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Degradation of transparent conductive oxides: Interfacial engineering and mechanistic insights

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ABSTRACT

Transparent conductive oxides (TCOs) are a known failure mode in a variety of thin film photovoltaic (PV) devices, through mechanisms such as resistivity increase and delamination. Degradation science studies of these materials, as well as most PV systems, have primarily utilized industry standard qualification protocols, which are not designed to be used as lifetime prediction tests. This work applies a data science approach to this engineering challenge, utilizing commercially available TCOs and subjecting them to an array of stressors, including environmental and material stressors. Optical, electrical and surface sensitive TCO property metrics were monitored and analyzed en mass. Different degradation mechanisms and modes were observed when different stressor combinations were applied; TCO surfaces are sensitive to the proportion of water and light in an exposure, yellowing of the TCO only occurs when humidity and UV light are combined, and PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)) application results in hazing and roughening of aluminum-doped zinc oxide (AZO). Using multi-variate analytics and plotting critical material properties against one another in a mechanistic plot, trade-offs between properties and the activation of different degradation mechanisms become readily apparent. In addition to a survey of failure modes of TCOs, a possible solution to the degradation of AZO was examined: the application of an organofunctional silane layer. The application of a thin APTES (3-aminopropyltriethoxysilane) film nearly eliminated the observed edge effects and greatly reduced the resistivity increase caused by damp heat exposure of AZO.

1. Introduction

The transparent electrode is a constituent of numerous optoelectronic devices, including photovoltaic (PV) devices, display and touch screens, and organic light emitting diodes (OLEDs). A variety of materials are used as transparent electrodes; active areas of research include transparent conductive oxides (TCOs), conductive polymers, such as PEDOT:PSS [1,2], and nanowire networks, such as silver nanowires [3,4]. The device context and expected lifetime of the application determine material durability requirements. PV is a long-lifetime application that involves a myriad of environmental stressors; TCOs are widely used as transparent electrodes in PV, and TCO degradation is a critical failure mode in many PV technologies [5–8]. Delamination at the TCO-absorber and TCO-glass interfaces has been reported in thin film silicon [9–11], copper indium gallium selenide (CIGS) [7,12,13], and organic PV (OPV) technologies [14–17]. Interfacial degradation is often an avenue for delamination and device failure, and control of interfaces is important to device performance [11,17–19]. Additionally, voltage-biased electrochemical corrosion of the TCO can lead to cracking [9,10,20], and increased resistivity and structural changes (including roughening and pitting) are widely observed in a number of optoelectronic devices [7,21–23,12].

In optoelectronic applications, TCO surfaces are often modified with one or more thin interfacial layers (IFLs), such as polymers, organofunctional silanes, and small molecule adsorbates [11,17,24–27]. These modifications are designed to improve device performance by controlling the TCO work function, optimizing rates of charge-carrier transfer, and increasing the compatibility of the polar TCO with nonpolar materials used in OPVs and OLEDs.

Although IFLs can enhance initial device performance, the effect of the IFL on the device's lifetime performance must also be

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considered. 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 to improve device efficiency and adhesion between the ITO (indium tin oxide) TCO and the polymer absorber layer [17]. However, PEDOT:PSS is highly acidic and hygroscopic, causing corrosion of the TCO layer (via dissolution of the indium from the In_2O_3 matrix) [15–17,28] and water-related damage to the entire device [8,29]. Other commonly used IFLs are organofunctional silanes; these have been used for decades as coupling agents between organic materials and inorganic surfaces, including in OPV and OLED devices to improve performance [30,31,19]. Silanes are an excellent candidate for interfacial layers in PV devices due to their dipole-like structure, their customizability, and their established use in commercial processes [24,32,33]. With respect to OLED device stability, incorporating a silane interlayer at the ITO/PEDOT:PSS interface has been shown to block the detrimental interaction between PEDOT:PSS and ITO over a short time frame [14].

For lifetime and degradation science (L&DS), the ideal outcome of an accelerated exposure is to provide rapid, straightforward insights into the lifetime performance of a material or device [34–37]. In an L&DS study, normal experimental approaches are complemented with an epidemiological approach using data science and statistical analytics. Materials, samples, and devices are considered as a system, and responses under applied stress are observed using a stress and response framework perspective [34]. All exposure conditions (stressors) and all experimentally measured properties are considered variables, and methods of exploratory data analysis (EDA) are used to identify relationships among variables. This data science approach complements the traditional hypothesis driven approach; new, statistically significant degradation modes and mechanisms can be uncovered by the addition of EDA, and detailed statistical analysis of the variables can provide confirmatory insights [38]. From these data, the next step in L&DS can be taken: developing predictive (prognostic) models demonstrating the observed relationships, enabling exploration of the materials and device performance for real world application [39,40]. Mechanistic degradation models, semi-gSEM (semi-supervised by domain science, generalized Structural Equation Models) can be developed to capture the system's response to stressors [35,41]. Here, the first steps in an L&DS study are conducted on TCOs.

Current industry standard tests were developed as qualification standards for safety marketability, not as lifetime predictors, generating a need for L&DS. Recent studies and colloquial knowledge have questioned whether these industry standard exposures are accurate predictors of real world degradation mechanisms [5,42,43]. Whereas degradation studies of TCOs and TCO devices have been conducted, most have focused on various forms of damp heat testing [9–11,7,21–23,12,44]. The present study broadens the literature, showing that comparison of multiple stressor combinations, including environmental and situational stressors, is necessary to provide insight into degradation mechanisms, including enabling comparison and cross-correlation of performance under accelerated and real world conditions.

In this study, a L&DS approach is applied to the engineering challenge of TCO degradation; illumination, humidity and temperature stressors are applied in various combinations to commercially available TCOs, exploring encapsulation, a polymer stressor (PEDOT:PSS), and a proposed protective silane interfacial layer (3-aminopropyltriethoxysilane, APTES). The optical, surface, and electrical properties of the TCOs were monitored, yielding insights into mechanisms of TCO degradation.

2. Experimental procedures

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 5 cm) were purchased commercially. Samples were subjected to exposures in 168 or 336 h (1 or 2 week) increments (steps) for a total of 1000 to 2526 h of exposure, and samples were removed at 6 time increments during the exposure. After each exposure step, 2–3 samples were removed, cleaned, and characterized. All samples were saved after exposure as part of a retained sample library for further studies. Samples were exposed in one of 4 configurations; open-faced, edge seal encapsulated, edge seal encapsulated with PEDOT:PSS, or open-faced with silane.

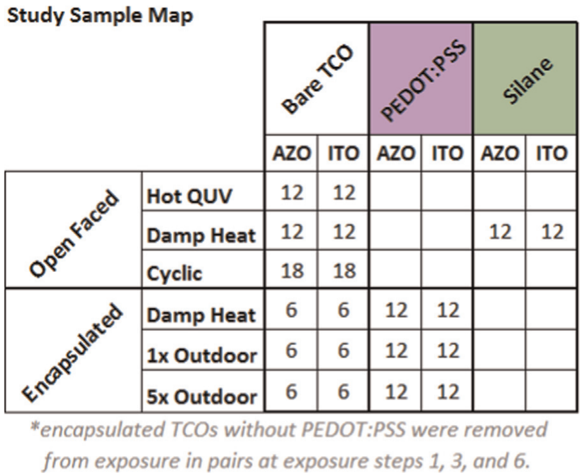
Averaged data are shown in the results section and, where applicable, a *t*-test was performed on the raw data to confirm statistically significant difference [45]. The optical and electrical properties of FTO were found to be robust under all exposure conditions used in this study (open faced accelerated), an observation consistent with the literature [21,46]. ITO was also statistically robust for many of the monitored exposure conditions and evaluation variables. A total of 234 samples were exposed; the subsets showcased in the results and discussion are shown in Fig. 1 [38].

This study is done in the spirit of open [47–50] and reproducible science [47,51,52]. Data were analyzed using open source software, the R programming language [53–56]. All data and the R analysis code to reproduce these analyses are available under an open data license at https://hml15@bitbucket.org/vuvlab/13od-lemiretcos.git [57].

2.1. Measurements of TCO properties

All samples were cleaned before and immediately after exposure to remove any environmental test chamber contaminants before data collection [58]. 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). Contact angle data were collected first to minimize time-dependent surface contamination in room air conditions. Then optical measurements were taken, followed by the resistivity measurements.

Contact angle values were collected by taking the averages of 50-frame video measurements at 5 locations on 2 samples (5 water videos from one sample, 5 diiodomethane videos from the other sample). Transmission spectra were obtained using an



Study Sample Map

		Bare TCO		PEDOT:PSS		Silane	
		AZO	ITO	AZO	ITO	AZO	ITO
Open Faced	Hot QUV	12	12				
	Damp Heat	12	12			12	12
	Cyclic	18	18				
Encapsulated	Damp Heat	6	6	12	12		
	1x Outdoor	6	6	12	12		
	5x Outdoor	6	6	12	12		

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

Fig. 1. Matrix showing the number of samples, exposure type and exposed sample configuration. Samples were removed, tested, and stored in a retained sample library at 6 time increments throughout the exposure duration.