Charge transport and recombination in bulk heterojunction solar cells studied by the photoinducted charge extraction by linearly increasing voltage technique

Attila Mozer
University of Wollongong, attila@uow.edu.au

Serdar Sariciftci
Johannes Kepler University

Laurence Lutsen
University of Hasselt

Dirk Vanderzande
University of Hasselt

R Osterbacka
Abo Akademi University

See next page for additional authors

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Abstract

Charge carriermobility and recombination in a bulk heterojunctionsolar cell based on the mixture of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-phenylene vinylene] (MDMO-PPV) and 1-(3-methoxycarbonyl)propyl-1-phenyl-(6,6)-C_{61} (PCBM) has been studied using the novel technique of photoinduced charge carrier extraction in a linearly increasing voltage (Photo-CELIV). In this technique, charge carriers are photogenerated by a short laser flash, and extracted under a reverse bias voltage ramp after an adjustable delay time (t_{del}). The Photo-CELIV mobility at room temperature is found to be $\mu = 2 \times 10^{-4}$ cm^2 V^{-1} s^{-1}, which is almost independent on charge carrier density, but slightly dependent on tdel. Furthermore, determination of charge carrier lifetime and demonstration of an electric field dependent mobility is presented.

Keywords

recombination, charge, heterojunction, cells, extraction, linearly, voltage, studied, transport, solar, technique, increasing, bulk, photoinducted

Disciplines

Engineering | Physical Sciences and Mathematics

Authors

Attila Mozer, Serdar Sariciftci, Laurence Lutsen, Dirk Vanderzande, R Osterbacka, M Westerling, and G Juska

Charge transport and recombination in bulk heterojunction solar cells studied by the photoinduced charge extraction in linearly increasing voltage technique

A. J. Mozer[a)] and N. S. Sariciftci
Linz Institute for Organic Solar Cells (LIOS), Johannes Kepler University Linz, Austria

L. Lutsen and D. Vanderzande
Limburgs Universitair Centrum and IMEC (IMOMEC), Diepenbeek, Belgium

R. Österbacka and M. Westerling
Department of Physics, Åbo Akademi University, Turku, Finland

G. Juška
Department of Solid State Electronics, Vilnius University, Lithuania

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Experimental determination of the mobility of photoinduced charge carriers in thin film (100–300 nm) organic photodiodes, and particularly in bulk heterojunction solar cells is not straightforward. Mobility in bulk heterojunction solar cells has been investigated using a time-of-flight (TOF) technique,[1] or has been calculated from the transfer characteristics of a field effect transistor (FET).[2] The applicability of both of the above techniques have limitations: The TOF technique, in which the transit time of a two-dimensional sheet of photogenerated charge carriers drifting through a sample of known thickness is determined, requires large films thicknesses with high optical density (o.d. > 10).[3] For bulk heterojunction solar cells, this requires at least 1 μm thick film of the photoactive blend, which is 3–10 times thicker than what the optimum performance of such device requires.[4] The performance of bulk heterojunction solar cells[5] as well as charge carrier mobility is shown to be morphology dependent, which may change by increasing the film thickness up to several microns.[6] Moreover, the number of charge carriers in a TOF experiment is limited to ~10% of the capacitive charge.[3] The maximum charge carrier concentration can be calculated according to c [cm^{-3}] $= 0.1((\varepsilon\varepsilon_0 U)/(d^2 e))$, where ε is the low-frequency dielectric constant ($\varepsilon \sim 3$), ε_0 is the vacuum permittivity, U is the applied voltage ($U \sim 10$ V, corresponding to 10^5 V cm^{-1}), d is the film thickness ($d \sim 1$ μm) and e is the elementary charge. Using the above values, $c \sim 1 \times 10^{14}$ cm^{-3} is calculated, which is orders of magnitude lower than the charge carrier concentration in an AM (air mass) 1.5 illuminated solar cell. In the FETs, on the other hand, the motion of electric field induced charges on the surface of an insulating dielectric is

monitored, which hardly resembles the operational condition of a sandwich type solar cell. In addition, charge carrier mobility in an FET may also strongly dependent on the morphology,[7] i.e., the morphology of the thin (<20 nm), phase separated[8] layer near the insulator, which may be altogether different from the morphology of the bulk.

In this letter, we demonstrate a technique of photoinduced charge carrier extraction in a linearly increasing voltage (Photo-CELIV)[9] applied to determine *simultaneously* the charge carrier mobility and lifetime of the carriers in bulk heterojunction solar cells with an active layer thickness of a few hundred nanometers. The experimental setup consists of a nanosecond laser (Coherent Infinity 40-100 Nd:YAG), a delay generator (Stanford Research DG 535), a function generator (Stanford Research DS 345), and a digital storage oscilloscope (Tektronix TDS754C). The sandwich type structure (Fig. 1) consists of an ITO-coated transparent electrode, 100 nm poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) layer, 260 nm (measured by a semiconductor profiler) active layer prepared by spin coating of a 1:4 weight ratio mixture of MDMO-PPV:PCBM solution (5 mg/ml polymer in chlorobenzene), and Aluminum as cathode (active area of ~3 mm^2, Al thickness is 80 nm). This device exhibits power conversion efficiency (η) at simulated AM 1.5 illumination of $\eta \sim 1.8\%$ as characterized in a solar simulator unit. The MDMO-PPV polymer was synthesized by the sulphinyl precursor route[10] by the group of D. Vanderzande, and PCBM was purchased from Rijksuniversiteit Groningen (J.C. Hummelen). The device was mounted in a cryostat, and illuminated from the ITO side by a 3 ns, 532 nm laser pulse for bulk photogeneration of charge carriers.

The pulse sequence and the schematic response of the Photo-CELIV technique are shown in Fig. 1. The response of

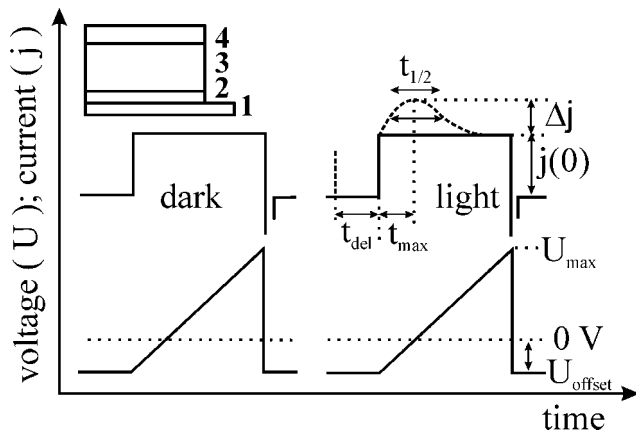[a)]Electronic mail: attila.mozer@jku.at

FIG. 1. Pulse sequence and a schematic response of the Photo-CELIV technique. The device structure is also displayed, and consists of (1) glass (2) ITO+100 nm Pedot-PSS (3) MDMO-PPV:PCBM 1:4 weight ratio (4) aluminum.

FIG. 2. Measured Photo-CELIV curves at (a) various delay times (t_{del}) between the light pulse and the voltage pulse; (b) various incoming light intensity at fixed $t_{del}=5$ μs; and (c) various U_{max}.

a dielectric upon application of a voltage ramp is a square-shaped current transient with the plateau value corresponding to the capacitive displacement current $j(0)=A \times \varepsilon\varepsilon_0/d$, where A is the voltage rise speed $A=dU/dt$. From $j(0)$ the RC time of the setup can be calculated, which is 2×10^{-8} s in the measurements presented herein. If charge carriers are extracted from the dielectric, an additional extraction current is detected. From the time when the extraction current reaches its maximum value (t_{max}), the mobility (μ) can be calculated as Eq. (1)[11]

$$\mu = \frac{2d^2}{3At_{max}^2\left[1+0.36\dfrac{\Delta j}{j(0)}\right]} \quad \text{if } \Delta j \leqslant j(0). \qquad (1)$$

Using Eq. (1), the re-distribution of the electric field during charge extraction is considered, which enables mobility measurements in conductive samples with relatively high carrier concentrations.[11] When a reverse bias voltage ramp is applied to the device (Aluminum connected to the positive terminal), no charge extraction is detected in the dark. However, the short laser flash generates charges, which undergo recombination, or alternatively, extracted under the built-in field. The built-in field may be compensated by the application of a forward bias dc offset voltage (U_{offset}). Therefore, charge carriers can be extracted after an adjustable delay time determining their lifetime (τ), and their mobility (μ) is determined according to Eq. (1).[12]

Recorded Photo-CELIV curves at various delay times are shown in Fig. 2(a). As the delay time increases, the maximum of the extraction current decreases and t_{max} slightly shifts to longer times. The former is the effect of charge carrier recombination, and the latter indicates decreasing mobility. The applied maximum voltage was 3 V, and U_{offset} =−0.75 V, which is near the built-in voltage of the device (measured open circuit voltage 0.8 V). Using the U_{offset} value of −0.8 V, charge carriers are injected in the dark, and subsequently extracted together with the light induced charge carriers upon application of the voltage ramp. This effect is slightly present at U_{offset}=−0.75 V, [note the small extraction in the dark CELIV curve in Fig. 2(a)]. The built-in field could be more precisely compensated in devices without using PEDOT-PSS under layer due to the reduced injection
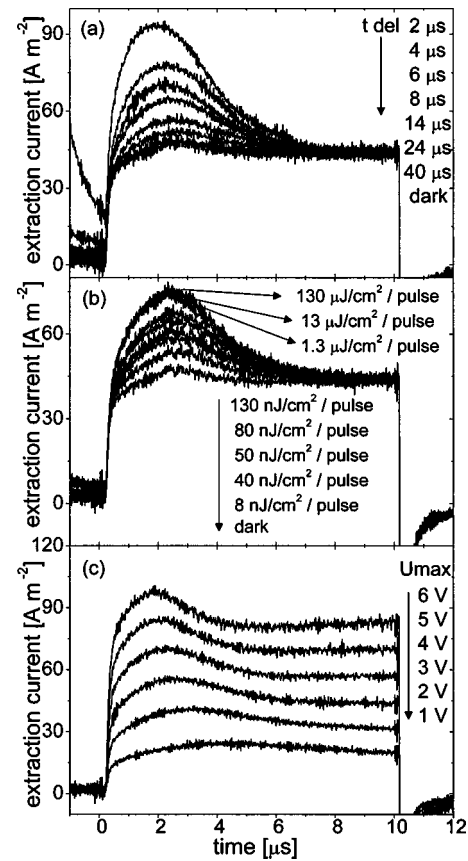
current at −0.75 V forward bias, however, the measured mobility values are not significantly affected by this change.

In the next experiment, the incoming light intensity was varied by using o.d. filters, and the charge carriers were extracted after 5 μs fixed delay time [Fig. 2(b)]. The extraction current saturates at light intensities above 1 μJ/cm^2/pulse. Such light intensity independent recombination kinetics in the μs−ms regime at higher illumination has been reported earlier by transient absorption measurements,[13,14] and has been attributed to thermally activated (slow) recombination of charge carriers exhibiting a power law decay as $\sim t^{-\alpha}, \alpha$ =0.4.[15] At illumination intensities <1 μJ/cm^2/pulse, the maximum of the extraction current is decreasing, however, t_{max} remains almost constant indicating that the mobility in these charge carrier concentrations (around 1.6 $\times 10^{15}$ to 1.7×10^{14} cm^{-3}) is nearly constant. Finally, voltage dependent (U_{max}) Photo-CELIV curves has been recorded at fixed 15 μs delay time [Fig. 2(c)]. The capacitive current step $j(0)=(dU/dt) \times \varepsilon\varepsilon_0/d$ is increasing as U_{max} increases, and the t_{max} shifts to shorter times indicating the electric field dependence of the mean carrier velocity.

The mobility is plotted versus delay time in Fig. 3(a). The mobility decreases up to ~10 μs, and remains almost constant ($\mu=2 \times 10^{-4}$ cm^2 V^{-1} s^{-1}) for further delays. The initial decay of mobility may be related to the energy relaxation of the charge carriers[12,16] towards the tail states of the density of states distribution, where a dynamic equilibrium is attained.[17] Further indication is given by the voltage (electric field) dependence of mobility at short (5 μs) and long (15 μs) delay times [Fig. 3(b)]. The electric field in the
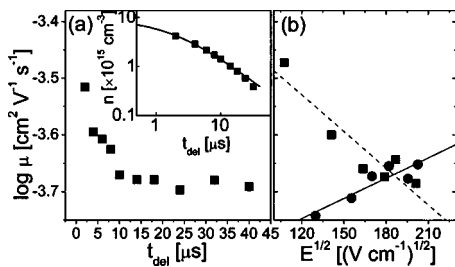
FIG. 3. Photo-CELIV mobility as a function of delay time (a) and the electric field (b) at (■) 5 μs or (●) 15 μs after the light pulse. Inset: Concentration of extracted charge carriers as function of delay time and the fit.

CELIV experiment varies constantly, and can be averaged as $E_{CELIV} = (A \times t_{max})/d$.[18,19] The calculated electric field dependence follows positive field dependence as expected for typical disordered semiconductor at longer delay times ($t_{del} = 15$ μs), yet shows a negative dependence at short delay times ($t_{del} = 5$ μs).

The inset of Fig. 3(a) shows the concentration of extracted charge carriers as a function of the delay time. The decay does not follow a power law ($t^{-\alpha}$) as was observed in Refs. 13 and 14. A bimolecular decay law, with the decay rate dn/dt changing from t^{-1} to the equilibrium bimolecular decay rate of t^{-2} [20] is indicated by these studies. The concentration decay is, therefore, fitted using a time-independent (nondispersive) recombination as $dn/dt = -\beta n^2$, where n is the concentration of charge carriers and β is the bimolecular recombination coefficient. The analytical solution is given by $n(t) = n(0)/[1 + (t/\tau_B)]$, where $n(0)$ is the initial ($t=0$) concentration of photogenerated charge carriers and $\tau_B = (n(0)\beta)^{-1}$ is the bimolecular lifetime. From the fit to the concentration decay we obtained $n(0) = 9 \times 10^{15}$ cm^{-3} and $\tau_B = 1.7 \times 10^{-6}$ s, yielding a bimolecular coefficient $\beta = 6 \times 10^{-11}$ cm^3 s^{-1}.

The different recombination law calculated from delay time-dependent Photo-CELIV as compared to the transient absorption (TA) measurement of Refs. 13 and 14 might arise from the fact that in the Photo-CELIV technique only charge carriers with reasonable mobility are extracted, yet in the TA, all charges including deeply trapped (immobile) carriers are also detected. On the other hand, the number of un-extracted charge carriers can be calculated from the end of the pulse extraction current, which is minimal at room temperature indicating that charge carrier trapping on the applied time (frequency) time scale is not significant.

An important question considered is the sign of the majority carriers detected in the Photo-CELIV technique. It has been argued by Mihailetchi *et al.* that the charge transport in the 1:4 weight percent MDMO-PPV: PCBM blend is dominated by electrons rather than holes.[21] ToF measurements[1] as well as FET studies[2] showed that mixing these two materials in 1:4 ratio results in fairly balanced charge transport. More recently, Meltzer *et al.*[22] have shown that the electron and hole mobility is more balanced as it was previously assumed, and reported very similar values for the hole mobility as obtained by the Photo-CELIV technique presented herein. From these Photo-CELIV measurements we cannot directly determine which sign of charge carrier is more mobile. Changing the time scale of the voltage pulse between 1 μs up to 1 ms, only one peak is detected. Finally, the shape of

the Photo-CELIV transients can be analyzed by a parameter $t_{1/2}$ to t_{max}[9] as illustrated in Fig. 1, which is 1.2 for ideal nondispersive transients. The $t_{1/2}$ to t_{max} values calculated for the transient shown in Fig. 2(a) are ~1.6 at short time delays, and gradually reaches the ideal nondispersive value of 1.2 at longer time delays (>10 μs) further indicating that a time-dependent energy relaxation of the charge carriers occurs. A more detailed study including the temperature dependence of the Photo-CELIV mobility will be published.

In summary, the technique of Photo-CELIV has been introduced to *simultaneously* determine the mobility and the lifetime of the photogenerated charge carriers in bulk heterojunction solar cells. It is found that the mobility is decreasing with increasing time delays, which is related to the energy relaxation of the charge carriers towards the deeper states of the density of states distribution. The mobility is found to be rather insensitive to the charge carrier concentration, and weakly dependent on the applied electric field.

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