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Charge Carrier Recombination in Bulk Heterojunction Organic Solar Cells

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1. Introduction

Photovoltaic phenomenon was first observed by E. Becquerel (Becquerel) in 1839. He observed the electric current-lit silver electrode, immersed in the electrolyte. In 1894, taking advantage of the observed photoconductivity phenomenon in amorphous selenium the semiconductor solar cell was developed.

The very first silicon p-n junction solar cell was made in 1954, energy conversion efficiency of which was 6% and the energy price \$200/W did not seem promising for wide application. Later, the development of satellites needed to provide sustainable energy sources and the cadmium sulfid, cadmium telluride, gallium arsenide and more efficient solar cells of other materials were created.

The first solar cell breakthrough was something like of the 1970 year, feeling the lack of oil, which oncreased interest in alternative energy sources. The basic raw materials, in addition to crystalline silicon, a polycrystalline silicon, were also amorphous silicon and other, suitable for thin solar cells, materials. Although, due to the high cost of these energy sources, extracted energy was only a small part of total energy production, but the lending spread as energy sources in various areas of small devices such as mobile phone, calculators, meteorological instruments, watches and so on. A solar powered cars and even solar powered aircraft were constructed. Major Solar cells used for the purification of salt water, as well as supply power to isolated objects: mountains, islands or jungle living population.

The second and much greater solar energy use breakthrough occurred in the first decade of the twenty-first century. This is caused by the earth's climate warming due to the increasing threat of thermal energy and the increasing CO₂ in the atmosphere. Many governments in many ways stimulated the solar energy lending. Germany in the decade from 1994 to 2004, installed as much as 70 times more solar energy equipment, and now is installed more than 1GW: produced over 3TWh energy, which cost around 0.5 €/kWh. In Japan solar power energy is less costly than the heat. The main price of solar energy is caused by the installation const - ~ 1€/W. Till 2004 there have already been installed over 1GW, while in 2006, the world's installed 6.5 GW. In 2007, the European Union in the fight against climate warming threat committed by 2030 to achieve that 25% of the total energy from alternative sources, mainly from the Sun. It should be around 1200 GW, the cost should not exceed 0.1 €/kWh. Another reason for the needed alternative energy sources is projected oil and gas resource depletion.

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Crystalline silicon still remains the unrivaled leader in the development of solar cells. However, the demand of renewable energy sources stimulated a search for a new, low-cost technologies and materials. Hydrogenated amorphous silicon (a-Si:H) has long been regarded as one of the most promising materials for development of cheap, lightweight and technologically solar cells. However, a-Si:H solar cells degraded in high intensity-light. Thus, forward-looking, more efficient microcrystalline ($\mu\text{c-Si:H}$) and nanocrystalline silicon (nc-Si:H) solar cells began to compete successfully with a-Si:H.

The first organic materials were investigated for more than a hundred years ago and for a long time the widest application, in scope of optoelectronics, was electrography. However, in 1977 A. J. Heeger, A. G. MacDiarmid and H. Shirakawa showed that the π -conjugated polymers can be doped, and change the properties of substances. This work demonstrated the possibility use polymers to create optoelectrical devices, resulted in huge interest and in 2000 was awarded the Nobel Prize. During the period from 1977 on the base of π -conjugated polymers has been built a number of electronic and optoelectronic devices: diodes, field effect transistors, sensors, photodiodes, etc. On 1993 - 2003 years π -conjugated polymers have been investigated in order to create a light-emitting diodes (OLED) and their systems, and these studies culminated in the creation of a colour OLED matrix, which is adapted to different types of displays. Recently, organic polymers mainly involved studies of organic solar cells and other organic electronics appliances, effectiveness of which is determined by the drift and recombination of charge carriers.

In order to develop efficient solar cells it is necessary the maximum possible the light absorption, the carrier photogeneration quantum efficiency, and that all photogenerated carriers be collected in a solar cell electrodes. The collection of charge carriers depends on their mobility and recombination. Thus, the investigations of carrier mobility and their density dependencies on the electric field, temperature and material structure are essential for the formation of understanding of charge carrier transport in these materials, which is essential to find effective new inorganic and organic materials and to development of new optoelectronic structures.

One of the main factors limiting efficiency of organic solar cells (OSC) is charge carrier recombination. In crystals, where the carrier location uncertain, recombination is caused by the probability to transfer energy: or emit photon - radiation recombination, or to another electron - Auger recombination, or induction phonons through the deep states. The latter depends on the density of deep states. In disordered structures, with a lot of localized states, should be very rapid recombination, but there recombination is caused by the meeting probability of electron and hole in space, as the only their meeting at a distance closer than the Coulomb radius causes their recombination (named Langevin), likely as gemini recombination. It is valid only if the energy dissipation or jump distance is less than the Coulomb radius. Thus, the Langevin bimolecular recombination is ordained by the mutual Coulomb attraction drift time, because under this attraction electron is moving toward the nearest hole, while at the same time, due to diffusion, with equal probability in any direction. The Langevin recombination time can be expressed as:

$$\tau_L = \int_0^r \frac{dx}{(\mu_n + \mu_p)F} = \frac{\varepsilon\varepsilon_0}{e(\mu_n + \mu_p)n} \quad (1)$$

Here μ_n, μ_p are electron and hole mobility, respectively; $F = e / 4\pi\varepsilon\varepsilon_0 x^2$ is strength of Coulomb electric field; n is density of charge carriers ($1/n = 4\pi r^3 / 3$), and r is a mean

distance between electron and hole. Thus, from the expression of Langevin bimolecular recombination coefficient $B_L = e(\mu_n + \mu_p) / \varepsilon \varepsilon_0$ it is clearly seen that recombination is caused by the features of charge carrier transport. In bulk heterojunction organic solar cells the reduced Langevin recombination is observed.

In this work we describe methods of investigation of charge carrier recombination in disordered structures, where stochastic transport of charge carriers complicates interpretation of experimental results: integral time of flight (i-TOF) (Juška et, 1995), using of which allows easily estimate the temperature dependence of recombination coefficient; charge carriers extraction by linearly increasing voltage (CELIV) (Juška et, 2000, a), which allows independently measure relaxation of density and mobility of photoexcited charge carriers; double injection current transient (DoI) (Juška et, 2005; Juška et, 2007), which is additional method of investigation of charge carrier recombination and, which allows to measure dependence of recombination coefficient on electric field.

In this study we represent how using current transient methods may be cleared up the features of charge carrier transport and recombination in disordered inorganic and organic materials. The microcrystalline silicon and π -conjugated polymers have been investigated as a typical inorganic and organic material.

2. Investigation methods

The disordered structure of material causes that mobility of charge carriers is low, because their motion is slowed down by the interaction with spectrum of the local states. Thus, the classical investigation methods: the Hall and magnetoresistance measurements are invalid. The carrier transport in disordered inorganic and organic materials, conductivity (σ) of which is low, is studied using time-of-flight (TOF) method. However, the conductivity of many π -conjugated polymers is high and does not fulfill the latter condition. Thus, for their investigation has been adapted and refined microcrystalline hydrogenated silicon (μ c-Si:H) used the extraction of charge carriers by linearly increasing voltage (CELIV) method. The latter method allows to investigate the transport properties of charge carriers both in conductive and low conductivity materials. For investigation of charge carrier transport and recombination the double injection current (DoI) transient method is promising as well.

2.1 TOF method

Time-of-flight method is widely used for investigation of transport, trapping-retrapping and recombination of charge carriers in disordered materials and structures. This method is applicable only for investigation of low conductivity materials, i.e. where the Maxwell relaxation time exceeds the duration of transit time (t_{tr}) of charge carriers through the interelectrode distance (d):

$$\tau_\sigma = \frac{\varepsilon \varepsilon_0}{\sigma} \gg t_{tr} = \frac{d^2}{\mu U} \quad (2)$$

TOF method is based on the current transient measurement when photogenerated of the same sign charge carriers is moving in the electric field (E) created in the interelectrode distance (d) of the sample and during a drift time (t_{tr}) the package achieves an opposite electrode. The simplicity and efficiency of method meant that it is a widely used for study of mobility (μ), trapping (τ_t) and lifetime of charge carriers (τ) in low conductivity ($\tau_\sigma > t_{tr}$)

materials. Low conductivity of material ensures that during the drift of photogenerated charge carriers through interelectrode distance the density equilibrium charge carriers will be too low to redistribute the electric field inside the sample, and the electric field will be steady at the moment of charge carrier photogeneration, i.e. $RC < t_{\text{del}} < \sqrt{\tau_{\sigma} t_{\text{tr}}}$ (here R is total resistance of measurement system and sample electrodes, C is geometric capacitance of sample). TOF method, dependently on amount of initial injected charge (Q_0) and, also, on characteristic time RC of measurement system, is divided into a number of regimes.

Small charge drift currents (SCDC). This regime is ensured when an amount of photogenerated charge is much less than an amount of charge on sample electrodes at given voltage (U_0), i.e. $eL = Q_0 \ll CU_0$. Here L amount of charge carriers photogenerated by pulse of light. In this regime there are a few cases:

- a. **current (diferencial) regime ($t_{\text{tr}} > RC$).** In case of strong absorption of light ($\alpha d \gg 1$, α is absorption coefficient) and nondispersive transport, the shape of pulse of photocurrent transient is close to rectangular, duration of which is t_{tr} (Fig. 1a, $L = 0,3$), and from the area of current transient the Q_0 can be estimated. In case of weak absorption of light ($\alpha d \ll 1$), charge carriers are photogenerated in the bulk of sample, thus, the shape of photocurrent pulse is triangular, which's duration is t_{tr} , and area is equal $Q_0/2$. The dispersive transport of charge carriers, due to dependence of charge carrier mobility on time, causes that pulse of current transient did not demonstrate obvious break points, from which will be possible to estimate t_{tr} (even if $\alpha d \gg 1$). In this case, if the current transient is represented by a double-log scale ($\lg j = f(\lg t)$), the turning point corresponds the t_{tr} .
- b. **charge (integral) regime ($t_{\text{tr}} < RC$).** Even in case of strong absorption of light and nondispersive transport of charge carriers the shape of photocurrent pulse is not so informative as in current regime (Fig. 1a, $L = 0,3$): the drift time of charge carrier package is estimated as halftime ($t_{1/2}$) of rise time of photocurrent pulse, i.e. $t_{\text{tr}} = 2 t_{1/2}$. The magnitude of photocurrent pulse is equal to amount of charge (Q) collected onto the sample electrodes during the charge carrier drift time. In case of bulk absorption of light, the magnitude of photocurrent pulse is equal $Q/2$, and $t_{\text{tr}} = 3,41 t_{1/2}$

If the voltage of backward direction is applied onto solar cell electrodes and, by short pulse of light the charge carrier pairs are photogenerated, the photocurrent pulse of their drift is observed, from which's duration (t_{tr}) the mobility of the charge carriers of the same polarity as illuminated electrode is estimated. An amount of drifting charge carriers is estimated from the area of photocurrent pulse, from which, when amount of absorbed quanta of light is known, the quantum efficiency is evaluated (Fig.1).

In case of trapping with characteristic trapping time τ or in case of stochastic transport, after photogeneration, the shape of photocurrent pulse is decreasing, and, from the area of photocurrent pulse, estimated dependence of amount of photogenerated charge carriers on voltage follows Hecht's dependence (Eq. (3)). From the latter dependence the $\mu\tau$ -product, which determines both the diffusion and drift lengths of charge carries, and causes effectiveness of solar cell, is estimated.

$$\frac{N}{N_0} = \frac{\mu\tau E}{d} \left(1 - \exp\left(-\frac{d}{\mu\tau E}\right) \right) \quad (3)$$

Space charge limited photocurrent (SCLP). In this case an amount of photogenerated charge is higher than charge on sample electrodes at U_0 , i.e. $Q_0 \gg CU_0$. The shape of photocurrent pulse depends on Q_0 (Fig. 1a), and strongly absorbed light ($\alpha d \gg 1$) creates reservoir of charge carriers at the illuminated electrode, from which not more than CU_0 charge package can drift to the opposite electrode. This package is moving in growing electric field, thus, in case of nondispersive transport and when $t_{tr} > RC$, drift time is $t_{SCLC} = 0,78 t_{tr}$, which is estimated from the spike of current transient (Fig. 1a). When $t > t_{SCLC}$, current flows until the whole charge is extracted from reservoir and the second turning point, at extraction time (t_e), appears on the pulse of photocurrent. An amount of charge extracted from the reservoir (Q_e), as well as t_e , depend on recombination speed of charge carriers in reservoir.

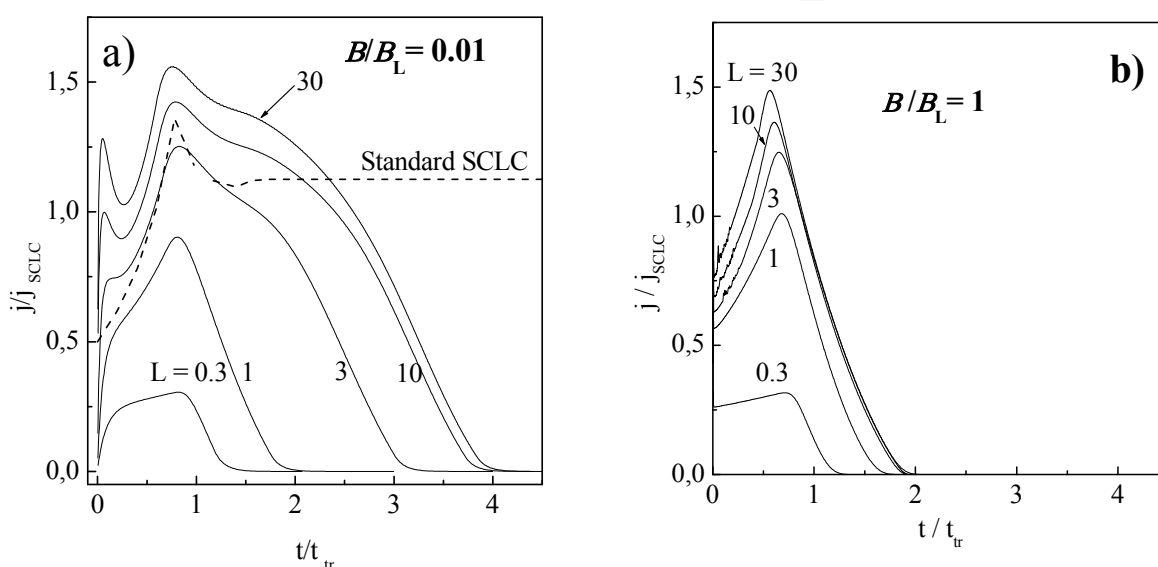


Fig. 1. Numerically modelled photocurrent transients of charge carrier drift dependence on exciting light intensity in case when $B/B_L = 0.01$ (a), and when Langevin recombination prevails (b). Density of photogenerated charge carriers is normalised to amount of charge on sample electrodes in SCLC regime

For investigation of charge carrier recombination by photocurrent transient methods the dependence of collected onto sample electrodes charge on intensity of photoexciting light pulse is measured (Pivrikas et, 2005). When, due to increasing intensity of light pulse, the amount of photogenerated charge achieves amount of charge carriers on sample electrodes ($Q_0 = CU_0$), the TOF regime changes from small charge drift current (SCDC) to space charge limited current (SCLC) (Fig. 2a). Further increase of light pulse intensity not follows by increase of photocurrent, but increases the duration ($t_e \geq t_{tr}$) of photocurrent pulse, which is caused by the extraction of charge carriers from reservoir. The faster charge carrier recombination in reservoir, the shorter extraction time (t_e), and, when recombination is very fast, $t_e \rightarrow t_{tr}$. Thus, the dependence of t_e on intensity of exciting light pulse L gives information about recombination process in charge carrier reservoir: dependence as $t_e(L) \approx \ln L$ indicates that monomolecular recombination prevails; if, at high intensity of light pulse, t_e saturates with L , then the bimolecular or of higher order of charge carrier recombination prevails.

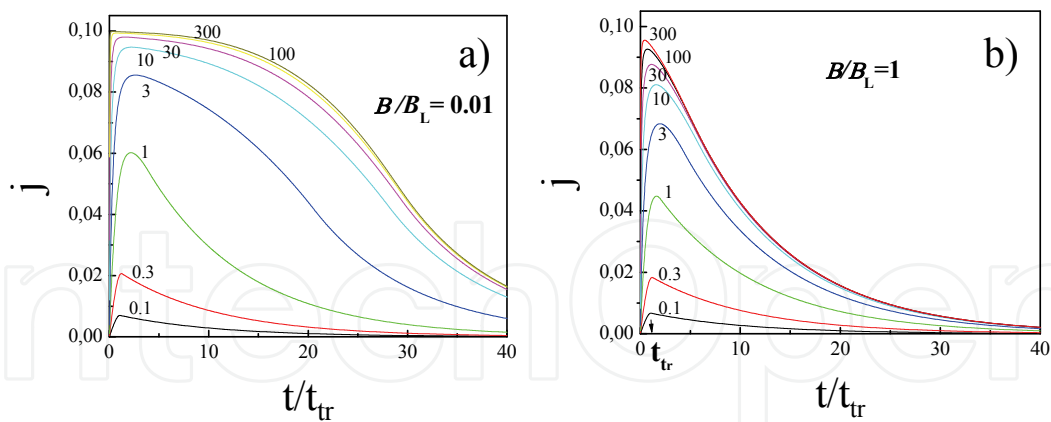


Fig. 2. Numerically modelled integral TOF current transients ($RC = 10 t_{tr}$)

In organic polymers the bimolecular recombination typically is of Langevine-type. The photocurrent transients of this case are shown in Fig. 2b, and the maximal amount of extracted charge is estimated as:

$$\frac{Q}{CU} = 1 - \exp\left(-\frac{eL}{CU}\right) \tag{4}$$

The maximal amount of extracted charge $Q = CU$.

When the bimolecular recombination is weaker than Langevin's one, from the saturation of extraction time, which is estimated as difference of photocurrent pulse halwidths at space charge limited and at small charge regimes, i.e. $t_e = t_{1/2} (L > 1) - t_{1/2} (L < 1)$, the ratio of bimolecular recombination coefficient (B) with Langevin's one according to expression:

$$\frac{B}{B_L} = \frac{t_{tr}^2}{t_e(t_e + t_{tr})} \frac{1}{\alpha d} \tag{5}$$

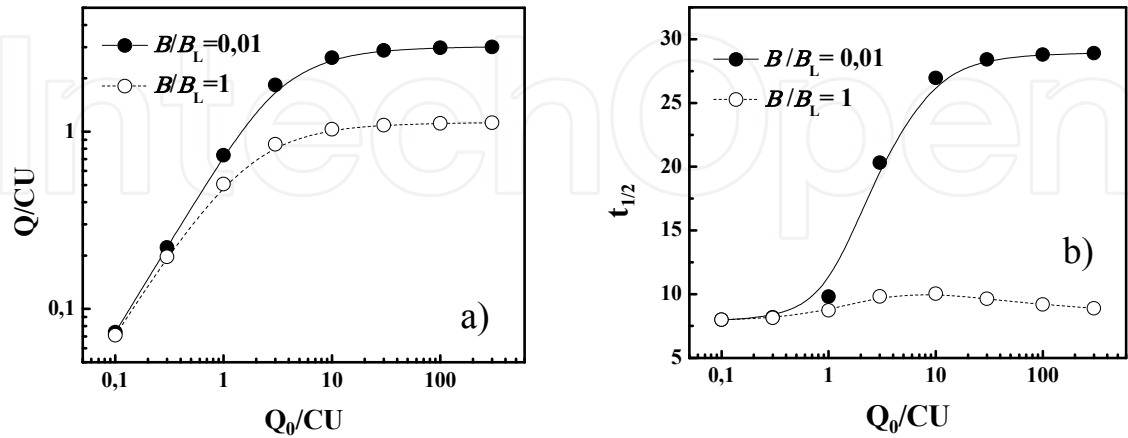


Fig. 3. Dependencies of amount of extracted charge Q (a) and of photocurrent halfwidth (b) on amount of photogenerated charge in case of Langevin and reduced bimolecular recombination

Here α is absorption coefficient. However, it is easier to measure the recombination coefficient using integral TOF when $RC > t_{tr}$ (Pivrikas et al, 2005). The examples of numerically modelled transients are demonstrated in Fig.2. Using this method the coefficient of bimolecular recombination is estimated as (Fig. 3):

$$B = \frac{edS}{t_e Q} \quad (6)$$

2.2 Charge carrier extraction by linearly increasing voltage (CELIV) method.

Method has the advantage that it is suitable for investigation of both high and low conductivity materials (Juška et al, 2000 a; Juška et al, 2004). After the triangular voltage pulse is connected to the sample electrodes in backward direction, the current caused by geometric capacitance of sample ($j(0)$) and conductivity current Δj are observed (Fig. 4).

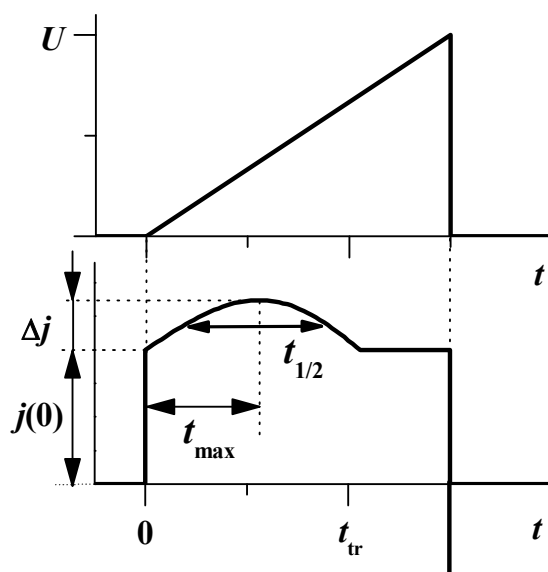


Fig. 4. Voltage pulse and current density observed by CELIV method

The measuring device is very simple: triangular pulse voltage generator and oscilloscope. Another advantage is that after triangular pulse of voltage is applied onto sample electrode, there is no initial, caused by capacitance, current peak, which disturb to monitor drift current in conductive materials.

The current transients were calculated by using standard solution method from continuity, current and Poisson equations in case when one of electrodes is blocking: Schottky or $p-i$ barrier, or even special structure with isolating sublayer. From Poisson equation when density of equilibrium carriers is n_0 the extraction depth l ($0 \leq l \leq d$) is estimated:

$$\frac{Q(t)}{\varepsilon \varepsilon_0} = \frac{en_0 l(t)}{\varepsilon \varepsilon_0} = E(0,t) - E(d,t), \quad (7)$$

here Q is the amount of extracted charge, $E(0,t)$ and $E(d,t)$ are the magnitudes of electric field at the front and back electrodes correspondingly.

From the continuity equation:

$$\frac{dQ}{dt} = j_d = \sigma_0 E(d, t), \quad (8)$$

In case of linearly increasing voltage $U = A t$ and

$$\int_0^d E dx = At = E(d, t) \cdot d + \frac{E(0, t) - E(d, t)}{2} \cdot l(t),$$

the Rikati equation is obtained for $l(t)$

$$\frac{dl(t)}{dt} + \frac{\sigma}{2\epsilon\epsilon_0 d} l^2(t) = \frac{\mu A t}{d},$$

Then the current transient is

$$j(t) = \frac{\epsilon\epsilon_0 A}{d} + \frac{\sigma}{\mu} \left(1 - \frac{l(t)}{d} \right) \left(\frac{\mu A t}{d} - \frac{\sigma}{2\epsilon\epsilon_0 d} \cdot l^2(t) \right), \quad (9)$$

The first component is caused by capacitance, and second one by conductivity.

When $\tau_\sigma = \epsilon\epsilon_0 / \sigma \gg t_{tr}$

$$j(t) = \frac{A}{d} \left[\epsilon\epsilon_0 + \sigma t \left(1 - \frac{\mu A t^2}{2d^2} \right) \right], \text{ when } t < d \sqrt{\frac{2}{\mu A}} = t_{tr}, \quad (10a)$$

$$j(t) = \frac{A}{d} \cdot \epsilon\epsilon_0 = j(0), \text{ when } t > t_{tr} \quad (10b)$$

From experimentally observed current transient the thickness of sample and/or dielectric permittivity may be estimated:

$$\frac{\epsilon\epsilon_0}{d} = \frac{j(0)}{A}, \quad (11)$$

The dielectric relaxation time may be estimated as

$$\tau_\sigma = \frac{2}{3} \cdot t_{\max} \frac{j(0)}{\Delta j}, \quad (12)$$

The mobility of equilibrium charge carriers can be estimated as

$$\mu = \frac{2d^2}{3A t_{\max}^2} \text{ if } \Delta j \leq j(0), \text{ i.e. } \tau_\sigma \geq t_{tr} \quad (13)$$

$$\mu = \frac{\tau_\sigma d^2}{A t_{\max}^3} \text{ if } \Delta j \gg j(0), \text{ i.e. } \tau_\sigma \ll t_{tr}$$

The bulk conductivity of sample follows from:

$$\sigma_{bulk} = \epsilon\epsilon_0 \left. \frac{dj}{dt} \right|_{t=0} / j_0. \quad (14)$$

The density of charge may be calculated from:

$$p_0 = \frac{2}{ed} \int_0^\infty \Delta j dt \quad (15)$$

In Fig. 5 there are demonstrated the results of modelling without trapping and with single trap level (Juška et al, 2000, b). For high and low A the modelling very well reproduces $t_{\max}(A) \approx A^{-0.5}$ and $A^{-0.33}$, predicted by Eq. (13). When trapping is accounted then in both limiting cases the same expressions for t_{\max} and Δj like without trapping are obtained, if one substitute μ by (μf) , where f is the trapping factor or for single trap $f = \tau_C / (\tau_C + \tau_R)$, where τ_R is the release time.

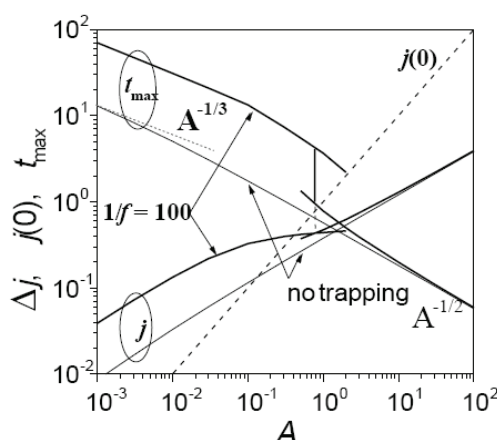


Fig. 5. Numerical modelling results of dependencies of Δj , t_{\max} , $j(0)$ on A . $A = 1$, when $t_{tr} = \tau_\sigma$. Bold lines demonstrate dependencies when shallow trapping is accounted ($\tau_C = 1$, $\tau_R = 100$); lines correspond case when shallow trapping is absent. Density of current is normalized to magnitude of $j(0)$, when $A = 1$, and time is normalized to τ_σ

The basic measurable parameters of CELIV Δj , t_{\max} depend on charge carrier interaction with trapping states, and this is reflected in dependencies of t_{\max} and Δj (Fig. 6). Numerical modelling (Juška et al, 2000 b), taking into account energy distribution of trapping states as $N(E) \sim \exp(-E^2/2\delta^2)$, demonstrate that measurements of $\Delta j(A) \sim A^\beta$ and $t_{\max}(A) \sim A^\gamma$ dependencies in various temperatures and electric fields, while choosing such A that $\Delta j \cong j(0)$, and estimating the rates of change as coefficients $\beta = \frac{d(\ln j)}{d(\ln A)} \Big|_{\Delta j=j(0)}$ and

$\gamma = \frac{d(\ln t_{\max})}{d(\ln A)} \Big|_{\Delta j=j(0)}$, the nature of charge carrier interaction with trapping states can be

cleared up, i.e., which charge carrier transport model is prevailing (Fig. 6):

1. if $\mu(F)$ dependence is caused by stochastic transport, then $(\beta - \gamma) = 1$, $(\beta + \gamma) < 0$;
2. if $\mu(E)$ dependence is caused by Poole-Frenkel type dependence of micromobility on electric field ($\mu \sim \exp(a\sqrt{E})$) then $(\beta - \gamma) > 1$, and $(\beta + \gamma) < 1$, and the latter is independent or decreases with increasing a (T decreases);
3. if the characteristic release from trapping states time τ_R depends on electric field, i.e. $\tau_R \sim \exp(-b\sqrt{E})$ then, when b increases, $(\beta - \gamma) > 0$, and $(\beta + \gamma)$ increases or even changes the sign.

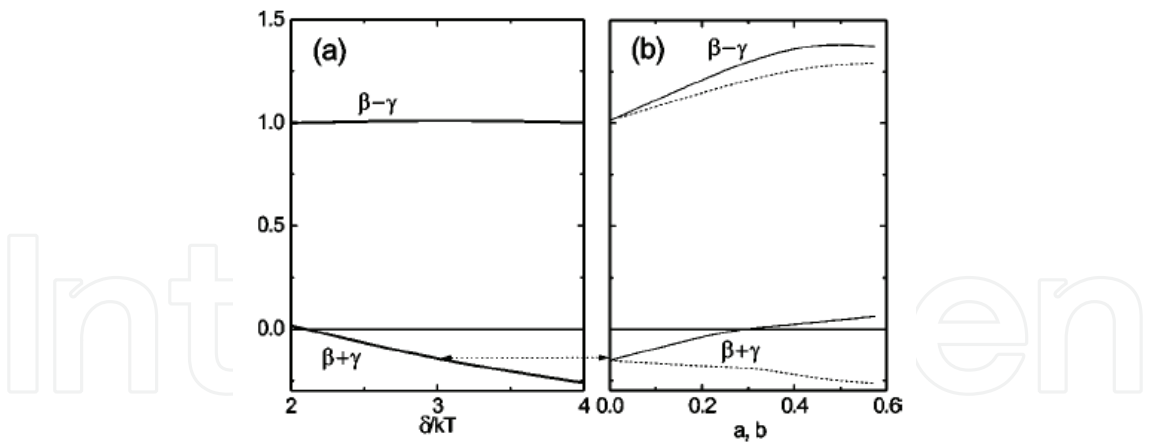


Fig. 6. Numerical modelling results of $(\beta + \gamma)$ and $(\beta - \gamma)$ dependencies on: (a) parameter δ/kT of Gaussian distribution of localized states; (b) Poole-Frenkel parameters a (doted line) and b (line) when $\delta/kT = 3$

2.3 Photo-CELIV method

Photo-CELIV method demonstrate even more opportunities where, by short pulse of light, photogenerated charge carriers are extracted by delayed (delay time t_{dU}) triangular pulse of voltage (Fig. 7) (Österbacka et al, 2004). Measurements of amount of extracted charge dependence on the delay time t_{dU} allow investigation of the relaxation of charge carrier density and mobility, independently. The latter are important in case of stochastic transport.

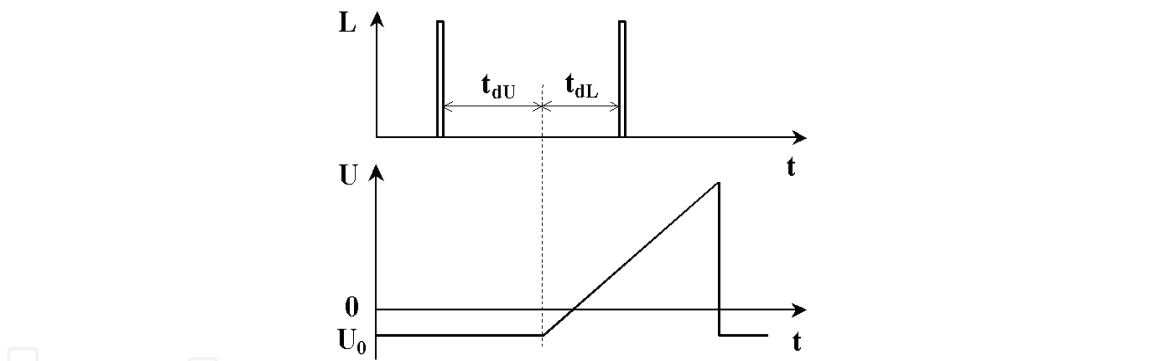


Fig. 7. Time chart of photo-CELIV method

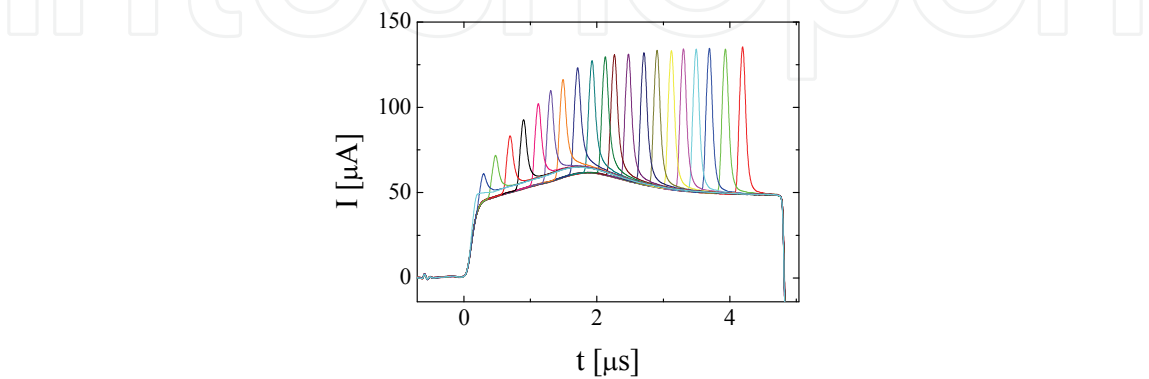


Fig. 8. Photocurrent transients of photo - CELIV for different t_{dL}

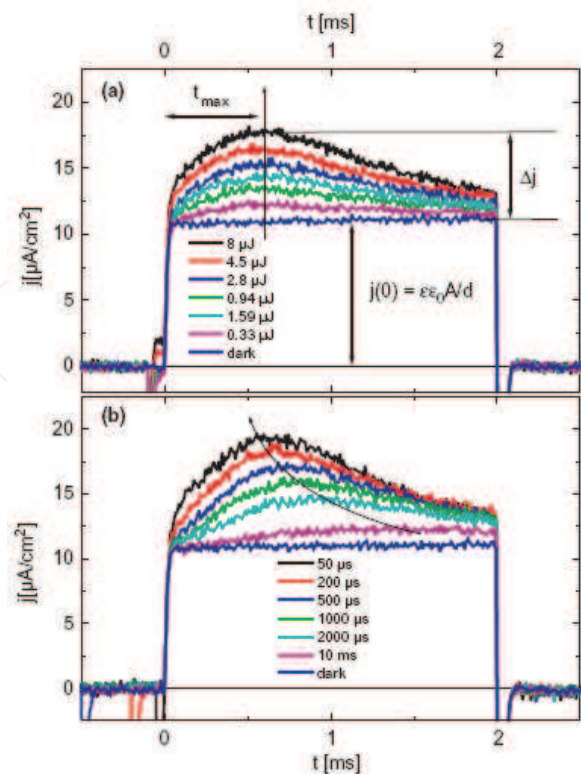


Fig. 9. Photocurrent transients of photo-CELIV at different intensity of pulse of light and fixed delay time (a), and at different delay time t_{dU} and fixed intensity of pulse of light (b) in RRa-PHT layer

2.4 Double injection current transient (DoI) method.

After the voltage is applied onto solar cell’s electrodes in forward direction, the double injection current is observed. When the dielectric relaxation time is longer than charge carrier drift time ($\tau_{\sigma} = \epsilon\epsilon_0/\sigma \gg t_{tr}=d/\mu E$), in case of bimolecular Langevin recombination, the whole injected charge carriers recombine while moving through interelectrode distance, and the observed current transient matches space charge limited current transient in case of sum of mobilities of both sign carriers.

When the recombination is weaker, then, after the drift time (t_{sl}) of slower charge carriers, an amount of injected charge carriers and, at the same time, current increases till saturates, due to recombination. Thus, the dependence of saturated density of current on voltage is:

$$j = 2\sqrt{\frac{e\epsilon\epsilon_0\mu_n\mu_p(\mu_n + \mu_p)}{B}} \frac{U^2}{d^3} = 2\epsilon\epsilon_0\sqrt{\frac{B_L}{B}} \mu_n\mu_p \frac{U^2}{d^3} \text{ , when } \tau_{\sigma} \gg t_{tr}; \tag{16}$$

From the shape of current transient pulse it is possible evaluate whether recombination is of Langevin-type or weaker. In Fig. 10 there are shown measurable parameters, from which the transport and recombination values is estimated. The sum of mobilities of both sign charge carriers as

$$\mu_n + \mu_p = 0.8 \frac{d^2}{Ut_{sc}} \tag{17}$$

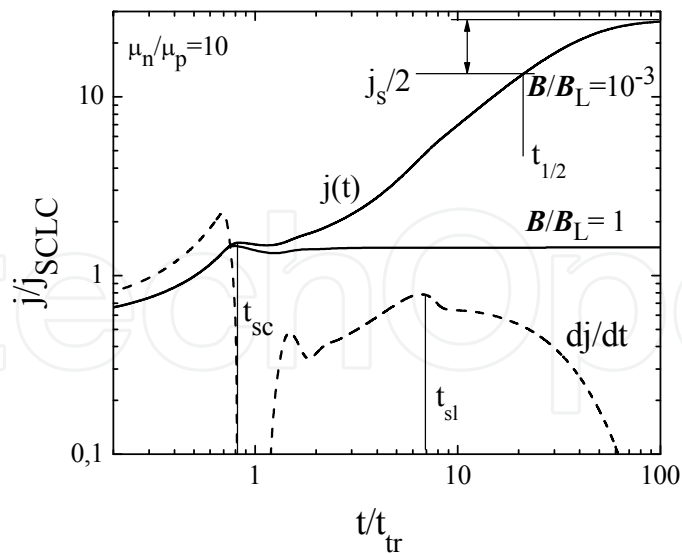


Fig. 10. Transients of double injection currents into dielectric in cases of Langevin and reduced bimolecular recombination or in other case

$$\mu_n + \mu_p \cong \frac{j_{\text{SCLC}} d^3}{\varepsilon \varepsilon_0 U^2} . \tag{18}$$

The mobility of slower charge carriers

$$\mu_{\text{sl}} = 0.8 \frac{d^2}{U t_{\text{sl}}} . \tag{19}$$

The coefficient of bimolecular recombination

$$B = \frac{\ln 3}{2} e (\mu_n + \mu_p) \frac{U}{j_s t_{1/2} d} . \tag{20}$$

In case of plasma injection into semiconductor, when dielectric relaxation time is shorter than charge carrier transit time ($\tau_\sigma = \varepsilon \varepsilon_0 / \sigma \gg t_{\text{tr}} = d / \mu E$), after ambipolar transit time of charge carriers ($t_a = t_m$), an amount of injected plasma, and, thereby, the current, increases till, due to recombination, saturates.

$$j(t) = \begin{cases} \sigma E \left(1 - \frac{2}{3} \frac{t}{t_a} \right)^{\frac{1}{2}} , & t < \frac{5}{6} t_a \\ \frac{3}{2} \sigma E + \left(j_s - \frac{3}{2} \sigma E \right) \tanh \left(B \Delta n_s \left(t - \frac{5}{6} t_a \right) \right) , & t > \frac{5}{6} t_a \end{cases}$$

$$j_s = \frac{8}{9} e \sqrt{\frac{(\mu_p + \mu_n) \mu_p \mu_n (n_0 - p_0)}{B}} \cdot \frac{U^{3/2}}{d^2} = \frac{8}{9} \cdot \frac{U}{d} \varepsilon \varepsilon_0 \sqrt{\frac{B_L}{B} \cdot \frac{1}{\tau_\sigma t_a}}, \text{ when } \tau_\sigma \ll t_a. \quad (21)$$

From the maximum of differential of current transient, using Eq. (22), the ambipolar mobility (μ_a) is estimated:

$$t_m \left(\frac{dj}{dt} \right)_{\max} = t_a = \frac{5}{6} \cdot \frac{d^2}{\mu_a U}. \quad (22)$$

Using Eq. (23), the coefficient of bimolecular recombination is:

$$B / B_L = 0.45 \frac{\tau_\sigma t_m}{t_{1/2}^2}. \quad (23)$$

From shape of double injection current pulse the information about charge carrier trapping is obtained (Fig. 11) (Juška et al, 2008). During the trapping of the slower charges, after the transit time, through the interelectrode distance, of faster charge carriers, the space charge limited current is flowing through the sample till the whole trapping states are filled in by slower charge carriers (“hole trapping” in Fig. 11). When the trapping of faster charge carriers is dominating, the current is decreasing and begins to increase after trapping states are filled in (“electron trapping” in Fig. 11). Thus, the integration of current until time when the current starts to rise, allows evaluate density of trapping states.

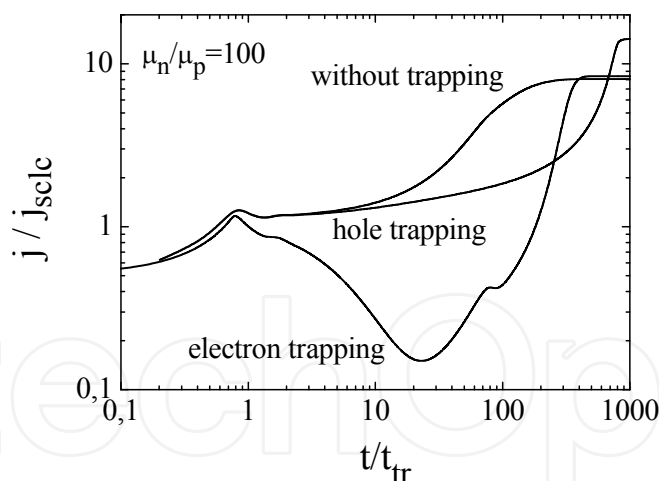


Fig. 11. Numerical modelling of double injection current transients when trapping is absent and when faster or slower charge carriers are trapped

The high capacitance of thin solar cells, immediately after application onto electrodes of rectangular pulse of voltage, causes high initial spikes of current, which complicates measurement and analysis of double injection current transients. To around the latter problem is possible by modification of DoI method, i.e. immediately after forward voltage pulse to apply the pulse of backward direction, and to measure the extraction current transient (Fig. 12) (Juška et al, 2006).

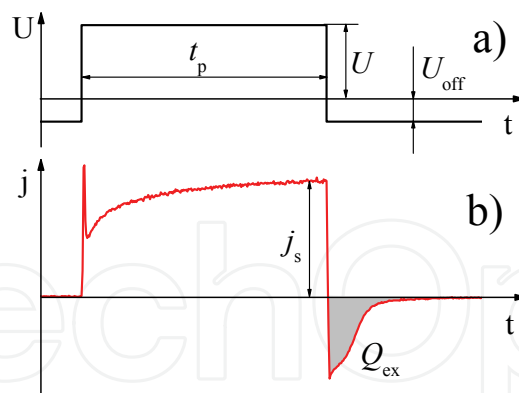


Fig. 12. Time charts of voltage pulse (a) and transients of double injection and extraction currents

The integral of extraction current gives an amount of extracted charge, from which's dependence on duration of injecting voltage (Fig. 13), the charge carrier mobility and bimolecular recombination coefficient can be estimated as:

$$B = \frac{\ln 3}{2} \frac{edS}{t_{1/2}Q_s}. \tag{24}$$

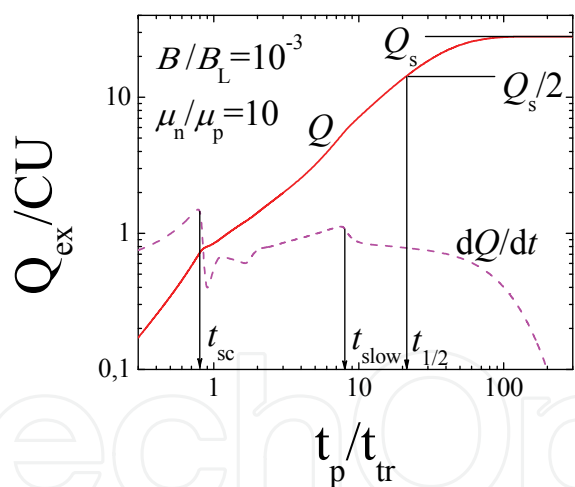


Fig. 13. Dependence of extracted charge on duration of injecting voltage pulse

3. Experimental results

3.1 Amorphous and microcrystalline silicon

Light-induced degradation of amorphous hydrogenated silicon (a-Si:H) is a serious problem of a-Si:H based photovoltaic solar cells. The most probable driving force for a-Si:H degradation is the energy (more than 1 eV) released during nonradiative bimolecular recombination of electron-hole pairs (which prevails at high light intensity) and that is why the discovery of mechanism of this recombination is of great importance.

For the study of bimolecular recombination coefficient (B) we have proposed the photoelectrical method (Juška et al, 1995), which is based on the measurement of extraction time (t_e) of the charge carrier reservoir using the space-charge limited photocurrent (SCLP) transient method. This method gives a possibility to estimate the monomolecular recombination time from the shape of the t_e dependence on the light intensity (L) and the bimolecular recombination coefficient B from the saturated value of t_e . These photoelectrical measurements demonstrated that the bimolecular recombination begins to prevail if charge carrier density is approximately 10^{17} cm^{-3} , and $B \approx 10^{-9} \text{ cm}^3/\text{s}$. In a-Si:H layers it was observed the reduced bimolecular recombination, which, possibly, is reduced because electron and hole, immediately after photogeneration, are separated by internal random potential field. Fig. 14 demonstrates that the bimolecular recombination coefficient is lower in a-Si:H layers, which are deposited at high grow speeds (internal random field is greater), and that temperature dependence of B is stronger than that of high-quality amorphous silicon layers.

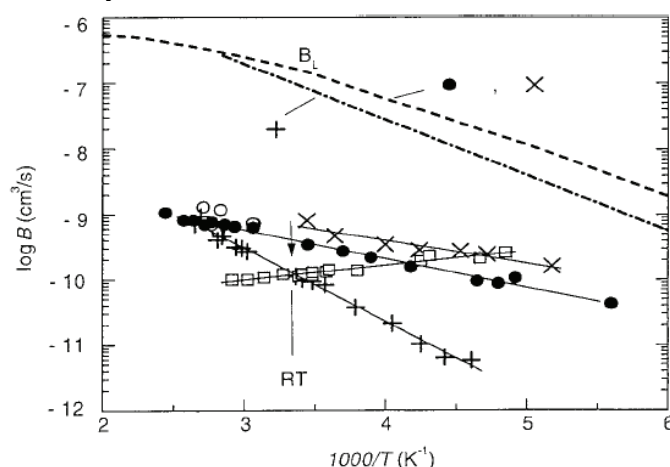


Fig. 14. Dependence of bimolecular recombination coefficient of electrons (●) and holes (○) on temperature in: high grade a-Si:H (x, ●, ○), high deposition rate a-Si:H (+) and $\mu\text{c-Si:H}$ (□) layers. Temperature dependencies of Langevin recombination coefficient (B_L)

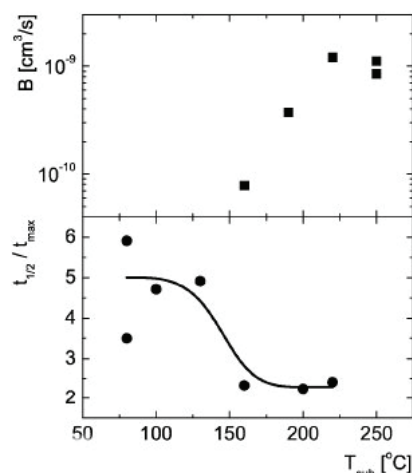


Fig. 15. Dependencies of bimolecular recombination coefficient B and dispersion parameter, estimated as $t_{1/2}/t_{\text{max}}$ from CELIV (Fig. 4), on substrate temperature during deposition of $\mu\text{c-Si:H}$ layer

In similar way the internal random potential influences bimolecular recombination in microcrystalline hydrogenated silicon ($\mu\text{c-Si:H}$). The temperature of substrate during deposition of $\mu\text{c-Si:H}$ strongly influences the magnitude of internal random potential, and, through the latter, influences dispersion of charge carrier transport. Thus, decreasing of the substrate temperature leads to increase of dispersion of charge carrier transport, but decreases coefficient of bimolecular recombination (Fig. 15).

3.2 π -conjugated polymers

Recently, the great opportunity to create enough effective, large area and low-cost organic solar cells (OSC) increased interest in π -conjugated polymers, but also has raised several problems. First of all, in disordered materials, which include π -conjugated polymers, the mobility of charge carriers, due to hopping, is low ($\mu \ll 1 \text{ cm}^2/\text{Vs}$) in comparison with crystalline materials, and the mean hopping distance of charge carriers is shorter than Coulomb radius. In turn, the low charge carriers jump distance results in a low photogeneration quantum efficiency and conditions the diffusion-controlled, Langevin type charge carrier recombination. Latter is caused by, the diffusion and Coulomb inter-traction field controlled, meeting probability of electron and hole in space. On the other hand, in order to OSC current density would be comparable with the crystalline semiconductors the density of photogenerated charge carriers should be much higher than in the crystalline solar cells.

The density of charge carriers, due to bimolecular recombination, causes small their lifetime because $\tau = (Bn_i)^{-1}$. However, for effective OSC, it is necessary that the lifetime of charge carriers should be higher than their drift time through the interelectrode distance in intrinsic electric field, i.e. $\tau > t_{\text{tr}}^i = d^2 / \mu U_i$ (U_i is intrinsic potential). Thus, for higher than 5% efficiency of OSC, when open circuit voltage is $\sim 0.5 \text{ V}$, thickness of sample is 300 nm , it is necessary that density of photocurrent will be higher than $15 \text{ mA}/\text{cm}^2$, and $\mu B_L / B > 5 \times 10^{-3} \text{ cm}^2/\text{Vs}$. Thus, the bimolecular recombination limits efficiency of organic solar cell in region of high intensity light, and ratio of bimolecular recombination coefficient with Langevin's one allows evaluate effectiveness of materials and structures.

As a model material for investigation of features of bimolecular recombination was chosen π -conjugated polymer RRa PHT. In RRa PHT layer the TOF current transients were nondispersive at low intensity of light pulses. With increase of intensity of the light pulse, the shape of photocurrent transient changes to the classic SCLC kinetics, and, at a very high intensity of light, its shape stopped to change (Fig. 16). An amount of extracted charge linearly increased with intensity of light and saturated in the region of high light intensity, when $Q_e / CU_0 = 1$. Such saturation of the $Q_e(L)$ dependence is the consequence of Langevin recombination (See Eq. (4)).

To assess the coefficient of Langevin recombination, it is necessary to know the charge carriers mobility, when the electric field is zero, because in the depth of photogeneration the electric field is shielded by the carriers. By measuring the hole mobility dependence on electric field strength and by extrapolation to $E = 0$, the hole mobility was evaluated as $\mu_p(E = 0) = 6.5 \times 10^{-6} \text{ cm}^2/\text{Vs}$, and, considering that the mobility of electrons at least by one order lower than of the holes, $B_L = 4 \times 10^{-12} \text{ cm}^3/\text{s}$ was estimated.

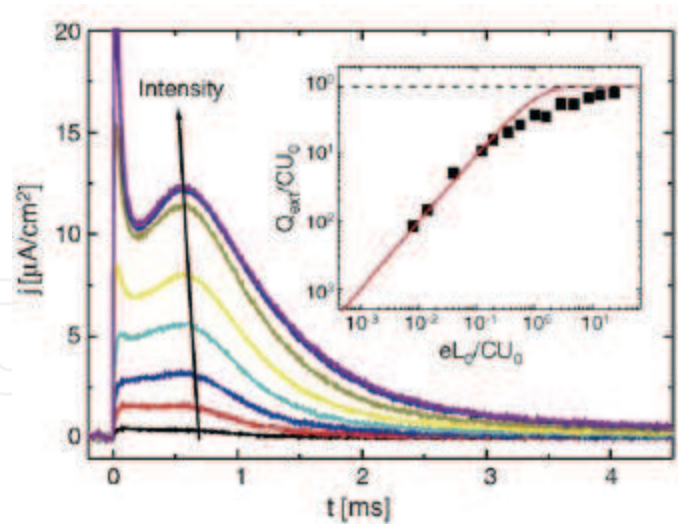


Fig. 16. TOF transients of photocurrent for different intensity pulse of light. Thickness of RRa PHT layer is 8 μm , $E = 10^5 \text{ V/cm}$

For direct measurements of photogenerated charge carrier density and mobility relaxation on time, the photo-CELIV method was used. From the duration t_{max} (see Fig. 4) the mobility of charge carriers and from integral of conductivity current ($\frac{1}{e} \int_0^\infty \Delta j dt$, here Δj is density of conductivity current) the density of charge carriers (p) at given t_{dU} (see Fig. 7) are estimated. The presence in the structure of intrinsic electric field has been compensated by offset voltage. Possible inaccuracy of this method can be caused by spatially distributed intrinsic electric field, which separates photogenerated charge carriers, thereby, decreasing recombination.

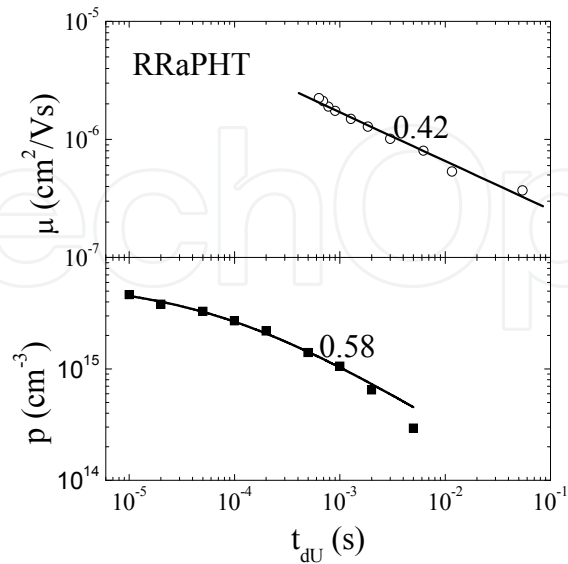


Fig. 17. Charge carrier mobility and density dependencies on t_{dU} . Solid line is $p(t)$ results according $B(t) = e\mu(t) / \varepsilon\varepsilon_0$ in case of Langevin recombination

In Fig. 17 the typical for RRa PHT mobility and density dependencies of hole on time are demonstrated. Fitting of mobility relaxation as $\mu = at^{-0.42}$ gives that Langevin recombination coefficient changes with time too, i.e. $B(t) = e\mu(t)/\varepsilon\varepsilon_0$. Thus, charge carrier density follows expression

$$p(t) = \frac{p(0)}{1 + p(0)B \int_0^t \mu(t)dt} . \quad (25)$$

Therefore

$$p(t) = \left(\frac{1}{p(0)} + \frac{e}{\varepsilon\varepsilon_0} \cdot \frac{at^{0.58}}{0.58} \right)^{-1} . \quad (26)$$

which is shown by solid line in Fig. 17. The coincidence of experimental results and theory confirms that, in low mobility organic material, bimolecular recombination is of Langevin-type. So, the same result has been obtained from the saturation of SCLC transients with intensity of light (Pivrikas et al, 2005 [5]).

3.3 Recombination in conjugated polymer/fullerene bulk heterojunction solar cells

One of possibilities reduce bimolecular recombination is to make junction of two organic material layers, in one of which are mobile the electrons and in another one the holes. The excitons, immediately after photoexcitation, are destroyed by electric field of heterojunction and separated electrons and holes are moving each of its transport material to sample electrodes. However, in organic polymers the diffusion distance not exceed 100 nm. Thus, an efficiency of such solar cell would be low because the thickness of solar cell would be approximately 100 nm and absorption of light weak. From Fig. 18a follows, that, oppositely to MEH PPV (poly(2-methoxy-5-(2'-ethylhexykoxy)-1,4-phenylenevinylene) layer, the heterojunction of MEH PPV/perilene more effectively separates photogenerated pairs, i.e. the charge carrier reservoir is created and an amount of collected charge approximately twice exceeds CU_0 (Fig. 18b). Supporting the latter experimental result, the numerical modelling, taking into account the Langevin recombination, demonstrates that, in case of bulk absorption of light and of small resistor, causing extraction current, an amount of extracted charge can exceed CU a few times, too. Thus, the obtained experimental results do not deny the Langevin recombination in heterojunction.

Another charge carriers bimolecular recombination reduction method has been identified investigating a-Si:H and μ c-Si:H layers: separate photogenerated charge carriers by an internal random field in space, so, that they move towards the electrodes in different ways. This method has been used for organic semiconductor structures: layer cast mixing transporting materials of holes and electrons. Such a bulk heterojunction blends allow to expect a significant reduction of bimolecular recombination, as in the bulk of samples created excitons are in the vicinity to heterojunctions. When they disintegrate, resulting electrons and holes moving towards each of its material to the contrary of the electrodes, i.e. separated in space.

Experimentally there were investigated bulk heterojunctions of various organic polymers with PCBM.

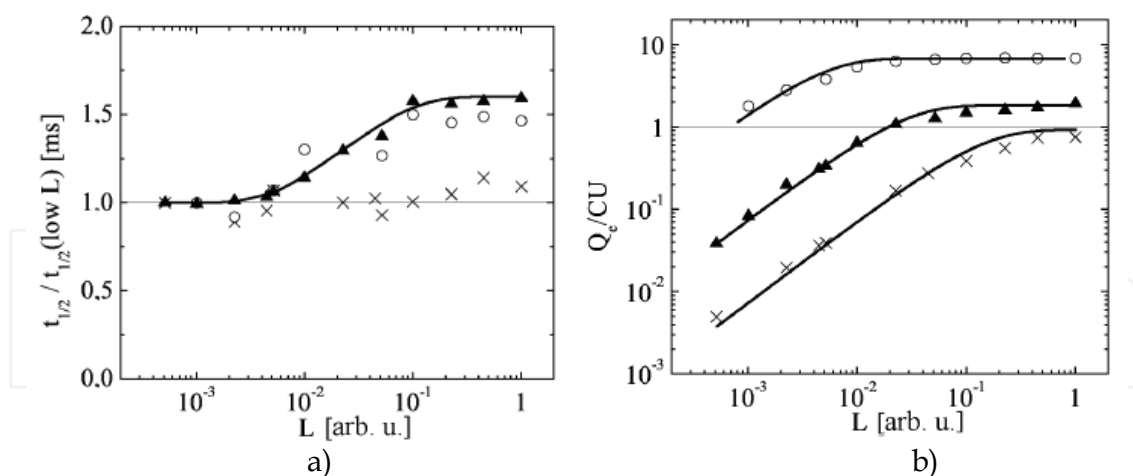


Fig. 18. Dependencies of TOF current transient halfwidth (a) and of collected charge (b) on the intensity of light pulse: x - MEH PPV, ▲ - perilene/MEH PPV junction, O - MEH PPV:PCBM blend

Time-dependent mobility and recombination in the blend of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-phenylene vinylene] (MDMO-PPV) and 1-(3-methoxycarbonyl)propyl-1-phenyl-(6,6)- C_{61} (PCBM) is studied simultaneously using the photoinduced charge carrier extraction by linearly increasing voltage technique (Mozer et al, 2005).

Photo-CELIV transient at various delay times, light intensities and applied voltages have been recorded, and the charge carrier mobility and lifetime simultaneously studied. It is found that, shortly after photoexcitation, both the charge mobility and the recombination are time-dependent (dispersive) processes, which is attributed to the initial relaxation of the charge carriers towards the tails states of the density of states distribution. The results confirm that the recombination dynamics within the studied μs - ms time scale is a thermally activated process rather than a temperature independent tunneling. The obtained time-dependent mobility values are used to directly describe the recombination dynamics (see Fig. 19 and Fig. 20). Density decay of charge carriers fitted according to Eq. (25).

Therefore results suggest that the recombination dynamics is nearly Langevin-type, i.e. controlled by diffusion of the charge carriers towards each other.

3.4 Recombination in P3HT:PCBM Bulk Heterojunction Organic Solar Cells

In poly(3-hexylthiophene): 1-(3-methoxycarbonyl) propyl-1-phenyl[6,6] C_{61} (P3HT:PCBM) bulk heterojunction solar cells, a reduction of the Langevin recombination is commonly observed after thermal treatment. This treatment has been shown to modify significantly the nanomorphology of the photoactive composite, inducing a crystallization of both the donor and the acceptor phases (Pivrikas et al, 2007). In Fig. 21 the experimentally measured results using integral TOF SCLC regime are presented. By comparing experimentally measured bimolecular recombination coefficient B with calculated Langevin recombination coefficient B_L , it was shown that $B/B_L \approx 10^{-3}$.

According to (Adriaenssens et al, 1997), if the reduction of bimolecular recombination is caused by random potential, the bimolecular recombination has follow $B \approx B_L \exp(-\Delta E/kT)$ dependence on temperature (here ΔE is mean random potential energy). Thus, the activation energy of B has to be higher than one of B_L , while experimentally it is obtained an opposite result. In case if bimolecular recombination is caused by tunnelling, the B/B_L ratio will

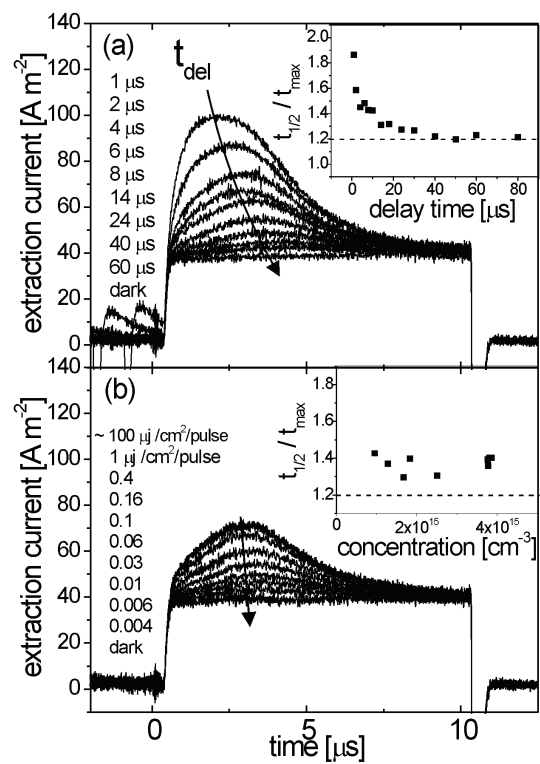


Fig. 19. Photo-CELIV transients recorded at 300 K at (a) various delay times at fixed light intensity; (b) varying illumination intensities attenuated using optical density filters at fixed 5 μs delay time. The voltage rise speed A was 4 V/10 μs. The insets show the calculated dispersion parameters $t_{1/2}$ to t_{max} versus delay time and the concentration of the extracted charge carriers, respectively.

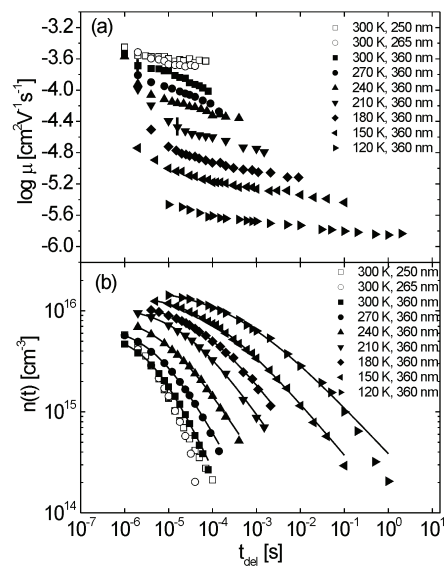


Fig. 20. Mobility (a) and the density (b) of extracted charge carriers versus the delay time for samples with different active layer thickness. Charge carrier mobility and density measured for the 360 nm device. Density relaxation of charge carriers fitted according to Eq. (25)

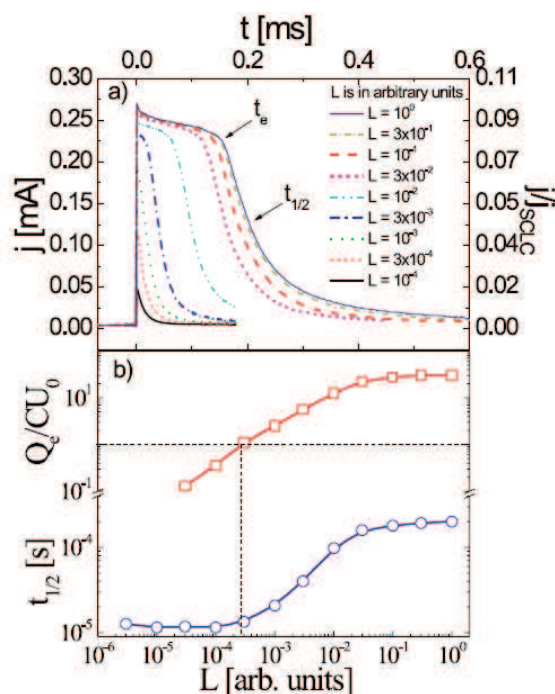


Fig. 21. Dependencies of integral TOF photocurrent transients (a), and of Q_e/CU_0 and $t_{1/2}$ on intensity of light pulse in RRP3HT:PCBM bulk heterojunction. Horizontal dotted line (b) corresponds $Q_e = CU_0$

demonstrate strong dependence on electric field. However, as is obvious from experimental results, this is not a case. The increasing of random potential also did not cause reduction of B/B_L ratio. In blend of segmented electron and hole transporting materials the meeting of charge carriers of opposite sign may be limited by charge carriers of lower mobility. However, this is insufficient to explain such big reduction of bimolecular recombination in RRP3HT:PCBM blend. This can be explained by, that the interface between polymer and acceptor materials, decreases Coulomb interaction, which suppress gemini and bimolecular recombination as it was proposed in (Arkhipov Heremans & Bäessler, 2003).

Furthermore, double injection current transients (DoI) and photo-CELIV measurements revealed, that the reduced B depends on the charge carrier density as in the case of Auger recombination (Juška et al, 2008). The same conclusion followed from transient photo voltage and transient photo absorption spectroscopy experiments (Shuttle et al, 2008). In the recent transient absorption spectroscopy experiments (Nelson, 2003) it was suggested that this type of relaxation is caused by a stochastic transport attributed to an exponential tail of localized states. However photo-CELIV and TOF experiments showed that the photocurrent relaxation is caused by the charge carrier's recombination (Pivrikas et al, 2005).

In this work, we are demonstrating that the reduction of B and its dependence on charge carriers density is caused by the two dimensional Langevin recombination (Juška et al, 2009).

Sirringhaus (Sirringhaus et al, 1999) showed that the mobility across and along the lamellar structure differs more than 100 times, which led to the fact that the recombination of charge carriers is mainly taking place in the two-dimensional lamellar structure. When spacing between lamellas $l \ll r_m$, r_m is determined by $\pi r_m^2 l = 1/n$. Then the recombination probability

$$f_{2D} = \frac{1}{t_m} = \frac{3\sqrt{\pi}}{4} \cdot \frac{e(\mu_n + \mu_p)}{\varepsilon\varepsilon_0} (l \cdot n)^{3/2} = \gamma_{2D} n^{3/2}. \quad (27)$$

where γ_{2D} is 2D recombination parameter. Hence, in two dimensional case, the bimolecular recombination coefficient will be reduced in comparison with one of the three dimensional case as

$$\frac{B_{2D}}{B_{3D}} = \frac{3\sqrt{\pi}}{4} l^{3/2} n^{1/2}.$$

For RRP3HT $l \cong 1.6$ nm (Sirringhaus et al, 1999) and, for example, when $n = 10^{16} \text{cm}^{-3}$, $\beta_{2D}/\beta_{3D} = 6 \times 10^{-3}$, and that is close to experimental results of Ref. (Pivrikas et al, 2007).

In the 2D recombination case, using Eq. (27), the equation governing the decay of the charge carriers is:

$$\frac{dn}{dt} = G - \gamma_{2D} n^{5/2}. \quad (28)$$

where G is the rate of the photogeneration or double injection. Similar dependencies were observed experimentally: $dn/dt \propto n^{2/6}$ (Shuttle et al, 2008). According to Eq. (28), after excitation by short pulse of light, the decay of the density of charge carriers is described as:

$$n(t) = \left(n_0^{-3/2} + \frac{3}{2} \gamma_{2D} t \right)^{-2/3} \propto t^{-2/3} \Big|_{n_0 \rightarrow \infty}, \quad (29)$$

here n_0 is initial density of photogenerated charge carriers. The similar dependence is observed using photo-CELIV technique (Fig.22).

In the case of 3D Langevin recombination $n(t) \propto t^{-1}$. It is worth to notice, that the slower than $n(t) \propto t^{-1}$ dependence can be observed due to the mobility dependence on time (stochastic transport), as it was shown in regiorandom poly(3-hexylthiophene) (Pivrikas et al, 2007). However, it is established by photo-CELIV that the mobility does not depend on the delay time after excitation (Fig. 22). That is why this explanation is not valid for the RRP3HT:PCBM blends. Another technique, which allows investigation of recombination process, is DoI current transient technique (Juška et al, 2007).

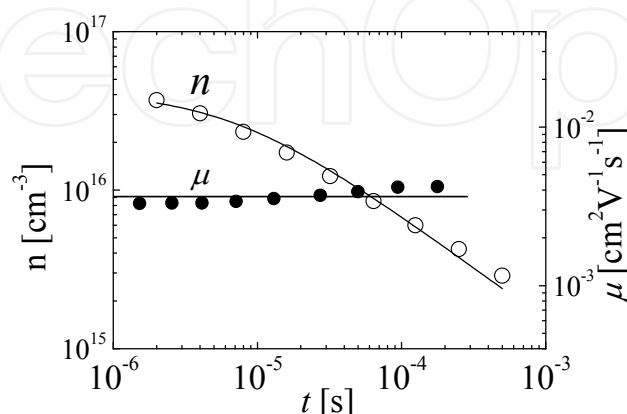


Fig. 22. Measured using photo-CELIV dependencies of mobility and density of electrons on time in annealed RR-P3HT:PCBM bulk heterojunction.

In the case of 3D Langevin recombination volt-ampere characteristics and DoI current transients corresponds to the sum of the space charge limited currents of electrons and holes, because the injected charge carriers will recombine completely within the interelectrode distance. In Fig. 23a numerically modelled DoI current transients are shown for the both 3D and 2D Langevin recombination cases for different distance l and ratios between fast and slow charge carriers mobilities μ_f / μ_{sl} .

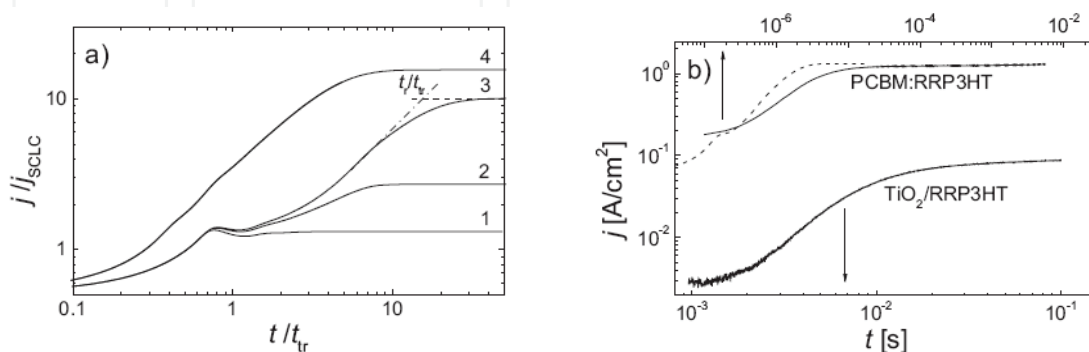


Fig. 23. Numerically modelled DoI current transients: a) in the case of 3D Langevin recombination (1) and 2D Langevin recombination for [(2) $l = 10$ nm, (3) $l = 1$ nm and $\mu_f / \mu_{sl} = 10$, (4) $l = 1$ nm and $\mu_f / \mu_{sl} = 1$]; both the time scale and current are normalized to transit time t_{tr} and SCLC of faster charge carriers, respectively. (b) DoI current transients: solid lines – measurements of RRP3HT:PCBM bulk heterojunction ($d = 1.4$ μm , $U = 9$ V) and TiO₂/RRP3HT ($d = 0.6$ μm , $U = 4$ V) structure; dashed line – numerically modelled DoI current transient for RRP3HT:PCBM structure ($\mu_n = 10^{-2}$ cm²/Vs, $\mu_p = 2.5 \times 10^{-3}$ cm²/Vs, $l = 1.6$ nm)

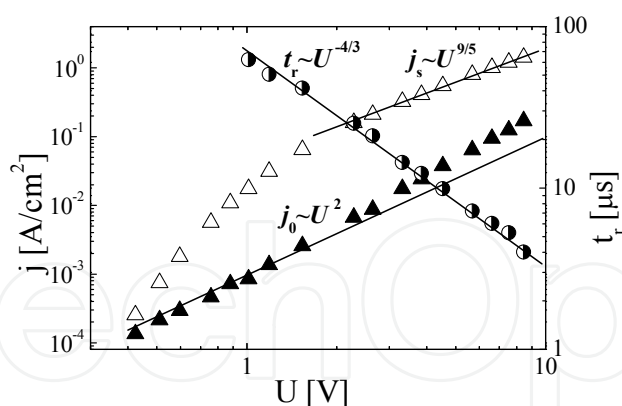


Fig. 24. The dependencies of initial current j_0 , saturation current j_s and recombination time t_r on voltage in the case of double injection.

In the case of 2D Langevin recombination the current-voltage characteristics can be obtained from Eq. (16) in the same way as in Ref. (Juška et al, 2006): $j \propto U^{9/5} / d^{13/5}$, while the saturation time of the DoI current transient is $t_r \propto U^{-6/5}$. The observed experimental results (Juška et al, 2007) are very close to these dependencies.

The comparison of DoI current transients obtained experimentally and numerically modelled using $\mu_n = 10^{-2}$ cm²/Vs, $\mu_p = 2.5 \times 10^{-3}$ cm²/Vs and $l = 1.6$ nm (obtained from X-rays

studies (Sirringhaus et al, 1999) of RRP3HT:PCBM blend is presented in Fig. 23b. The ratios between initial and stationary currents are in good agreement with experiment giving the same l value, and the discrepancy in current rise times could be explained by not taken into account dispersion of the charge carrier transport.

So, the observed increase of DoI current in RRP3HT:PCBM bulk heterojunction and TiO_2 /RRP3HT structures and good fit of numerical modelling with experimental data in RRP3HT:PCBM, proves that recombination takes place in RRP3HT. The slower rise of current in TiO_2 /RRP3HT structure is caused by the lower electron mobility and deep trapping (Juška et al, 2008).

By the integral mode TOF method, where the RC time constant of the measurement setup is much larger than the transit time of the charge carriers ($RC \gg t_{tr}$) we can determine the 2D recombination parameter γ_{2D} in lamellas and its temperature dependencies in more convenient (Pivrikas et al, 2005) and straightforward way because it is independent on material's parameters. In the case of 3D Langevin recombination, the current transient saturates as a function of light-intensity and the amount of extracted charge slightly exceeds CU (when $\alpha d \gg 1$; $Q_{ex} = CU$, therefore $t_{ex} = 0$). In the case of 2D Langevin recombination, the charge carrier extraction time t_{ex} , when collected charge saturates with light intensity, is estimated in the similar way as in the case of reduced bimolecular recombination (Juška et al, 1995):

$$t_{ex} = \left(\frac{2}{3\gamma_{2D}} \right)^{2/5} \left(\frac{ed}{j_{ex}} \right)^{3/5} \propto j_{ex}^{-3/5}, \quad (30)$$

where j_{ex} is extraction current, which could be varied by changing loading resistor or applied voltage. In the case of the reduced bimolecular recombination $t_{ex} \propto j_{ex}^{-1/2}$.

In Fig. 25b the extraction time as a function of the density of extraction current in different structures containing RRP3HT is shown. Since t_{ex} shows the same dependence on the extraction current density j_{ex} , it can be concluded that the recombination is taking place in RRP3HT and it is governed by the 2D Langevin recombination.

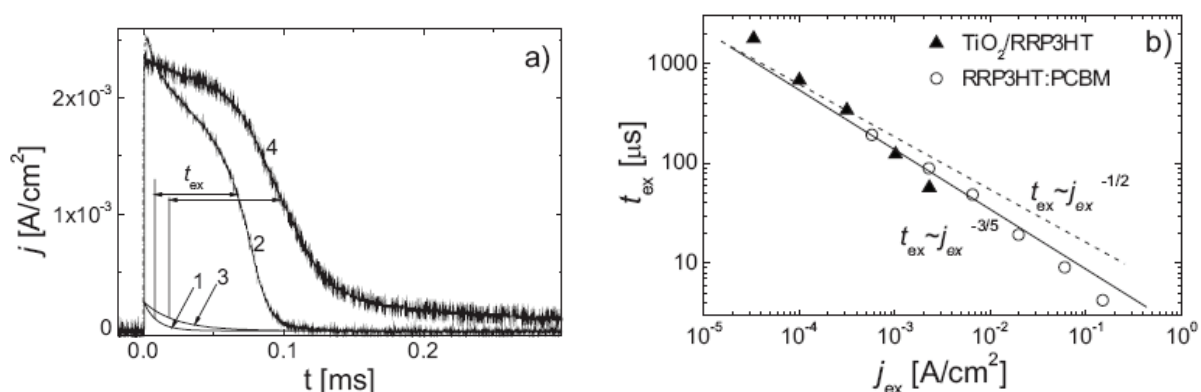


Fig. 25. Current transients of charge carrier extraction (a) observed by integral TOF: small charge drift current (1, 3) and transient of saturated on light intensity photocurrent (2, 4) in TiO_2 /RRP3HT structures and RRP3HT:PCBM bulk heterojunction, respectively.

Measurement of extraction time is indicated. Dependencies of extraction time (b) on the extraction current density in TiO_2 /RRP3HT structures and RRP3HT/PCBM bulk heterojunction

4. Conclusion

In this work there are demonstrated the methods of investigation of charge carrier recombination in organic solar cells, where stochastic transport of charge carriers complicates interpretation of experimental results: charge carriers extraction by linearly increasing voltage (CELIV), which allows independently measure relaxation of density and mobility of photoexcited charge carriers; double injection current transient, which is additional method of investigation of charge carrier recombination and, which allows to measure dependence of recombination coefficient on electric field; integral time of flight (SCLC), using of which allows easily estimate the temperature dependence of recombination coefficient.

Experimentally it is shown, that the decay of the density of photogenerated charge carriers in the blend of MDMO-PPV:PCBM is of 3D Langevin-type, which is typical for organic materials, and in annealed samples of RRP3HT and bulk heterojunction solar cells of RRP3HT:PCBM it is of 2D Langevin-type recombination in the lamellar structure.

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