

BACK ELECTRODE INFLUENCE ON OPTO-ELECTRONIC PROPERTIES OF ORGANIC PHOTOVOLTAIC BLEND CHARACTERIZED BY KELVIN PROBE FORCE MICROSCOPY

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Abstract

Organic photovoltaic (PV) system consisting of P3HT:PCBM blend layer was prepared with an aluminum (Al) back electrode. After the final thermal annealing the Al layer was partially removed. Kelvin Probe Force Microscopy (KPFM) was used to measure photovoltage response to illumination by a solar spectrum light as a function of time (up to 3 weeks). Comparison of the same KPFM measurement on the areas with and without Al revealed differences in both morphology and photovoltage response to illumination. The data are discussed with view to reducing degradation of organic PV devices.

Keywords: Organic photovoltaics, Kelvin Probe Force Microscopy, degradation

1. INTRODUCTION

Organic photovoltaic (PV) devices are considered promising as a renewable energy source due to their carbon-based nature, ease of fabrication, or the capability of preparation on structured or even flexible substrates. Standard device architecture is so-called bulk-heterojunction (BHJ) where the donor and acceptor materials are mixed together and create an interpenetrating network. Their moderate power conversion efficiency (current record is 13.2 % by Heliatek GmbH, commercially available modules <3 % [1]) is still high enough for several specific applications (functional building designs, wearable electronics, etc.). However, if unprotected against environmental conditions their usable lifetime is still strongly limited by degradation [2].

One of the possible methods to assess the degradation properties of organic blends with high spatial resolution is Kelvin probe force microscopy (KPFM). KPFM is a regime of atomic force microscopy for measuring and imaging surface potential. Thus it can detect any changes in electronic properties under defined conditions (e.g. as a function of time, illumination, gas exposure, etc.). KPFM has been successfully used for study of degradation of organic blend layers as well [3-5]. Since then it turned out that the properties of a completed organic PV device are significantly influenced by the back metal electrode [6]. Therefore, in this contribution we focus on comparison of opto-electronic properties (as detected by KPFM) of an organic PV device made of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-Phenyl C61 butyric acid methyl ester (PCBM) both directly on a pristine blend layer and on an area from where the metal electrode was removed after finalizing the device.

2. EXPERIMENTAL

Corning glass substrates with indium tin oxide (ITO) transparent electrode (by Delta Technologies, Ltd., $R_s = 5-15 \Omega/\text{sq}$) were cleaned by ultrasonication in acetone, isopropanol, and deionized water before use. PEDOT:PSS (by Heraeus Clevios™) was spin-coated on the ITO surface (3000 rpm, 30 s) and dried (170 °C, 20 min, hotplate). Pre-heated (50 °C) solution of P3HT:PCBM (by BASF) was spin-coated (1500 rpm, 60 s) on the PEDOT:PSS layer and dried (90 °C, 60 min, oven). 50 nm thick aluminum (Al) bars were thermally evaporated through a metal shadow mask on top of the sample. The sample was thermally annealed (150 °C, 30 min, hotplate). After the final thermal annealing Al was partially removed by Scotch tape so that the active

organic layer below was exposed for characterization. The area with no Al deposition is referred to as pristine BHJ area further in the text; the area from which the deposited Al was removed is referred to as uncovered BHJ.

KPFM was measured by an NTEGRA Prima system (NT-MDT) using Cr/Pt coated silicon cantilevers (Multi75E-G, BudgetSensors). Two-pass amplitude modulated KPFM was used. In this regime the topography profile is captured during the first pass in semicontact mode. Then the tip is kept at a constant height (defined by Δz , dz) over the sample surface and a DC bias voltage (optimized by a closed loop) is used to minimize tip oscillations induced by an AC voltage applied between the sample and the tip. The resulting DC bias voltage represents the contact potential difference between the materials of the tip and the sample. Typical parameters for the KPFM used in this experiment were AC voltage 2 V, $dz = -5$ nm, scan rate 0.3 Hz.

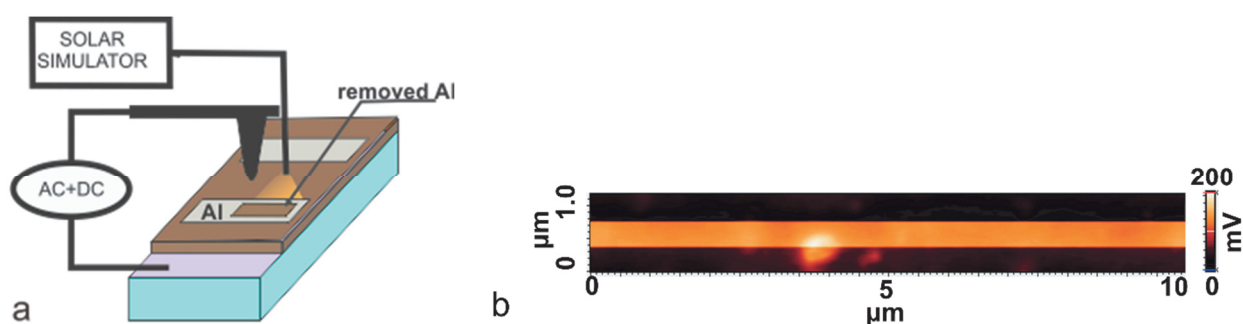


Figure 1 a) Schematics of the experimental setup; b) typical KPFM image in dark (bottom and top parts) and under illumination (middle part)

Illumination induced effects were studied by using a solar simulator (Solar LightLine A1, ScienceTech, inc.). The output of the solar simulator was coupled into a quartz optical fiber that leads the light near the scanning tip of the AFM and illuminated the surface from approx. 3 cm distance (**Figure 1a**). In this configuration the light intensity is somewhat lower than the regular AM1.5 illumination, yet the spectrum remains the same. The KPFM characterization was performed in the following way: the first 10 scanlines were measured in dark, next 10 scanlines under illumination, and the final 10 scanlines in dark again. The scanline was 10 μm long to cover a representatively large areas. The typical resulting image is shown in **Figure 1b**. The experiment was repeated many times during time period of three weeks on both pristine active layer surface and on an area from where the Al thin film was removed.

3. RESULTS AND DISCUSSION

Figure 2 shows optical microscopy views of the blend layer. The pristine area (**Figure 2a**) looks smooth with needle-like features tens of micrometers long, the uncovered BHJ area shows more or less round spots of 10 μm in diameter in average (**Figure 2b**). Similar differences between the pristine and uncovered BHJ areas were observed not only on various locations within the particular sample, but on other control samples that were prepared and treated in similar way as well. Therefore it is assumed to be the result of the presence of Al on the blend layer during the final annealing step. Similarly looking needle-like structures were observed recently on the same type of organic PV device [6] and they were attributed to PCBM crystals. Al layer is believed to prevent the PCBM from crystallization [7], which fits well to the fact that no needle-like structures are observed in **Figure 2b**.

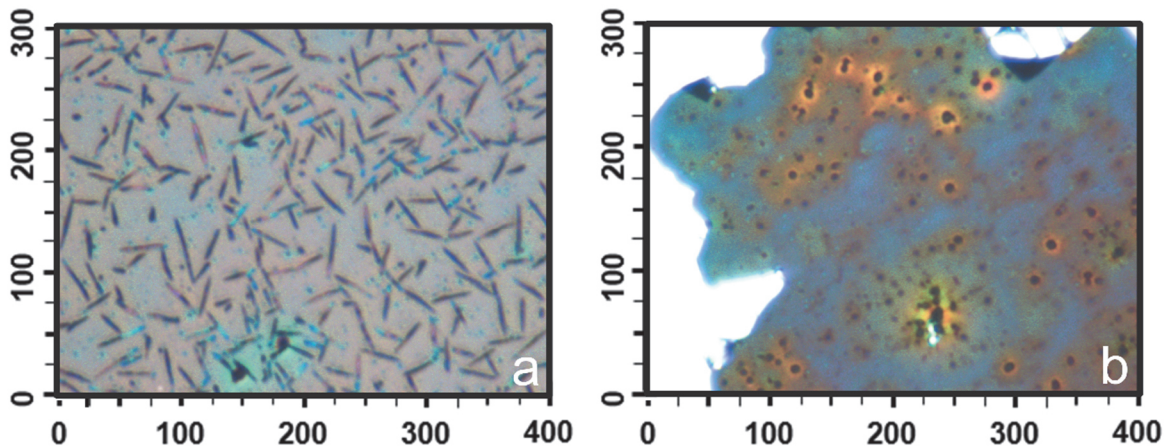


Figure 2 Optical microscopy images (area 400 x 300 μm²) of the pristine area (a) and the area from where Al was partially removed (b). White regions correspond to residual Al having high optical reflectivity

Figure 3a plots the changes in the surface potential under illumination as a function of time on the freshly fabricated device. There is no visible change in the surface potential under illumination at the pristine area and the surface potential is leveled at +450 mV during the whole measurement cycle. At the uncovered area the surface potential moves from the initial level at approx. -50 mV to +40 mV under illumination and then it moves to -60 mV after illumination switching off. The changes occurred within one scan line, which takes 6.7 s.

In the long-term evolution plot in **Figure 3b** the individual measurement cycles are shrunk to a vertical lines. Their heights thus correspond to the extent of the response to the illumination. The plot shows that the photovoltage response at the uncovered area is well resolvable (50-100 mV) all the time during the three week period and follows the trend in decreasing the magnitude of surface potential change. At the pristine area the photovoltage is small (within 15 mV, when resolvable). Note that between the measurements the sample was physically moved in the AFM microscope and thus the individual measurements are not from exactly the same positions. The long-term change in the surface potential can be split into two regions: quick region during the first 3 days (from +450 mV to +70 mV), and slower decrease down to -30 mV within the rest of the period (18 days), as shown in **Figure 3b**. Based on the KPFM results only it cannot be clearly resolved what the reason for this long-term change is. As it occurs mainly at the pristine area, it most likely reflects either absorption of air humidity that was previously evaporated during the thermal annealing or oxidation of one of the blend components [8].

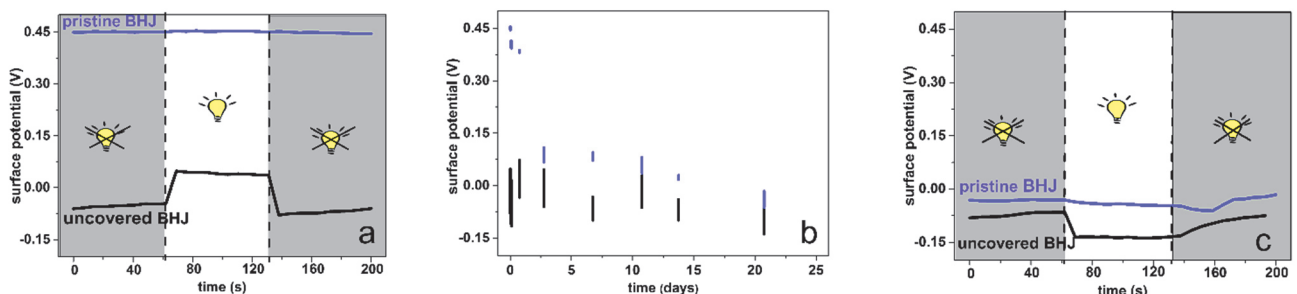


Figure 3 Line profiles of the KPFM images the pristine (violet) and uncovered (black) BHJ areas at the beginning (a), during long term time period (b), and after three weeks from fabrication (c)

Figure 3c shows the detailed photo-responses at the end of the three week experiment. At the pristine area the photo-response is negligible (observed variations cannot be correlated with the times of illumination switching on/off) and the absolute surface potential is lower and closer to the one at the uncovered area. The

photovoltage at the uncovered area in **Figure 3c** is still detected, but it looks differently now. First of all, the response to illumination is inversed, compared to the one observed on the fresh device. This inversion is observed from the third day after the sample fabrication. Such behavior is highly surprising and its origin is unknown so far. Based on the long-term evolution of surface potential (**Figure 3b**) the transition occurs at approx. the same time when the rapid decrease in surface potential at the pristine area is finished. The initial high surface potential (that most likely corresponds to lower work function) may enable redistribution of charge carriers within the material that is not allowed afterwards. Recently, it has been reported that organic PV devices undergo a so called burn-in process, which is a rapid decrease in energy conversion efficiency within a few minutes or hours after fabrication under illumination [9]. Considering that in our experiment the three days correspond to several minutes of illumination, the burn-in process and the changes in surface potential may be of similar origin. Thus quality of encapsulation by the back electrode is highly important. Actual roles of back electrode material, structure, and gas permeability still remain to be elucidated. Second noticeable change is that the surface potential changes from -65 mV to -135 mV under illumination and returns slowly to -75 mV after the illumination is switched off. This indicates changes in carrier recombination mechanism, namely slower recombination which may be due to better spatial separation of the photo-excited charge carriers. Further experimental work is needed to study these two effects in more detail.

4. CONCLUSION

KPFM was used to study changes in surface potential and photovoltage of an organic PV device during three weeks. Measurements were performed both on a pristine organic blend layer and on an area from where the Al back electrode was removed. It was observed that the two areas look differently in optical microscopy and also their opto-electronic properties are different. The surface potential and photovoltage of the material that was annealed under the Al electrode is more stable during the three weeks. Thus quality of encapsulation by the back electrode is highly important. At the area where no Al was deposited the surface potential was initially higher by approx. 0.5 V and decreased significantly in time. The decrease happens in two regimes: fast (the first three days) and slow (the rest of the experiment). The period of fast regime corresponds to the time when the photovoltage at the uncovered area is positive before it switches to negative. This suggests possible correlation with burn-in process in organic PV devices.

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