Nanoscale electrical characterization of semiconducting polymer blends by conductive atomic force microscopy (C-AFM)

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Abstract

For the first time local electrical characteristics of a blend of two semiconducting polymers were studied with conductive atomic force microscopy (C-AFM). The investigated mixture is potentially interesting as the active layer in plastic photovoltaic devices. Besides conventional topography analysis of morphology and phase separation, the internal structure of the active layer was investigated by observing the current distribution with nanoscale spatial resolution. Similar to force spectroscopy, current imaging spectroscopy was performed during scanning the sample surface. Different types of current–voltage (I–V) characteristics were extracted from the array of spectroscopic data obtained from each point of the scans, and local heterogeneities of the electric characteristic were determined and discussed.

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1. Introduction

Polymer electronics, one of the most promising modern technologies, is based on the use of semiconducting polymers. The central part of many organic electronic devices, such as organic light emitting diodes or plastic photovoltaic devices, is the active layer, which has a typical thickness of about 40 to 100 nm. In this thin film, electric current is converted to light or vice versa. Whereas in conventional, inorganic photovoltaic devices free charges are formed almost
instantaneously upon light absorption, in organic semiconductors excitons, which are dissociated at a junction of a p- and a n-type material are created. The p- and n-type materials differ by the value of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), which allows for the charge separation at the interface. At present, the most efficient design for the active layer is based on the concept of bulk heterojunction, in which both components form an interpenetrating network with nanometer-scale size domains [1]. Ultimately, such a design maximizes the interfacial area for exciton dissociation, and limits the recombination because of the fast transport of free electrons and holes to the electrodes.

The chemical composition and the local organization of the active layer induced by the applied processing conditions have been identified as important parameters for the efficiency of charge separation in the active layer, and thus for the performance of an organic photovoltaic device. For example, Refs. [2–5] have discussed the influence of the morphology of the active layer on electrical characteristics and performance of plastic electronic devices. Therefore, the understanding of the relation between morphology and local electrical properties in the active layer is a key element for improving the device performance.

Measurements with scanning probe microscopy (SPM) methods allow for obtaining high-resolution topography information and surface properties of the sample at the same time. In previous studies, scanning tunneling microscopy (STM) has been used for investigation of semiconducting polymers [6–8]. In particular, the current–voltage (I–V) characteristics at the surface of poly(phenylenevinylene) (PPV) samples, widely used in organic photovoltaic devices, have been studied and modeled [7,8]. However, STM is only able to probe (semi-) conductive surfaces, since a current between tip and sample is used to keep a constant tip–sample distance and to probe the topography. This means that in STM measurements topography and electrical information are linked, and especially for electrically heterogeneous samples like bulk heterojunctions separation of electrical data from topography is difficult.

Other SPM techniques suitable to study organic semiconductors are scanning near-field optical microscopy (SNOM) and atomic force microscopy (AFM). Near-field optical microscopy and spectroscopy have been used to study aggregation quenching in thin films of MEH–PPV [9]. The obtained results suggest that the size of aggregates in thin films must be smaller than the resolution limit of SNOM of roughly 50 nm. Further, SNOM has been applied to map topography and photocurrent of the active layer of an organic photovoltaic device [10,11]. However, the reported spatial resolution was only about 200 nm, which is too low for detailed morphology analysis of, e.g. a thin film bulk heterojunction where the optimal phase separation is expected to be 10–20 nm. AFM equipped with a conductive probe, on the other hand, is able to overcome the abovementioned problem of STM and provides a higher resolution than SNOM. However, to prevent or minimize sample surface damage operation conditions and especially the tip load on the sample has to be adjusted carefully. Measuring the surface in contact mode with a voltage applied between tip and sample allows for obtaining the topography and the current distribution simultaneously. This method is called conductive or current sensing AFM (C(S)-AFM) [12,13]. The resolution of C-AFM is as small as the tip–sample contact area, which can be less than 20 nm. Nowadays, this method is widely used for the characterization of inorganic semiconductors [12–21], and its potential for the study of electrical properties of organic materials has been demonstrated [22–31]. For example, single crystals of sexithiophene have been studied [23], 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 studied [27] and the spatial current distribution and I–V characteristics of the samples were discussed. However, a study of the spatial distribution of electrical properties of semiconducting polymer blend has not been performed by applying C-AFM yet. In the present work we describe results of local topography and electrical measurements with C-AFM on a blend.
of two semiconducting polymers, which act as the active layer for organic photovoltaic devices.

2. Materials and methods

The studied blend includes two conjugated polymers: poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO–PPV) as electron donor and poly[oxa-1,4-phenylene-(1-cyano-1,2-vinylene)-(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene)-1,2-(2-cyanovinylene)-1,4-phenylene] (PCNEPV) as electron acceptor. The average molecular weights of the MDMO–PPV and PCNEPV used were 570 and 113.5 kg/mol, respectively, as determined by GPC using polystyrene standards. The chemical structures of the polymers are presented in Fig. 1. Both components cannot crystallize. It was shown that a similar mixture is interesting for photovoltaic applications, and detailed studies of the performance of polymer photovoltaic devices based on these materials have been described in Ref. [2]. The power conversion efficiency of such a photovoltaic device using this particular blend as active material can be up to 0.75% under standard conditions (AM1.5, 1000 W/m²). The samples studied consist of a glass substrate with an ITO layer (Philips Research), a spin-coated PEDOT:PSS (Baytron-P, Bayer) layer and a spin-coated active layer. The latter is based on a 1:1 mixture by weight of MDMO–PPV and PCNEPV. The solutions for spin-coating contained 0.25%wt of each component in chlorobenzene. The solution was stirred overnight at 50 °C and at 70 °C for 1 h immediately prior to spin coating. Such samples represent working photovoltaic devices, except for the missing metal back electrode.

For SPM measurements we used a commercial SPMs Solver P47H and Solver LS (both NT-MDT, Russia) equipped with optical microscopes. The cantilevers used were CSC12 (Micromash), NSG11 (NT-MDT), and conductive tips of both types with an additional Au-coating. A typical force constant of the cantilever used for electrical measurements was about 0.65 N/m, and the radius was below 50 nm. Since the polymers are sensitive to oxygen, the AFM measurements were performed in a glove box (Unilab, MBRAUN) having nitrogen atmosphere with oxygen and water levels below 1 ppm. The ITO layer was grounded during all SPM measurements. Current–voltage (I–V) characteristics were measured under illumination. The Fermi levels for ITO, PEDOT:PSS and gold, respectively, are 4.7, 5.2 and 5.1 eV [4,27]. For the reason of better illustration, Fig. 2 shows a scheme of the experimental setup for C-AFM measurements.

3. Results and discussion

Thickness measurements of the active layer were performed by AFM operated in intermittent
contact (IC) mode (also known as “tapping” mode). For this purpose, the sample was carefully scratched by a knife and the height of the active layer was measured. Due to the stronger adhesion of PEDOT:PSS on ITO or glass, compared to the adhesion of the active layer on PEDOT:PSS, the active layer could be removed selectively. Fig. 3 shows the boundary between the active layer and the PEDOT:PSS substrate (Fig. 3a) and the corresponding cross-section of the scratched area (Fig. 3b). The average thickness of the active layer was found to be 27 nm. The high-resolution topography image of the active layer shows more details of the local organization of the sample (Fig. 3c). Domains with a lateral size of up to 300–400 nm slightly stick out of the surface of the sample. The presence of these domains is a clear indication for the occurrence of phase separation in the active layer. The rms roughness of the sample surface is about 1.5 nm as determined from Fig. 3c, and height variations are significantly smaller than the film thickness. The size of the domains can be adjusted by using components with different molecular weight or molecular architecture (e.g. side chains). More details on how to control the phase separation of the MDMO–PPV/PCNEPV blend are described elsewhere [2,5]. In the present study we use PCNEPV with a relatively high molecular mass so that domains formed in the film samples are large. This will be helpful for further experiments; especially for obtaining the lateral distribution of the electrical properties with C-AFM. It should be noted that this blend is not the optimal choice for best device performance; smaller domains with sizes below 50 nm are preferred [2].

Measurements of the electrical current distribution over the sample surface were performed with an Au-coated tip. In such an experiment the tip plays the role of the back electrode but having a much more localized contact area. A voltage was applied to the tip and the ITO front electrode was grounded (Fig. 2). For conductive AFM measurements the tip was kept in contact with the sample surface while the current through the tip was measured. In contrast to operating in IC mode, contact mode is characterized by a strong tip-sample interaction that can lead to destruction of
the surface, especially in the case of soft polymer samples. Therefore, the load applied to the tip during C-AFM has to be small enough to reduce sample destruction and, at the same time, it must provide a reliable electric contact. We usually operated with a load of about 10–20 nN. The contact cantilevers used for C-AFM are suitable for operation in IC as well as contact mode so that nondestructive testing of the sample surface could be performed before and after the C-AFM measurements. C-AFM measurements of the same sample area were done several times and resulted in completely reproducible data. Subsequent analysis of the surface performed in IC mode showed almost no destruction of the sample surface; only minor changes were detected.

A topography image and the corresponding current distribution measured at +8 and −8 V on the tip are shown in Fig. 4. All images were acquired subsequently so that some drift occurred. All pronounced domains in the topography image (Fig. 4a) correlate with regions of minimal current in the C-AFM image (dark areas in Fig. 4b).

From the energy level diagram (Fig. 1) it follows that the difference between the HOMO level of MDMO–PPV and the Fermi level of both electrodes is rather small so that we expect ohmic contacts for a hole injection and strong energy barriers for electrons. 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. The energy difference between the HOMO and LUMO of PCNEPV and the Fermi levels of both electrodes is about 1 eV, which means that a large barrier for electron injection exists in the structure ITO/PEDOT:PSS/PCNEPV/Au-tip (some changes of barrier heights are possible when contact between metal electrodes and organic material occurs [4,23]). Because the hole mobility of a n-type polymer is typically smaller than that of a p-type polymer a hole only

Fig. 4. C-AFM images of the same area: (a) topography, (b) current distribution image with a positive bias at $U_{\text{tip}} = +8 \text{V}$, the white arrow in (b) indicates a domain with reduced current, (c) current distribution image with a negative bias at $U_{\text{tip}} = -8 \text{V}$. Black arrows indicate same domains for easy identification.
current through the MDMO–PPV is larger than for PCNEPV in both bulk and contact limited regimes. Therefore we assume that the observed contrast in Fig. 4b is due to a hole current, flowing through MDMO–PPV rich phase.

However, C-AFM measurement also shows regions with a current value lying in between that of the MDMO–PPV matrix and the PCNEPV domains. An arrow on Fig. 4b marks one of these regions. These areas might be assigned as PCNEPV domains inside the active layer that are possibly covered by MDMO–PPV.

It is reported that the electrical contrast measured by C-AFM at the surface of samples depends on sign of the voltage applied [23]. As shown in Fig. 4c, the C-AFM measurements at negative bias on the tip showed drastic changes of the contrast in the current images compared to positive bias (Fig 4b). PCNEPV domains again showed only little current at low load, however MDMO–PPV showed a heterogeneous spatial current distribution. These electrical heterogeneities indicate small grains with a typical size of 20–50 nm, which differs by the value of current. A similar structure was observed on MEH–PPV films [27]. In the case of MEH–PPV, the authors attribute these sub-structures to a special and very local organization of the film.

In addition to topography and current sensing analysis, current imaging spectroscopy was performed as well. The procedure of such measurements is similar to the so-called “force volume” technique [32], which implies measurements of the force–distance curve at each point of a scan in order to get complete information about lateral distribution of mechanical properties at the surface. Here, we extend this method to measurements of electrical properties of the sample [18]. Current–distance ($I$–$z$, at constant voltage) and current–voltage ($I$–$V$, for constant distance; always in contact) dependencies were collected at each point of a scan. The procedure of such measurements is shown schematically in Fig. 5.

An array of $128 \times 128$ $I$–$z$ curves at $+8$ V on the tip was obtained in order to study the influence of the applied load on the distribution of current. An $I$–$z$ curve at one point was obtained by movement of the tip by the scanner in $z$ direction. In our experiment first we bring the tip in contact with the sample surface, then the scanner with attached tip is moved up 60 nm, and finally moves down for 160 nm while simultaneous performing measurements of the local current (Fig. 6). The change of the $z$-position of the scanner, when tip–sample contact occurs, leads to both the bending of the lever and penetration of the tip in the sample. Additional experiments showed that the penetration depth in the range of the used load is much smaller than lever bending, i.e. the load can be roughly estimated from the $z$ movement of the scanner: $F = k \Delta z$, where $k$ is cantilever force constant and $\Delta z$ is scanner displacement calculated from the first point were tip–sample contact

Fig. 5. Schematic illustration of $I$–$V$ measurements at 9 consecutive points. The dark gray area represents a PCNEPV rich domain, the brighter areas, the MDMO–PPV rich matrix.

Fig. 6. Current–distance ($I$–$z$) behavior of the MDMO–PPV matrix and PCNEPV domains. The direction from right to the left corresponds to the approaching of the tip to substrate surface.
occurs. The cross-section of the obtained array of $I$–$z$ curves shows the distribution of the current at the sample surface for a certain $z$-position of the scanner (or load). Movement from point to point was executed in contact mode under small load (above 20 nN in our experiments). As a result the destructive action of the lateral force is reduced significantly. It is also possible to perform such measurements in IC mode, thus making the measurements of polymer topography more precise. For the sample studied here we obtained similar results with current imaging spectroscopy performed in both contact and IC mode.

Fig. 6 demonstrates $I$–$z$ curves measured in the PCNEPV domains and the MDMO–PPV matrix. For loads in the range 10–30 nN the current is approximately constant, but for an increased load of more than 30 nN the current starts to rise rapidly. In case of PCNEPV a similar trend could be measured, however, because PCNEPV is a less good hole conductor current values are on a lower level compared with MDMO–PPV. This probably means that current measurements on PCNEPV need a higher tip–sample interaction compared to MDMO–PPV. Even a strong penetration of the sample surface by the tip may be required.

Detailed analysis of the electric characteristics of organic photovoltaic devices includes measuring of $I$–$V$ curves. We have performed similar measurements in each point of a scan. In order to get acceptable lateral resolution an array of $128 \times 128$ $I$–$V$ curves was obtained on an area of $1.2 \times 1.2 \mu$m$^2$, which corresponds to a pixel resolution of better than 10 nm. From the analysis of these data, three different $I$–$V$ characteristics were extracted (Fig. 7): one represents PCNEPV rich domains, and the other two represent different positions in the MDMO–PPV matrix. The current through the PCNEPV is again much lower than the current through MDMO–PPV at both polarities of voltage in the range up to 10 V. For a positive potential at the tip, $I$–$V$ curves of MDMO–PPV have a similar shape at any position. On the other hand, negative bias at the tip leads to significant differences between $I$–$V$ curves obtained at different positions at the sample surface, evidenced by the asymmetrical shape of some of the $I$–$V$ curves.

It is known that $I$–$V$ curves measured by C-AFM can be asymmetrical even for an electrically symmetrical structure. Such an asymmetrical $I$–$V$ characteristic has been shown for the structure Au-electrode/organic semiconductor/Au-tip [23]. The injection of holes from the gold-coated tip was found more efficient than injection from a gold substrate. The same situation is observed in our experiment: the average hole current through MDMO–PPV is smaller at the negative bias on the tip. For a model device ITO/PEDOT:PSS/organic semiconductor/Au-electrode hole injection from PEDOT:PSS into organic materials was found being more efficient than from a sputtered Au top electrode in Ref. [4]. Despite presence of PEDOT:PSS layer in our sample the hole injection from the tip is more efficient. This fact can be explained by influence of the tip, in particular, by the high electric field at the tip end caused by tip shape [23]. Moreover, probably mechanical stress of the surface under the tip is influencing the electrical properties. At the same time, other areas of MDMO–PPV have nearly symmetrical $I$–$V$ characteristics as it is expected for an electrically symmetrical structure. Since the current heterogeneities in the MDMO–PPV matrix are reproducible when the same place is scanned several times, it may be concluded that they reflect local different
molecular organization of the MDMO–PPV, as already discussed for Fig. 4c and 7.

4. Conclusions

To the best of our knowledge, for the first time spatially resolved variations of the local electrical properties of a photovoltaic blend of two semiconducting polymers, the electron donor MDMO–PPV and acceptor PCNEPV, have been studied by current–distance and current–voltage measurements applying conductive AFM. The C-AFM measurements clearly showed the phase separation of the components of the blend. Moreover, additional PCNEPV domains inside the active layer as well as heterogeneities in the MDMO–PPV matrix could be detected. This makes this technique very useful for studying blends containing semiconducting polymers. The \( I-V \) and \( I-z \) measurements confirm that under illumination hole current occurs mainly in the MDMO–PPV rich areas.

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