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Influence of composition and heat-treatment on the charge transport properties of poly(3-hexylthiophene) and [6,6]-phenyl C$_{61}$-butyric acid methyl ester blends

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Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C$_{61}$-butyric acid methyl ester (PCBM) blends have been demonstrated to form highly efficient polymer photovoltaic devices. In this letter, the time-of-flight technique is used to investigate the influence of composition and heat treatment on charge transport properties of P3HT and PCBM blends. The transport of electrons and holes both display a transition from dispersive to nondispersive and return to dispersive again as the percentage of PCBM increases. A balanced mobility of both electron and hole is obtained at a composition of 1 : 1 weight ratio, and it is nearly independent of the electrical field in the range of our test. The increase in carrier mobility is attributed to the formation of a more-ordered structure in the blend. This structural ordering is further enhanced by slowly evaporating the solvent during film formation which results in additional increase in carrier mobility. However, no such effect is observed in thick films ($\sim$200 nm), indicating the presence of such high-degree ordering due to heat treatment. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2045554]

Polymer photovoltaic devices show a promising future in large area, flexible, low cost, and light-weight applications. The bulk heterojunction composed of blends of low-band-gap polymer and methanofullerences have been demonstrated to achieve high efficiency.[1] The transfer of photogenerated electrons from donor (polymer) to acceptor (methanofullerences) is very efficient in the bulk heterojunction due to its large interface for charge transfer. This process typically occurs within $\sim$100 fs. Among the candidates of polymers for photovoltaic applications, poly(3-hexylthiophene) (P3HT) is found to be very promising due to its low band gap, (2.14 eV) good solubility, thermal and environmental stability,[2] and high hole mobility.[3] Preliminary research on the electronic properties of [6,6]-phenyl C$_{61}$–butyric acid methyl ester (PCBM) and P3HT have been investigated by several groups.[2,4] The transfer of photoinduced charges from P3HT to PCBM has been proven by the quenching of photoluminescence in P3HT.[4] Photovoltaic (PV) cell using blends P3HT and PCBM has been demonstrated to achieve high-power conversion efficiency up to 4.4% under 100 m/Wcm^2 of AM1.5 global irradiation.[5] It is found that the device performance depends strongly on composition[6] and heat-treatment condition.[5] In contrast to the poly-(phenylenevinylene)-derivative : PCBM blend system, the device with highest efficiency has the composition of 1 : 1 weight ratio.[6] Although the electronic property between P3HT and PCBM has been investigated by several groups, the carrier transport properties of films fabricated using such a blend are not well understood.

In this letter, the effects of material composition and heat treatment on the charge transport properties are investigated by the time-of-flight (TOF) technique. The samples studied in this work consist of a single polymer blend layer sandwiched between an indium–tin–oxide (ITO) anode and an Al cathode. In the active polymer blend layer, P3HT is the electron donor and PCBM is the electron acceptor. The chemical structures of P3HT and PCBM and the electron transport process are shown in Fig. 1. The P3HT : PCBM weight ratios vary from 0 : 1 (pure P3HT) through 2 : 1, 1 : 1, 1 : 2 to 1 : 3, corresponding to a PCBM weight percentage of 0%, 33%, 50%, 66%, and 75%, respectively. The thickness of the polymer blend layer varies from 0.7 to 1.53 μm. For the photocurrent transient measurement, the samples are under applied biases from 0 to 20 V and are illuminated through the ITO electrode using a nitrogen laser (λ=337 nm, τ=4 ns, 10 Hz). The incident power of the laser is kept small enough to avoid buildup of photoexcited charge in the samples, which ensures the constant electrical field distribution across the polymer blend layer. The transient current caused by the laser in the presence of an external applied electrical field is reflected by the voltage on the variable serial resistor in the circuit. The voltage signal across the resistor is amplified by an SR560 voltage preamplifier before being recorded by a Tektronix™ oscilloscope. The output resistor of SR560 is 50 Ω. By choosing the polarity of the electrical field applied to the samples, the transport of electrons and holes can be studied separately. The *RC* time constant of the cell and circuit is much smaller than the transit time. All measurements are performed at room temperature. Carrier mobility (μ) can
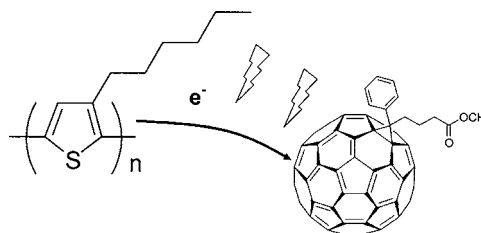

FIG. 1. Chemical structure of P3HT and PCPM. Electrons are transferred from P3HT to PCBM under illumination.
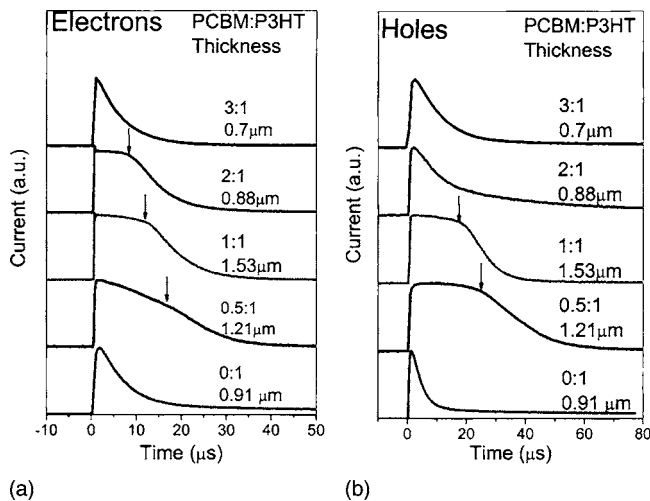
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FIG. 2. Photocurrents for (a) electrons and (b) holes from samples with different compositions.

be calculated from $\mu = d^2/Vt_{\mathrm{tr}}$, where V is the applied bias, d is the thickness of the polymer film, and t_{tr} is the transit time. For nondispersive charge transport, the transit time is taken as the inflection point in the decay of the current from its plateau value. For dispersive transients, the transit time is obtained at the intercept of the pretransit and post-transit asymptotes of the photocurrent as plotted on a double logarithmic scale.

Fig. 2 shows the typical electron and hole transient photocurrents for samples with different compositions. The transport of electron and hole in pure P3HT is highly dispersive, which agrees with the results reported before.[7] Due to the irregular photocurrent profile of our samples, the hole and electron mobilities of pure P3HT are difficult to extract. The transports of electron and hole become nondispersive when a small amount of PCBM (33%) is added into P3HT. A clear plateau followed by a tail in the photocurrent profile is observed. This transition is obvious for the hole transport. The fast initial decay of the TOF signal is limited by the time resolution of the experimental setup. For electron photocurrent, the inflection of the plateau region and exponential decay region is not well defined because the photocurrent, or electron packet, decays in the plateau region. There are two possibilities causing the decrease of photocurrent (electrons packet) during the plateau region (transport period): the trapping of transporting carriers and the recombination of transporting carriers.[8] It has been demonstrated that the photocurrent will decrease significantly during the plateau region when traps with opposite polarity charges were introduced into the polymer film.[8] However, in our samples, there is no significant difference in photocurrent prior and after introducing charge traps in the film. Thus, it is reasonable that there is some recombination of electrons and holes in the sample with 33% PCBM.

When the percentage of PCBM is increased to 50%, the photocurrent profiles for both electrons and holes have a well-defined nondispersive profile, indicating a more-ordered structure is present and the electron mobility increases to 1×10^{-4} cm^2 V^{-1} s^{-1}. The recombination of electrons and holes is thus negligible. Nondispersive transport switches to dispersive when the composition increases to 3:1. A similar transition from nondispersive back to dispersive occurs for hole transport at the composition of 2:1. The transition from
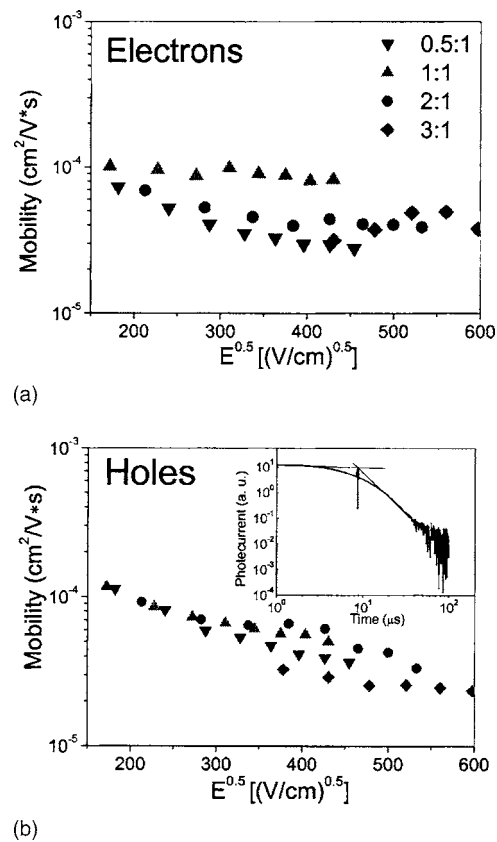

FIG. 3. Electrical field dependence of (a) electron and (b) hole mobility for samples with different compositions. The inset of (b) shows how transit time is obtained in the dispersive photocurrent profile.

dispersive to nondispersive and again to dispersive is also observed in the polyfluorene:PCBM system when the PCBM percentage is increased.[9] Generally, the nondispersive photocurrent profile indicates a more-ordered structure (topological or energetical). In the P3HT:PCBM system, electrons are transported through the PCBM matrix while holes are transported through P3HT matrix. Thus, it shows that the P3HT:PCBM blend provides a more-ordered structure than pure P3HT when an adequate amount of PCBM is introduced. However, at higher percentage of PCBM (75%, for example), large-scale phase segregation occurs and the structure returns to the disordered state,[10] which is indicated by the dispersive transport behavior of electrons and holes. Also, we notice the composition at which transition from nondispersive to dispersive occurs, for the transport of electrons (3:1) and holes (2:1) is different, which shows that the degree of order for P3HT and PCBM is different at different compositions. At a 1:1 wt–ratio blend, both electron and hole transports are clearly nondispersive, and this coincides with the PV cells with best performance.[6]

The electrical field dependence of electron and hole mobilities has been investigated in this letter. According to the Poole–Frenkel law, by plotting mobility as a function of the square root of electrical field ($\sqrt{E}$), a linear relation can be found between the $\ln\mu$ and $\sqrt{E}$. However, as shown in Fig. 3, the mobilities of electrons and holes for all compositions only show weak dependence with the electrical field at high electrical field and even slight negative dependence at low electrical field. The negative electrical field dependence of mobility in P3HT has been studied in detail in Refs. 11–14. It is demonstrated that such phenomenon in P3HT
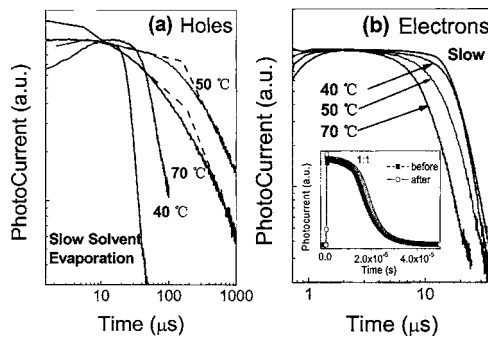
FIG. 4. Photocurrent of (a) holes and (b) electrons for the thick film at different solvent evaporation rates; inset of (b): photocurrent of device with 1:1 composition before and after heat annealing.

originates from the small energetic, but large spatial disorder,[13,14] instead of the experimental artifact related to the TOF technique. The 1:1 ratio sample has a more-ordered structure, which is illustrated by the relatively small changes in mobility with electric field.

It is found that the device performance is very sensitive to the heat-treatment condition and the solvent evaporation rate. The heat treatment shows different effects on films with different thicknesses. For example, in thin devices (~43 nm active layer), thermal annealing significantly increases both short-circuit current and the fill factor of the devices; in devices with an active layer as thick as 210 nm, the heat treatment only has an effect on the fill factor. In order to find out how heat treatment affects the device performance, TOF measurement has been performed to study the change of mobility upon those heat treatments. However, for TOF measurement, the thickness of the films must be thick enough to ensure that the charge transport region is much wider as compared to the light absorption region. Therefore, only thick films are studied by the TOF experiment.

To study the effect of the solvent evaporation rate on the charge transport properties, films with slow and fast solvent evaporation rates (samples are subjected to heat at 40, 50, and 70 °C to accelerate the evaporation rate) are prepared with P3HT:PCBM composition of 1:1. The TOF results are shown in Figs. 4(a) and 4(b), respectively. Figure 4(a) shows that the higher rate of solvent evaporation, the more dispersive the transport of holes, in the mean time, the hole mobility reduces rapidly (ten time less for the device backed at 50 °C than the slow evaporation device). On the other hand, the electron mobility increases slightly with increasing evaporation rate, as shown in Fig. 4(b). The higher mobility and more nondispersive transport behavior indicate a more-ordered structure forms in the slow evaporation film. It has been reported that P3HT tends to form better self-ordering for the drop casting films.[15] This can be explained by considering that slow evaporation of solvent will provide a longer time period for P3HT to self-organize and form an ordered structure, thus enhancing the hole transport property of the solar cell. Absorption spectra of slow evaporated film

show much more pronounced vibronic shoulders than fast evaporated film, which is another indication of the presence of a higher degree of ordering.[5]

The effect of thermal heat treatment on thick films is also studied by TOF. The electron photocurrents for the sample with composition 1:1 before and after annealing are shown in the inset of Fig. 4(b). No obvious improvement of the carrier transport property is found. This result agrees with the fact that baking of thick film devices does not increase short-circuit current. It is clear that the improvement in device performance is not caused by higher carrier mobility. The fill factor is greater for devices with thick films that are postproduction heat treated. It is believed that the serial resistance is reduced after annealing.

In summary, we have studied the effect of composition and heat treatment on the charge transport properties of the P3HT:PCBM blend by TOF measurement. The photocurrents of electrons and holes show an anomalous transition from dispersive to nondispersive and return to dispersive again as the PCBM percentage increases. This behavior indicates the formation of an ordered structure forming at an adequate concentration of PCBM. Slow evaporation tends to further fascinate the ordering of P3HT:PCBM, and thus results in higher carrier mobility of such films.

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