Available online at www.sciencedirect.com

ScienceDirect

Organic Electronics 9 (2008) 149–154

Organic Electronics

www.elsevier.com/locate/orgel

Letter

Conductive atomic force microscopy (C-AFM) analysis of photoactive layers in inert atmosphere

Alexander Alexeev [a], Joachim Loos [b,*]

[a] Nanotechnology-MDT Co, Moscow, Russia
[b] Eindhoven University of Technology, Department of Chemical Engineering and Chemistry,
Laboratory of Materials and Interface Chemistry, and Laboratory of Polymer Technology, and Soft Matter Cryo-TEM Research Unit,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received 9 August 2007; received in revised form 12 October 2007; accepted 14 October 2007
Available online 24 October 2007

Abstract

Conductive atomic force microscopy (C-AFM) measurements have been performed on the MDMO-PPV/PCBM system which is potentially interesting for applications as active layer in polymer solar cells (PSCs). It is demonstrated that C-AFM analysis performed in air for ambient conditions provides only inadequate information about the local electrical properties. The main reason is that the samples chemically degrade when in contact with air. Moreover, we speculate that also the adsorbed water layer interferes with reliable nanoscale electrical measurements. In contrast, when performed in inert atmosphere C-AFM analysis offers consistent results of e.g. the *I–V* characteristics with lateral resolution better than 50 nm, and is able to detect local heterogeneities of these *I–V* characteristics at the sample surface.

PACS: 07.79.Lh; 68.37.Ps; 73.61.−r

Keywords: Conductive atomic force microscopy; Polymer solar cell; Morphology; Photoactive layer; Inert atmosphere

---

1. Introduction

In general, performance measurements of polymer solar cells (PSCs) are carried out on operational devices having at least the size of square millimetres to centimetres. On the other hand, the characteristic length scale determining the functional behaviour of the bulk heterojunction photoactive layer is in the order of 10 nm (exciton diffusion length) to about 100–200 nm (layer thickness) [1–3]. The morphological requirement for the photoactive layer in a high-performance PSC is nanoscale phase separation, which provides large interface area for exciton dissociation and, at the same time, continuous pathways for free charge carrier transport to the appropriate electrodes. Further, it is well-known that the local organisation dominantly controls the functional behaviour of devices. Thus, it is necessary to obtain property data of nanostructures with nanometre resolution to be able to establish structure-property relations that link length scales from local nanostructures to macroscopic devices.

---

* Corresponding author. Tel.: +31 40 2473034.
E-mail address: j.loos@tue.nl (J. Loos).

1566-1199/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.orgel.2007.10.003

In this respect, a very useful analytical tool is conductive atomic force microscopy (C-AFM) [4,5]. Because AFM uses the interaction force between probe and sample surface as feedback signal, both topography and conductivity of the sample can be mapped independently. Theoretically, the resolution of C-AFM is as small as the tip-sample contact area, which can be in the few nanometre range. C-AFM is widely used for the characterization of electrical properties of organic semiconductors. For example, single crystals of sexithiophene have been studied [6], where the *I–V* characteristics of the samples were measured. Several electrical parameters such as grain resistivity and tip-sample barrier height were determined from these data. In another study, the hole transport in thin films of MEH-PPV was investigated and the spatial current distribution and *I–V* characteristics of the samples were discussed [7]. Recently, the distribution of electrical characteristics of polymer blends was studied by C-AFM [8–11].

It is well-known that the performance of most PSC as well as of organic electronic systems in general, drops dramatically after short-time exposure to air, especially when illuminated by light [12]. While some groups have already taken care to perform their C-AFM measurements in a dry nitrogen atmospheres thereby achieving good correlation with device properties [8], it is more common to perform C-AFM in air under ambient conditions. It is the purpose of our study to clearly demonstrate that the local electrical properties of nanostructures in the photoactive layer of PSCs changes when C-AFM measurements are performed at ambient conditions; and as consequence the obtained results are not comparable with data gained from device characterisation. At the same time, we would like to point out that C-AFM measurements performed in the inert atmosphere of a glove box provide more reliable information on electrical properties of organic nanostructures and allow establishing structure-property relations of functional polymer systems at the nanometre length scale.

2. Experimental

2.1. Materials

For the present study, 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM) [13] was synthesized in the University of Groningen, the Netherlands, and poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) [14] was obtained from Philips Research Eindhoven, the Netherlands. The molecular weight of the MDMO-PPV was 570 kg/mol as determined by GPC using polystyrene standards. Poly(ethylenedioxythiophene)-poly(styrenesulfonate)(PEDOT:PSS) was purchased from Bayer AG, Germany. The energy level diagram for materials used in this work is presented in Fig. 1.

2.2. Specimen preparation

The samples studied consist of a glass substrate with an ITO layer (kindly provided by Philips Research, the Netherlands), a spin-coated PEDOT:PSS layer (Baytron-P, Bayer) and a spin-coated photoactive layer. The latter is based on a 1:4 blend by weight (MDMO-PPV/PCBM) initially dissolved in toluene. The spin coating conditions were optimized such that the thicknesses of the photoactive layers were below 100 nm. These samples represent working photovoltaic devices, except for the missing metal back electrode. All sample preparation steps were performed in a glove box (Unilab, MBRAUN, Germany). We are aware that applying toluene as solvent forces large scale phase separation between MDMO-PPV and PCBM, which provides photoactive samples better suited for C-AFM investigations but not for optimum performance in PSCs.

2.3. Characterization

For AFM measurements Solver P47H and NTegra-Aura were used (both NT-MDT, Russia). The cantilevers used were CSC12 (Micromash, Estonia) coated with an additional Au-layer for conductivity measurements. A typical force constant of the cantilevers was about 0.65 N/m, and the radius was below 50 nm. C-AFM experiments were performed with AFM installed in a glove box, which had a

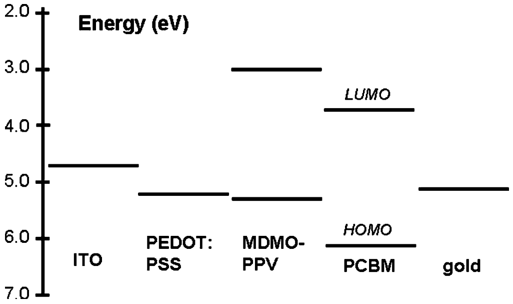

Fig. 1. Energy level diagram for the materials used in present work (energy levels according to Ref. [15]).

nitrogen atmosphere with oxygen and water levels below 1 ppm; only few experiments were carried out at ambient conditions. The ITO layer was grounded during all C-AFM measurements performed in the glove box. The C-AFM measurements for ambient conditions in air were performed with grounded tip.

3. Results and discussion

MDMO-PPV/PCBM is one of the systems best studied for applications as photoactive layer in high-efficient PSCs; efficiencies of about 2.5% have been reported for optimized preparation conditions [16]. Further, it has been demonstrated that the performance of devices having these compounds as blend in their photoactive layers decreases immediately when exposed to air [17]. For this reason, we have chosen the blend MDMO-PPV/PCBM as a model system for our C-AFM experiments.

Fig. 2 shows a series of C-AFM images obtained at ambient conditions in air of a thin PCBM/MDMO-PPV film spin-coated from toluene solution. For such preparation conditions PCBM and MDMO-PPV phase segregate, and PCBM forms large nanocrystalline domains embedded in the MDMO-PPV matrix [15,18]. All images were acquired with a tip coated with a gold layer. The topography image (Fig. 2a) shows that the PCBM domains (bright areas) have maximum diameters of about 500 nm. Phase segregation is responsible for the high roughness of the film: the PCBM domains stick out of the film plane few tens of nanometres.

Figs. 2b and c represent the current distribution image for bias voltages at the tip of −2.3 V (Fig. 2b) and +10 V (Fig. 2c), respectively, measured at the same sample area as the topography image. For negative bias at the tip good contrast is obtained between the electron donor (p-type

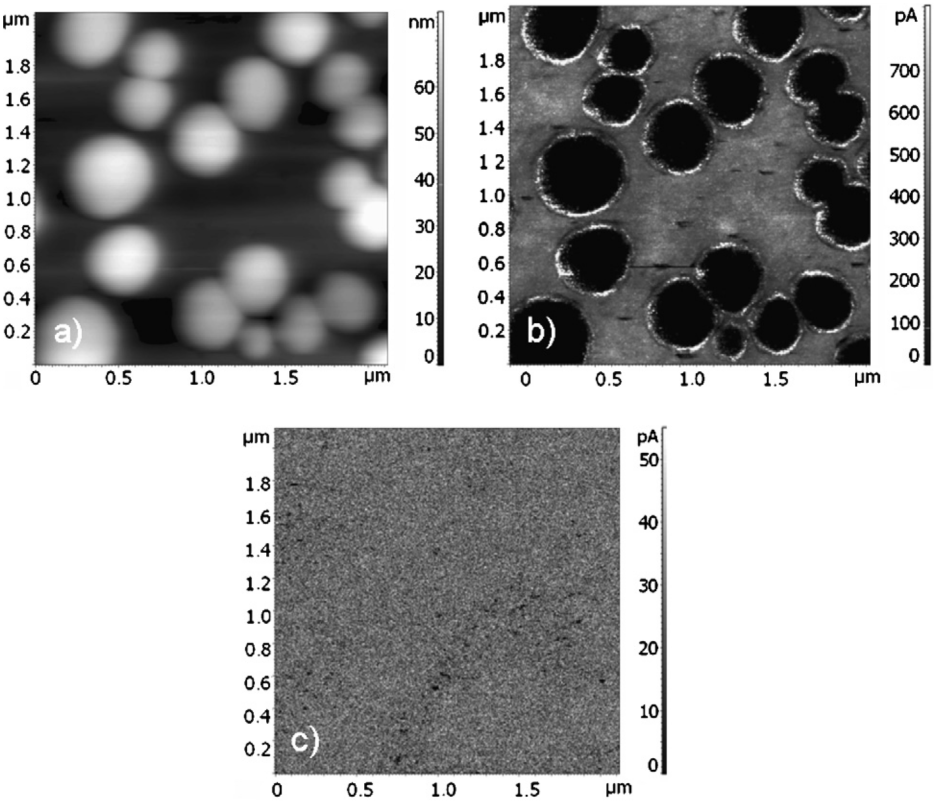

Fig. 2. C-AFM image series acquired at ambient conditions in air of a thin PCBM/MDMO-PPV film spin-coated from toluene solution: (a) topography image, and current distribution images of the same area for (b) a negative bias at the tip of −2.3 V, and (c) for a positive bias at the tip of +10 V. The very slight contrast (c) is caused by some superposition with topography information during the current measurements.

semi-conductor) and the electron acceptor (n-type semi-conductor) materials in the sample. From the corresponding energy level diagram (Fig. 1) it follows that the difference between the HOMO level of MDMO-PPV and the Fermi levels of both electrodes (ITO/PEDOT:PSS and Au-tip) is rather small so that we expect ohmic contacts for hole injection and strong energy barriers for electrons [6,19]. Therefore a hole only current through the MDMO-PPV is expected for both polarities of voltage in a ITO/PEDOT:PSS/MDMO-PPV/Au-tip structure. On the other hand, we can conclude that areas of low current level correspond to the electron acceptor materials, i.e. PCBM (Fig. 2b). This interpretation is in accordance with the above-mentioned topographical observations (Fig. 2a). For positive bias at the tip, however, no differences between the two phases can be obtained, and the measured overall current level is below the noise level of our experimental setup.

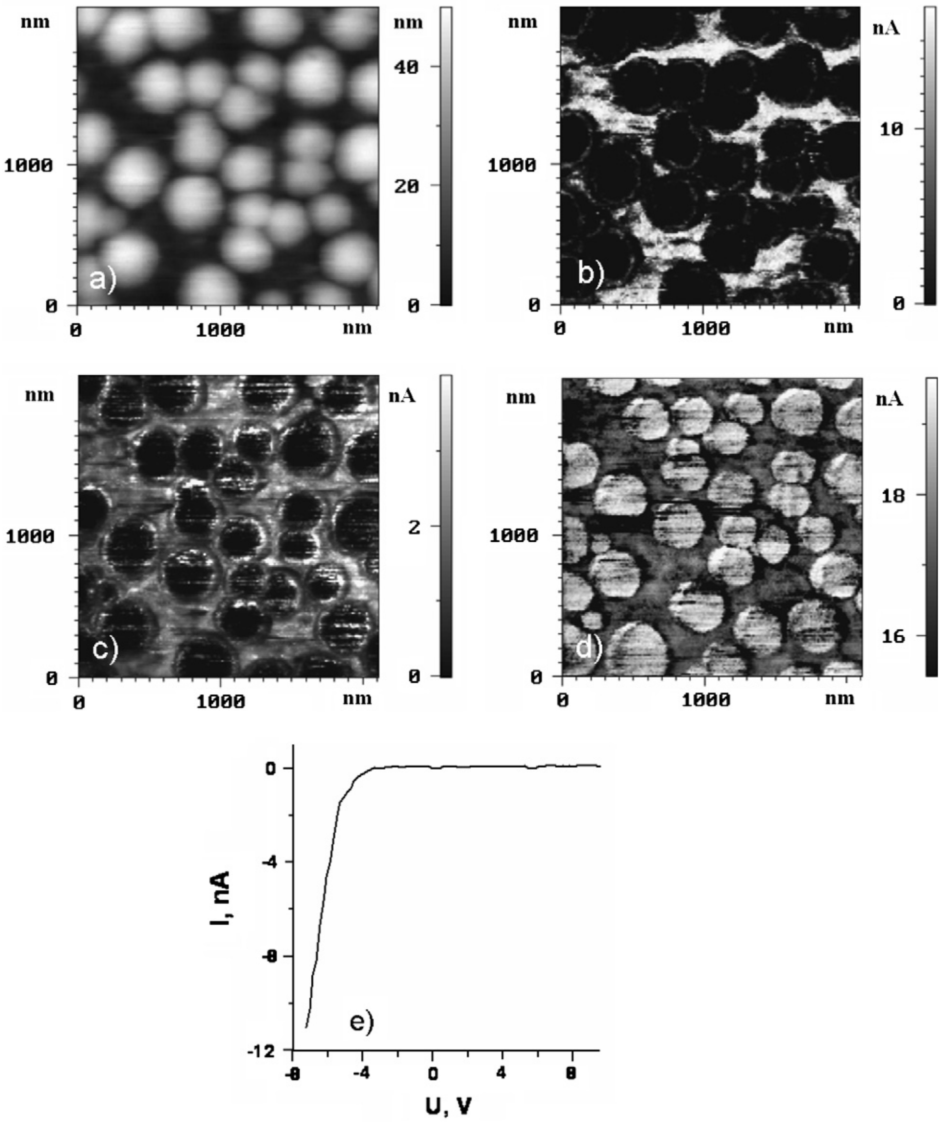

Fig. 3. (a) Topography of a PCBM/MDMO-PPV thin film sample obtained in contact mode; (b)–(d) C-AFM images acquired in the inert and water free atmosphere of a glove box showing the current distribution of the same sample area for (b) a positive bias at the tip of +10.0 V, (c) for a negative bias at the tip of −5 V, and (d) for a negative bias at the tip of −10 V, (e) *I*–*V* curve obtained on pure PCBM film spin-coated on glass/ITO/PEDOT:PSS.

Since the materials under investigation are sensitive to oxygen and at ambient conditions the always-present water layer on top of the sample surface interferes with nanometre scale electrical measurements, which has been reported recently for the case of surface potential measurements [20], we have performed additional C-AFM experiments on the same MDMO-PPV/PCBM system but in inert atmosphere. For this purpose, we have assembled the C-AFM setup in a glove box filled with nitrogen atmosphere and an oxygen and water level below 1 ppm.

Fig. 3 presents C-AFM measurements of a MDMO-PPV/PCBM sample for such an experimental setup with lateral resolution better than 50 nm. For negative bias at the tip of −5 V similar features are observed as discussed for Fig. 2b (Fig. 3c): the dark areas represent PCBM domains with low current embedded in the MDMO-PPV matrix showing higher current. Contrary to measurements performed in air, also for the positive bias value at the tip of +10 V good contrast between the phases is observed (Fig. 3b). Beside some little drift of the area probed during the two successive C-AFM measurements with positive and negative bias, PCBM domains can be recognised as dark areas embedded in the bright MDMO-PPV matrix in Fig. 3b and c. Around the PCBM domains ring-like structures are seen having higher current (Fig. 3b–d and Fig. 2b), which might be caused by more efficient charge collection at the domain interface [11]. Probably, an existing mixed-phase of PCBM and MDMO-PPV at the interface may enhance charge mobility, as reported for blends of polythiophene with polyethylene or polystyrene [21]. For negative bias at tip of −10 V the contrast of the current image is inversed: the current through the PCBM-rich phase is higher than the current through the matrix (Fig. 3d). Such contrast changes can be explained by analysing corresponding *I–V* measurements performed on a pure PCBM film: current above the noise level is detected only at high negative bias on tip (Fig. 3e).

4. Conclusions

C-AFM is a reliable analysis technique providing local information of electrical properties of functional polymer systems, when applied in inert atmosphere. In air most samples chemically degrade, and the present molecular water layer interferes with adequate measurements. Applying C-AFM on the functional blend MDMO-PPV/PCBM reliable current contrast images of the PCBM domains embedded in the MDMO-PPV matrix are acquired with lateral resolution better than 50 nm. Details of the interface between the two components are visualised and discussed. Currently, investigations of various photoactive layer systems are in progress applying higher lateral resolution in the order of 10–20 nm to identify features having similar length scale as the exciton diffusion length.

Acknowledgements

We would like to thank Svetlana v. Bavel for her support for sample preparation. Part of the work is embedded in the research program of the Dutch Polymer Institute (DPI projects #326 and #524), and additional financial support is appreciated by the Ministry of Economic Affairs of the Netherlands via the Technologische Samenwerkings project QUANAP (SenterNovem TSGE3108).

References

[1] G. Yu, A.J. Heeger, J. Appl. Phys. 78 (1995) 4510.
[2] J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, A.B. Holmes, Nature 376 (1995) 498.
[3] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science 270 (1995) 1789.
[4] C. Shafai, D.J. Thomson, M. Simard-Normandin, G. Mattiussi, P.J. Scanlon, Appl. Phys. Lett. 64 (1994) 342.
[5] P. De Wolf, J. Snauwaert, T. Clarysse, W. Vandervorst, L. Hellemans, Appl. Phys. Lett. 66 (1995) 1530.
[6] T.W. Kelley, C.D. Frisbie, J. Vac. Sci. Technol. B 18 (2000) 632.
[7] H.-N. Lin, H.-L. Lin, S.-S. Wang, L.-S. Yu, G.-Y. Perng, S.-A. Chen, S.-H. Chen, Appl. Phys. Lett. 81 (2002) 2572.
[8] C. Ionescu-Zanetti, A. Mechler, S.A. Carter, R. Lal, Adv. Mater. 16 (2004) 385.
[9] A. Alexeev, J. Loos, M.M. Koetse, Ultramicroscopy 106 (2006) 191.
[10] O. Douheret, L. Lutsen, A. Swinnen, M. Breselge, K. Vandewal, L. Goris, J. Manca, Appl. Phys. Lett. 89 (2006) 032107.
[11] D.C. Coffey, O.G. Reid, D.B. Rodovsky, G.P. Bartholomew, D.S. Ginger, Nano Lett. 7 (2007) 738.
[12] J. Morgado, R.H. Friend, F. Cacialli, Synt. Met. 114 (2000) 189.
[13] J.C. Hummelen, B.W. Knight, F. LePeq, F. Wudl, J. Yao, C.L. Wilkins, J. Org. Chem. 60 (1995) 532.
[14] H. Becker, H. Spreitzer, W. Kreuder, E. Kluge, H. Schenk, I. Parker, Y. Cao, Adv. Mater. 12 (2000) 42.
[15] H. Hoppe, N.S. Sariciftci, J. Mat. Chem. 16 (2006) 45.
[16] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, Adv. Funct. Mater. 11 (2001) 15.
[17] F. Padinger, T. Fromherz, P. Denk, C. Brabec, J. Zettner, T. Hierl, N. Sariciftci, Synth. Met. 121 (2001) 1605.
[18] X. Yang, J.K.J. van Duren, R.A.J. Janssen, M.A.J. Michels, J. Loos, Macromolecules 37 (2004) 2151.

[19] N. Koch, A. Elschner, J. Schwartz, A. Kahn, Appl. Phys. Lett. 82 (2003) 2281.
[20] H. Sugimura, Y. Ishida, K. Hayashi, O. Takai, N. Nakagiri, Appl. Phys. Lett. 80 (2002) 1459.
[21] S. Goffri, C. Müller, N. Stingelin-Stutzmann, D.W. Breiby, C.P. Radano, J.W. Andreasen, R. Thompson, R.A.J. Janssen, M.M. Nielsen, P. Smith, H. Sirringhaus, Nat. Mater. 5 (2006) 950.