The Mobility and Decay Kinetics of Charge Carriers in Bulk Heterojunctions

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Plastic solar cells based on so-called "bulk heterojunctions", in which a blend of conjugated polymer donor and acceptor molecules forms a three-dimensional network, have shown efficiencies over 2.5 %. For this type of solar cells, the transport properties of the photo-induced charge carriers are thought to limit the efficiency. We have studied in this work the transport properties in thin films of blends on an inert substrate, which were photoexcited with a nanosecond visible laser pulse producing free charge carriers. The change in conductivity was measured using the Time-Resolved Microwave Conductivity technique (TRMC), which relieves us of having to apply electrodes.

For PCBM/MDMO-PPV blends, we have studied the effect of the weight fraction of PCBM (W_{PCBM}) on the mobility and recombination kinetics of the charge carriers. For all blends, the wavelength dependence of the photoconductivity in the range 420 to 700 nm closely resembled the photon attenuation spectrum indicating that photoexcitation of both components contributes to mobile charge carrier formation. The product of the quantum yield for charge separation, □, and the sum of the charge carrier mobilities, □□, was determined from the maximum (end-of-pulse) value of the transient photoconductivity.

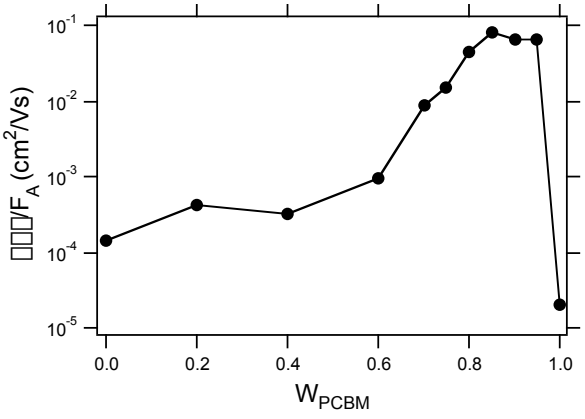

Figure 1. The dependence on W_{PCBM} of the values of □ □□, corrected for their attenuation derived on 500 nm irradiation for the lowest intensity used.

On excitation at 500 nm, □□□ remained almost constant in going from W_{PCBM} = 0.2 to 0.6 with an average value of 0.6□10^{-3} cm^2/Vs. Above W_{PCBM} = 0.6, the mobility and lifetime increased dramatically and a maximum mobility value close to 0.1 cm^2/Vs for W_{PCBM} = 0.85 was found. These observations are explained by the occurrence of phase separation above W_{PCBM} = 0.6, resulting in the formation of highly mobile electrons within PCBM-rich aggregates.

For photovolatic cells based on an electron accepting polymer (PCNEPV) and MDMO-PPV, a two orders of magnitude increase in photoconductivity was observed after annealing the blend at 100°C for 3 hours. The optical absorption spectrum of the bulk heterojunction shows only a minor change upon annealing. For both un-annealed and annealed samples the photoconductivity is proportional to the incident laser when intensities less than 5.0□10^{13}, and 3.0□10^{12} photons/cm^2/pulse, respectively are used. However, for the latter sample the photoconductivity is two orders of magnitude larger. Though we cannot exclude that this is partly caused by an increase of the mobility of the charge carriers, we propose that this increase is related with the occurrence of phase separation in the polymer/polymer film, resulting in PCNEPV rich parts. On absorption of a photon, charge separation occurs, yielding a bound electron/hole pair at the polymer/polymer interface. Due to increased diffusional motion of the electron in the PCNEPV rich parts, dissociation of the electron/hole pair is favoured. In this way, the electron can escape from its geminate counterpart, which retards effectively the geminate recombination present in the un-annealed sample.

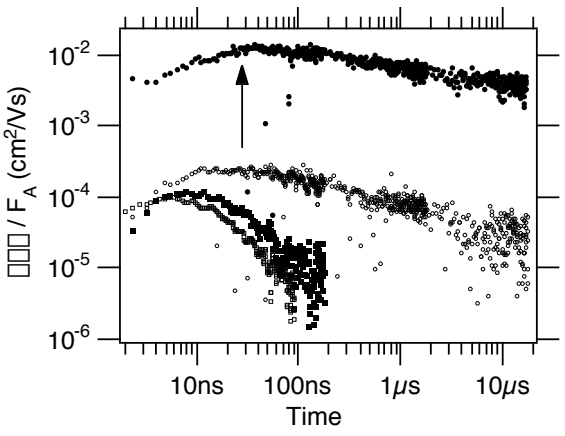

Figure 2. TRMC transients corrected for optical attenuation observed on photoexcitation of a MDMO-PPV layer (squares) and a 1:1 blend (circles) before (open markers) and after the heat treatment (filled markers). For the MDMO-PPV film hardly any increase is observed on annealing.