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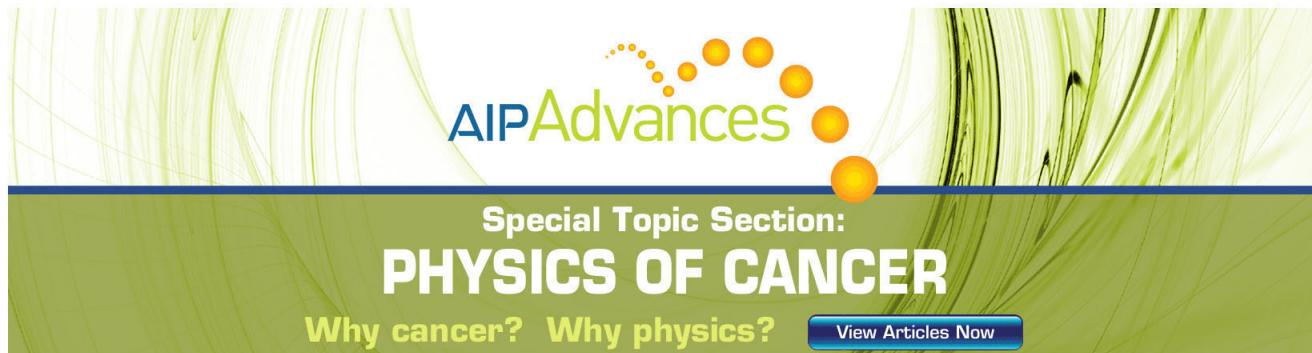## Additional information on Appl. Phys. Lett.

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Effects of solvent and annealing on the improved performance of solar cells based on poly(3-hexylthiophene): Fullerene

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Polymer solar cells based on poly(3-hexylthiophene):[6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM) were fabricated using two different solvents. P3HT:PCBM films casted from chlorobenzene solution absorb more red light than the films casted from chloroform solution. After thermal annealing, the films casted from chloroform show higher absorption than the films casted from chlorobenzene. Solar cells made from P3HT:PCBM chlorobenzene solution show no change in the white light power conversion efficiency (2.2%) after annealing. Solar cells processed from P3HT:PCBM chloroform solution show a white light power conversion efficiency of 1.5% without thermal annealing and 3.4% after the thermal annealing. The stated efficiencies are not corrected for the spectral mismatch. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1929875]

Polymer photovoltaic devices are a renewable, alternative source of electrical energy. During the last few years, increased effort of many research groups was devoted to the development of solar cells based on conjugated polymers. Using poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene]:[6,6]-phenyl-C_{61}-butyric acid methyl ester (MDMO-PPV:PCBM), polymer solar cells with white light power conversion efficiency of 3.3% on glass substrates[1] and of 3% on flexible substrates[2] were realized. Regioregular poly(3-hexylthiophene) (P3HT) appears to be one of the most suitable conjugated polymers to date for polymer solar cells. It combines a lower band-gap in comparison to MDMO-PPV and a high degree of intermolecular order leading to high carrier mobilities. Because of these facts it is less surprising that the newest top results concerning the conversion efficiency were obtained using this material. Presently, the state of the art is an external AM1.5 power conversion efficiency of 3.5% with P3HT:PCBM, where further improvement of device performance was realized by postproduction treatment with simultaneously annealing and applying an external electric field.[3]

Several works were already published related to the relationship between the nanomorpholgy of the organic photoactive layer (bulk heterojunction) and the performance of the polymer solar cells.[4–6] The morphology of this layer can be strongly affected by the processing conditions used such as the donor–acceptor composition, the solvent and the thermal annealing of the organic layer. Shaheen *et al.* found that the use of toluene as solvent for the MDMO-PPV:PCBM system led to a coarser phase separation than for chlorobenzene.[4]

In this work we report on the effects of the processing conditions on the light absorption of P3HT:PCBM layer and on the performance of the polymer solar cells processed from these layers. The chemical structures of P3HT and PCBM are given elsewhere.[3] For the measurement of the absorption spectra P3HT:PCBM layers (1:1 and 1:2 wt %) were spin coated from chlorobenzene and chloroform solutions on ITO coated polyester foils. The absorption spectra of the nonannealed layers were measured, then these layers were heated at 100 °C for 10 min and measured again. The measurements were carried out by an UV-VIS-NIR spectrometer UNICAM UV 300 (Thermo Spectronic).

Figure 1 shows the absorption spectra of P3HT:PCBM composite films (1:2 wt %) casted from chloroform and chlorobenzene solutions before and after thermal annealing at 100 °C. The absorption maximum of the film casted from

FIG. 1. Absorption spectra of P3HT:PCBM composite films (1:2 wt %) casted from chloroform (CF) and chlorobenzene (CB) solutions before and after thermal annealing at 100 °C.

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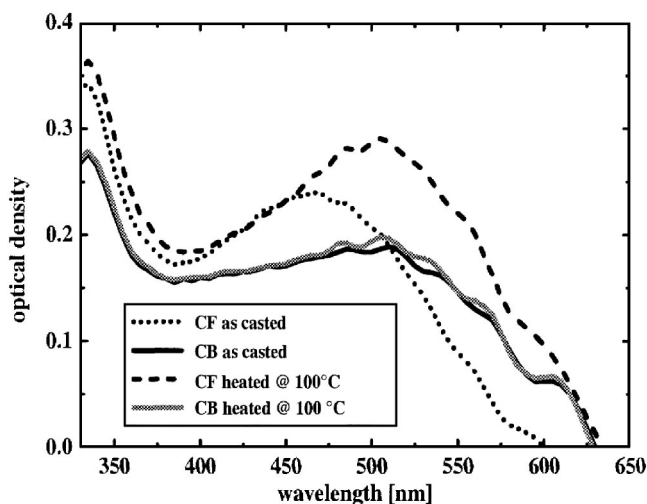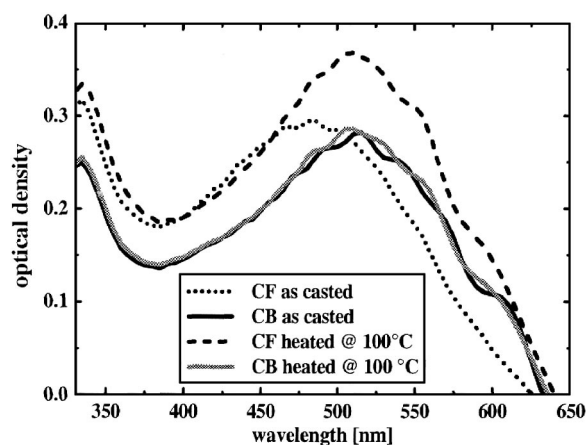
FIG. 2. Absorption spectra of P3HT:PCBM composite films (1:1 wt %) casted from chloroform (CF) and chlorobenzene (CB) solutions before and after thermal annealing at 100 °C.

TABLE I. Comparison of device parameters of PET/ITO/PEDOT:PSS/P3HT:PCBM/Al polymer solar cells with different P3HT:PCBM compositions and process by different solvents (chlorobenzene CB and chloroform CF).

Composite	V_{OC} (mV)	I_{SC} (mA/cm²)	FF	$\eta_{AM1.5}$ (%)
1:1 in CB	600	9.2	0.4	2.2
1:2 in CB	700	3.6	0.4	1.0
1:1 in CF nonannealed	600	6.2	0.4	1.5
1:1 in CF annealed	630	10.9	0.49	3.4

chloroform solution is observed at a wave length of 460 nm. This maximum is observed at 510 nm when the film is casted from chlorobenzene solution. The absorption band edge of the films casted from chloroform and chlorobenzene solutions are observed at 600 and 630 nm, respectively. The peak at 335 nm in both spectra is caused by PCBM.[7] This indicates that the degree of the P3HT chain ordering[8] is higher in the case of using chlorobenzene. After thermal annealing of the two layers the PCBM peak as well as the whole spectrum of the film casted from chlorobenzene remains unchanged, while the absorption spectra of the film casted from chloroform changes significantly. The maximum absorption peak is redshifted by 50 nm, the absorption band edge is shifted from about 600 to 630 nm. The changes in the absorption spectrum of the film casted from chloroform solution upon annealing are due to the molecular diffusion of PCBM out of the polymer matrix, which increases the degree of the P3HT chain ordering.[9] That indicates the same type of increased structural order caused by thermal annealing and by changing of the solvent from chloroform to chlorobenzene.

Using a P3HT:PCBM composite (1:1 wt %) and the two solvents chlorobenzene and chloroform we found the same behavior (Fig. 2): after thermal annealing no change in the absorption spectrum of the film casted from chlorobenzene solution and redshifted of the absorption spectrum of the film casted from chloroform solution are observed.

Comparing the absorption spectra of P3HT:PCBM films with different composition ratio (1:1 and 1:2 wt %) casted from chlorobenzene, we found that the maximum absorption peak and the absorption band edge are redshifted only by 5 nm upon going from 1:2 to 1:1 wt % (Figs. 1 and 2). After the thermal annealing, this shift remains. For P3HT:PCBM films casted from chloroform solution with 1:1 and 1:2 wt % the difference is devious. For the nonannealed films the maximum absorption peak is shifted from 475 to 485 nm and the absorption band edge is shifted from about 600 to 625 nm changing the composition from 1:2 to 1:1 wt %. After annealing the shift becomes smaller: the maximum absorption peak is shifted from 505 to 510 nm and the absorption band edge is shifted from 630 to 635 nm changing from 1:2 to 1:1 wt %. Several other peaks obtained in the spectral range 400–630 nm in (Figs. 1 and 2) are due to thin film interferences, which indicate smooth surface and interface morphology of the active layer. The am-

plitude of the interference pattern is smaller for films casted from chloroform than for films casted from chlorobenzene, because the films casted from chloroform solution are thicker than the films casted from chlorobenzene solution.

We conclude that molecular diffusion of PCBM in the P3HT matrix is higher in the films casted from chloroform in comparison to films casted from chlorobenzene solutions, which destroys the self-organization structure of P3HT and reduces the absorption of the organic layers in the green spectral region. This effect depends on the amount of PCBM in the composite and is very pronounced in the case of using chloroform solution. After thermal annealing the absorption around 510 nm is further increased. This effect is due to the improved ordering of the conjugated polymers in the film by reducing the free volume and the defect density at the interface created during solvent evaporation[10] as well as by the improved interchain interactions.[11] The effect of the solvent and the thermal annealing on the morphology is investigated by x-ray diffraction. $2\theta/\theta$ scans prove that P3HT crystallizes after annealing. The results of these investigations will be published elsewhere.

Polymer solar cells were fabricated using 5 × 5 cm² flexible ITO coated polyester foils (175 μm biaxially oriented and thermally stabilized polyethylene terephthalate film coated with 100 nm ITO, trade name: T-MOX 60 purchased from CADILLAC PLASTIC GmbH/Germany, surface resistance: 60 $\Omega/\square$). P3HT was supplied from Sigma-Aldrich Chemie GmbH/Germany and PCBM came from the laboratory of the Hummelen Group at University of Groningen. A 100 nm layer of poly(3,4-ethylene-dioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS) was spin coated onto the substrate (dried on a hot plate at 80 °C for 5 min at clean room conditions) followed by a 100–200 nm layer of the P3HT:PCBM (1:1 or 1:2 wt %) blend. An aluminum top electrode (80 nm) was deposited in vacuum through a shadow mask. Device preparation and characterization were realized at clean room conditions without protection against air and moisture. The device design is described elsewhere.[2] For cell characterization a 100 mW/cm² white light from a Steuernagel solar simulator was used to apply AM1.5 conditions during illumination. The calculated efficiencies were not corrected for the spectral mismatch.

Table I summarizes the photovoltaic parameters of the cells investigated during this work. Figure 3 shows the current–voltage characteristics of PET-foil/ITO/PEDOT:PSS/P3HT:PCBM/Al solar cells under white light illumination (100 mW/cm²) for P3HT:PCBM 1:1 and 1:2 wt % using chlorobenzene (CB) solvent. The open circuit voltage (V_{OC}) of the cell based on a 1:2 composition is 100 mV higher than that of the cell based on a 1:1 composition. Because the same
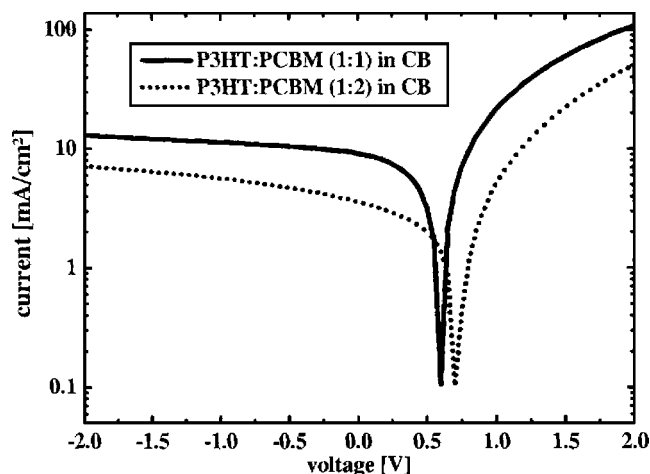
FIG. 3. Current–voltage characteristics of PET-foil/ITO/PEDOT:PSS/ P3HT:PCBM/Al solar cells under white light illumination (100 mW/cm²) for P3HT:PCBM 1:1 and 1:2 wt % using chlorobenzene (CB) as solvent.

donor and acceptor in the both cells were used the difference in V_{OC} values cannot be explained by the energy difference between the LUMO of the acceptor and the HOMO of the donor.[12] Instead it can be explained by the partial coverage of the cathode by PCBM,[13] which is higher by using the 1:2 than by 1:1 composition. The short circuit current (I_{SC}) of the cell based on a 1:1 composition is obviously higher than that of the cell based on 1:2 composition. This significant difference is due to the differences in optical density and to the different absorption in the green spectral region of the photoactive layer (Figs. 1 and 2) as well as due to the partial damage of the absorber–metal interface caused by the formation of voluminous PCBM clusters in the cell processed from 1:2 composition. The fill factor (FF) of both cells is identical and amounts to 0.4. Consequently, the energy conversion efficiency of the cell based on 1:1 composition ($\eta_{AM1.5}$ =2.2%) is higher than that of the cell based on 1:2 composition (1.0%). No enhancement in the performance of both cells was obtained after annealing of the cells.

A change of the solvent used for the 1:1 P3HT:PCBM composition from chlorobenzene to chloroform leads to lower I_{SC} and $\eta_{AM1.5}$. V_{OC} and FF do not change (Table I). The lower I_{SC} of cells prepared using chloroform is due to the lower absorption compared to the cell prepared using chlorobenzene (Fig. 2). After thermal annealing of the cell prepared using 1:1 P3HT:PCBM composite from chloroform solution the performance of the cell is improved. V_{OC} becomes 30 mV higher, I_{SC} and FF increase to 10.9 and 0.49 mA/cm², respectively, and as a consequence, $\eta_{AM1.5}$ amounts to 3.4%. The series resistance of the nonannealed cell is 11.7 Ω cm². After the thermal annealing decreased the series resistance to 6.6 Ω cm². The series resistance includes the bulk and the contact resistance and is given by the (inverse) slope of the $I-V$ curve at higher voltage where the curve becomes linear: $R_s = (I/V)^{-1}$. The improvement of the performance after thermal annealing can be explained as follows: before annealing P3HT has an amorphous structure caused by the higher concentration of fullerene. During annealing PCBM diffuses out of the polymer matrix to form a percolated network with improved electron transport

properties.[9] Photoluminescence experiments have shown that almost all excitations created in the as-casted P3HT:PCBM composition (by 1:1 wt % ratio) are quenched and provide charges. The fact that I_{SC} and FF increase after the thermal annealing must be due to the fact that not all photogenerated charges in the as-casted composition can be collected at the electrodes and recombine either geminately or nongeminately in the active layer of the solar cell. After the thermal annealing the nanoscale phase separation occurs and pure PCBM phase builds a percolating network. By this the negative charges injected from P3HT into a pure PCBM phase delocalize and do not easily recombine with the holes in the P3HT matrix. The building of PCBM percolating network in the MDMO-PPV:PCBM composition could be achieved by the optimization of the wt % ratio of the two components.[14] In addition P3HT crystallizes and has a more planar backbone structure, the interchain interactions enhances, the morphological structure of the P3HT:PCBM film is improved by reducing the free volume and the density of morphological defects at the interface (between P3HT chains and PCBM phase) created during evaporation of the solvent and consequently the absorption of the film increases. The charge transfer and the electronic transport properties are improved as well. The enhanced absorption and electron transfer and transport lead to a higher I_{SC}. The more ordered structure improves the contact between electrodes and photoactive film, which decreases the series resistance of the cells and increases the current as well as the fill factor.

In summary, we have found that the processing conditions (solvent, P3HT:PCBM composition, thermal annealing) strongly effect the optical properties of the P3HT:PCBM films. The improved absorption of the composite films, the enhancement of the degree of polymer chain ordering lead to an improved performance of polymer solar cells based on poly(3-hexylthiophene):fullerene.

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