Polymer solar cells with enhanced lifetime by improved electrode stability and sealing

Roland Roesch *, Kai-Rudi Eberhardt, Sebastian Engmann, Gerhard Gobsch, Harald Hoppe

Institute of Physics, Ilmenau University of Technology, 98684 Ilmenau, Germany

ABSTRACT

Charge carrier extracting electrodes are shown to control the long term stability of state-of-the-art polymer solar cells. Especially low work function metals like aluminum as electron extracting contact and their interface to the photoactive material are identified to be very unstable due to oxidation and delamination, even under superior sealing conditions. In this study we deliberately employed a solution processible titanium oxide interlayer between the photoactive layer and the electron transporting metal contact to study the impact of this layer, in combination with a variation of metal back electrodes and different sealing conditions on overall device long term stability. An automated lifetime testing setup for in-situ *IV*-characterization and different imaging techniques, namely lock-in thermography and luminescence imaging, were used for investigation of time dependent photovoltaic behavior and laterally resolved degradation features.

A titanium oxide/aluminum bilayer as electron extracting contact revealed to be very stable, exhibiting ~100 h of lifetime without any sealing and approximately 18,000 h extrapolated operation time with superior glass–glass sealing, reaching commercially usable dimensions of device stability.

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1. Introduction

Photovoltaics as one source of renewable energy is supposed to be one of the major human energy sources in the future. Due to its low maintenance requirements and its very high variability, large power plants as well as small isolated applications are easily installable and operable. Furthermore, the costs for energy from photovoltaics are mainly driven by the investment costs, i.e. the price per installed watt peak. One of the main aims of thin film photovoltaic technologies is, besides flexibility, its low cost production, which is achievable due to low material consumption. Thin film photovoltaics based on semiconducting polymers has, in addition, another major advantage: its solution processable material components including photoactive layer materials allow fast, large-scale and thus cost effective coating techniques, further reducing the production and investment costs [1,2]. Their recent catch-up race to power conversion efficiencies around 10%, comparable to other thin film photovoltaic technologies [3], ultimately paves the way for polymer-based photovoltaics to enter commercial markets. However, the main disadvantage of polymer photovoltaics to date, its low device stability, prevents it from being the main thin film technology in the field. Although device stability and degradation mechanisms of polymer solar cells were studied since 10 years [4–6], device' lifetime was limited between hours to days and weeks within the field of research for a long time. Inverted polymer solar cell structures [7] and extreme sealing conditions lead the way to ~5000 h of operational lifetime for polymer solar cells comprising poly(3-hexylthiophene) (P3HT) as photoactive material [8–10]. Recently it was shown by Peters et al. [11] that using poly[[9-(1-octylnonyl)–9H-carbazole–2,7-diyl]–2, 5-thiophenediyl–2,1,3-benzothiadiazole–4,7-diyl–2,5-thiophenediyl] (PCDTBT) [12] instead of P3HT leads to twice the lifetime (~10,000 h) under the same extreme sealing conditions, comprising glass–glass sealing and getter materials. Together with its higher potential in power conversion efficiency approaching 7% [13], PCDTBT exhibits superior properties compared to P3HT and making it worth to be maxed out further in terms of device lifetime.

For "non-inverted" P3HT based polymer solar cells it was already shown that replacing the low work function cathode by a solution processible titanium oxide interlayer [14,15] between photoactive layer and metal cathode results in considerably improved device lifetime [16–18]. Using this type of metal oxide interlayer in PCDTBT based polymer solar cells resulted in power conversion efficiencies of more than 6%, without the need of low-work function metals as cathode material [19].

In this report we combine the advantages of PCDTBT, i.e. higher power conversion efficiency and improved intrinsic stability compared to P3HT, together with the advantage of a solution processible titanium oxide layer to increase the lifetime of "non-inverted" sealed and unsealed polymer solar cells toward long term applications.

* Corresponding author. Tel.: +0049 3677 693210; fax: +0049 3677 693173.
E-mail address: roland.roesch@tu-ilmenau.de (R. Roesch).

2. Materials and methods

2.1. Sample preparation

Polymer solar cells were prepared on indium tin oxide (ITO) covered glass substrates. On top a poly[3,4-(ethylenedioxy)–thiophene]:poly(styrene sulfonate) (PEDOT:PSS, Clevios PH) layer was spin coated from an aqueous dispersion as hole transport layer (HTL), followed by a drying step at 180 °C for 15 min. Subsequently the photoactive layer consisting of electronic grade poly[[9-(1-octylnonyl)–9H-carbazole–2,7-diyl]–2,5-thiophenediyl–2,1,3-benzothiadiazole–4,7-diyl–2,5-thiophenediyl] (PCDTBT, 1-material Inc.) and phenyl C_{61} butyric acid methyl ester (PCBM, Solenne) blended in a ratio of 1:2 and dissolved in chloroform with a polymer concentration of 0.4 wt% was deposited on top of the HTL by spin coating. Thereafter a under-stoichiometric titanium oxide (TiO_x) layer was deposited from solution on top of the photoactive layer and annealed under ambient atmosphere as detailed elsewhere [14,15]. A spin coating speed of 3000 RPM for 1 min resulted in a TiO_x-layer thickness of ~10 nm.

To complete the layer stack, the metal back electrode (aluminum or silver) was deposited by physical vapor deposition. A template within the sample holder ensured a device active area of 0.5 cm^2. Hereupon devices were finally sealed by glass plates and epoxy resin. Two different epoxy resins were used, one heat curable (Araldite 2k) and one UV-curable (DELO LP655). The curing process was either done at a temperature of ~80 °C for 30 min or under UV-light of 365 nm wavelength for 3 min. Fig. 1 depicts a schematic cross section and a visual top view image of such a device. Initial IV-characterization was performed under simulated AM1.5 sunlight at 1000 W/m^2, with a class A solar simulator (16S300 single port solar simulator, Solar Light Company Inc.). Furthermore, external quantum efficiency (EQE) was determned to validate the photocurrents (PVE300 System, Bentham Instruments).

2.2. Automated lifetime testing

In order to determine the lifetime of the devices, IV-characteristics under constant illumination were taken in a self-build automated lifetime testing setup. A metal halide lamp was used to illuminate the samples with approximately 1000 W/m^2, resulting in a device temperature of ~45 °C. An emission spectrum is given in Fig. 2(a). Although this spectrum shows considerable deviations to a standard AM1.5 spectrum, this light source fulfills the requirements of a large area device degradation testing setup, especially in providing a better spectral match in the UV-light region as compared to halogen or standard sulfur plasma lamps [20]. Addressing individual devices was carried out by a multiplexer (Keithley 7700,
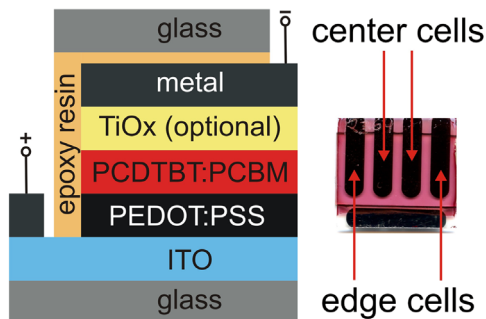
Keithley Instruments) and the IV-characterization itself was done by a source measurement unit (Keithley 2400, Keithley Instruments) every 30 min. Automation of IV-characterization was done via computer control. Furthermore temperature, humidity and light intensity were monitored, thus the setup fulfills all requirements of level 1 laboratory testing conditions under illumination ("ISOS-L-1") [20]. Fig. 2(b) shows a photograph of the degradation setup described above.

2.3. Luminescence imaging and lock-in thermography

Luminescence imaging [21] and lock-in thermography [22] were used for lateral investigation of deficiencies of thin (and light emitting) electronic devices via optical or electrical excitation. Both methods have been adapted successfully to polymer solar cells and modules for quality control and degradation analysis [23–31].

In this report electroluminescence imaging (ELI) was used to identify any deficiencies related to charge carrier injection and thus the electrodes, since the devices were excited with a defined constant forward current [32]. The light emitted from the photoactive layer was collected with a back-illuminated and cooled silicon charge coupled device camera.

Dark lock-in thermography (DLIT) was performed by applying a square wave signal to the device under test, either in forward or reverse direction. The heat dissipation of all current flows within the device was imaged by an InSb focal plane array detector (640 × 512 pixels) with a temperature sensitivity of ~20 mK in the detection range of 3–5 μm. To further increase the temperature sensitivity, a software-based lock-in algorithm was performed for each pixel of the camera and resulted in ~50 μK sensitivity. It is noteworthy that DLIT is able to detect any heat dissipation within the sample, for example even the photovoltaic operation itself and not only defects such as shunts.

3. Results and discussion

3.1. Unsealed solar cells

As a first step, completely unsealed solar cells with either bare aluminum or TiO_x/aluminum cathode were prepared. The photovoltaic parameters short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and power conversion efficiency (PCE) as a result of the IV-characteristics are shown in the first two rows of Table 1.

Fig. 1. Schematic cross-section of a polymer solar cell investigated in this study (left) and top view image of such a cell (right). In the image, "center" and "edge" cells are marked, which is essential for interpretation of imaging results later in the report. Please note that the cross section is not true to scale.
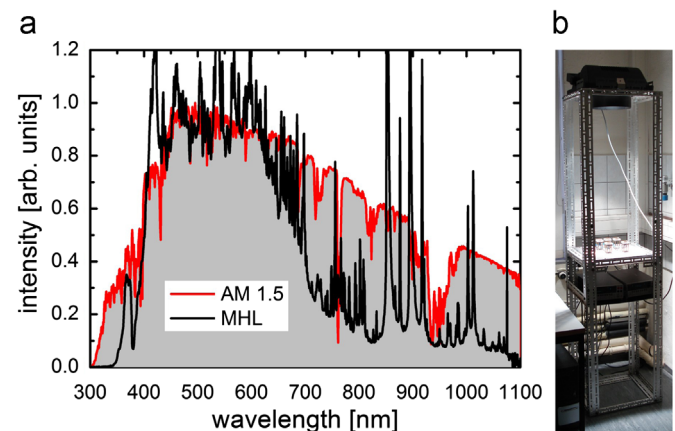

Fig. 2. (a) Metal halide lamp (MHL) emission spectrum versus the AM1.5 standard spectrum . Differences can be observed especially in the UV and NIR range. (b) Photograph of the self-built automatic degradation setup.