Application Note

Exploring the properties of organic semiconductors for photovoltaic applications with the NanoWizard® AFM

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Introduction

Energy conversion is one of the hottest topics in today's research community. In photovoltaics, sunlight is used as a reliable and clean source of energy to generate electricity. Photovoltaic devices have to be simple and have low build cost. In this paper, organic photovoltaics are shown as an alternative to conventional solid state semiconductors. Organic photovoltaic cells (OPVC) are based on spatial structures (e.g. layers) of conductive or semiconductive polymers, often referred to as organic electronics. In these, the polymer or small organic molecules (dye doped OPVC) are used to accomplish the functions of collecting solar photons, converting the photons to electrical charges and transporting the charges to an external circuit. However the efficiency of conversion in OPVC devices is currently one order of magnitude lower than solid state based cells. This is related to the lower charge mobility caused by nanoscale morphology and energy level mismatch in the hetero-junction in such structures. Here, using AFM with its superior spatial resolution in combination with local electrical measurements (e.g. conductive AFM) under optical excitation is demonstrated as a powerful tool to gain insight into the underlying processes. The schematic setup of the system is presented in Fig. 1.

This report shows the analysis of the morphology and electrical properties of a photoconductive polymer as a simple model system for more complex OPVC's in correlation with exposure of light and defined environmental conditions.

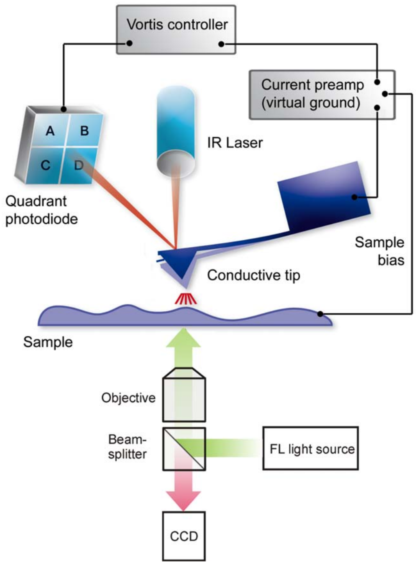

Fig. 1: Schematic representation of the used setup. The topography and conductivity of the sample is investigated by conductive AFM (top). Optical excitation of the sample is realized through the objective by a flourescence light source from the bottom.

Conductive AFM under controlled gas environment (N_2) on inverted microscope

All experiments described here were carried out using the JPK NanoWizard® NanoScience AFM in combination with an inverted research grade microscope (Zeiss,

Fig. 2: Experimental setup used for the investigations. The NanoWizard® AFM with the mounted conductive module is integrated into an inverted microscope (Zeiss, AxioObserver), which rests on an active vibration platform (Accurion, micro 40). The tubes are connecting the closed chamber CAFM module with a nitrogen source. The microscope is equipped with transmission illumination (condenser), fluorescence illumination and a CCD camera.

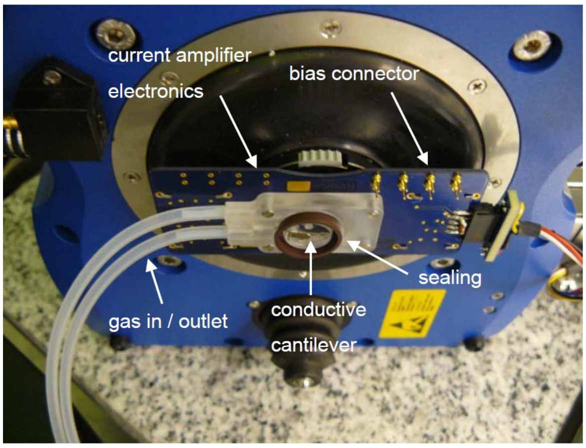

***Fig. 3:** JPK conductive AFM module with closed chamber mounted at the AFM head.*

AxioObserver) with fluorescence illumination (see Fig. 2). Conductivity measurements were performed using the JPK Conductive AFM module (see Fig. 3). This module carries a closed chamber which can be flushed with an inert gas (e.g. nitrogen) to avoid unwanted degradation of the polymer caused by intercalated water and oxygen. An integrated current to voltage converter is located as close as possible to the tip for highest current resolution (down to 1.5 pA). The module also applies the necessary bias voltage between the sample and conductive AFM tip. Silicon contact mode cantilevers with a force constant of 0.3 N/m and a conductive Cr/Pt coating (NanoWorld) were used.

The polymer film was prepared on a transparent coverslip

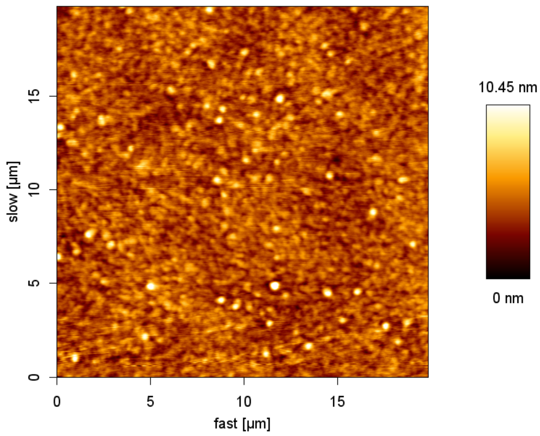

***Fig. 4:** Height image of polymer surface coated on ITO.*

ITO/glass substrate. ITO (Indium Tin Oxide) is a transparent conductive electrode and is highly suitable to be used to easily couple the electrical measurements to light. A thin layer of PEDOT:PSS was spin-coated onto the ITO coated glass substrate. The substrate was then baked in a N_2 environment. Subsequently, the P3HT:PCBM blended solutions were spin-coated on the PEDOT:PSS resulting in a bulk heterojunction film of about 100 nm.

The ITO substrate was electrically connected to the JPK conductive AFM module. In Fig. 4, an AFM height image of the resulting topography of the polymer film is shown.

Test of the electrical tip-sample contact using force spectroscopy

The electrical contact between the conductive AFM-tip and the sample in a conductive AFM experiment can be proven by recording the current signal while approaching and retracting the tip relative to the sample surface. If the tip is brought into mechanical contact, a current should be detectable.

Fig. 5, shows the corresponding force distance curve. When the AFM-tip gets into contact with the sample for the first time during the approach, a jump of the current to 10 pA can be observed. On pulling back the tip, the cur-

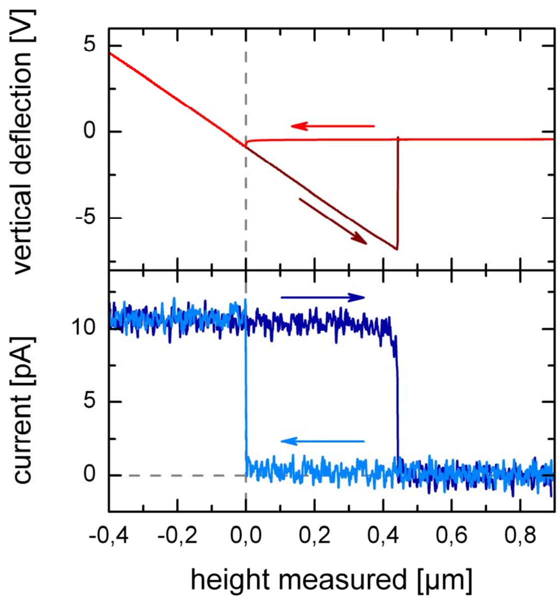

***Fig. 5:** Force-distance and current-distance curves on the prepared polymer film (bias = +1V).*

rent keeps the level until the tip is out of contact with the sample.

Generation of charge carriers by in-situ illumination

The local photocurrent of different regions in the blend film can be studied using conductive AFM with external optical excitation. The AFM-tip was brought into contact to the sample at a predefined position (bias voltage of +5V) and illuminated with a wavelength of λ = 470 nm (blue) by using the fluorescence capabilities of the inverted optical microscope. While the illumination was periodically switched on and off using the shutter of the Zeiss microscope, the photocurrent was recorded over time. In Fig. 6, the results of this measurement are presented. A direct coupling between the illumination and the observed photocurrent is easily visible. If the illumination is switched on, the photocurrent jumps from a value close to zero to a value of about 80 pA. This is an indication of free charge carriers induced by the illumination of the sample.

Additionally to the previous experiment, current-voltage (I-V) curves can also be recorded enabling the investigation of the dependence of the observed photocurrent on the bias voltage being applied between tip and sample.

In Fig. 7, I-V curves are shown having been taken at the same position as before (bias: -10V…+10V, 5V/s). In order to see the effect of the illumination of the polymer film, two curves are shown with and without illumination respectively. A comparison reveals an increase of approximately two orders of magnitude of the current for high bias voltages when the illumination is switched on.

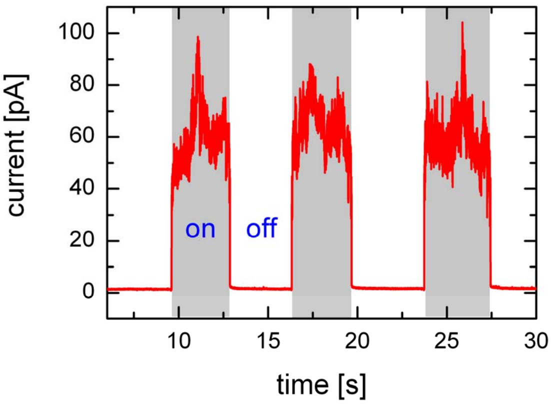

Fig. 6: *CAFM current measurement over time, while the cantilever was in contact with the sample. The illumination was switched on and off periodically as indicated in the graph.*

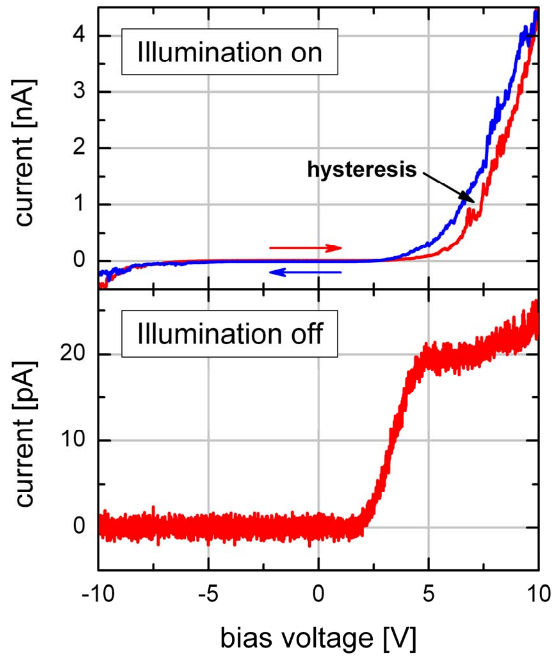

Fig. 7: *Dependence of the observed photocurrent on the bias voltage, when the illumination is switched on (top) or off (bottom).*

Additionally, a hysteresis can be observed when the illumination is switched on, i.e. the observed current depends on the fact whether the bias voltage is increased or decreased.

Conclusion and Outlook

AFM and conductivity measurements combined with optics are a powerful tool to study the behavior of optically active polymers with respect to light.

Variations of the conductivity in conjugated polymer blends can be easily identified with the help of conductive AFM current mapping. This technique can be applied to probe the charge transport and current distribution of phase-separated conjugated polymer blends in the nanometer scale which is useful for understanding the morphology and structure relationship of bulk heterojunction materials. It can play an important role for the microscopic understanding and optimization of conjugated polymer-based solar cells.

Literature

[1] D. Coffey and D. S. Ginger, *Time-Resolved Electrostatic Force Microscopy*, Nature Materials 5, 735-740 (2006).

[2] D. Coffey, O. G. Reid, D. B. Rodovsky, G. P. Bartholomew, D. S. Ginger, “Mapping Local Photocurrents in Polymer/Fullerene Solar Cells with Photoconductive Atomic Force Microscopy,” Nano Letters 7, 738-744 (2007).

[3] M. Dante, J. Peet, T.-Q. Nguyen, “Nanoscale Charge Transport and Internal Structure of Bulk Heterojunction Conjugated Polymer/Fullerene Solar Cells by Scanning Probe Microscopy”, The Journal of Physical Chemistry C 2008, 112, 7241.

[4] T. A. Bull, L. S. C. Pingree, S. A. Jenekhe, D. S. Ginger, C. K. Luscombe, "The Role of Mesoscopic PCBM Crystallites in Solvent Vapor Annealed Copolymer Solar Cells", ACS Nano 2009, 3, 627.