# Stability of polymer solar cells: Dependence on working pressure

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## ABSTRACT

We investigated the degradation behavior of polymer/fullerene solar cells processed at different working pressures during the deposition of the metal back electrode by physical vapor deposition (PVD). The temporal development of the photovoltaic parameters was determined with a homemade automated degradation setup for constant irradiation of $\sim$1000 W/m$^2$ in air.

The initial device efficiency improved with evacuation time. The device stability itself depended also on the PVD working pressure: the larger the PVD pressure, the more pronounced was the fast decay of the performance. As reactive remnants, still present within the evaporation chamber due to the larger PVD working pressure, seemed to contribute to the so-called device "burn-in", yielding overall stronger decays for larger PVD working pressures. As a consequence a trade-off between final base working pressure and pumping time seems to be a requirement for cost-effective industrial evaporation processes.

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## 1. Introduction

Organic photovoltaic devices as renewable, next generation energy resources have matured during the last years. The major advantages compared to traditional silicon photovoltaics are flexibility, low weight and roll-to-roll processibilty [1]. Since power conversion efficiencies of polymer solar cells approaching 10% [2] for liquid processing and vacuum processing [3], and outdoor long-term stabilities for polymer solar modules of more than 1 year [4] have been reported, commercialization becomes worthwhile. However, the existing lack in power conversion efficiency and device stability compared to silicon photovoltaics have to be overcome by a better cost structure. Beside the costs for raw materials, processing costs play a main role, especially when vacuum processes are applied, e.g. for metal back electrode deposition.

The pressure ($p$) over time ($t$) dependence for a recipient evacuated by a vacuum pump in the ideal case is given by

$$-\frac{dp}{dt} = \frac{S}{V} \cdot p \tag{1}$$

with pumping speed $S$ and volume $V$. Integration of Eq. (1) yields

$$p(t) = p_0 \cdot e^{-\frac{S}{V} \cdot t} \tag{2}$$

with $p_0$ as base pressure at $t=0$.

Unfortunately this simple equation is only feasible for rough vacuum. In the high vacuum region leakages become dominant

which results in a pressure dependence of the effective pumping speed. The time needed to decrease the pressure in a recipient, called evacuation time, then increases disproportionately high with decreasing pressure [5].

Therefore an optimal working pressure has to be found for evaporation of metal electrodes, small enough to enable efficient device functionality and stability but as large as possible for allowing short evacuation times. In terms of commercialization of roll-to-roll production of polymer solar cells and modules, investment and especially production costs of expensive vacuum processes have to be weighted carefully against the benefits of such a technology.

The approach in this work is to investigate the efficiency and long time stability of polymer solar cells based on poly[3-hexylthiophene] and phenyl C$_{61}$ butyric acid methyl ester processed at different working pressures during metal back electrode physical vapor deposition.

## 2. Experimental

### 2.1. Materials and sample preparation

Polymer solar cells investigated in this work were prepared on indium tin oxide (ITO) covered glass substrates. On top a poly[3,4-(ethylenedioxy)-thiophene]:poly(styrene sulfonate) (PEDOT:PSS, Clevios) layer was spin coated from an aqueous dispersion as hole transport layer (HTL), followed by a drying step in air at 180 °C for 15 min. Subsequently the photoactive layer made of electronic grade poly[3-hexylthiophene] (P3HT, Merck) and phenyl C$_{61}$ butyric acid methyl ester (PCBM, Solenne) blended in a ratio of

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2:1 and dissolved in chlorobenzene with a polymer concentration of 1.2 wt% was deposited on top of the HTL also by spin coating technique under inert gas atmosphere. Thereafter the metal back electrode (aluminum) was deposited by physical vapor deposition (Auto 306, Edwards). A template within the sample holder ensured a device active area of 0.5 cm². Hereupon devices were annealed at 150 °C for 8 min and finally sealed between glass plates by epoxy resin, both under inert gas atmosphere [6]. Fig. 1 depicts a schematic cross section (a) and a visual image (b) of such a device. Initial IV-characterization was performed under simulated sunlight at 1000 W/m², AM1.5 from a Class A solar simulator (16S300 single port solar simulator, Solar Light Company Inc.).

The choice of applicable working pressures during physical vapor deposition was limited by two facts. First the pressure had to be low enough to enable physical vapor deposition due to limitations of the mean free path $l$

$$l = \frac{k_B T}{\sqrt{2}\pi d^2 p} \tag{3}$$

with $k_B$ as Boltzmann constant, $T$ as temperature, $d$ as particle diameter and $p$ as pressure. For air at room temperature and a pressure of $1 \times 10^{-4}$ mbar a mean free path of 1 m is achieved, approximately meeting the dimensions of a vacuum chamber and thus limiting the working pressure at its upper end. The second limit was given by the pumping speed $S$ of the vacuum pump used and the leakages of the vacuum chamber. Both limitations resulted in a set of investigated working pressures that is enlisted in Table 1 together with the correlated pumping time. It has to be noted that the roughing pump needed almost 10 min before the high vacuum pump could overtake within the used system.

## 2.2. Automated degradation setup

In order to determine the time dependence of the devices' IV-characteristics under constant illumination, a homemade automated degradation setup was established. A metal halide lamp (MHL) was used to illuminate the samples with approximately 1000 W/m². An emission spectrum is given in Fig. 2(a). Although this spectrum
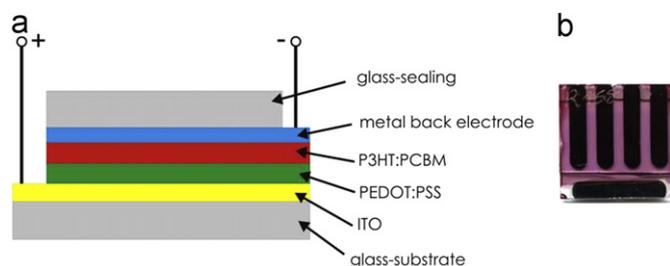


**Fig. 1.** Schematic cross section (a) and visual image (top view, b) of a polymer solar cell investigated in this study.

**Table 1**
List of applied working pressures during metal back electrode physical vapor deposition and correlated pumping times. $5 \times 10^{-7}$ mbar is almost the final pressure of the system.

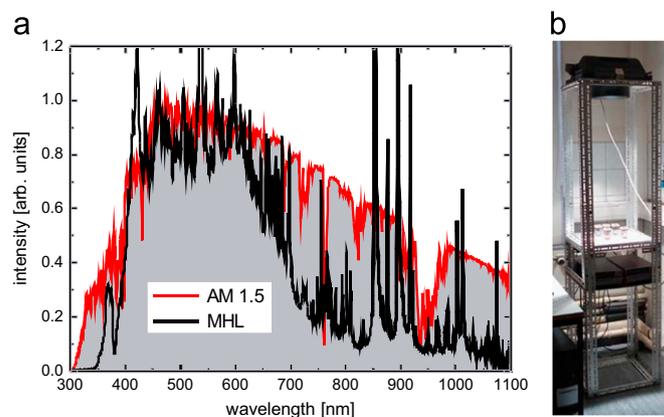| Pressure (mbar) | Pumping time (min) |
| --- | --- |
| $1 \times 10^{-4}$ | 10 |
| $1 \times 10^{-5}$ | 15 |
| $1 \times 10^{-6}$ | 30 |
| $5 \times 10^{-7}$ | ~180 |



**Fig. 2.** (a) Metal halide lamp in comparison with the AM1.5G solar spectrum. Between 350 and 700 nm the overlap of both spectra is particularly good, and (b) photograph of the homemade automated degradation setup.

reveals some deviations to a standard AM1.5 spectrum, this light source fulfils the requirements of a large area device degradation testing setup, which were defined and published by the participants of the ISOS-3 conference, held in Roskilde, Denmark in October 2010 [7]. Electrical circuitry 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 achieved via computer control. Together with temperature, humidity and light intensity tracking this automated degradation setup fulfils all requirements of level 1 laboratory testing conditions under illumination "ISOS-L-1" [7]. Fig. 2(b) shows a photograph of the degradation setup described above.

## 3. Results/discussion

### 3.1. Initial IV-characteristics

Initial IV-characterization under illumination of $\sim 1000$ W/m² already revealed differences in the solar cell parameters, i.e. power conversion efficiency (PCE), fill factor (FF), open circuit voltage ($V_{OC}$) and short circuit current density ($J_{SC}$) (compare with Fig. 3). Each circle or cross in Fig. 3 stand for the parameter of one solar cell.

PCE was approximately 10–15% smaller for $1 \times 10^{-4}$ mbar than for all other working pressures, induced by reduced $J_{SC}$ and FF. In contrast $V_{OC}$ was almost constant for all working pressures.

While the reduced FF could be attributed to oxygen induced p-doping of the P3HT [8], that results in formation of a space charge region in front of the anode due to additional mobile holes, a lower $J_{SC}$ could either be explained by the same fact or by additional implications on the metal back electrode by oxidation during and after the deposition process, due to oxygen containing reactants (called only oxygen below) present in the surrounding atmosphere and in the photoactive layer. Most probably oxygen was already present within the photoactive layer and/or HTL before deposition with a working pressure of $1 \times 10^{-4}$ mbar, since parts of device processing took place in air and a pressure of $1 \times 10^{-4}$ mbar corresponds to approximately 0.1 ppm oxygen content in a well performing glove box. For working pressures lower than $1 \times 10^{-4}$ mbar physisorbed oxygen was able to diffuse out of the half-finished products before metal back electrode deposition, which is, of course, a time dependent process. However, the almost constant $V_{OC}$ for all devices indicated an electrically intact photo-active layer/metal back electrode interface.