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Charge-carrier transport and recombination in thin insulating films studied via extraction of injected plasma

G. Juška,[*] G. Sliaužys, K. Genevičius, and K. Arlauskas
Department of Solid State Electronics, Vilnius University, Saulėtekio 9 III K, 10222 Vilnius, Lithuania

A. Pivrikas
Department of Physics, Åbo Akademi University, Porthansgatan 3, 20500 Turku, Finland
and Graduate School of Materials Research, Universities of Turku, Turku, Finland

M. Scharber
Konarka Austria, Altenbergerstrasse 69, A-4040 Linz, Austria

G. Dennler and N. S. Sariciftci
Linz Institute for Organic Solar Cells, Johannes Kepler University, Linz, Austria

R. Österbacka
Department of Physics and Center for Functional Materials, Åbo Akademi University, Porthansgatan 3, 20500 Turku, Finland
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We show how charge-carrier transport and recombination in thin insulator films are directly measured using the technique of extraction of injected plasma. This technically simple technique is complementary to the well-known time-of-flight technique. We use this technique on bulk-heterojunction solar cells, where the double-injection current into an insulator is found, and we show how to use the extraction of the injected plasma to independently and simultaneously measure the charge-carrier mobility and bimolecular recombination coefficient in these films. A simple analytical solution to calculate the bimolecular recombination coefficient from an injected charge is derived. We found that the extracted charge follows a linear dependence as a function of applied voltage and saturates as a function of offset voltage, leading to the conclusion that almost all of the injected charge is extracted at high offset voltages. Therefore, we can directly measure the charge-carrier mobility and bimolecular recombination coefficient from the extracted charge as a function of voltage pulse duration. Moreover, the charge-carrier bimolecular recombination coefficient ($\beta = 2.2 \times 10^{-12}$ cm^3/s) is found to be strongly reduced compared to Langevin-type coefficient, as previously shown.

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I. INTRODUCTION

Bulk-heterojunction solar cells (BHSCs) are promising candidates for large-scale production due to cheap, roll-to-toll fabrication possibilities.[1] When trying to achieve high power conversion efficiency it is very important to understand the overall efficiency limiting factors, e.g., charge-carrier generation and extraction.[2] To measure these parameters in low-mobility materials the time-of-flight (TOF) and charge-carrier extraction by linearly increasing voltage (CELIV) techniques are often used.[3,4] However, the application of these techniques for samples with film thickness of less than 1 μm is complicated because the photogeneration region is comparable with the sample thickness. Furthermore, the high sample capacity allows only the integral-mode (charge) TOF method to be used.[5] This makes the interpretation of the results more complicated.

In this work we demonstrate the technique of extracting injected plasma, i.e., injected electrons and holes that approximately neutralize each other.[6] We show how to measure the charge-carrier transport and recombination parameters when double injection (DI) current into an insulator is present ($\tau_\sigma > t_{tr}$, where τ_σ is the dielectric relaxation time, and t_{tr} is the charge-carrier transit time through the sample). Previously DI current has been studied in inorganic semiconductors.[6–11] DI limited by monomolecular charge-carrier recombination[12] and in the presence of traps[13,14] was used to clarify device performance and the underlying principles of transport and recombination in *p*-type germanium, *p*-*i*-*n* silicon diodes, and other semiconductors. Moreover, for efficient light emission DI is necessary. In organic light-emitting devices DI transients have been studied.[15–19] We have previously shown how to use DI current transients into a semiconductor ($\tau_\sigma < t_{tr}$) to study charge transport and recombination in BHSCs.[20] DI into an insulator has not been widely studied before and there are no simple analytical solutions for the DI transients into an insulator. However, optical DI into an anthracene crystals has been performed to study the current density, electric field, and space charge distributions.[21]

In our experiment we show how to estimate the charge-carrier mobility and bimolecular recombination coefficient from the extraction of injected plasma for a BHSC with $\tau_\sigma > t_{tr}$.

II. THEORY

For high densities of injected charge carriers bimolecular carrier recombination will start to dominate.[22] In low-carrier-mobility materials, where Langevin-type charge-carrier recombination is expected, the injected charge carriers meet and completely recombine within the interelectrode region, and the current in thick films will therefore insignificantly exceed the space-charge-limited current[6] (SCLC)

$$j(U) = \frac{9}{8}\epsilon\epsilon_0(\mu_n + \mu_p)\frac{U^2}{d^3}. \tag{1}$$

Here ϵ is the dielectric permittivity, ϵ_0 is the relative permittivity, μ_n (μ_p) is the electron (hole) mobility, U is an external applied voltage, and d is the sample thickness. In this case the amount of injected electrons and holes is equal to $3CU/2e$ and the extracted charge Q_{ex} is

$$Q_{ex} = CU, \tag{2}$$

where C is the sample capacitance.

For the insulator case, i.e., $t_{tr} \ll \tau_\sigma$, and if the bimolecular recombination coefficient β is small compared to the Langevin coefficient $[\beta \ll \beta_L = e(\mu_n+\mu_p)/\epsilon\epsilon_0]$ then we can write the DI current as[6]

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

In this case the electrons and holes form a plasma, i.e., the amount of injected holes approximately equals the amount of injected electrons ($P \approx N$) and the total amount of charge carriers is much greater than the charge stored on the electrodes $[e(N+P) \gg CU]$. The charge-carrier accumulation and the subsequent increase in current are limited by recombination. In the case of reduced bimolecular carrier recombination the number of accumulated charge carriers in the film starts to increase approximately after the ambipolar drift time and we will get the following time dependence of the current:[6]

$$j(t) \propto \tanh(\beta \Delta n_s t), \tag{4}$$

where t is the time, and Δn_s is the density of saturated plasma as a function of time.

However, in thin films, the DI transient overlaps with the RC decay transient. Moreover, if the sample resistance is comparable to the internal resistance of the generator and oscilloscope (50 Ω), the sample resistance will cause an extra voltage drop over it, leading to a lower voltage over the film. Therefore, the sample resistance will limit the DI current. The best method to overcome this problem is to observe the behavior of accumulated charge carriers from the extraction current transients as a function of the injection pulse duration t_p (see Fig. 1). By solving the continuity equation with bimolecular charge-carrier recombination in a similar fashion as in the case of double injection into a semiconductor,[20] we can write the following relation:

$$Q_{ex}(t_p) = \int_{t_p}^{\infty} j_{ex}(t)dt \propto \tanh(\beta Q_s t_p/edS), \tag{5}$$

where j_{ex} is the extraction current and Q_s is the amount of injected charge saturated as a function of time due to recombination. In this case we can estimate the bimolecular recombination coefficient as

$$\beta = \frac{\ln 3}{2}\frac{edS}{t_{Q/2}Q_s}, \tag{6}$$

where $t_{Q/2}$ is the time when the injected charge is equal to half of its maximum value.

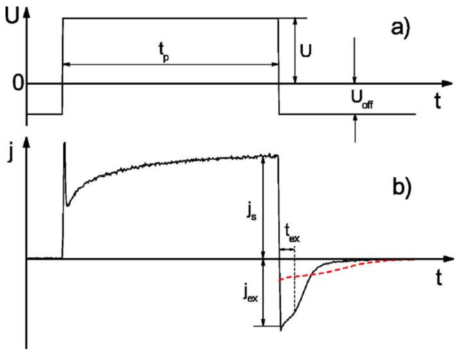

FIG. 1. (Color online) Schematic DI and extraction current transient setup showing the applied square-shaped voltage pulse with an applied voltage U, pulse duration t_p, and offset voltage U_{off} in (a) and typical DI current with extraction current transient in (b). The dashed line shows an extraction transient without offset voltage, and the full line with an offset.

When the amount of extracted charge and injection current are known we can estimate the sum of the charge-carrier mobilities:

$$t_{tr} = d^2/(\mu_n + \mu_p)U = Q_s/I_s, \tag{7}$$

where I_s is the double-injection current saturated as a function of time. The sum of the carrier mobilities can also be estimated from the time required for the injected carriers to meet according to SCLC conditions:[6]

$$Q_{ex}(t_p) = CU \quad \text{when } t_p = t_{tr}. \tag{8}$$

III. EXPERIMENT

The sandwich-type samples were made by doctor blading a 1:2 blend of regioregular poly(3-hexylthiophene) (RRPHT) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM) in chloroform on an indium tin oxide substrate coated with a thin poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) film. As the top electrode a thin lithium fluoride film followed by a semitransparent aluminum film was evaporated.

The sample thickness $d = 1.4$ μm. The dielectric relaxation time in the sample $\tau_\sigma \approx 100$ μs $\gg t_{tr} \approx 0.1-1$ μs at room temperature for the voltages used.

In Fig. 1(a) a schematic picture of the externally applied voltage pulse and Fig. 1(b) a typical experimental DI transient response are shown. A square-shaped voltage pulse with a variable pulse duration t_p and voltage amplitude U is applied and current transients are recorded in the oscilloscope [Fig. 1(b)].

In the beginning the current transient is governed by the displacement current of the external RC circuit with a char-

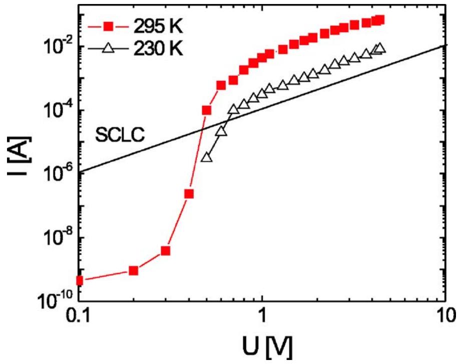

FIG. 2. (Color online) Current-voltage characteristics measured at room temperature (open triangles) and at 230 K (closed squares). The straight lines show the calculated SCLC using the obtained mobility $\mu \approx 10^{-3}$ cm^2/V s.

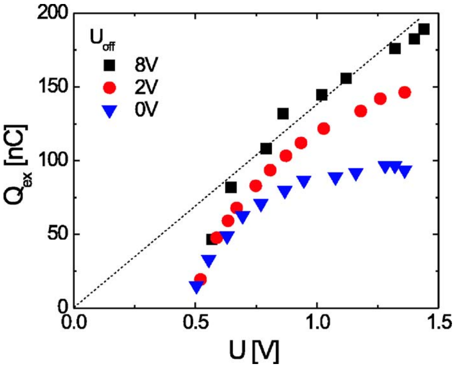

FIG. 3. (Color online) Extracted charge Q_{ex} as a function of applied external voltage U measured for different offset voltages U_{off}. The dotted line shows the theoretical linear dependence [Eq. (3)] of the extracted charge on the applied voltage.

acteristic time constant τ_{RC}. After τ_{RC} the double-injection current starts to dominate and the current transient shows an increase with subsequent saturation due to bimolecular charge-carrier recombination.[20] A negative offset voltage U_{off} is applied to fully extract the accumulated charge carriers.

IV. RESULTS AND DISCUSSION

In Fig. 2 the stationary current as a function of voltage for two temperatures is shown. The measurements were performed with a very low resistance of the voltage source and current meter in order to obtain as high as possible voltage drop over the film.

At very low applied voltages the current is diffusion driven as has been observed in similar films,[20] whereas at high voltages the current is proportional to the voltage squared $I \propto U^2$. The experimentally measured current value is much higher than the calculated (room temperature) SCLC value shown as a straight line in Fig. 2. The stationary SCLC is calculated using the sum of charge-carrier mobilities obtained by using Eq. (7) and Fig. 5 below ($\mu \approx 10^{-3}$ cm^2/V s).

The shape of the current transient in Fig. 1 and the fact that $I \propto U^2$ shows that double injection of plasma is active and that the DI current is limited by bimolecular carrier recombination. Since the DI current is much larger than the SCLC the bimolecular charge-carrier recombination is strongly reduced compared to the Langevin type, $\beta/\beta_L \ll 1$, as expected in these materials.[22]

In order to study the amount of charge that is extracted from or recombines in the reservoir, we have measured the extracted charge Q_{ex} by integrating the extraction current transients as a function of applied voltage U for different offset voltages U_{off}, as shown in Fig. 3.

We measured the extracted charge from 0.5 V when the DI current becomes significant. In the case when DI is limited by the bimolecular recombination into an insulator the extracted charge is directly proportional to the applied voltage $Q_{ex} \propto U$ [as seen from Eq. (3), $j \propto Qv \propto U^2$, $v \propto U$, and therefore $Q \propto U$, where v is the charge-carrier drift velocity]. The deviation from the linear dependence is most significant at low offset voltages (around the built-in potential), as is seen in Fig. 3. The reason is that it takes a longer time to extract all of the carriers, allowing more time for carriers to recombine. At higher offset voltages the extracted charge follows a linear dependence above 0.6 V of an applied offset voltage at 8 V. This clearly shows that most of the injected plasma is being extracted from the sample without significant carrier recombination.

The extracted charge, extraction time, and extraction current as a function of offset voltage are shown in Fig. 4.

As can be seen in Fig. 4 the extracted charge saturates as a function of offset voltage. This again shows that most of the injected plasma is being extracted from the sample. Therefore, one can use the amount of extracted charge to calculate the bimolecular recombination coefficient using Eq. (5).

The extraction time t_{ex} decreases as a function of offset voltage, because at higher offset voltages less time is required to extract the reservoir of charge carriers. The built-in potential is measured from the linear dependence of extraction current when it is extrapolated to zero offset voltage and is found to be U_{bi}=0.65 V.

The advantage of the technique of extraction of injected plasma is that we can directly and independently measure the

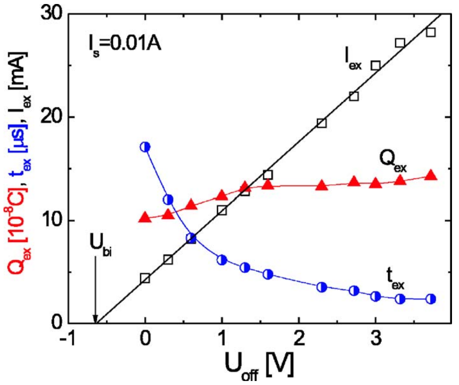

FIG. 4. (Color online) The extracted charge Q_{ex} (closed triangles), extraction time t_{ex} (half filled circles), and extraction current I_{ex} (open squares) shown as a function of applied offset U_{off} voltage at a constant stationary DI current of 0.01 A.

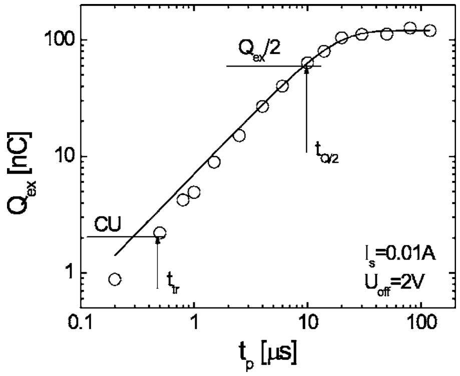

FIG. 5. Extracted charge as a function of injecting voltage pulse duration t_p. The solid line is a fit to Eq. (5).

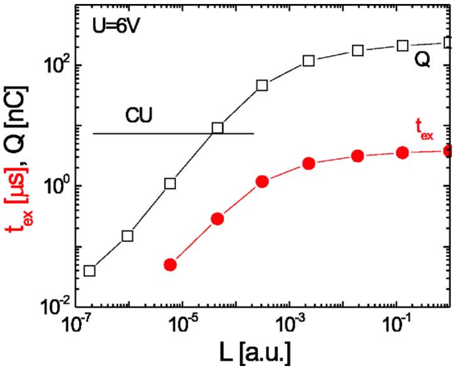

FIG. 6. (Color online) The extracted charge Q (open squares) and the extraction time t_{ex} (closed circles) as a function of laser light intensity measured using integral TOF mode.

bimolecular recombination coefficient. The extracted charge as a function of injecting voltage pulse duration t_p is shown in Fig. 5. The extracted charge $Q_{ex} \gg CU$ confirms that the bimolecular recombination coefficient is reduced compared to the Langevin-type recombination coefficient.

At short pulse durations the extracted charge follows near to linear dependence, whereas at long pulse durations the extracted charge saturates due to the charge-carrier recombination. In Fig. 5, the solid line is a fit of the experimental data points to Eq. (5). Since most of the injected charge is extracted from the sample, we can calculate $\beta = 2.2 \times 10^{-12}$ cm^3/s by using either Eq. (5) or Eq. (6) at an electric field $E \approx 10^4$ V/cm.

Moreover, the technique of extraction of injected plasma allows us to directly measure the charge carrier mobility in our BHSC. By using Eq. (8) when the extracted charge is equal to CU the transit time t_{tr} can be directly found from the experimentally measured data and the sum of both carrier mobilities is estimated to be 0.02 cm^2/V s. We checked this by performing integral-mode TOF measurements and found charge-carrier mobility of 0.02 cm^2/V s and independent of electric field. The carrier mobility measured using the differential TOF technique matches well with previous results of 0.01–0.02 cm^2/V s. However, the carrier mobility values obtained by using the saturated current as a function of time and extracted charge from Eq. (7) are lower than those values. This discrepancy is probably due to the charge-carrier trapping which would result in decreased equilibrium carrier mobility.

We have also used the TOF technique to directly and independently measure the bimolecular recombination coefficient value in these bulk-heterojunction solar cells, which allows us to compare these values and verify the plasma extraction technique.

In the TOF technique the charge-carrier reservoir is created by using a short laser light pulse (with wavelength 532 nm) and β is estimated from the saturated extracted charge Q and reservoir extraction time t_{ex}.[22]

In Fig. 6 the extracted charge and extraction time are shown as functions of laser light intensity. The extracted charge also demonstrates saturation at a level which is much higher than the CU value. The extraction half-time also increases and saturates as a function of light intensity. By using Eq. (4) from Ref. 22 we can directly calculate $\beta = 3.6 \times 10^{-12}$ cm^3/s using the saturated extracted charge Q and extraction time t_{ex} as shown in Fig. 6.

Having the total extracted charge Q and extraction time t_{ex} at highest light intensities, by using an equation derived elsewhere,[22] we again directly calculate the bimolecular recombination coefficient measured using the TOF technique as $\beta = 3.6 \times 10^{-12}$ cm^3/s when $E = 0$.

V. CONCLUSIONS

In conclusion, we have shown how the technique of extraction of injected plasma can be used to characterize charge-carrier transport and recombination in thin insulating films. The presence of double-injection current limited by bimolecular carrier recombination in bulk-heterojunction solar cells was observed. A simple analytical solution to estimate the bimolecular recombination coefficient is derived, and since it was found that most of the injected charge is extracted at high applied offset voltages, the charge-carrier bimolecular recombination coefficient and carrier mobility are directly calculated from the extracted charge, which is convenient to measure experimentally. By comparing the results obtained using both TOF and plasma extraction techniques we conclude that in RRPHT-PCBM bulk-heterojunction solar cells the bimolecular charge-carrier recombination is strongly reduced, $\beta/\beta_L \ll 1$, which confirms the previously observed results; the recombination coefficients obtained using both techniques are in a very good agreement. Moreover, both the sum of electron and hole mobilities and the bimolecular recombination coefficient are experimentally and independently measured by using the technique of extraction of injected plasma.

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*Electronic address: gytis.juska@ff.vu.lt

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