FTO films was measured using a Keithley 2400 Source and Lucas Labs four point probe (which penetrates slightly into the film – the ITO film was too thin to use this tool). For details on the resistivity measurements, see appendix B. Microscope images were collected with a Leica DM 2500M microscope at 5x magnification to observe edge effects of AZO.

The baseline characteristics of the TCOs are presented in Table 3.1 and the baseline transmission spectra are presented in Figure 3.2. Baseline data was taken on more than 24 samples for each material type.

Table 3.1. Baseline properties of the TCOs.

<table>
<thead>
<tr>
<th>Property</th>
<th>AZO</th>
<th>ITO</th>
<th>FTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellowness Index (arb.)</td>
<td>5.24 ± 0.06</td>
<td>5.91 ± 0.03</td>
<td>3.48 ± 0.04</td>
</tr>
<tr>
<td>% haze</td>
<td>0.60 ± 0.02</td>
<td>0.08 ± 0.02</td>
<td>15.4 ± 0.1</td>
</tr>
<tr>
<td>L* (arb.)</td>
<td>93.43 ± 0.01</td>
<td>94.668 ± 0.008</td>
<td>92.31 ± 0.02</td>
</tr>
<tr>
<td>a* (arb.)</td>
<td>-1.22 ± 0.05</td>
<td>-0.077 ± 0.003</td>
<td>-0.272 ± 0.006</td>
</tr>
<tr>
<td>b* (arb.)</td>
<td>3.22 ± 0.02</td>
<td>3.14 ± 0.02</td>
<td>1.89 ± 0.02</td>
</tr>
<tr>
<td>Water contact angle (degrees)</td>
<td>7.5 ± 0.3</td>
<td>4.3 ± 0.2</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td>Diiodomethane contact angle (degrees)</td>
<td>22 ± 2</td>
<td>30.3 ± 0.8</td>
<td>5.7 ± 0.3</td>
</tr>
<tr>
<td>Total Surface free Energy (mN/m or mJ/m²)</td>
<td>81.5</td>
<td>80.2</td>
<td>82.2</td>
</tr>
<tr>
<td>center Resistivity (ohms/sq.)</td>
<td>9.58 ± 0.09</td>
<td>47.3 ± 0.3</td>
<td>7.64 ± 0.05</td>
</tr>
<tr>
<td>Supplier Specified Film Thickness (nm)</td>
<td>800-900</td>
<td>35</td>
<td>400</td>
</tr>
</tbody>
</table>

3.3 Exposure Parameters

Five exposure protocols were used, 3 accelerated, and 2 real world: ASTM G154 X2.1-Cycle 4 ("cyclic"), Modified ASTM G154 X2.1-Cycle 4 ("5 suns UV"), IEC 61626 ("damp
Figure 3.2. The % transmission baselines for all three TCO materials.

heat, "DH"), and outdoor exposures at 1x and 5x concentrations on a dual-axis tracker (see Table 3.2). Note that ASTM G154 X2.1-Cycle 4 is one of a commonly used set of irradiance settings; in this case, the irradiance that is approximately equivalent to 5 suns of UV light at 340 nm. The 5x outdoor exposure used front surface aluminized hexagonal mirror concentrators to concentrate the sunlight, such that the final irradiance is 5 times the suns irradiance.

3.4 Cleaning Procedure

Given the importance of cleaning procedures to TCO surfaces, preliminary exposure studies, and the exposure chambers and protocols, all samples were cleaned before exposure and immediately after exposure, before data were collected, to obtain data only
Table 3.2. Exposure parameters used in this study.

<table>
<thead>
<tr>
<th>Exposure Name</th>
<th>Conditions</th>
<th>Equipment</th>
<th>Stressors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified ASTM G154 X2.1-Cycle 4, &quot;5 suns UV&quot;</td>
<td>70 °C and 1.55 $W/m^2/nm$ @ 340 nm</td>
<td>QUV Spray</td>
<td>Heat, UV light</td>
</tr>
<tr>
<td>IEC 61646.10.13, &quot;damp heat&quot;, &quot;DH&quot;</td>
<td>85 °C, 85% relative humidity</td>
<td>CSZ ZPH8</td>
<td>Heat, Humidity</td>
</tr>
<tr>
<td>ASTM G154 X2.1-Cycle 4, &quot;cyclic&quot;</td>
<td>8 h @ 70 °C, 1.55 $W/m^2/nm$ @ 340 nm, 4 h @ 50 °C with spray in dark</td>
<td>QUV Spray</td>
<td>Heat, UV light, Humidity</td>
</tr>
<tr>
<td>Outdoor 1x</td>
<td>Cleveland weather June-October</td>
<td>dual-axis tracker</td>
<td>Heat, Sunlight, Humidity</td>
</tr>
<tr>
<td>Outdoor 5x</td>
<td>Cleveland weather June-October, front surface mirror concentrator</td>
<td>dual-axis tracker</td>
<td>Heat, Sunlight, Humidity</td>
</tr>
</tbody>
</table>

of the TCO material. This process only removed environmental test chamber (ETC) contaminants that would not be present in a real world application (ex: chamber gasket lubricant on open-faced TCO samples), and should not be harsh enough to change/remove surface changes inflicted by the exposure. Contact angle and surface free energy data were always collected first, followed by optical measurements, and lastly the resistivity measurements. Measurements were done in this order to ensure a clean surface for contact angle measurements and to reduce introducing surface species before optical measurements.

Sample cleaning involved a series of 10 min sonications in 30 °C solvents (acetone, isopropanol, DI water), drying under nitrogen gas, and a 15 min UV ozone clean at 60 °C (Novascan PSDP-UV8T). Note that gentle scrubbing with an optical wipe was used after the IPA sonication to remove strongly adhered surface species after various exposures.
Initially, a sonication process of a detergent sonication followed by two DI water sonica-
tions was used instead of the solvents, however, it was observed visually that the deter-
gent was insufficient to remove strongly adhered ETC contaminants, and the methodol-
gy was modified. The contact angle and surface free energy data of the detergent and
solvent cleaned samples are still comparable, as the primary determinant of the surface
energy is determined by the UV ozone clean; ETC contaminants would primarily affect
the optical data by increasing the haze because they would adhere to the back glass sur-
face.

3.5 Encapsulation Process

The encapsulation was accomplished by wet etching the ITO and AZO samples with
50:50 concentrated HCl:H₂O solution to remove the edges, cleaning, applying a 1/3 of 10
mm width of Quanex Solargain™ Edge Tape - SET LP03 (WVTR 0.3 g/m²/day at 100%
Relative Humidity (RH), 37.8 °C), followed by lamination in a mini module laminator
at 90 °C and 500 mPa after 10 min evacuation. The detailed lamination procedure can
be found in Appendix C. The encapsulation was intended to merely control the water
ingress to and ETC contamination of the sample, not completely eliminate moisture in
the system. Once moisture had penetrated the encapsulated cell, some incubation time
was allotted, to be more comparable to open-faced exposures. To determine when mois-
ture had penetrated the edge seal, a pair of color changing Absorbant Industries humid-
ity sensors (30%RH and 60%RH) were encapsulated in the same manner as the pseudo-
cells, and placed in the exposure with the TCO samples. When the color of the humidity
dot changed, the corresponding relative humidity percentage had been reached. For the
damp heat exposure, the humidity sensors showed that the inside of the encapsulated
cell had reached at least 60% RH in less than 24 hours, therefore the damp heat exposure was conducted on a 6 week basis, like the open-faced. For the outdoor exposures, the humidity dots were placed outdoors with the samples, and one week after the humidity dots were judged to show humidity inside the cell, the first set of samples were removed from exposure, and then at two week increments for 6 time steps. For the 5x exposure, the first set of samples were removed after 677 hours of exposure, while the first samples from the 1x exposure were removed after 845 hours.

3.6 PEDOT:PSS

For samples aged with OLED-grade PEDOT:PSS, the as received polymer from Clevios (PVP AI4083, resistivity of 750 Ω cm, solids 1.75%) was spun coat onto the etched, cleaned TCO before lamination. The polymer was spun at 4000 rpm for 40 s and post baked for 10 min at 150 °C. The PEDOT:PSS was wiped from the edges of the glass with a DI water dampened optical wipe, then samples were stored in nitrogen until encapsulation, a total of less than 10 minutes of air exposure. Post exposure, the PEDOT:PSS was removed with a DI water dampened optical wipe, and the TCO cleaned as normal.

3.7 Silanization

For open-faced silanized samples, after TCO cleaning, APTES (3-aminopropyltriethoxysilane) films were deposited in a 1% v/v silane/anhydrous toluene solution for 60 mins at 65 °C, followed by a series of solvent rinses (anhydrous toluene, chloroform, methanol), drying under nitrogen, and a 10 min bake at 120 °C. Before exposure, the contact angle measurements of the silane+TCO stack were taken on the freshly deposited samples. Post exposure, the samples were cleaned, omitting the UV-ozone
step, and only contact angle measurements taken on the silane+TCO stack. The APTES layer was then removed with a UV-ozone clean for 40 minutes at 60 °C, and each sample confirmed for silane removal with water contact angle measurements. The sample was then re-cleaned and data taken on the TCO as normal.
4 Exploratory Data Analysis and Results

4.1 EDA Pairs Plots and Correlation Coeff for Data Analysis

The raw data and R code used for these analyses can be found on BitBucket.org, 13ms-LemireTCOs.

The following is a walk through of how the data collected were processed and analyzed. First, the data were subsetted and plotted in pairs plots. A subset is defined by the material type, the configuration and the exposure type, and is represented by a small box in Figure 3.1. Figure 4.1 is an example of a pairs plot, in this case for AZO open-faced in damp heat. The pairs plots for all subsets in this work can be found in Appendix A.

The pairs plot contains every variable measured (except % transmission) plotted against every other variable, for as many points as are available. The left most column of graphs are the scatter plots for each variable plotted as a function of time, and the top row is time plotted as a function of every variable. This means that the data plotted are mirrored over the diagonal of the pairs plot, and the axes swap, allowing one to examine, for example, both yellowness index as a function of haze, and haze as a function of yellowness index. The primary objective is to quickly glean trends, then delve in and examine individual plots, which are read as any scatter plot, yielding insights about
Figure 4.1. Raw data pairs plot of AZO in damp heat.

how closely two variables are related and in what manner they are related. The first 5 variables (YI, Haze, L*, a*, b*) are optical data collected with the Hunterlab colorimeter. The next 5 variables (Water CA, Diiodo CA, SFE tot, SFE disp, SFE polar) are the water and diiodomethane contact angles, and the total, dispersive and polar surface energies. The last set of variables (edges, centers, sides) are the resistivity measurements by location on the sample. Resistivities taken in the center of the sample are presented throughout
the rest of this document, as they are the least prone to edge effects. ITO and AZO were also exposed with APTES layers, whose surface energy data is presented as the last data in their pairs plots, denoted by "S" before the variable description.

The scatter plots show how the variable trends with time and other variables, possibly lending mechanistic insights (linearly, exponentially, etc). It allows a huge amount of data to be examined at the same time, and to look at variable-variable relationships that are otherwise hidden by only examining variable-time relationships. Much of the analysis here is on variable-time graphs, however, a short insight into variable-variable relationships will be examined in chapter 8.

After examining the pairs plots, the linear correlation coefficient function is applied to the data. These coefficients are calculated from the complete pairs of data and yields on a scale from 0 to ±1 how linearly correlated the two variables are, where 0 is no correlation and ±1 is completely correlated. The table of linear correlation coefficients for the same AZO open-faced in damp heat is shown in Figure 4.2. The color intensity is increased every 0.1 increment, using Excel conditional formatting, such that 1 is the darkest blue, and 0 is white. In this work, a correlation coefficient above ±0.7 is considered reasonably highly correlated.

![Figure 4.2. Linear correlation coefficients of AZO in damp heat.](image-url)
If the pairs plot and colored correlation coefficient chart are then overlaid, a quick visual is provided, highlighting variables and plots that may yield insights. Comparing the different subsets colored pairs plots, differences in responses can be quickly gleaned. For example, comparing AZO open-faced damp heat exposure to AZO open-faced 5 suns UV exposure, the plots and correlation coefficient coloring quickly demonstrate there is more trending and response in the damp heat exposure (e.g. Figure A.1 vs. Figure A.2).

Figure 4.3. Raw data pairs plot of AZO in damp heat.
One cannot rely on only the correlation coefficient, as it only assesses linear relationships, and would not show a large coefficient for a more exponential or quadratic relationship. Thus, plots were deemed potentially indicative if they had a large correlation coefficient and/or clear visual trending.

Following identification as a potentially indicative plot, the individual graph is then individually examined for significance. A meaningful graph demonstrates reasonably clear trending over a reasonable magnitude for the variable. Meaningful magnitudes were determined by comparing the relative scatter of the baseline and known specifications of the tools used. Typically, changes were of a smaller magnitude in the optical data (yellowness index, % haze, L*, a*, b*), given the low variation in the baseline data and the precision of the instrument. Water and diiodomethane contact angles needed to demonstrate at least a 2-5 degree difference, and the surface energies calculated from the contact angles needed to change by at least 2 mN/m² to be meaningful. AZO and FTO resistivities needed a change of greater than 2 Ohms/sq, while ITO measurements looked for a slightly greater change, due to the lack of precision of the instrument. Observations of the meaningful graphs for each individual subset are made here, before comparing exposure types and configurations in the discourse.

4.1.1 Baselines

A large set of baseline data was taken for each material, however, every sample was not baselined. For those subsets in which all samples were entirely baselined, they are analyzed as is. For those subsets with incomplete or no baseline data, the totality of the baseline data for the material was appended to the subset. This was deemed reasonable because the samples were assumed to be "sub-samples" of a larger "sample material", 

and in fact, the tested samples were cut from module size sheets. These baseline adjustments can be seen in the R code. This baseline correction includes all the trials with PEDOT:PSS; all the 0 points in the following graphs are the totality of the bare TCO, not depositing then immediately removing the PEDOT:PSS layer. Silane 0 point data are taken post-deposition, with the APTES on the TCO, unless otherwise noted.

4.2 AZO

4.2.1 Open-faced Configuration

5 Suns UV. There is little change observed for AZO in the 5 suns UV exposure. In fact, the only changes observed were in the form of step changes that may have benefited the material. Figure 4.4 shows a step change increase in hydrophilicity of the AZO surface. No other changes of significance were observed for AZO in 5 suns UV.

![AZO 5 suns UV: Water contact angle vs. Time](image)

Figure 4.4. Water contact angle vs. time for AZO in 5 suns UV.
Damp Heat. Comparatively, there is extreme change seen in AZO in the open-faced damp heat exposure. This can be viscerally grasped from the many dark-shaded plots in Figure A.2. Figure 4.5 shows the step change to increased hydrophobicity, the opposite of the 5 suns UV exposure.

![AZO Damp heat: Water contact angle vs. Time](image)

Figure 4.5. Water contact angle vs. time for AZO in damp heat.

The most dire change is seen in the resistivity increase (Figure 4.6). The AZO resistivity increases 250% in open-faced damp heat over 1000 hours of exposure. The trend appears somewhere between linear and exponential.

When APTES, the silane interfacial layer, was applied, the degradation of the AZO film due to damp heat was less catastrophic, although the same variables were found to be indicative of the degradation trends (Figure A.3). The water contact angle of the AZO, seen in Figure 4.7, showed an increase over its baseline.
Figure 4.6. Center resistivity vs. time for AZO in damp heat.

Figure 4.7. Water contact angle vs. time for AZO in damp heat with APTES. Note, 0 point data are the bare AZO contact angles; no silane had yet been deposited.

The resistivity, shown in Figure 4.8, increased with exposure time by approximately 50%.
Figure 4.8. Center resistivity vs. time for AZO in damp heat with APTES.
**Cyclic.** In the cyclic open-faced exposure, a quasi combination of the 5 suns UV and damp heat exposure, all material properties (optical, surface, electrical) demonstrated trending. As seen in Figure A.4, there are many strongly linear trends with time, especially in the optics and resistivity. Figure 4.9 show the increases in both yellowness index and % haze with exposure time for the AZO films. There are also strong relations seen in the L* and b* values, which are components of the yellowness index and haze.

![AZO Cyclic: Yellowness Index vs. Time](image1.png) ![AZO Cyclic: % Haze vs. Time](image2.png)

Figure 4.9. Yellowness index and % haze vs. time for AZO in cyclic.

A step increase in the surface free energy occurs within the first 168 hours of cyclic exposure, as seen in Figure 4.10, which is the only increase in surface free energy found in this work.

Finally, there is also a steady increase in the resistivity of the AZO film, seen in Figure 4.11. The magnitude of this increase is smaller than that of either damp heat exposure configurations.
Figure 4.10. Total surface free energy vs. time for AZO in cyclic.

Figure 4.11. Center resistivity vs. time for AZO in cyclic.
4.2.2 Encapsulated Configuration

**Damp Heat.** When encapsulated, the water vapor transmission rate to the film surface is controlled, but not eliminated. However, the response of the AZO film to damp heat when encapsulated is more muted than the open-faced response, evidenced by the lack of strongly correlated variables in Figure A.5. The primary variables that demonstrated a response were the surface properties. The water contact angle demonstrates a step increase in the first 168 hours of exposure, shown in Figure 4.12.

![Figure 4.12. Water contact angle vs. time for AZO encapsulated in damp heat.](image)

The AZO films were also encapsulated with PEDOT:PSS in damp heat. With the PEDOT:PSS layer, increased degradation beyond just encapsulated is observed, as demonstrated by the correlation coefficient coloring in Figure A.6. There is a step change in the yellowness index at 168 hours of exposure, as seen in Figure 4.13.
Figure 4.13. Yellowness index vs. time for AZO encapsulated with PEDOT:PSS in damp heat.

The water contact angle trends with time, seeming to increase and then suddenly decrease again at 840 hours of exposure time (Figure 4.14).

Finally, there is a step change in the resistivity with time, shown in Figure 4.15.
Figure 4.14. Water contact angle vs. time for AZO encapsulated with PEDOT:PSS in damp heat.

Figure 4.15. Center resistivity vs. time for AZO encapsulated with PEDOT:PSS in damp heat.
Outdoor 1x. All outdoor samples, with or without PEDOT:PSS, were encapsulated, as open-faced configuration has little relation to real world applications. There was little response from the 1x concentration outdoor encapsulated samples, which is to be somewhat expected, as it typically takes a few years for a device to fail in the field, while these were exposed for a few months. As can be seen in Figure A.7, the most distinct response was from the water contact angle. Figure 4.16 shows an initial step change in the water contact angle for the AZO surface.

![AZO 1x Encapsulated: Water contact angle vs. Time](image)

Figure 4.16. Water contact angle vs. time for AZO encapsulated in 1x outdoor.

Additionally, the resistivity appears to increase slightly with exposure time, shown in Figure 4.17.

When encapsulated with PEDOT:PSS and placed under 1x outdoor conditions, there is, like damp heat, an increased response over just encapsulated, again seen in the trends and increased correlation coefficient coloring of the pairs plot, Figure A.8. Pulling out
Figure 4.17. Center resistivity vs. time for AZO encapsulated in 1x outdoor.

the key variables, Figure 4.18 shows a steady increase in haze with exposure time, also reflected in the trends of $L^*$, $a^*$, and $b^*$.

In this case, the diiodomethane contact angle was most indicative of surface changes, demonstrating a step change after the first exposure step (Figure 4.19).

There was also an increase in resistivity with exposure time, shown in Figure 4.20.
Figure 4.18. Haze vs. time for AZO encapsulated with PEDOT:PSS in 1x outdoor.

Figure 4.19. Diiodomethane contact angle vs. time for AZO encapsulated with PEDOT:PSS in 1x outdoor.
Figure 4.20. Center resistivity vs. time for AZO encapsulated with PEDOT:PSS in 1x outdoor.
Outdoor 5x. To accelerate the outdoor aging process and study high sun concentration effects, samples were encapsulated and placed outdoors under 5x concentration using a front-surface aluminized, hexagonal concentrator. When encapsulated, the strongest response was seen in the surface properties, gleaned from Figure A.9. Specifically, the water contact angle showed a steady increase with exposure time, as shown in Figure 4.21.

![AZO 5x Encapsulated: Water contact angle vs. Time](image)

Figure 4.21. Water contact angle vs. time for AZO encapsulated in 5x outdoor.

At 5x outdoor exposure, when encapsulated with PEDOT:PSS, there is again an increased response over just encapsulation, seen in the darker coloring of Figure A.10. There are significant optical effects, in the yellowness index and the haze, seen in Figure 4.22. Both show an increase with exposure time.

In this case again, the diiodomethane contact angle is most surface sensitive, demonstrating a step change after the first exposure increment, shown in Figure 4.23.
Figure 4.22. Yellowness index and % haze vs. time for AZO encapsulated with PEDOT:PSS in 5x outdoor.

Figure 4.23. Diiodomethane contact angle vs. time for AZO encapsulated with PEDOT:PSS in 5x outdoor.
Lastly, there is also an increase in the resistivity of the AZO at 5x outdoor with PEDOT:PSS, Figure 4.24.

![AZO 5x Encap. w/ PEDOT:PSS: center Resistivity vs. Time](image)

Figure 4.24. Center resistivity vs. time for AZO encapsulated PEDOT:PSS in 5x outdoor.

### 4.3 ITO

Now we will examine ITO variable responses in the same exposures as AZO. ITO is known to be a more stable TCO material than AZO\textsuperscript{17,28,29}, and thus the responses from the films are expected to be smaller.

#### 4.3.1 Open Faced Configuration

**5 suns UV.** First, the gentlest exposure, ITO in a constant 5 suns worth of UV irradiance. Looking at Figure A.11, there are some optical changes in a* and L*, highlighted by the
correlation function, however they do not appear in the yellowness index or % haze measurements, and the change is too small to be meaningful. Thus, they are noted as changing, but their significance is unclear. In contrast, the surface changes were large enough to warrant investigation. The water and diiodomethane contact angles are shown in Figure 4.25. ITO’s water contact angle seems to decrease then increase again, while the diiodomethane undergoes an initial step change increase.

Figure 4.25. Water and diiodomethane contact angles vs time for ITO open-faced in 5 suns UV.
Damp Heat. Like AZO, the primary changes for ITO in the open-faced damp heat exposure were in the surface energy and resistivities, seen in Figure A.12. The diiodomethane contact angle, seen in Figure 4.26, increases with exposure time.

![ITO Damp heat: Diiodomethane contact angle vs. Time](image)

Figure 4.26. Diiodomethane contact angle vs time for ITO in damp heat.

While the correlation coefficient is a middling value (0.62), the ITO resistivity does seem to undergo an initial step change in damp heat, shown in Figure 4.27.

ITO was also exposed to damp heat with the APTES layer. The % haze, total surface free energy and center resistivity show possible changes with exposure time in Figure A.13 though none distinctly. There was a distinct response from the silane surface energies, taken post solvent clean, before removing the silane. As seen in Figures 4.28 and 4.29, there is a step change in the contact angles at 168 hours of exposure.

Lastly, there does seem to be a slight step increase in the resistivity of the ITO with exposure, as can be seen in Figure 4.30.
Exploratory Data Analysis and Results

Figure 4.27. Center resistivity vs time for ITO in damp heat.

Figure 4.28. Silane water contact angle vs time for ITO with APTES in damp heat.
Exploratory Data Analysis and Results

Figure 4.29. Silane diiodomethane contact angle vs time for ITO with APTES in damp heat.

Figure 4.30. Center resistivity vs time for ITO with APTES in damp heat.
Cyclic. In the cyclic combined stressor exposure, the ITO showed some optical degradation, as well as surface changes, which are expressed in Figure A.14. The yellowness index shows a steady decrease, while the haze shows an increase, shown in Figure 4.31. Although these changes are small, the ITO thin film will only display small changes and the instrument’s precision is a small fraction of the range represented. These changes are also present in $b^*$, highlighted in Figure A.14.

**Figure 4.31.** Yellowness index and % haze vs time for ITO open-faced in cyclic.

There are some small, unclear changes in the water and diiodomethane contact angles, and the resistivity with exposure time.
4.3.2 Encapsulated Configuration

**Damp Heat.** Encapsulated ITO was exposed to damp heat, and the effects on optics, surface energies and resistivities are shown in Figure A.15. The $L^*$ has a strong, and for this variable, relatively large increase with time, shown in Figure 4.32.

![ITO Damp heat Encap.: $L^*$ vs. Time](image)

*Figure 4.32. $L^*$ vs time for ITO encapsulated in damp heat.*

There is also an increase in the diiodomethane contact angle, shown in Figure 4.33.

As in several other exposures of ITO so far, there is an initial step change in the resistivity, which can be seen in Figure 4.34.

ITO encapsulated with PEDOT:PSS was also exposed to damp heat. The variable responses can be seen in Figure A.16. $L^*$ again demonstrates a steady increase with exposure time, as seen in Figure 4.35.
Figure 4.33. Diiodomethane contact angle vs time for ITO encapsulated in damp heat.

The diiodomethane water contact angle again increases with time (Figure 4.36). There may also be some small step change in the resistivity at the first 168 hours, shown in Figure 4.37.
Figure 4.34. Center resistivity vs time for ITO encapsulated in damp heat.

Figure 4.35. L* vs time for ITO encapsulated with PEDOT:PSS in damp heat.
Figure 4.36. Diiodomethane contact angle vs time for ITO encapsulated with PEDOT:PSS in damp heat.

Figure 4.37. Center Resistivity vs time for ITO encapsulated with PEDOT:PSS in damp heat.
**Outdoor 1x.** The response of all variables for ITO encapsulated and exposed at 1x outdoor conditions can be seen in Figure A.17. There was very little degradation apparent in these samples. This is expected, given the small response in the AZO films, and that the ITO films are known to be more stable. There may be a step change in the resistivity at the first exposure step.

When encapsulated with PEDOT:PSS and exposed outdoors at 1x, there was a slightly larger magnitude response (Figure A.18). However, the response variables remained the same; most prominently the resistivity demonstrates a step change after the first time increment (Figure 4.38).

![Figure 4.38. Center resistivity vs time for ITO encapsulated with PEDOT:PSS in 1x outdoor.](image)

**Outdoor 5x.** Increasing the intensity of the exposure, ITO was encapsulated and exposed outdoors at the 5x concentration. The response of the observables can be seen in
Figure A.19, colored by the linear correlation coefficient. The two variables that demonstrate trends with exposure time are water contact angle and resistivity. The water contact angle shows a step change with exposure time, as seen in Figure 4.39.

![ITO 5x Encap.: Water Contact angle vs. Time](image)

Figure 4.39. Water contact angle vs time for ITO encapsulated in 5x outdoor.

As in many of the other exposures, the resistivity of the ITO shows a step change with the first exposure increment (Figure 4.40).

When exposed with PEDOT:PSS at 5x concentration outdoors (Figure A.20), ITO displayed similar results to encapsulated without PEDOT:PSS (Figure A.19). The resistivity again displayed a step change after the first exposure step, as shown in Figure 4.41.
Figure 4.40. Center resistivity vs time for ITO encapsulated in 5x outdoor.

Figure 4.41. Center resistivity vs time for ITO encapsulated with PEDOT:PSS in 5x outdoor.
4.4 FTO

FTO is known in the literature and the field to be the most stable of the TCOs studied here. After being subjected to three different open-faced exposures, and demonstrating essentially no degradation, it was eliminated from the encapsulated exposure.

4.4.1 5 suns UV

The most degradation FTO displayed was in the 5 suns UV exposure. As can be seen in Figure A.21, only the optical measurements demonstrate trending with exposure time. The yellowness index displays a step increase at 168 hours of exposure, as seen in Figure 4.42. However, the magnitude of the change is barely outside the scatter of the baseline, so the change is noted but not of concern.

Figure 4.42. Yellowness index vs. time for FTO open-faced in 5 suns UV.
While the yellowness increased, the haze decreased with exposure time, as seen in Figure 4.43.

![FTO 5 suns UV: % Haze vs. Time](image)

Figure 4.43. Haze vs. time for FTO open-faced in 5 suns UV.

### 4.4.2 Damp Heat

The damp heat exposure affected the % haze and diiodomethane contact angle of the FTO, gleaned from Figure A.22. Specifically, the haze shows a step decrease after 168 hours of exposure, shown in Figure 4.44. This decrease is comparable to that in the 5 suns UV exposure.

The initially very low diiodomethane contact angle increases significantly over the 1000 hours of exposure time, as seen in Figure 4.45. This change is reflected in the decrease of the dispersive component of the surface energy, "SFEdisp" (Figure A.22).
4.4.3 Cyclic

Even when stressors were combined in the cyclic exposure, still the only effect was on the haze, as demonstrated by Figure A.23. The % haze dropped at the first exposure step, shown in Figures 4.46.
Figure 4.45. Diiodomethane contact angle vs. time for FTO open-faced in damp heat.

Figure 4.46. Haze vs. time for FTO open-faced in cyclic.
4.5 Remarks on EDA Plots

What is made clear from the examination of the pairs plots and correlation coefficients of all subsets is that the primary variables which demonstrate degradation are the yellowness index, % haze, water contact angles, and center resistivity measurements. As such, these are the primary variables that will be used to compare between exposure types and configurations. Additionally, it should be noted for every subset except AZO open-faced cyclic, the total surface free energy decreased with exposure time, regardless of material, either as a step change or a steady decrease, typically from 82 mJ/m\(^2\) to between 76 mJ/m\(^2\) and 79 mJ/m\(^2\). The cause of this extremely consistent change is unclear, however, for surface insights, water and diiodomethane contact angles have been found to be the most sensitive metric of change.

It was also observed that AZO is the "canary in the coal mine"; it demonstrates the first and most response of the three TCOs. As such, in the discussion of the data, AZO will be examined first, then ITO and FTO, as it will set the maximum of the response scale and put the other degradation into perspective. Through the discussion averages of the data are plotted as a function of exposure time, with the standard deviation of the mean as the associated error, and a t-test for point checks of data comparison. The methodology for these calculations is now discussed.

4.6 Error Analysis

It should be noted for all of the error analysis that the majority of the time increments have two samples on which data was taken. The cyclic open-faced exposure had three samples at each time increment for each material, and some encapsulated AZO data
points have only one sample due to breakage during un-encapsulation. Therefore, the error analysis is as accurate and generous as it can be made with two samples at each time increment.

### 4.6.1 Standard Deviation

For these data, the standard deviation has been calculated between samples (rather than within samples, where multiple data points were sometimes available). With the exception of the R-chek, based on examination of baseline data and tool specifications, the error in the tool accuracy has been judged negligible in comparison to sample scatter - the variation of the samples was observed to increase with exposure time. The R-chek measurements, used to read the resistivity of ITO, have been corrected with respect to the distance to the edge of the sample in accordance with the R-chek manual. See Appendix B for the details of this correction, and see the R code for the calculation.

To calculate the standard deviation of the mean, the following procedure was used. The function takes the standard deviation of a variable between samples by time increment, by using the aggregate function. The built in standard deviation function in R uses $N - 1$. This value is then divided by the square root of the number of observations at each time increment. In the R code, this function is denoted as "sdevm".

### 4.6.2 T-test

The t-test was utilized for comparisons of subsets, or step changes within a subset. For example, the t-test was applied to determine if one exposure type caused significantly more yellowness than another exposure type, at each time increment. It was also applied to determine if a step change in a variables response was significant. The built in t-test in R was utilized, and the p-values extracted, using the "alternate" function as necessary to
denote "greater" or "less" when comparing data. P-values from the t-test were analyzed, and anything lower than 0.055 was considered a statistically significant result.
5 Discussion: Comparison of TCO Changes in Exposures

This chapter discusses the degradation of each material property for each TCO in each of the exposure configurations. Graphs presented here are averages with error bars, which are the standard deviation of the mean. The methodology for these calculations are in Chapter 4. Here changes in each of the primary material properties of interest will be examined, starting with optics, then interfaces, and then conductivity.

5.1 AZO

5.1.1 Accelerated Exposures, Open-faced Configuration

Optical Properties. A change in the yellowness index was seen only in the cyclic exposure. As shown in Figure 5.1, the cyclic exposure yellowness index is consistently higher than the damp heat or 5 suns UV exposure after approximately 336 h of exposure time.

To ensure that these are in fact statistically significant differences, a t-test (methodology in Chapter 4) was performed at each time step between cyclic and the other exposures, testing if the cyclic averages were significantly greater. The p-values of the t-test, shown in Table 5.1, confirm that after 336 hours, the cyclic yellowness index averages higher than that of the damp heat or 5 suns UV exposure. It could then be reasonably
inferred that the increase in yellowness is due to the combination of water and UV light stressors, as these stressors alone (damp heat and 5 suns UV) did not increase yellowness. An increase in yellowness of AZO films was also found by visual inspection by Messerschmidt et al.\textsuperscript{34}

Table 5.1. T-test p-values of yellowness index comparison. Note, p-values < 0.055 are considered statistically significant.

<table>
<thead>
<tr>
<th>Exposure Time</th>
<th>Cyclic vs. DH</th>
<th>Cyclic vs. 5 suns UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1824</td>
<td>0.0147</td>
</tr>
<tr>
<td>168</td>
<td>0.4813</td>
<td>0.1411</td>
</tr>
<tr>
<td>336</td>
<td>0.0285</td>
<td>0.0253</td>
</tr>
<tr>
<td>504</td>
<td>0.0237</td>
<td>0.0337</td>
</tr>
<tr>
<td>672</td>
<td>0.0013</td>
<td>0.0059</td>
</tr>
<tr>
<td>840</td>
<td>0.0556</td>
<td>0.0013</td>
</tr>
<tr>
<td>1008</td>
<td>0.0023</td>
<td>0.0007</td>
</tr>
</tbody>
</table>
There is also an increase in haze during the cyclic exposure which is not observed in the 5 suns UV exposure, Figure 5.2. There is an uncertain increase in the damp heat haze, which may be due to environmental test chamber contaminants soiling, strongly adhered to the glass side of the sample.

A structural breakdown in the AZO film is also apparent in the transmission spectra, indicated by changes in the interference fringes. Comparing Figures 5.3 and 5.4, we see that the damp heat exposure shows a reduction in the peak-trough height of the fringe, indicating a roughening of the film’s top surface, whereas the cyclic exposure has a frequency shift in addition to peak-trough height reduction, indicating a change in film thickness in addition to surface roughening. It is unclear whether the film thickness change is due to a decrease in film height from the exposed surface, a change in the glass/TCO interface, or possibly a different location on the AZO film. However, the simplest explanation is a film thickness reduction, related to the surface roughening.
The cyclic exposure also has an increase in the infrared region of the spectra, which, as observed by Sundaramoorthy et al, is likely related to a reduction in free carriers.\textsuperscript{11}

Figure 5.3. % transmission changes for AZO over the damp heat exposure. (Thanks to Kelly Peterson)

Figure 5.4. % transmission changes for AZO over the cyclic exposure.
**Interfacial Properties.** Due to the polar nature of a TCO surface, the water contact angle is an excellent indicator of change on the top surface, which will make an interface with the solar cell device. In Figure 5.5, each of the exposures appears to maintain a different water contact angle throughout the exposure, damp heat becoming more hydrophobic, 5 suns UV more hydrophilic, while the cyclic maintained its initial water contact angle. The t-test p-values again demonstrate that these values are distinctly different (Table E.1). These surface differences likely come from water effects; the most hydrophilic samples came from the exposure with no water, and the most hydrophobic samples were from the wettest exposure. The cyclic has a lower water contact angle than damp heat, which would suggest there is a drying out type phenomenon during the hot, UV light portion of the exposure.

![AZO Water contact angle vs. Time](image)

Figure 5.5. Water contact angle in the open-faced accelerated exposures.
It should also be noted here that AZO is subject to delamination-type edge effects in both damp heat and cyclic exposures. Micrograph images of the edge of the AZO film are shown in Figure 5.6.

![Micrograph of edges of AZO, shelf aged, damp heat and cyclic. Microscope at 5x magnification. (Thanks to Ina Martin)](image)

The damp heat effects appear as a ring around the entire edge of the sample, where moisture had access to the interface between the AZO and the glass. It appears that the damp heat exposure is in the process of peeling away, while the edges of the AZO film have completely flaked away in the cyclic exposure. Again, this is most likely a water effect, and in the case of the cyclic complete delamination, a water and thermal cycling effect.

**Electrical Properties.** Lastly, as the most unstable TCO studied here, and as a key material property, we now examine the resistivity of the AZO in these open-faced exposures.
Clearly seen in Figure 5.7, the damp heat exposure has an extreme affect on the resistivity of the AZO film, increasing by 2.5 times the original value. Damp heat is also more aggressive than either the cyclic or 5 suns UV exposure. The cyclic and 5 suns UV exposure are comparable until 1000 hours in electrical degradation, demonstrated by the p-values (see Table E.2). As with the other degraded properties of the AZO film, this degradation can be attributed essentially entirely to water. These results are also consistent with the literature understanding of AZO degradation with water.11,12,17,19,34,35

![AZO Center Resistivity vs. Time](image)

**Figure 5.7.** Resistivity increase for AZO in open-faced accelerated exposures.

### 5.1.2 Accelerated vs. Outdoor Exposures

In this section the degradation of encapsulated AZO films is considered, in both outdoor and accelerated exposures, versus the open-faced exposures we just examined.
**Optical Properties.** While the intention of the encapsulation process was to control but not eliminate moisture, it does not appear in the optical responses that the AZO degraded similarly in the encapsulated configuration as the open-faced configuration. Figure 5.8 shows the yellowness index and haze of the AZO samples in all the previously examined open-faced exposures as well as the data of the 1x and 5x outdoor and damp heat encapsulated samples. The primary meaning of this data is that the open-faced and encapsulated configurations are not easily comparable, in that there is insufficient response from the encapsulated samples to demonstrate degradation and make comparisons. A longer exposure time or a more permeable edge tape may solve this problem.

![AZO YI vs Time](image1.png)  ![AZO %Haze vs Time](image2.png)

**Figure 5.8.** Yellowness index and % haze do not degrade when encapsulated in any outdoor or accelerated exposures.

**Interfacial Properties.** While the optical properties show no degradation when encapsulated in any exposure, there is an apparent change in the water contact angle, as was observed in Chapter 4. In the open-faced configuration, the water contact angle was highly dependent on the exposure type. In Figure 5.9, initial step changes in the water contact angle can be seen for all the encapsulated configurations, with the largest
Discussion: Comparison of TCO Changes in Exposures

5.1 AZO

5.1.2 Damp Heat Exposures

Electrical Properties. As seen in Figure 5.10, the material response was low for the encapsulated samples. Figure 5.10 shows no significant increase in resistivity with exposure time for any of the encapsulated AZO samples in any exposure.

5.2 ITO

5.2.1 Accelerated Exposures

Optical Properties. As seen in Figure 5.11, ITO’s optical properties did not degrade in any open-faced exposure configuration. There may have been some small amount of haze increase for all of the exposures. Transmission spectra confirm that the transmission is constant for all exposure types.

Interfacial Properties. As noted in Chapter 4, the water contact angle of ITO did change with exposure. In Figure 5.12, a trend in water contact angle similar to that of AZO is found in the hydrophilicity of ITO. The 5 suns UV exposure is most hydrophilic, and the...
damp heat is the most hydrophobic, again ranked in order of increasing water present in the exposure. The t-test p-values (see Table E.3) are consistent with the error bars on the plot, meaning that for approximately half the time steps, the damp heat water contact angle is distinctly higher than the cyclic exposure, and at all points, the 5 suns UV is the most hydrophilic.

**Electrical Properties.** The resistivity of ITO in damp heat, cyclic and 5 suns UV are presented in Figure 5.13. There appears to be no degradation in the 5 suns UV exposure. There may be an increase over the course of the cyclic exposure. Damp heat appears to have an initial step change at the first 168 hours of exposure. If the t-test is taken on the damp heat baseline versus all the rest of the data, it is found that the average of
Figure 5.10. Resistivity changes for AZO in outdoor and accelerated exposures.

Figure 5.11. Yellowness index and haze of ITO do not degrade in open-faced accelerated exposures.

the exposed data is statistically significantly higher than the baseline, with a p-value of 7.36e-8. Given that the only exposures which show even a possibility of electrical degradation are those with humidity as a stressor, these results seem to tie water to the mild
Figure 5.12. Water contact angle changes for ITO in open-faced accelerated exposures.

degradation of electrical performance in ITO. This is consistent with the literature and would likely be exacerbated by an applied voltage in the presence of water.\textsuperscript{20,29}

5.2.2 Accelerated vs. Outdoor Exposures

As with AZO, ITO was studied in an encapsulated configuration in damp heat, 1x and 5x outdoor. These data are now compared to the open-faced accelerated exposures.

**Optical Properties.** The resilience of the optical properties of the ITO was maintained in both damp heat and outdoor encapsulated exposures. It was observed in Chapter 4 that $L^*$ shows an increase with exposure time in damp heat. While the trend can be clearly observed in Figure 4.32, the magnitude is very small and no other optical measurement changes significantly.
Interfacial Properties. As was observed in the open-faced exposures, a difference in the water contact angle between exposure types was apparent. In Figure 5.14, the damp heat encapsulated samples show a step increase in the water contact angle, much like that of the open-faced exposure, while the outdoor 1x and 5x exposures maintain a lower water contact angle for longer, more like the cyclic exposure. This would suggest that UV light, even when the ITO is encapsulated, helps maintain hydrophilicity.

Electrical Properties. It was seen in the open-faced exposure that there was little electrical degradation, as it was only observed in a step change in the damp heat exposure. When encapsulated and placed in any of the exposures, there is again a step change in the resistivity of the ITO (Figure 5.15). The point in the 5x exposure at 1349 hours of exposure is an outlier, which is the average of an outlier and reasonable trending point.
Almost all the encapsulated ITO resistivities fall above those of the open-faced exposures. It is possible this is due to part of the encapsulation process, possibly related to the butyl edge tape, as mentioned previously for the water contact angles. While the encapsulated study was conducted after the open-faced study, it is unlikely that shelf aging caused this increase, as resistivity measurements of reserved ITO samples have been found to be shelf stable.

### 5.3 FTO

In the literature and field, FTO is known to be the most stable of the TCOs studied here. Thus the expected response is very small, and indeed, there is no response from the
Discussion: Comparison of TCO Changes in Exposures

Figure 5.15. Resistivity changes for ITO in outdoor and accelerated exposures. Curiously, the only distinct change was in the haze value of the FTO. Starting at nearly 16% haze, as seen in Figure 5.16, there is a decrease of 2-3% after 336 hours of exposure in all open-faced exposures. The t-test was used to compare data before and after the step change in the haze for each exposure type. The p-value for the step change in damp heat exposure at 168 hours is 4.97e-7. The p-value for the step change in 5 suns UV exposure after 163.8 hours is 5.22e-8. The p-value for the step change in cyclic exposure after 326.6 hours is 0.0010. It is unclear why there is a change in the % haze of the FTO in the open-faced exposure, given that all the exposures affected it equally.

However, as a result of this extreme stability, FTO was not examined in any encapsulated configurations. A study with PEDOT:PSS might be warranted if FTO becomes surface or electrical properties.
Discussion: Comparison of TCO Changes in Exposures

Figure 5.16. Haze changes for FTO in open-faced accelerated exposures.

a serious consideration for organic photovoltaics, and conducting a study with applied voltage or different device-like configurations is recommended.
6 Discussion: Effects of PEDOT:PSS

6.1 Water Effects: Comparison to bare TCO

Knowing that different exposure types cause different degradation mechanisms, it is also important to examine different exposure configurations, such as placing the TCO in a device context, to observe interactions with other layers during degradation. A layer of PEDOT:PSS, which is known to damage ITO\textsuperscript{14–16,21}, incorporated into a glass-glass edge-seal only lamination forms a first approximation of the environment a TCO would see if used in an OPV device. Note, in all graphs, only one encapsulated subset without PEDOT:PSS exposure is shown; all encapsulated without PEDOT:PSS data were comparable, so only one is given as a reference to reduce visual crowding. Also, the 0 point data for all PEDOT:PSS data are bare TCO baselines before any PEDOT:PSS has been applied, as noted in section 4.1.1.

6.1.1 AZO

Damp Heat exposures with PEDOT:PSS. The application of PEDOT:PSS demonstrates greater degradation than bare AZO in damp heat. AZO with PEDOT:PSS encapsulated in damp heat sees an increase in yellowness index, shown in Figure 6.1. Additionally, AZO has a higher haze paired with a lower water contact angle (Figure 6.2) and a decrease in the transmission with smoothing of the interference fringes (Figure 6.3). These
indicate a roughening of the AZO surface, also known to occur without the presence of PEDOT:PSS\textsuperscript{6,17,19}, and this roughening may also cause a film thickness change from etching away material from the surface.

Figure 6.1. Effect of PEDOT:PSS layer and aging on AZO yellowness index.

Figure 6.2. Effect of PEDOT:PSS layer and aging on AZO haze and water contact angle.
Discussion: Effects of PEDOT:PSS

Outdoor Exposures with PEDOT:PSS. When AZO encapsulated with PEDOT:PSS is exposed to 5x concentration outdoors, the haze is greater than or equal to PEDOT:PSS hazing in just damp heat. The water contact angle is even lower in 5x outdoor than damp heat exposure (Figure 6.4). Additionally, the % transmission is significantly reduced in the 5x exposure compared to the damp heat exposure, as seen in Figure 6.5, compared to Figure 6.3. This implies that the hazing mechanism may be accelerated by light or UV radiation.

Resistivity of AZO with PEDOT:PSS. However, this photo-induced mechanism does not appear to be related to the resistivity increase mechanism, as the outdoor 5x exposure resistivity is comparable to that of the damp heat exposure, showing no extra acceleration.
Discussion: Effects of PEDOT:PSS

Figure 6.4. Haze and water contact angle changes in AZO in damp heat and real world exposures, suggesting possible photo-sensitive mechanism.

Figure 6.5. % transmission changes for AZO with PEDOT:PSS in the 5x outdoor exposure. (Thanks to Kelly Peterson)
Figure 6.6. Resistivity changes in AZO in damp heat and real world exposures, suggesting photo-sensitive mechanism.
6.1.2 ITO

As demonstrated in Chapter 4, the only optical change with the application of PEDOT:PSS was a small change in $L^*$ in damp heat exposure. However, as noted before, this is a very small change and is not apparent in the yellowness index or % haze of the ITO films, although there may be a slight increase in yellowness index that is not yet large enough to call statistically significant.

The only changes apparent for ITO with PEDOT:PSS are in the interfacial properties, and even these are unclear, demonstrating differences, but no trending. Shown in Figure 6.7, there are differences in the water and diiodomethane contact angles between exposure types. In the 1x and 5x outdoor exposures, a consistently low water contact angle is maintained. The diiodomethane contact angle of the damp heat with PEDOT:PSS is higher after 504 hours than any of the outdoor exposures.

![Figure 6.7](image)

Figure 6.7. Effect of PEDOT:PSS layer and aging on ITO interfacial properties, demonstrated by water and diiodomethane contact angles.

This set of data suggests there are interfacial changes, however, in totality, they are inconclusive and not elucidated by the surface free energies. Additionally, in the 5x outdoor exposure the PEDOT:PSS layer itself became hydrophobic in the exposure area at
the longest exposure times. Figure 6.8 shows the hydrophobic region of the PEDOT:PSS, and the water contact angle of this area of PEDOT:PSS is $86^\circ$, as opposed to the unexposed area, which is approximately $26^\circ$. The reason for this extreme change in the nature of the PEDOT:PSS is unclear, though it could perhaps be due to change in the chemical structure of the polymer blend. This has also not been noted in the literature before.

![Image](image.png)

*Figure 6.8. The perfect outline of the hexagonal area of exposure is defined by water on the hydrophobic PEDOT:PSS on ITO from 5x outdoor exposure.*

The PEDOT:PSS does not accelerate the resistivity increase of ITO in any exposure type (Figure 6.9). There does appear to be the same initial step change in resistivity discussed in Chapter 5.
Figure 6.9. Effect of PEDOT:PSS layer and aging on ITO resistivity.
6.2 Mechanistic Insights of PEDOT:PSS Degradation

From these data, PEDOT:PSS is detrimental to the performance of AZO, optically and at the interface. It causes a distinct increase in yellowness index, as well as hazing. A visual comparison between damp heat and 5x outdoor samples can be seen in Figure 6.10. While the exposures with light as a stressor (1x and 5x outdoor) do seem to exacerbate the hazing of the AZO, there is little trending with exposure time; the hazing/roughening does not get appreciably worse with time. This, coupled with the examination of the images in Figure 6.10, seems to indicate that most of the degradation of the AZO from PEDOT:PSS actually occurs during the deposition of PEDOT:PSS.

Figure 6.10. Image of the hazing of AZO samples by PEDOT:PSS application. The PEDOT:PSS has been removed from the AZO in these images.

The bulbous puddle-like features in Figure 6.10 are actually the initial deposition area of the PEDOT:PSS immediately before the spin coating process. While the puddle of PEDOT:PSS only remained on the AZO surface in that position for perhaps 5 seconds at
most, the outlines are clearly visible even after over 2500 hours of exposure outside. This would also explain the non-trending variations seen in the % haze values (Figure 6.4) and the fact that the hazy areas are not restricted to only the exposed areas of the TCO. This is consistent with the way PEDOT:PSS is known to degrade ITO, in that when water is present, the etching ability of the PEDOT:PSS is enhanced; at deposition, there is water present as a solvent. DeJong et al. found that ITO was etched during spin coating of PEDOT:PSS. A simple confirmation would be to deposit and immediately remove the PEDOT:PSS layer, and take surface and optical measurements.

The chemistry of the hazing reaction of PEDOT:PSS with AZO is unknown, but it is likely similar what is known in the literature, in which the acidic PEDOT:PSS etches and dissolves In\(^+\) ions into the device. It is also likely, that if the mechanism is similar, sufficiently long exposure to PEDOT:PSS might eventually affect the electrical properties of the AZO through damage to the thin film structure.

The bulk degradation seen in the ITO with PEDOT:PSS was less than expected based on literature results. It is possible that with the addition of an electrical stressor, this degradation mechanism may become more apparent. The changes in the hydrophilicity of the PEDOT:PSS itself with exposure to highly concentrated sunlight may be an interesting insight into the photosensitive nature of PEDOT:PSS itself. It seems likely from the water and diiodomethane contact angle data that there are interfacial changes of the ITO, but it is so far unclear precisely what those might be. The use of more samples, additional stressors, and possibly thicker films of ITO are suggested to clarify this degradation.
7 Discussion: Effects of Silane Interfacial layer

7.1 Interfacial Engineering

Interfacial degradation is often an avenue for delamination and device failure, and increasingly, studies are discovering the importance of the interface to many device properties and functions.\textsuperscript{10,16,40,42} Given the degradation observed in the AZO and the changes of the ITO surface properties, these two TCOs were exposed with a silane interfacial/barrier layer to attempt to reduce degradation. FTO demonstrated no degradation, and therefore was not included in this study. ITO and AZO with the silane layer were exposed in an open-faced configuration to damp heat to determine the ability of the silane to protect the TCO from degradation.

7.1.1 Baseline of Silane Properties

The library of silanes is immense; the hydrolyzable group and the organofunctional group can be customized, tuning the surface energy, the thickness and the nature of the film and interface. The silane chosen for this study, APTES, is well characterized in
Discussion: Effects of Silane Interfacial layer

APTES is a tri-functional silane; it can form up to 3 bonds with surfaces or other APTES molecules, forming multi-layers as opposed to just monolayers. The structure of APTES is shown in Figure 7.1.

![Figure 7.1. Structural formula of APTES](image)

Baseline surface energy properties of the silane on the TCOs were measured. Table 7.1 shows the water and diiodomethane contact angle data and surface free energies of APTES on AZO and ITO. In comparison to bare, naturally hydrophilic TCO (see Table 3.1), the APTES-coated TCOs are hydrophobic with a much lower total SFE. This is a potential benefit to the TCO when exposed to a humid environment; however, for the construction of a solar cell, this may create additional challenges. PEDOT:PSS is hydrophilic, meaning that the bonding between PEDOT:PSS and a silane would be weaker than that between the PEDOT:PSS and TCO. This might transfer delamination problems to the silane-PEDOT:PSS interface, rather than eliminating them. It is possible that a silane could be used to replace the PEDOT:PSS layer.

### 7.1.2 Other Considerations

Percent transmission and resistivity measurements demonstrated that the silane layer did not interfere with the optical or electrical performance of the TCOs. The yellowness
Table 7.1. Baseline Surface energies and contact angles of APTES on ITO and AZO

<table>
<thead>
<tr>
<th></th>
<th>Water contact angle</th>
<th>Diiodomethane contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AZO</td>
<td>ITO</td>
</tr>
<tr>
<td>Water contact angle</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>61° ± 8°</td>
<td>55° ± 4°</td>
</tr>
<tr>
<td>Diiodomethane contact</td>
<td></td>
<td></td>
</tr>
<tr>
<td>angle</td>
<td>38° ± 3°</td>
<td>34° ± 3°</td>
</tr>
<tr>
<td>Total SFE</td>
<td>53.6 mJ/m² ± 0.7 mJ/m²</td>
<td>62.6 mJ/m² ± 2 mJ/m²</td>
</tr>
<tr>
<td>Disperse SFE</td>
<td>40.7 mJ/m² ± 0.4 mJ/m²</td>
<td>42.7 mJ/m² ± 0.6 mJ/m²</td>
</tr>
<tr>
<td>Polar SFE</td>
<td>12.9 mJ/m² ± 0.5 mJ/m²</td>
<td>19.9 mJ/m² ± 1 mJ/m²</td>
</tr>
</tbody>
</table>

index was affected minimally, and neither haze nor transmission were affected perceptibly. The silane application did not change the baseline resistivity of the TCO. Stack resistivity is not studied here, as the primary interest is in the TCO and the method of measuring resistivity penetrates the silane layer. Thus it is not clear if this, albeit thin, interfacial layer would cause the stack resistivity to increase, although preliminary studies of incorporation into an OPV device do show a slightly reduced efficiency for multilayer silane films (less than 20%, Thanks to Ina Martin).

Initially, all of the accelerated exposures were to be studied with silane interfacial layers in an open-faced configuration. However, during initial testing with a different silane molecule, allyltriethoxysilane (ATES), the 5 suns UV exposure removed the silane over the exposure time. Post-exposure, solvent-cleaned contact angles were inhomogeneous across the surface of each sample, ranging from silane levels of hydrophobicity,
to solvent cleaned TCO hydrophilicity. The 5 suns UV exposure likely acted as a gentle 
UV Ozone clean, which slowly removed the silane from the TCO surface. The silane was 
not tested in an encapsulated configuration, which could prevent the removal in the UV 
exposures; further studies are recommended to determine if encapsulation is sufficient 
to maintain the silane layer.

It should also be noted that for the edge seal tape used in the encapsulated study, 
Quanex recommends applying a silane to increase adhesion of the edge seal tape. The 
application of a silane may then be able to serve two purposes at once, to protect the 
TCO as a water barrier and to increase the adhesion of the outer water barrier.

7.2 Silane layers in Accelerated Exposures

ITO and AZO were silanized and then exposed to damp heat in an open-faced configu-
ration. Again, all 0 point data for the silane samples, unless otherwise noted, were taken 
post-deposition, with the silane on the TCO.

7.2.1 ITO

The only effect of the silane on the ITO film was to change the optical properties. The 
silane on ITO decreased the yellowness index of the ITO by 6%, and may have increased 
the % haze to at most 3%, as can be seen in Figure 7.2 These small changes may be due 
to the interface of the ITO and APTES, or possibly due to the deposition process of the 
silane. The silane had no effect on the resistivity in damp heat, as seen in Figure 7.3, or 
on any other properties.
7.2.2 AZO

The more unstable AZO film saw a much more drastic change in degradation when silanized. AZO’s yellowness index was increased by 12%. This change, like in the ITO,
is small and does not trend with time. It may also be due to interfacial changes or the deposition of the silane.

However, the APTES layer had a significant benefit for the electrical and structural properties of the AZO. Shown in Figure 7.4, the APTES layer inhibits the resistivity increase caused by damp heat exposure for AZO. As opposed to a 250% increase in open-faced damp heat, there is only a 59% increase in the resistivity when protected by the APTES layer (the encapsulated damp heat AZO is included for visual reference).

![AZO Center Resistivity vs. Time](chart.png)

**Figure 7.4.** Resistivity of bare and APTES-treated AZO as a function of exposure time. Encapsulated AZO in damp heat is included as a reference point.

Additionally, the silane mostly eliminated the delamination-type edge effects seen in open-faced AZO in damp heat exposures. A microscope image of the AZO edge is shown in Figure 7.5, showing that the edge of the 1000 hour silanized AZO sample has
less degradation than the open-faced damp heat. As opposed to the 1-2 mm of edge delamination-type effects surrounding the entire sample, the silane reduces these to less than 1 mm in only a few locations around the edge of the sample. These improved results are attributed to the APTES layer acting as a water barrier, protecting the water sensitive AZO.

![Image](image1.png)

**Figure 7.5.** The delamination type edge effects seen in AZO in damp heat are significantly reduced by APTES. (Thanks to Ina Martin)

While preventing resistivity increase and reducing edge effects are highly desirable outcomes of using a silane interfacial layer, this is not a comprehensive study of silanes in full cell context. Some unintended side effects of using a silane interfacial layer may include decreased adhesion at the silane/PEDOT:PSS interface, as discussed previously. The resistivity is also of the TCO itself, so stack resistivity effects are unknown at this time.
Unlike previous chapters, this chapter discusses the use of accelerated testing to gain insights to the lifetime and degradation of materials and devices. Recently, there has been an increasing number of calls for more realistic accelerated tests, on the basis that the stressors in the current accelerated qualification testing may not be representative of how the device will perform during its lifetime.\textsuperscript{2,49} A reasonable test is defined as one which induces the same mechanistic degradation as seen in the real world. A test encompasses not only the environmental stressors, such as heat, light and humidity, but application dependent stressors, such as a device configuration in a grid context. This is a difficult task to accomplish, as the real world is a complex, dynamic, multi-stressor environment. Replicating multiple stressors in an accelerated exposure is much more difficult than a single stressor, but a single stressor (e.g. water) may not induce the same degradation as two or more stressors together (e.g. applied voltage and water). Additionally, devices deployed in the Sahara will see different stressors than devices deployed in Florida, than devices deployed in Germany. How can one degradation testing standard, or one device design, predict accurately and perform optimally for 25 years in all of these
environments? It has been proposed that qualification standards adopt multiple qualitative ratings, as opposed to a pass-fail test, to more accurately report the diversity of this challenge.\(^\text{49}\)

Here, the data and degradation presented in Chapters 5, 6, and 7, will be re-examined for literature established and newly observed degradation mechanisms, and the exposure types subjected to a reasonableness check. The discussion will include optical changes, electrical changes, and surface and structural changes.

### 8.1 Optical Changes

#### 8.1.1 Environmental Stressors Only

The optical changes which occurred in the open-faced TCO films were:

- Initial drop in FTO % haze in all exposure types
- Increase in AZO yellowness index and % haze in cyclic exposure

Starting with the FTO, given that all the exposure types decreased the % haze, and that the only common stressor between the exposures was elevated temperature (50-85 °C), this suggests that the FTO "annealing" in the air decreased the haze of these films. It was postulated earlier that this might also be a water effect; it may be that the water in the ambient air (5 suns UV exposure) is sufficient for this change, but adding water (damp heat) does not increase the change.

In the AZO yellowness, we have a perfect example of our multi-stressor test inducing new mechanisms. Neither in damp heat nor in 5 suns UV alone does the yellowness index demonstrate any changes. However, in the cyclic exposure, which alternates hot UV light and hot water, there is an increase in the yellowness index with time. The chemical mechanism which produces an increased yellowness is unknown, but we can surmise
from these data that it is a product of the combination of UV light and water on the AZO film.

Now to the reality check; this yellowness increase is seen in the accelerated cyclic exposure, which sprays water on the samples for 4 hours, then exposes them to 5 suns worth of UV light for 8 hours, all at elevated temperature. This set of conditions seems like a decent approximation of the cyclic nature of outdoors plus an acceleration factor, so if we compare the cyclic and 5x outdoor exposures, we might expect them to induce similar mechanisms, such as yellowness increase. Figure 8.1 shows this comparison, and it appears as though at the end of the 5x outdoor exposure the yellowness index has suddenly spiked to near cyclic exposure levels. Unfortunately, this final data point is not well corroborated (only one sample was tested due to breakage during un-encapsulation), but intellectually it would make sense that the yellowness should increase and that it should have a long delay time, given edge-seal encapsulation and the irregular watering of the sample during Cleveland summer. These results warrant further study, with longer outdoor exposures and more samples, but it seems promising that the cyclic exposure, even in the open-faced configuration may be a good acceleration of this real world degradation.

### 8.1.2 PEDOT:PSS and Environmental Stressors

As noted previously, PEDOT:PSS increases both yellowness and % haze of AZO films, and the majority of this degradation seems to be caused at the initial application of the PEDOT:PSS, rather than increasing throughout the exposure. This is consistent with the literature, which says that PEDOT:PSS degrades the TCO in the presence of water, primarily at deposition and if exposed to air.7,14
8.1.3 Silane Configuration

A change was seen in the yellowness index for both ITO and AZO with the application of the silane layer, although differently for the two TCOs. This small change did not trend with time but was present at the baseline and was constant throughout the exposure. It seems likely that this was due to the toluene in the silane deposition, which involved soaking the TCO in a silane-toluene solution for 1 hour. We do not attribute it to the 40 minute UV ozone clean to remove the silane because it is present at the baseline (when the silane was still on the TCO) and because the UV ozone comparable exposure, 5 suns UV, had no affect on the yellowness index. This may be avoided by using different silane application methods.
This effect, like the PEDOT:PSS, falls into the category of considerations related to the configuration and design of the device; what other chemicals will the material encounter not only during its lifetime but during manufacturing which may produce a lasting effect.

### 8.2 Electrical Changes

The general observations made previously in the course of the discussion, are that FTO is electrically stable, ITO appears to have an initial step change in resistivity for all exposure types, and that AZO’s resistivity is highly water sensitive. The water sensitivity of AZO, more specifically, ZnO is well known, and the resistivity increase thought to be primarily due to break down at grain boundaries.\(^{11,12,18,19,34}\) The cause of the initial increase in resistivity for ITO is unclear; although it seems like a "burn-in" type period, like that of a-Si modules, there is no literature knowledge of this type of effect for ITO. It may be that like the FTO % haze reduction, this occurs as a result of annealing in air.

Thinking of these effects from the point of view of finding reasonable exposures, only the AZO has a sufficient response to consider. Looking at the resistivities in the various exposure configurations, as seen in Figure 8.2, it certainly seems that the damp heat exposure is harsher than any other exposure, eliciting a perhaps exponential resistivity increase. However, without a response in the outdoor exposures, it is difficult to draw conclusions on the reasonableness of an exposure. Using the cyclic exposure, which preliminarily seems like a reasonable acceleration of the optical degradation of AZO, to compare to the damp heat, would indicate that damp heat is unreasonable as an accelerated test. Despite active spray with water for 4 hours, the AZO resistivity does not increase nearly as rapidly as the damp heat exposure. This additionally might imply that
there is a recovery time during the UV exposure time, drying the film and restoring some of the water damage. Ultimately, this requires more detailed work on relative acceleration factors, but the reasonableness the damp heat exposure is called into question.

![AZO Center Resistivity vs. Time](image)

**Figure 8.2.** A comparison of all exposure types and configurations and their affect on AZO resistivity.

### 8.3 Surface and Structural Changes

While there are no traditional structural measurements (like X-ray Diffraction, Scanning Electron Microscopy) taken on the TCOs here, the transmission curves and visual inspection have lent several insights into the structural degradation occurring in the AZO films. In several exposures, the interference fringes from the transmission curves lend insights to the film properties (see Figures 5.3, 5.4, 6.3, and 6.5). The peak-trough height
is sensitive to the smoothness of the surface and the frequency of the fringes are sensitive to the film thickness. It was found that water caused a roughening of the surface, while water plus UV light (cyclic exposure) cause both surface roughening and thickness changes. This is a perfect demonstration of the need to have multi-stressor tests to activate all the degradation mechanisms. Similarly, PEDOT:PSS caused both surface roughening and thickness changes in damp heat, and when the same configuration was placed outdoors at 5x concentration (an additional stressor), both mechanisms were enhanced, noticeably dropping the average % transmission of the film (Figure 6.5).

The edge effects mentioned in Chapters 5 and 7 are present in two exposure types; damp heat and cyclic open-faced. The delamination type edge effects are clearly water related, as they do not appear in the open-faced 5 suns UV exposure. As observed previously, it also appears from these images (Figure 5.6 and 7.5) that the damp heat is partway through the delamination process while the cyclic exposure completely delaminated and flaked away the AZO film, likely due to thermal cyclic in the exposure. The delamination may also affect the frequency of the interference fringes of the AZO film, in that damp heat shows no frequency shifting, but cyclic exposure does. Delamination of the TCO from glass is known to occur in the field, so to have that effect present in an accelerated exposure is appropriate, although a TCO is never exposed open-faced in a device nor extended all the way to the edge of the glass. Clear delamination effects have not yet been seen in the encapsulated samples, suggesting that these received a much lower dose of water.
8.4 Variable-Variable Trending

As noted in chapter 4, the power of the pairs plot is to be able to look at not only time trending, but variable trending. Such graphs can lend mechanistic insights into the degradation of materials, by relating otherwise unrelated properties. The relation of % transmission spectra to free carrier concentrations and resistivity has already been noted here and in the literature. Here, an example of two disparate properties are compared for mechanistic insights, using the canary material AZO.

In Figure 8.3, the yellowness index is plotted as a function of center resistivity for all open-faced exposures, 5 suns UV, damp heat, and cyclic. Previously, it was observed that only the cyclic exposure, with the combination of water and UV light, caused an increase in yellowness index (Figure 5.1). It was also shown that damp heat causes a drastic (250%) increase in resistivity, due to the presence of water, and cyclic demonstrates a smaller increase in resistivity, while 5 suns UV shows no electrical degradation. Figure 8.3 reinforces all of these observations; neither damp heat or 5 suns UV show an increase in yellowness index, but the combination of UV light and water (cyclic) does cause an increase in the yellowness index. This is a perfect demonstration of a multi-stressor versus a single-stressor exposure instigating different degradation mechanisms; had only damp heat or 5 suns UV tests been conducted on the AZO, degradation pathways would have been missed. It also suggests that the yellowing mechanism and the resistivity increase mechanism are mutually exclusive; damp heat shows a resistivity increase with no yellowness index increase.

It also appears that the cyclic exposure trend of yellowness index vs resistivity might demonstrate a saturation curve. An increase in resistivity is expected for AZO in cyclic
Figure 8.3. Comparison between Cyclic and Damp Heat exposures of yellowness index vs resistivity.

exposures, given the presence of water, and longer exposure times might yield more conclusive information about the interaction of these two mechanisms. More insights from these variable-variable plots should be yielded from semi-guided structural equation modeling techniques under development in the Solar Durability and Lifetime Extension Center.
8.5 Final Thoughts

From all the different degradation mechanisms induced from all the different exposure types, the need for accelerated exposures which can replicate real world degradation is emphasized. Single stressor exposures are useful for providing insights into which stressors a material, or device, are sensitive to, thereby deconvoluting the stressors. However, a single stressor exposure cannot induce the mechanisms which will be seen in the real world, nor can it induce mechanisms which require stressor interaction.
9 Conclusions

The degradation of transparent conductive oxides is a key aspect to the improvement of the lifetime of thin film photovoltaics. Here, we have considered a wide variety of exposure types and configurations, in an attempt to examine a broad variety of degradation mechanisms. Three common TCOs, AZO, ITO and FTO were subjected to damp heat, ASTM G154 5 suns UV and cyclic exposures, and two outdoor exposures at 1 sun and 5 suns concentrations. The materials were exposed in several configurations; open-faced, encapsulated, encapsulated with PEDOT:PSS and open-faced with APTES. Optical, electrical, and surface properties of the TCOs were monitored throughout the exposures to monitor the degradation of the films.

It was found that AZO was the most unstable of the TCOs, which agrees with the literature. AZO’s electrical properties were most severely affected by exposure to water, and delamination type edge effects were apparent. While UV light alone did not affect the AZO film, the combination of water and UV light, in the presence of heat, saw an increase in yellowness index and % haze, with a less severe increase in resistivity than damp heat. Additionally, the cyclic exposure completely delaminated the AZO from the edges, most likely as a result of combined water and thermal cycling.
The ITO studied here was perhaps more stable than some others in the literature. There was no optical degradation in any exposure. The water contact angle was sensitive to water and UV light, in that the water contact angle ranked the exposures from most to least UV light and least to most water. It appeared as though there was a step change increase in the resistivities in every exposure type.

FTO was not found to degrade in any exposure, although the % haze may have been sensitive to UV light exposure.

To simulate a real world OPV application, PEDOT:PSS was applied to AZO and ITO then the samples were edge-seal only encapsulated. AZO saw severe optical degradation merely from the application of PEDOT:PSS; an increase in yellowness index, an increase in % haze coupled with a decrease in water contact angle related to a surface roughening mechanism, which may be light sensitive. PEDOT:PSS on AZO did not however accelerate the resistivity increase. ITO, which is documented to react with PEDOT:PSS saw some unclear surface changes, but no other effects.

Organofunctional silanes were explored as a method to customize the TCO-absorber interface and to protect the TCO from environmental degradation. APTES was chosen for the degradation study in damp heat environment with AZO and ITO. APTES successfully protects the AZO film from edge effects of moisture ingress and helps maintain a lower resistivity over 1000 hours of damp heat exposure. There was little effect on the performance of ITO with the application of APTES. Both AZO and ITO saw small changes in yellowness index, most likely as a result of the long silane deposition in toluene. The protection for the AZO film provided by the APTES is a promising start, and further studies in other exposure types and other configurations (pseudo-cell and full cell) are suggested.
Finally, from this broad range of exposure types and configurations, as many varieties of degradation mechanisms are observed. As noted by numerous other professionals in solar technology, understanding and combating the mechanisms of degradation is important to the successful commercialization of all photovoltaic technologies.\textsuperscript{1,7,16,17,49} Current market qualification testing primarily serves to weed out infant mortality devices, but lends no insight into real world degradation mechanisms nor is predictive of the lifetime.\textsuperscript{49} It is observed here, in the case if AZO that the damp heat exposure may be an unreasonable test, while the cyclic may be a more reasonable test, based on comparable mechanisms to the outdoor exposures. These data and observations emphasize the need for a lifetime and degradation science approach that can convolute and deconvolute environmental stressors, outline mechanisms, and inform our accelerated tests to better relate to real world degradation.
10 Suggested Future Research

As with any research, there is always more exploration that can be conducted. The samples generated in this work have been stored for future analysis. This analysis should include structural and chemical characterization of the samples in each type of exposure, such as X-ray Diffraction, X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy. Ideally, these measurements should compliment the analysis already conducted, extending the understanding of the chemical changes involved in the degradation mechanisms. Calculations and analysis should also be conducted to relate the outdoor and accelerated exposure data. These calculations may be based on a scaled "dose" of stressors that the TCO was subjected to. The Solar Durability and Lifetime Extension Center is developing a semi-guided structural equation modeling technique which may prove useful to comparing mechanisms between accelerated and outdoor exposures.

To ensure the statistical robustness of the observations made here, more samples of the same and different TCOs should be subjected to these exposures, including an extension of the outdoor exposures. As part of corroborating and extending the data, improvements to the methodology of resistivity measurements for ITO and encapsulation procedure should be explored. Finally, examining various configurations and exposure
types with an additional electrical stressor on the TCO, given the literatures observations of the role electrical stress plays in degradation.

Extending beyond the parameters and mechanisms studied here, it is recommended to further explore the role of interfacial layers on degradation. This includes encapsulating the TCO-silane stack such that UV light can penetrate while preventing the small amount of ozone exposure (5 suns UV accelerated test), to determine if it is stable in UV light. Similarly, a TCO-silane-PEDOT:PSS stack should be exposed in a variety of exposures, to determine if the silane is an effective reaction blocking layer for long term use, up to and including a full cell design.
Appendix A
Pairs Plots and Correlation Coefficients

The raw data can be found LOCATION. Here is it presented in pairs plots. The method of analyzing the data is described in Chapter 4.
1 AZO

1.1 Open-faced Configuration

Figure A.1. Raw data pairs plot of AZO in 5 suns UV.

5 Suns UV.
Damp Heat. Bare

Figure A.2. Raw data pairs plot of AZO in damp heat.
Figure A.3. Raw data pairs plot of AZO in damp heat with APTES, a silane layer.
Figure A.4. Raw data pairs plot of AZO in cyclic.
1.2 Encapsulated Configuration

**Damp Heat.** Without PEDOT:PSS

Figure A.5. Raw data pairs plot of AZO, encapsulated in damp heat.
Figure A.6. Raw data pairs plot of AZO in damp heat, encapsulated with PEDOT:PSS.
**Outdoor 1x.** Without PEDOT:PSS

Figure A.7. Raw data pairs plot of AZO, encapsulated in 1x outdoor.
With PEDOT:PSS

Figure A.8. Raw data pairs plot of AZO in 1x outdoor, encapsulated with PEDOT:PSS.
Outdoor 5x. Without PEDOT:PSS

Figure A.9. Raw data pairs plot of AZO, encapsulated in 5x outdoor.
Appendix

With PEDOT:PSS

Figure A.10. Raw data pairs plot of AZO in 5x outdoor, encapsulated with PEDOT:PSS.
2 ITO

2.1 Open Faced Configuration

Figure A.11. Raw data pairs plot of ITO in 5 suns UV.

5 suns UV.
Damp Heat. Bare

Figure A.12. Raw data pairs plot of ITO in damp heat.
With Silane

Figure A.13. Raw data pairs plot of ITO in damp heat with APTES, a silane layer.
Figure A.14. Raw data pairs plot of ITO in cyclic.
2.2 Encapsulated Configuration

**Damp Heat.** Without PEDOT:PSS

![Raw data pairs plot of ITO in damp heat encapsulated](image)

Figure A.15. Raw data pairs plot of ITO in damp heat encapsulated.
Figure A.16. Raw data pairs plot of ITO in damp heat encapsulated with PEDOT:PSS.
Outdoor 1x. Without PEDOT:PSS

Figure A.17. Raw data pairs plot of ITO in 1x outdoor encapsulated.
Appendix

With PEDOT:PSS

Figure A.18. Raw data pairs plot of ITO in 1x outdoor encapsulated with PEDOT:PSS.
**Outdoor 5x. Without PEDOT:PSS**

Figure A.19. Raw data pairs plot of ITO in 5x outdoor encapsulated.
Appendix

With PEDOT:PSS

![Image: Raw data pairs plot of ITO in 5x outdoor encapsulated with PEDOT:PSS.]

Figure A.20. Raw data pairs plot of ITO in 5x outdoor encapsulated with PEDOT:PSS.
3 FTO

3.1 5 Suns UV

Figure A.21. Raw data pairs plot of FTO in 5 suns UV.
3.2 Damp Heat

Figure A.22. Raw data pairs plot of FTO in damp heat.
3.3 Cyclic

Figure A.23. Raw data pairs plot of FTO in cyclic.
Resistivity measurements were taken on samples in the locations shown in Figure B.1 for open-faced samples and edge-deleted/encapsulated samples. The center resistivities are taken to be the most accurate as they are furthest from an edge, and therefore less subject to edge effects of the four point probe measurement.

Figure B.1. Diagram of resistivity measurement locations on sample surface. Note: NOT TO SCALE.

Due to the width of the probes on the R-chek used to measure the ITO resistivity, the data has been adjusted to reflect the known edge errors given in the R-chek manual. The "edge" location data was multiplied by 0.8, the "center.top" and "center.bottom"
were multiplied by 0.91, and the "center" multiplied by 0.98, as per the manual recom-
mendations and measured distance. The side measurements were excluded, given their
distance varied over the width of the probe. This may have introduced some amount
of error for edge-deleted ITO samples, given that the probe is now closer to the edge,
however, the center is still assumed to be reasonably accurate.
Appendix C

Lamination Procedure

Lamination was accomplished with the use of a P Energy Mini-module Laminator, Model L036A. The recipe used in the laminator is presented here.

Table C.1. Laminator Recipe: Setpoints

<table>
<thead>
<tr>
<th>Step</th>
<th>Time (s)</th>
<th>Temperature (°)</th>
<th>Bladder Pressure (mBar)</th>
<th>Chamber pressure (mBar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>variable</td>
<td>90</td>
<td>400</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>240</td>
<td>90</td>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>variable</td>
<td>90</td>
<td>0</td>
<td>1000</td>
</tr>
</tbody>
</table>

The laminator was run blank twice with this recipe before laminating any samples, to "prime" the pumps and increase accuracy. The bladder pressure was typically within ±20 mBar of the set point; pressure would spike above the set point at the beginning of the step, then drop to below the set point and slowly climb again to above the set point. The initial and final width of the edge tape was monitored for consistency.
Appendix D
Shelf Stability

Figure D.1 shows the resistivity of samples stored over the course of 4 months. Given the small changes seen in the optics of the TCOs under degradation, it was assumed that the optics of the shelf stored TCOs were stable, confirmed by visual inspection.

Figure D.1. Graph demonstrating that the resistivity of all TCOs is shelf stable.
Appendix E

T-test P-values

This appendix contains the tables of t-test p-values referenced throughout the thesis.

1 AZO Degradation

Table E.1. T-test p-values of water contact angles in open-faced accelerated exposures comparison.

<table>
<thead>
<tr>
<th>Exposure Time</th>
<th>Cyclic vs. DH</th>
<th>Cyclic vs. 5 suns UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>168</td>
<td>8.42e-5</td>
<td>0.0021</td>
</tr>
<tr>
<td>336</td>
<td>0.0114</td>
<td>0.0236</td>
</tr>
<tr>
<td>504</td>
<td>0.0378</td>
<td>0.0004</td>
</tr>
<tr>
<td>672</td>
<td>3.04e-6</td>
<td>0.0001</td>
</tr>
<tr>
<td>840</td>
<td>0.0016</td>
<td>1.43e-5</td>
</tr>
<tr>
<td>1008</td>
<td>0.0002</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

Table E.2. T-test p-values of resistivities in open-faced accelerated exposures comparison.

<table>
<thead>
<tr>
<th>Exposure Time</th>
<th>Cyclic vs. 5 suns UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.997</td>
</tr>
<tr>
<td>168</td>
<td>0.5</td>
</tr>
<tr>
<td>336</td>
<td>0.5239</td>
</tr>
<tr>
<td>504</td>
<td>0.2017</td>
</tr>
<tr>
<td>672</td>
<td>0.2266</td>
</tr>
<tr>
<td>840</td>
<td>0.1229</td>
</tr>
<tr>
<td>1008</td>
<td>0.0302</td>
</tr>
</tbody>
</table>

2 ITO Degradation
Table E.3. T-test p-values of water contact angles in open-faced accelerated exposures comparison.

<table>
<thead>
<tr>
<th>Exposure Time</th>
<th>DH vs. Cyclic</th>
<th>Cyclic vs. 5 suns UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>168</td>
<td>0.0209</td>
<td>0.0095</td>
</tr>
<tr>
<td>336</td>
<td>0.4397</td>
<td>0.0003</td>
</tr>
<tr>
<td>504</td>
<td>0.0866</td>
<td>5.84e-5</td>
</tr>
<tr>
<td>672</td>
<td>0.0010</td>
<td>5.81e-5</td>
</tr>
<tr>
<td>840</td>
<td>0.0883</td>
<td>1.36e-6</td>
</tr>
<tr>
<td>1008</td>
<td>0.0395</td>
<td>0.0003</td>
</tr>
</tbody>
</table>
Complete References


