Double-injection current transients as a way of measuring transport in insulating organic films

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We propose a double-injection current transient technique for the study of charge-carrier transport in thin insulating films of low-mobility materials with reduced carrier bimolecular recombination compared to the Langevin type. This experimentally simple technique, allows us to estimate the sum of the faster carrier and the slower carrier mobility's ($\mu_f+\mu_s$) and the slower carrier mobility (μ_s). Furthermore, in thin films when the *RC* current overlaps the injection current transients we propose to estimate these transport parameters using the extracted charge as a function of injection pulse duration. The method is applied on bulk-heterojunction solar cells made from blends of regioregular poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene. We have experimentally verified the technique by measuring the charge carrier mobility's and compared them with results obtained using standard time-of-flight and carrier extraction using linearly increasing voltage techniques. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2736791]

I. INTRODUCTION

Organic semiconductors are promising materials for solar cells and light emitting diodes.[1] The operation and performance of these devices strongly depends on the charge transport. To clarify charge transport properties in thin films (sample thickness $d<1$ μm) using classical time-of-flight (TOF) and carrier extraction by linear increasing voltage (CELIV) methods is complicated, because the photogeneration region is comparable with the sample thickness. Also the large sample capacitance makes the *RC* time comparable with the transit time (t_{tr}). To extract transport properties from stationary current-voltage (I-V) characteristics is nontrivial due to the lack of dynamics.[2] Transient electroluminescence techniques have previously been used to study electron and hole mobility's in organic light-emitting devices where Langevin-type charge-carrier recombination is present.[3] However, the presence of reduced bimolecular carrier recombination in bulk-heterojunction solar cells[4] provide the means to study charge-carrier transport and recombination directly using the dynamics of current injection. We have previously shown how to estimate the ambipolar carrier mobility and the bimolecular recombination coefficient in bulk-heterojunction solar cells using double-injection (DoI) current transients into semiconductors[5] and insulators.[6] In this work we show how to clarify charge-carrier transport properties in insulating low-mobility materials using double-injection current transients.

II. THEORY

In homogeneous disordered low-mobility materials (i.e., hopping distance is shorter than the Coulomb radius) the carrier recombination is governed by the probability for them to meet in space. This type of recombination is described as bimolecular Langevin-type carrier recombination and the bimolecular recombination coefficient β_L is governed by the carrier mobilities[7]

$$\beta_L = e(\mu_n + \mu_p)/\epsilon\epsilon_0, \tag{1}$$

where $\epsilon\epsilon_0$ is the dielectric permittivity and μ_n and μ_p are the electron and hole mobility, respectively.

In case of double injection into an insulator (i.e., when the dielectric relaxation time $\tau_\sigma=\epsilon\epsilon_0/en\mu \gg t_{tr}$, where t_{tr} is the transit time of the faster carriers) when the recombination

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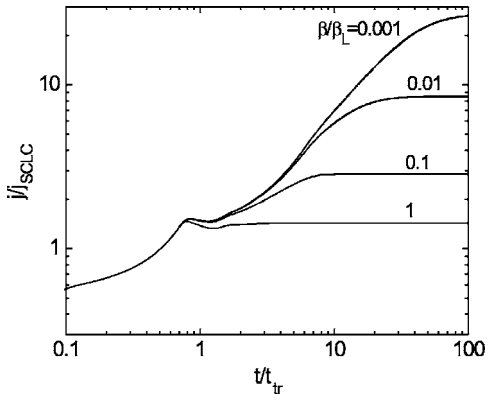

FIG. 1. Double-injection current transients calculated for different bimolecular recombination coefficients normalized to the Langevin coefficient β/β_L with $\mu_n=10\mu_p$.

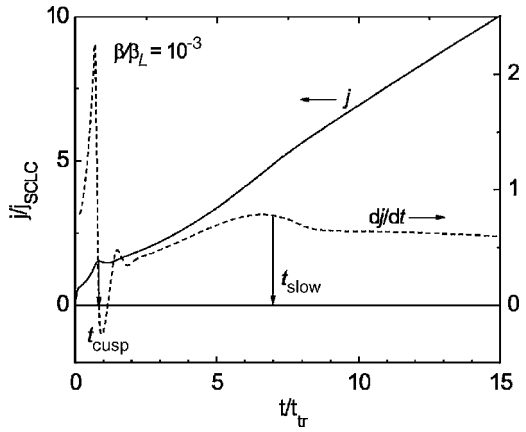

FIG. 2. Initial DoI current transient (solid line) and the time derivative (dashed line) of the current showing t_{slow}, the transit time of the slower carrier.

is of the Langevin type the charge carriers will completely recombine within the interelectrode distance. The observed stationary current-voltage dependence is then similar to the single-carrier (monopolar injection) space-charge limited current (SCLC) case,[8]

$$j_s(U) = C\epsilon\epsilon_0(\mu_n + \mu_p)\frac{U^2}{d^3}, \tag{2}$$

with C only insignificantly exceeding 1.

However, when the bimolecular recombination coefficient is much less than the Langevin coefficient ($\beta \ll \beta_L$), the amount of carriers increases with time within the interelectrode distance to finally saturate due to carrier recombination. If the recombination is bimolecular the steady state current can be written as[6]

$$j_s(U) = \epsilon\epsilon_0\sqrt{\frac{2\beta_L}{\beta}\mu_n\mu_p}\frac{U^2}{d^3}. \tag{3}$$

Figure 1 shows typical calculated current transients with different values of the bimolecular recombination coefficient β, when $\mu_n=10\mu_p$.

The typical cusp observed in the current transient is determined by the time when the injected charge carriers meet, i.e.,

$$t_{cusp} \approx 0.8\frac{d^2}{(\mu_n + \mu_p)U}, \tag{4}$$

whereas the following increase in the current (observed only when $\beta \gg \beta_L$) is caused by carrier accumulation in the film. At the time t_{slow},

$$t_{slow} \approx 0.75\frac{d^2}{\mu_{slow}U}, \tag{5}$$

the slower carriers reach the opposite electrode and a slight change of slope in the current increase is observed, clearly seen in the current derivative shown in Fig. 2.

The following current increase is caused only by carrier accumulation, until the current finally saturates due to recombination. After the slower carrier transit time t_{amb},

$$t_{amb} = \frac{d^2(\mu_n + \mu_p)}{\mu_n\mu_p U}, \tag{6}$$

the carriers are distributed evenly in the bulk (preserving charge neutrality) meaning that $n \cong p$. We can therefore simplify the differential equation describing the carrier recombination

$$\frac{\partial n}{\partial t} = G - \beta n^2, \tag{7}$$

where G is the generation rate of the carrier density n due to double injection,

$$G = \frac{CU}{edt_{amb}} = \frac{\epsilon\epsilon_0 U^2\mu_n\mu_p}{ed^4(\mu_n + \mu_p)}. \tag{8}$$

By solving Eq. (7) in the steady-state (i.e., $\partial n/\partial t=0$) and by using Eq. (8) we obtain (within a factor of 2) the saturated current density [Eq. (3)] by inserting into $j_s=en(\mu_n+\mu_p)U/d$. Using this simple approximation the time dependence of the charge carrier and current densities as a function of bimolecular recombination then obtains the simple form

$$n(t) = \sqrt{\frac{G}{\beta}}\tanh\left(\sqrt{G\beta}t\right), \tag{9}$$

and

$$j(t) = j_s\tanh(\beta n_s t), \tag{10}$$

where $n_s=j_s d^2/eU(\mu_n+\mu_p)$ is the saturated density of injected charge carriers.

Since the RC current overlaps with the initial part of the current transient and makes it difficult to estimate t_{cusp} in the current transient, we have recently suggested to use an alternate method, namely extraction of the injected charge.[6] We can measure the amount of injected charge by applying a reverse bias offset voltage (U_{off}) after the injecting (forward bias) pulse, given that all the injected carriers can be extracted. The numerically calculated extracted charge Q_{ex} as a function of injection pulse duration, t_p is shown in Fig. 3 and a clear resemblance with the DoI current transient is observed.

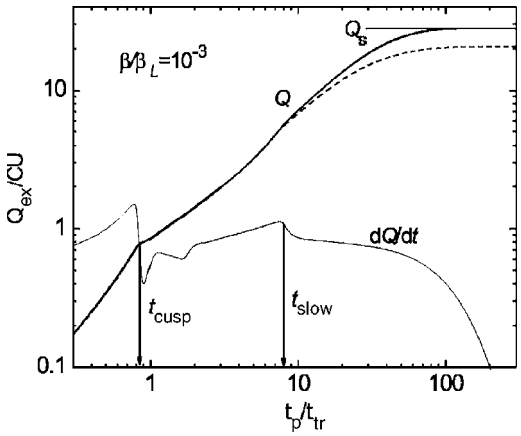

FIG. 3. Numerically calculated extracted charge and its derivative as a function of injection pulse duration. Extracted charge without recombination during the extraction (full line) and extracted charge when the recombination during the extraction is included for $\tau_{RC}=t_{tr}$ (dashed line).

From Fig. 3 it is clear that the extracted charge is approximately equal to CU when $t_p \approx t_{\mathrm{cusp}}$, therefore we can use that time to estimate the sum of both carrier mobility's $(\mu_n+\mu_p)$. The slower carrier transit time and mobility can be estimated from the time when $t_p=t_{\mathrm{slow}}$, i.e., when the maxima in the derivative of the extracted charge as a function of t_p, $Q_{\mathrm{ex}}(t_p)$, is seen (see Fig. 3).

The stationary carrier mobility $(\mu_n+\mu_p)$ can also be estimated using the ratio between the stationary current value J_s and the amount of extracted charge Q_s as follows:

$$\mu_n+\mu_p=\frac{d^2}{U}\frac{J_s}{Q_s}. \tag{11}$$

Unfortunately, due to carrier recombination during the extraction the amount of extracted charge carriers is smaller than the injected. The recombination loss depends on the load resistance which is limiting the extraction current. The numerically calculated extracted charge Q_{ex} for an unlimited extraction speed and for $\tau_{RC}=t_{tr}$ is shown in Fig. 3. It can be seen, that all charge carriers are extracted when the amount of injected carriers is small, but when the saturated current value j_s is reached an insignificant part of the extracted charge is lost due to recombination during the extraction.

III. EXPERIMENT

Sandwich-type samples were made from a 1:2 blend of regioregular poly(3-hexylthiophene) (RRPHT) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM) in chloroform by doctor blading the chloroform solution on a indium-tin-oxide (ITO) substrate coated with a thin poly(3,4-ethylenedioxythiophene) doped with polysulfonate styrene (PEDOT:PSS).[9] The sample thickness was $d=1.4\ \mu$m having a dielectric relaxation time $\tau_\sigma \approx 100\ \mu s \gg t_{tr} \approx 0.1-1\ \mu$s at room temperature in the used voltage range.

A square-shaped voltage pulse with a variable pulse duration t_p and amplitude U is applied over the sample and current transients are recorded in an oscilloscope. In Fig. 4 a schematic picture of the applied voltage pulse together with a typical DoI transient response is shown.

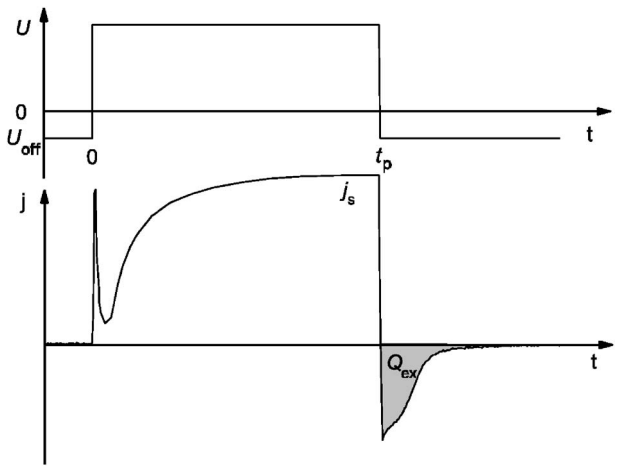

FIG. 4. Schematic DoI and extraction current transient setup showing the applied square-shaped voltage pulse with the magnitude U, pulse duration t_p, and offset voltage U_{off} together with typical DoI current response followed by the extraction current transient Q_{ex}.

In the beginning the current transient is governed by the displacement current of the external RC circuit with a characteristic time constant τ_{RC}. After τ_{RC} the DoI current starts to dominate and the current transient shows an increase with subsequent saturation due to bimolecular charge-carrier recombination. A negative offset voltage U_{off} is applied to extract the accumulated charge carriers. The extracted charge is estimated by integrating the current transient after the injecting voltage pulse is switched off and by subtracting the current transient without the injection pulse.

IV. RESULTS AND DISCUSSION

The experimentally measured stationary current-voltage dependence is shown in Fig. 5.

When the applied voltage is higher than the built-in potential the charge-carrier injection into the film starts. The fact that the DoI with reduced bimolecular carrier recombination is dominating is evident from the following experimental observations: (a) the dark current is proportional to U^2 [see Eq. (3)] and it's amplitude is much larger than the SCLC value calculated using the faster carrier mobility; (b) after the application of the voltage pulse the current continues to increase even after the transit time t_{tr}; (c) the extracted

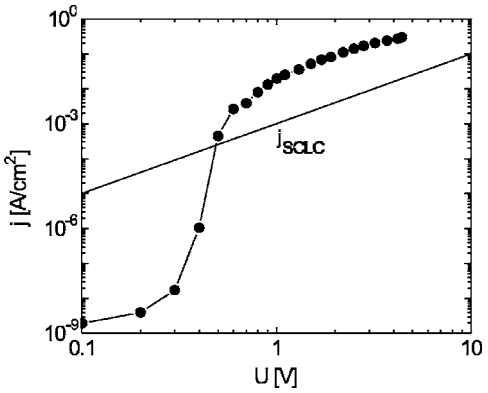

FIG. 5. Stationary current as a function of applied voltage compared with calculated SCLC current using the measured $\mu=10^{-2}$ cm^2/V s.

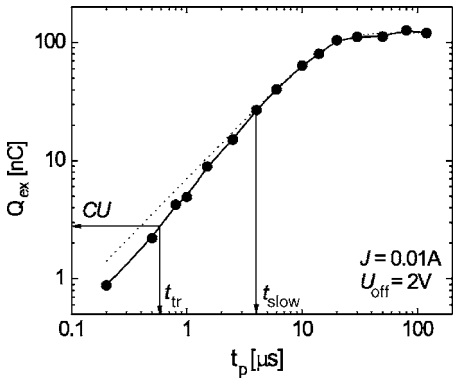

FIG. 6. Experimentally measured extracted charge as a function of the injection pulse duration. The dashed line is fit of the experimental data using Eq. (12).

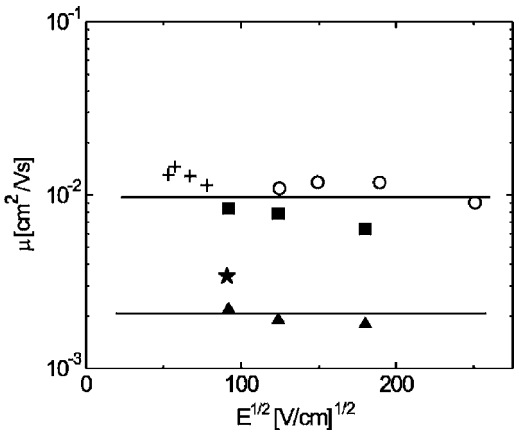

FIG. 7. Comparison of the measured charge-carrier mobility's as a function of electric field: μ_n using CELIV (crosses), μ_n using TOF (circles), $\mu_n+\mu_p$ using DoI (squares), slower carrier mobility μ_p using DoI (triangles), and μ_{sat} using DoI (star).

charge is much larger than CU. In bulk-heterojunction solar cells the electrons and holes are transported along different pathways. The size of the interpenetrating clusters and/or segments is much smaller than the film thickness, but more importantly also smaller than the Debye screening radius.[10] Therefore, we are in the regime corresponding to plasma injection into an insulator.[8]

Due to the film thickness, the RC current covers the initial part of the DoI current transient. Therefore, we extract the transport parameters from the extracted charge Q_{ex} as a function of pulse duration t_p as shown in Fig. 6. This is valid since we carefully check that we lose lesser than ≈30% of the injected charge due to recombination during the extraction.

The sum of both carrier mobility's $(\mu_n+\mu_p)$ is estimated from Fig. 6 using the time when the injecting pulse equals $CU[t_p \approx d^2/(\mu_n+\mu_p)U]$. Moreover, the mobility of the slower charge carriers, previously difficult to measure in thin films, is estimated for different electric fields using Eq. (5). Experimentally this is done by using the time when the extracted charge starts to follow the equation[6]

$$Q_{\mathrm{ex}}(t_p) = \int_{t_p}^{\infty} J_{\mathrm{ex}}(t)\,dt = Q_s \tanh\left(\frac{\beta Q_s t_p}{ed}\right), \tag{12}$$

i.e., when the experimental and calculated curves coalesce, in Fig. 6.

In Fig. 7 the obtained results of both the slowest mobility and sum of the mobility are compared to the measured electron mobility's using TOF and with the mobility of the faster carriers obtained using CELIV.

The very good agreement between the three independent techniques show that the faster carriers are electrons and the holes are slower. The sum of both carrier mobility's obtained using the stationary Q_s and J_s is smaller than the values obtained from the time when the extracted charge as a function of t_p equals CU. If the injected charge would not be fully collected due to recombination during extraction it would lead to a reduction of the mobility value even more. So we think, that the reduced stationary drift mobility is a result of shallow trapping, because Q_s also accounts for trapped carriers.

The estimation of the hole mobility is only approximate, but in photo-CELIV two extraction maxima corresponding to both carriers are not observed, which shows that the carrier mobility ratio is not large.

The obtained value of β from Eq. (12) and Fig. 6 is $\beta = 1.1\times10^{-11}$ cm^3/s which is in agreement with previously observed β in these films. Using the measured mobility at $\mu=10^{-2}$ cm^2/V s we calculate $\beta_L \cong 5.2\times10^{-9}$ cm^3/s leading to $\beta/\beta_L = 2.1\times10^{-3}$, which is in very good agreement with the previously reported recombination value.[6]

V. CONCLUSIONS

An experimentally simple technique is shown for the measurement of charge carrier transport in thin films where the bimolecular carrier recombination is reduced compared to the Langevin type. We have used the technique on bulk-heterojunctions solar cells and show how to experimentally estimate the sum of both carrier mobility's and the mobility of slower charge carriers. The modification of this technique, extraction of injected carriers,[6] allows us to further expand the measurable device thickness range and to estimate the carrier mobility by measuring the extracted charge as a function of injecting voltage pulse. The experimentally measured carrier mobility values in RRPHT/PCBM bulk-heterojunction solar cells are presented and compared to mobility values obtained using TOF and CELIV techniques.

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