Influence of aging climate and cathode adhesion on organic solar cell stability

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ABSTRACT

Recently, organic solar cells have demonstrated high power conversion efficiencies, but extrinsic device stability remains to be a challenge. Often, delamination of the cathode upon water ingress leads to a massive active area loss and to a strong decrease in efficiency. We present highly efficient organic solar cells with an oligothiophene-based donor and two different cathodes. Devices are aged at four different climates under continuous illumination. Al and $MoO_3/Cr/Al$ cathodes are compared. Additional interlayers are introduced for enhanced cathode adhesion. Aging in different climates reveals a strong dependency of the degradation speed on absolute humidity for standard Al cathodes. However, using additional interlayers, degradation seems to be almost decoupled from the applied climate and device degradation is slowed immensely. Parallel WVTR measurements of the AlO_x barrier allow for the assessment of absolute water quantities until devices are degraded to half of their initial efficiency: $24 \frac{g}{m^2}$ are found for standard Al cathodes, while devices with additional interlayers reach $58 \frac{g}{m^2}$. This difference is related to a completely different aging behavior, which trades strong short-circuit current density losses for moderate fill-factor losses.

1. Introduction

Recent developments in the area of organic solar cells (OSCs) has shown the great potential of this technology. With power conversion efficiencies over 13% [1], reasonable energy harvesting is possible with such devices. While these efficiencies are reached in lab samples under inert conditions, providing long-term stability emerges as a more pressing issue towards marketability. The strong susceptibility to moisture of organic electronic devices such as OSCs and organic light emitting diodes (OLEDs) is well known [2–4] and can be tackled by two fundamentally different approaches: First, better moisture barriers need to be developed to allow for less water ingress, leading to more stable devices. Necessary water vapor transmission rates (WVTRs) to achieve feasible lifetimes of five years and longer have been estimated to be in the range of 10^{-5}–$10^{-6} \frac{g}{m^2 d}$ [2]. Providing a flexible and highly transparent moisture barrier of this quality for large areas is extremely challenging, considering that available technology is only covering WVTRs several orders of magnitude higher. Though recent progress on barrier systems (e.g. atomic layer deposition (ALD) of oxide thin-films [5–7]) shows promising results, these solutions might be too expensive for a wide-spread commercial success of OSC. Second, device suscept-ibility towards ingress of reactive gas species needs to be actively reduced. Here, a detailed analysis of the actual degradation pathways must be performed. Most degradation studies on OSCs have so far reached the conclusion that moisture ingress is the most detrimental among all usually occurring gas species [2–4,8–10]. Upon ingress, the cathode, often consisting of an Al film, is oxidized. With an already limited adhesion of the metal to the organic layers, this easily leads to a local delamination of the cathode. The contact to the cell is lost and current from this area can no longer be extracted efficiently. The short-circuit current I_{SC} drops as active area is lost in a circular pattern around defects in the barrier [4,3,11,2]. Most graphically, this can be observed in dark spot formation of OLEDs, but the same mechanism can be found for OSCs [3]. It has been shown that interlayers between organics and electrode metal can yield higher device stability by slowing interface oxidation and promoting adhesion. Especially chromium [12], titanium [13,12], chromium oxide [14], and other oxides like MoO_3 [15] have been implemented successfully. Chromium is known to enhance the electrode adhesion [12,16,17], effectively preventing active-area loss.

We present a detailed study of the degradation of highly efficient OSCs [18] aged in various controlled climates under AM1.5G illumina-tion. The used devices are a well-known system, which has been applied to numerous investigations, showing very good reliability [18–20].
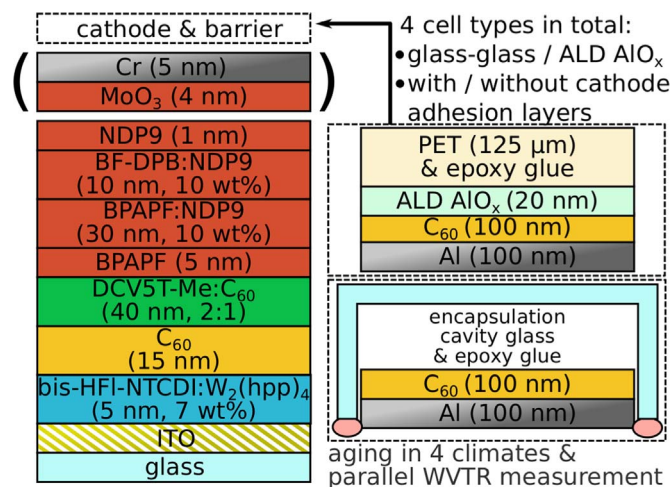

Fig. 1. Schematic depiction of OSC stacks, not to scale. Devices are deposited with or without additional interlayers below the Al cathode. For each type, encapsulation is either done using glass (reference samples) or ALD AlO$_x$ for climate-dependent aging.

Table 1

Aging climates used for the degradation of organic solar cells. Absolute humidities (AH) are calculated using the Magnus formula (Equation [23]).

temperature [°C]	RH [%]	AH [mbar]	remarks
65	50	126	ISOS-L3 standard condition[a]
38	53	35	same temperature/absolute humidity as other conditions, see below
38	75	50	same temperature (38 °C) as above
48.2	31	35	same absolute humidity (35 mbar) as above

[a] ISOS-L3 condition requires the sample to be kept at the maximum power point throughout the whole measurement. Here, parallel measurements necessitate open circuit conditions between data acquisition.

OSCs are intrinsically very stable and dominant degradation stems from electrode oxidation and delamination. We compare ALD encapsulation for extrinsic and glass-glass encapsulation for intrinsic degradation testing. Furthermore, we measure the WVTR of the ALD encapsulation with electrical Ca-Tests to calculate absolute water ingress. Using this extensive experimental setup, two types of n-i-p device are compared: One with a simple Al cathode and one with additional layers below the cathode to enhance its adhesion –MoO$_3$ and Cr. All OSC types are displayed in Fig. 1. For maximum experimental insight, we carefully choose four climates, see Table 1 for actual values: Standardized ISOS-L3 aging conditions [21]; two climates sharing the same temperature with different humidity, enabling a better deconvolution of water vs oxygen degradation; and lastly, another climate sharing the same absolute humidity with one of the above conditions, but at a different temperature. This allows for a rough estimation of purely temperature-activated processes without influences of moisture content. All climates are also chosen to work with saturated salt solutions providing the humidity, which is necessary for WVTR acquisition in the electrical calcium corrosion test system used in this investigation. By doing a parallel WVTR measurement on the barrier used for OSC encapsulation in the same climate, an absolute amount of water ingress can be calculated from the lifetimes.

2. Experimental

For this investigation, OSCs and electrical calcium corrosion tests (Ca-tests) for moisture ingress measurements are produced by vacuum evaporation. This is done in a customized multi-source vacuum deposition chamber (K. J. Lesker, UK) at a base pressure of 10^{-8} mbar. All presented OSCs are manufactured in a single deposition run.

Organic materials, Ca, and Al are deposited from electrically heated ceramic crucibles or pans (CreaPhys, Germany). Electrically heated tungsten evaporation boats are utilized for Cr and MoO$_3$. Layer thickness is controlled with oscillating quartz monitors. The system is attached to a nitrogen-filled glovebox to allow for inert handling of the samples. OSCs are deposited onto Corning Eagle XG glass with pre-structured ITO (Thin Film Devices, USA). For Ca-tests, Borofloat 33 glass (Schott, Germany) is used as substrate. The following materials are used in OSC and Ca-test deposition: C$_{60}$(CreaPhys, Dresden, Germany), 2,2-((3,4-dimethyl-[2,2:5,2:5,2:5,2-quinquethiophene]-5,5-diyl)bis(methanylylidene))dimalononitrile (DCV5T-Me), N, N'-bis(9,9-dimethyl-9H-fluoren-2-yl)-N,N'-diphenylbiphenyl-4,4-diamine (BF-DPB; Synthon, Wolfen,Germany), N, N-bis(fluoren-2-yl)naphthalenetetracarboxylic diimide (bis-HFl-NTCDI; synthesized in-house), tetrakis (1,3,4,6,7,8-hexahydro-2H-pyrimidol[1,2-a]pyrimidinato)ditungsten (W$_2$(hpp)$_4$), "Novaled P Dopant 9" (NDP9), 2,2-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6-TCNNQ; Novaled AG, Dresden, Germany), 9,9-bis[4-(N,N-bis(biphenyl-4-yl)amino)phenyl]-9H-fluorene (BPAPF; Lumtec, Hsin-Chu, Taiwan), molybdenum oxide (Sigma-Aldrich, Munich, Germany), aluminum, and chromium. For OSC devices, first a 5 nm layer of bis-HFI-NTCDI:W$_2$(hpp)$_4$ is deposited on the structured ITO as electron transport layer, this is followed by 15 nm of C$_{60}$, which serves two functions. It acts as hole blocker towards the donor-acceptor blend and also acts as active material, generating a minor share of the photocurrent. Afterwards, the active layer blend of DCV5T-Me (donor) and C$_{60}$ (acceptor) is evaporated in a 2:1 ratio and a thickness of 40 nm. During the deposition of this layer, the substrate is heated to 90 °C for morphological reasons. [18] Next a 5 nm layer of BPAPF serves as electron blocker and exciton reflector. Hole extraction is done using two hole transport layers in series BPAPF:NDP9 and BF-DPB:NDP9 in thicknesses of 30 nm and 10 nm, respectively. This facilitates hole extraction by matching energy levels of the adjacent layers. 1 nm of pure dopant is used as interface doping on top of the hole transport layers to generate a better electrical contact to the metal. In case of devices with additional interlayers, 4 nm of MoO$_3$ and 5 nm of Cr are evaporated for their adhesive properties, at this point in the stack. For all devices, 100 nm Al serve as top electrode, followed by 100 nm of C$_{60}$, which provides an in-house reference surface for the ALD barrier. For maximum comparability of the devices, this layer is deposited on all OSC devices regardless of encapsulation type. Structures of all non-proprietary molecules are shown in supplement Fig. S1. OSC stacks, cathode variations and encapsulation are displayed in Fig. 1. After deposition, OSCs are either encapsulated with AlO$_x$ thin-films or glass. Atomic layer deposition (ALD) of 20 nm AlO$_x$ is done at 100 °C reactor temperature in a Sentech SI ALD LL plasma-enhanced deposition system (Sentech Instruments GmbH, Germany). The following gases are used in 220 cycles of deposition: electronic grade trimethylaluminum (TMA) precursor, atomic oxygen precursor from oxygen plasma, and nitrogen gas with 99.9999% chemical purity for purging. To ensure mechanical and chemical stability of the barrier layer [22], an additional poly-ethylene terephthalate (PET) film (125 μm thick, Melinex, DupontTeijin Films Ltd., UK) is glued onto it using UV-cured XNR 5592 (Nagase ChemteX Corporation, Japan) epoxy. Reference samples are encapsulated using encapsulation glasses with gas cavities. A getter in the cavity binds ingressing moisture. Along the rim, cavity encapsulation glasses are glued onto the reference samples with UV-cured XNR 5592 epoxy.

External quantum efficiency (EQE) and current-voltage (IV) characteristics are measured in custom setups running custom LabView software. In both systems, multiple samples are fitted in sample holders on automated, moving trays for individual measurement. These are integrated into cabinets to reduce background illumination. For mismatch calculation, EQE measurements are done first, employing the following components: A 7265 DSP lock-In amplifier (Signal Recovery, USA) measures the current response to a chopped monochromatic probe light, generated with an Oriel® Apex xenon arc-lamp (Newport,