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## LETTER TO THE EDITOR

## Multilayer formation in spin-coated thin films of low-bandgap polyfluorene:PCBM blends

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### Abstract

Blends of the low-bandgap polymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (APFO-3) and the fullerene derivative [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) were spin-coated from chloroform solution into thin films, which were examined with dynamic secondary ion mass spectrometry. For blends with high PCBM content, the depth profiles show composition waves that were caused by surface-directed phase separation during spin-coating. The formation of such multilayer structures by spontaneous self-stratification is likely to have implications for optimization strategies for the performance of organic solar cells.

The bulk heterojunction structure, in which an electron-donating component intermingles with an electron-accepting component, is a concept that has proven its importance for organic solar cells and in particular polymer/fullerene solar cells [1]. In such a solar cell an exciton is formed in the polymer upon absorption of light and is separated at the interface between polymer and fullerene into an electron and a hole. In the generally accepted model, the electron-accepting fullerene derivative transports the electron to the metal electrode and the electron-donating polymer transports the hole to the ITO electrode. The need for efficient absorption gives rise to criteria regarding the polymer material and the film thickness, while the optimal film morphology in such a solar cell is a trade-off between the criteria for efficient charge generation and charge transport. The usual way to prepare the active layer of solar cells

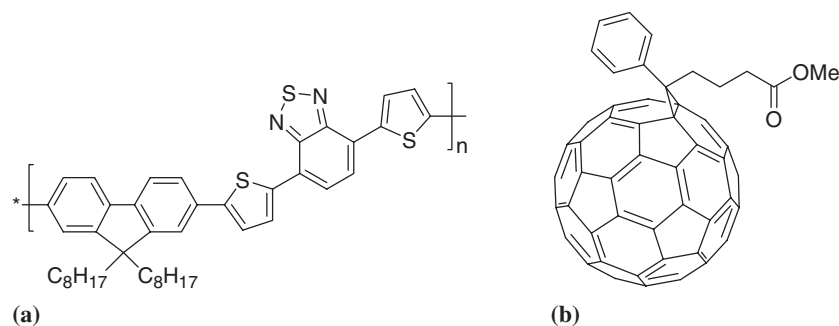
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is to spin-coat the film from a solution of polymer blend in a common solvent. An intimate mixing of the blend components is important for efficient charge generation and a continuous high-mobility path for the photo-generated charges to the electrodes is required for good charge transport. It was shown that the morphology of the spin-coated film has drastic effects on the performance of polymer/fullerene solar cells [2, 3]. Morphology modifications [4, 5] induced (by a change of the common solvent) in a blend of poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene) (MDMO-PPV) with the fullerene derivative [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) resulted in an enhanced conversion efficiency for this solar cell of 2.5% at AM 1.5 illumination [4]. Record conversion efficiencies of 4.9% were obtained for poly(3-hexyl thiophene) (P3HT) blended with PCBM after annealing post-treatments that affect the film morphology [6]. Another promising class of materials for photovoltaic energy conversion is low-band-gap polyfluorenes, e.g. poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-5,5-4',7'-di-2-thienyl-2',1',3'-benzothiadiazole] (APFO-3), with an extended absorption range, overlapping well with the solar spectrum. The highest conversion efficiency reported so far is 2.1% for a blend of APFO-3 and PCBM with 1:4 mass fractions of its components, spin-coated from a chloroform solution [7].

For thin solid films of polymer blends produced by spin-coating from solution, the film formation is characterized by rapid solvent quenching. Fast variations of thermodynamic and kinetic parameters make phase separation [8] a complex (non-quasi-static) process [9], often accompanied by interfacial instabilities [10–12] and resulting in non-equilibrium (often metastable) morphologies. The morphology depends furthermore on solubility and the surface energies of components and substrate [11]. Structure formation models [9, 13] suggest the initial formation of multilayers, which can either be frozen in [14, 15] or break up [12] by interfacial instabilities to yield lateral domains. Self-stratified lamellar structures, resulting from solvent quench in polymer blend films, have been observed [14, 15] and related with surface-directed phase separation [16]. Vertical phase separation and bilayer formation has also been reported for blends containing polyfluorene copolymers [17–22]. In turn, for fullerene (PCBM) blends with MDMO-PPV, lateral and vertical structural variations have been observed by electron microscopy methods [3, 5, 23, 24], but no spontaneous stratification was detected by dynamic TOF-SIMS [25].

Previously we have investigated the surface topography of thin films of the APFO-3:PCBM blend by tapping-mode AFM for a wide range of blend ratios (1:1 to 1:4 by weight) [26, 27] and found that the surface is flat with roughness values close to 1 nm [27]. The surface composition of a thin film of the APFO-3:PCBM blend with bulk ratio 1:4 was recently investigated by UV-photoemission spectroscopy and found to be 1:1, implying surface enrichment of APFO-3 [28]. Here we report on a study of the vertical structure of thin films of the APFO-3:PCBM blend, spin-coated from chloroform solutions on silicon substrates. The chemical structures of APFO-3 and PCBM are shown in figure 1. We use dynamic secondary ion mass spectrometry (SIMS) to analyse the vertical composition of the blend by depth profile analysis of the films, where the film is gradually sputtered by a scanning ion beam and the fragments simultaneously analysed by mass spectrometry. This technique is well established for both vertical and lateral mapping of the components in thin films of polymer blends, hence providing the 3D morphology [29]. We show for the first time that multilayers can be formed spontaneously during spin-coating of polymer/fullerene mixtures. The consequences of self-stratification, most enhanced for the 1:4 APFO-3:PCBM blends (where the highest conversion efficiency was reported), are discussed for the optimization of solar cell performance.

The synthesis of APFO-3 is described elsewhere [7]. The molecular weight ( $\overline{M}_w$ ) of APFO-3 was 11 800 ( $\overline{M}_n = 4900$ ). PCBM was purchased from the University of Groningen, The Netherlands. APFO-3:PCBM blend solutions in chloroform were prepared with a total

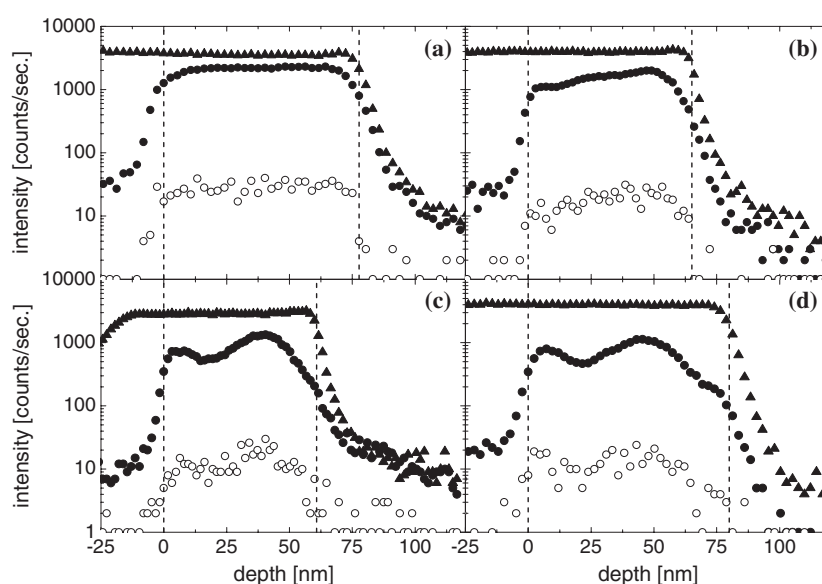


**Figure 1.** Chemical structures of (a) APFO-3 and (b) PCBM.

concentration of solids of  $12 \text{ mg ml}^{-1}$  and polymer:PCBM ratios of 1:1, 1:2, 1:3 and 1:4 by weight. The thin films were spin-coated on RCA-cleaned silicon substrates [30, 31]. The cleaning procedure is described elsewhere [26, 30] and leaves the surface hydrophilic. The spin speed was 1500 rpm and time  $\sim 80$  s, which resulted in a film thickness of  $70 \pm 10$  nm. The SIMS depth profiles (depth resolution of 10 nm) were obtained by a VSW apparatus equipped with a liquid metal ion gun (FEI Company) [29]. The sample material was sputtered with a  $\text{Ga}^+$  primary ion beam of 5 keV (2 nA) over a region of  $100 \mu\text{m} \times 100 \mu\text{m}$ , but only the secondary ions from the central (50%) part of the sputtered area were collected for analysis. The selected secondary ions were analysed in a quadrupole mass spectrometer (Balzers): clusters with mass to charge ratios ( $m/q$ ) equal to 16, 24, 26, 28, and 32 were recorded as labels for the blend components and substrate. To investigate the outermost region in detail all samples were covered with a 50–100 nm thick sacrificial layer of polystyrene to provide an additional region necessary for the equilibration of the sputtering process [32]. The film thickness was determined for each of the films using atomic force microscopy. Contact angles using formamide were determined on spin-coated films of pure PCBM and APFO-3, prepared from chloroform solutions ( $12 \text{ mg ml}^{-1}$ ), using contact angle equipment FTA 200 (First Ten Ångstroms, USA). The contact angles were converted into surface energy values by using the relation by Li and Neumann [33, 34].

The resulting SIMS depth profiles for spin-coated APFO-3:PCBM thin films with blend ratios 1:1, 1:2, 1:3, and 1:4 are shown in figure 2. The  $\text{CN}^-$  ions with  $m/q = 26$  and  $\text{S}^-$  ions with  $m/q = 32$  originate from APFO-3 and are therefore interpreted as a signature of the polymer. The conformity of the depth profiles of both signals gives additional strength to this assignment. We monitor also the signal at  $m/q = 24$  ( $\text{C}_2^-$ ) and the intensity of the secondary  $\text{O}^-$  ions ( $m/q = 16$ ). Even though PCBM contains oxygen, the  $m/q = 16$  label cannot unambiguously be assigned to PCBM, because it may originate from  $\text{S}^{2-}$  ions or from different sources. The depth profiles can be divided into three depth ranges: a sacrificial polystyrene layer, the APFO-3:PCBM blend layer (starting at 0 nm), and the silicon substrate covered by a thin native oxide layer. For all samples, the intensity profile of  $\text{C}_2^-$  ions is flat over both polymer regions, i.e. the polystyrene and the blend region, and decreases sharply at the interface with the substrate. The position of the substrate is verified by the profile of the  $\text{Si}^-$  ions ( $m/q = 28$ ) (not shown) and corresponds well with the position at which the  $\text{C}_2^-$  signal decreases to 50% (dotted line most to the right in figures 2(a)–(d)).

In the sample with blend ratio 1:1 (figure 2(a)), the flat  $\text{CN}^-$  and  $\text{S}^-$  profiles indicate a homogeneous distribution of the polymer in the film, implying the same for PCBM, while



**Figure 2.** Intensity versus depth profiles of negative ions with different  $m/q$  ratios: 24 ( $C_2^-$ )—solid triangles, 26 ( $CN^-$ )—solid circles, 32 ( $S^-$ )—open circles, obtained for APFO-3:PCBM thin films on Si substrates; APFO-3 to PCBM blend ratios are (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4. The dotted lines indicate the depths at which the  $CN^-$  signal has increased to 50% of its saturation value (left) and where the  $C_2^-$  signal has fallen to 50% of its maximum value (right).

the profiles of the sample with blend ratio 1:2 (figure 2(b)) show the initial formation of a polymer-depleted region at the substrate (depth 55–60 nm). For the sample with blend ratio 1:3, two maxima are observed in the depth profile of the polymer (figure 2(c)); one near the free surface (0–10 nm) and one at about 40 nm depth, i.e. near the middle of the film, indicating two polymer-enriched regions. The depletion of polymer near the substrate (45–60 nm) has also become more pronounced. The depth profile of the polymer in the sample with blend ratio 1:4, which is the common blend ratio for APFO-3:PCBM layers used in solar cells, is shown in figure 2(d). Here we observe even more clearly the surface segregation of polymer at the free surface, the second maximum in polymer content near the middle of the film (at about 45 nm), and finally a polymer-depleted region of about 20 nm wide near the substrate. We interpret the total depth profile of the sample with blend ratio 1:4 as a fourfold multilayer with an enrichment of APFO-3 at the free surface of the film, followed by a PCBM-enriched layer (and polymer depletion) under the immediate surface, then a subsequent polymer-rich central layer, and a PCBM enrichment (and polymer depletion) near the silicon substrate. The actual ratios of APFO-3 to PCBM in the various regions cannot be deduced from the SIMS profiles, because of the complex cluster-specific and environmental dependence of both the sputter rate and the detection sensitivity.

The vertical segregation of the blend components can be explained by their difference in surface energy. The surface energy of a homogeneous PCBM-film, determined from contact angle measurements, is  $38.2 \text{ mN m}^{-1}$ . The corresponding value for a homogeneous APFO-3 film is  $32.2 \text{ mN m}^{-1}$ . Since APFO-3 has a lower surface energy than PCBM it is attracted to the interface with air to lower the energy of the free surface. The higher surface energy of PCBM is more compatible with the high surface energy silicon substrate and the blend film is

enriched with PCBM at this interface. The cleaned silicon substrate is covered with a native  $\text{SiO}_x$  layer [30], for which a dispersive surface energy component of  $36.5 \text{ mN m}^{-1}$  is reported, the total surface energy being even higher [35]. At equilibrium the blend would thus form a bilayer structure. However, the spin-coating process does not allow the system enough time to reach this state and a four-layer structure is frozen in, in agreement with layered structures observed for spin-coated thin films of several polymer/polymer blend systems [15, 17, 36].

For thicker APFO-3:PCBM (1:4) films, spin-coated from a blend solution with a total solid concentration of  $30 \text{ mg ml}^{-1}$ , as is usually used for solar cells, the SIMS depth profiles (not shown) demonstrate a similar enrichment of the free surface with polymer and the corresponding compositional waves as in the case of the thinner films with blend ratio (1:4). In polymer solar cells made of APFO-3:PCBM (1:4), ITO covered with a thin film of the conducting polymer PEDOT:PSS is used as a bottom electrode. We also measured the SIMS depth profile of a film of the same APFO-3:PCBM (1:4) blend spin-coated on PEDOT:PSS/ITO (not shown) and found that it is similar to the one for the film on silicon (figure 2(d)). Polymer enrichment is observed at the free surface, followed by a depletion layer and a second polymer-enriched region. However, due to the overlap of label ions in the neighbouring layers at the interface between the blend and the PEDOT:PSS-coated ITO substrate, the determination of the exact position of this interface and the profile in this region is difficult and more work is in progress.

In a simple model, the charge transport in a bulk-heterojunction solar cell would benefit from a vertical segregation with enrichment of the electron-donating material at the hole-collecting PEDOT:PSS/ITO contact and of the electron-accepting component at the free surface, onto which the electron-collecting contact is later evaporated. The film structure revealed by SIMS of the APFO-3:PCBM (1:4) blend on silicon (figure 2(d)) and on PEDOT:PSS/ITO demonstrates instead an enrichment of the electron donor (APFO-3) at the free surface. In spite of this, a reasonably high conversion efficiency (2.1% [7]) is reached for solar cells made from the APFO-3:PCBM blend, suggesting that transport is not completely hampered by the vertical structure. However, more work is underway to optimize the solar cell performance given the new morphological information.

In summary, a depth profile of the polymer APFO-3 in a spin-coated thin film of the APFO-3:PCBM blend can be obtained by monitoring the  $\text{CN}^-$  and  $\text{S}^-$  intensities as a function of depth by dynamic SIMS. The depth profiles depend strongly on the blend ratio. While the blend with ratio 1:1 (by weight) showed a homogeneous film composition, vertical phase separation was observed for blend ratios 1:2, 1:3 and 1:4. A fourfold multilayer structure was formed in the APFO-3:PCBM (1:4) film, where the free surface is enriched with polymer and the substrate interface is partly depleted of polymer and consequently enriched with PCBM. The segregation is explained by surface energy differences and kinetic limitations. For a blend film prepared on PEDOT:PSS-coated ITO, enrichment of the free surface with APFO-3 is also found. The observed multilayer structure is, according to a simple model, not optimal for the performance of solar cells made from this blend. This new structural information implies that vertical morphology issues should be taken into account in optimization strategies for conjugated polymer blend devices.

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