

VILNIUS UNIVERSITY  
SEMICONDUCTOR PHYSICS INSTITUTE

Gytis Sliaužys

CHARGE TRANSPORT AND RECOMBINATION IN THE  
ORGANIC SOLAR CELLS

Summary of doctoral dissertation

Technological sciences, materials engineering (08T)

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## Introduction

The Earth's energy usage grows very rapidly while the fossil energy resources are decreasing. Therefore, interest in alternative and renewable energy resources is growing. The solar energy is very promising, because the solar panels directly convert sunlight into the electricity.

In 1839 A. E. Becquerel observed photoelectric effect in an electrode immersed in a conductive solution exposed to light [1]. In 1954 the first silicon solar cell was demonstrated at Bell Laboratories. The interest in organic semiconductors revived in the 1977, when A. J. Heeger, A. G. MacDiarmid and H. Shirakawa discovered conducting polymers [2].

The  $\pi$  conjugated polymers [3] and fullerene derivatives [4] are most popular materials for organic solar cells. The price of these materials is low and manufacturing technology is developed very well.

Organic semiconductors have strong light absorption, for example, in the MDMO-PPV (poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene) absorption coefficient  $\alpha$  is  $10^5 \text{ cm}^{-1}$ , when energy of the exciting light exceeds band gap energy 0.25 eV [3], while silicon solar cells shows the same absorption when exciting light energy exceeds band gap energy 1.88 eV. Therefore, thickness of organic solar cells could be significant thinner in comparison with silicon solar cells.

Theoretical calculation shows at maximum power conversion efficiency could be  $\sim 10\%$  for  $\pi$  conjugated polymer and PCBM (1-(3-methoxycarbonyl) propyl - 1 - phenyl - [6,6]-methano- fullerene) bulk heterojunction solar cells [5]. Experimentally this value has not been reached, today maximal power conversion efficiency of 5.5 % is achieved for low band-gap polymer and PCBM bulk heterojunction solar cells [6]. Therefore, it is very important to determine the charge carrier's transport and recombination features in organic solar cells.

## Aim and tasks of the work

1. The development of a double injection transients technique for the research of organic materials.
2. The investigation of the charge carrier transport and recombination features in organic solar cells.
3. The investigation of the influence of the annealing to charge carrier transport and recombination features in organic solar cells.

4. The investigation of the TiO<sub>2</sub>/RR-P3HT interface influence to the charge carrier photo generation and recombination.

### **Scientific novelty**

1. The double injection transients technique was used to determinate properties of the organic materials.
2. The properties of the charge carrier transport and recombination has been measured and compared by three the different techniques (TOF, CELIV and DoI).
3. The influence of the annealing to charge carrier transport and recombination properties in the organic solar cells has been investigated.
4. The trapping of the charge carriers in organic materials has been evaluated.

### **The statements presented for defence**

1. Double injection current transients technique is suitable for investigation of mobility, recombination and trapping of charge carriers in thin organic solar cells.
2. Reduced charge carriers recombination and increased of quantum efficiency after annealing are determined by nanostructure of material.
3. Electric field dependence of charge carrier recombination coefficient, observed by double injection technique, is determined by electric field dependence of charge carriers concentration and bimolecular charge carrier recombination coefficient dependence on charge carriers concentration.

### **Literature review**

This chapter presents the literature review of the organic solar cells and theirs materials. The hopping transport and bimolecular charge carrier recombination mechanism in organic materials are presented below.

### **Numerical modeling of double injection transients**

This chapter presents the numerical modeling of double injection current transients. The normalized parameters were used in our calculations. The dimensionless parameters help easily to compare experimentally obtained data to numerically calculated values. The calculated double injection current transients at different voltages, recombination, mobility and trapping conditions are presented here.

## Samples

The bulk heterojunction solar cells were made by doctor blading the chloroform solution of RR-PHT and PCBM on a glass substrate covered with indium tin oxide (ITO) coated with a thin film of poly(3,4-ethylenedioxythiophene) doped with polysulfonate styrene. As the top electrode a thin lithium fluoride film followed by a semitransparent aluminium film was evaporated. The treated samples were annealed at 125 °C for 15 minutes.

The RR-P3HT/TiO<sub>2</sub> films were made by dipping ITO substrates into the solutions of titanium salt with different precursors in order to make porous or flat TiO<sub>2</sub> surfaces. These films were dried at room temperature, annealed at 450°C for 15 minutes in air and transferred into the nitrogen atmosphere. The RR-P3HT film ( $d = 0.45 \mu\text{m}$ ) was spin coated from dichlorobenzene solution on top of TiO<sub>2</sub> and annealed at 125 °C for 15 minutes. The semitransparent gold electrode was thermally evaporated onto the top of structure.

All samples were sealed at nitrogen atmosphere.

## Measurements techniques

This chapter describes the methods and techniques, used in experimental research. Time of flight (TOF), charge extraction in a linearly increasing voltage (CELIV) and double injection (DoI) techniques were used to investigate properties of charge carrier transport and recombination. By using these techniques charge carrier mobility and bimolecular recombination coefficient dependences on electric field, temperature and charge carriers concentration were investigated in organic semiconductors and isolators.

The schematic TOF timing diagram is shown in Fig. 1. The sample is connected to the voltage pulse generator in reverse bias. After delay time ( $t_d$ ), which is longer than  $RC$  time, a short laser pulse of strongly absorbed light generates a delta shaped charge carriers distribution. The charge carriers travel in applied external electric field through the interelectrode distance. By using small charge (when  $Q \ll CU$ ) differential TOF technique (Fig. 1 a) charge carrier

mobility ( $\mu$ ) can be determined from  $\mu = \frac{d}{t_{tr} E}$ . At high light intensities integral TOF technique (Fig. 1 b) allows determination of the bimolecular charge carrier recombination

coefficient ( $B$ )  $B = \frac{CU}{Q} \frac{t_{tr}}{t_e} B_L$ , where  $B_L$  – Langevin recombination coefficient

$$B_L = \frac{e(\mu_e + \mu_h)}{\epsilon \epsilon_0} .$$

The schematic CELIV timing diagram is shown in Fig. 2. The idea of CELIV is based on the analysis of the extraction current transients when triangular pulse is applied to the sample with at least one blocking contact. The very first initial current step ( $j_0$ ) is caused by the geometric capacitance of the sample and can be used for estimation of either the dielectric

constant or the thickness  $d = \frac{\epsilon \epsilon_0 A}{j_0}$  of the active material. The rise speed of the current following  $j_0$  is caused by the bulk conductivity of the sample or by the most conductive part in the device. The time to reach the extraction current maximum  $t_{max}$  is used for the estimation of

the drift mobility of charge carriers  $\mu = \frac{2}{3A} \frac{d^2}{t_{max}^2}$ . By subtracting the current transient recorded in light from the dark current transient we get the photo generated charge carrier's concentration  $n$ .

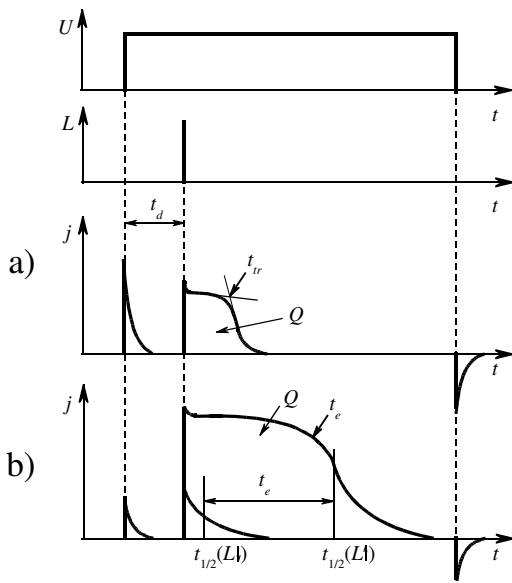


Fig. 1. Voltage, light pulses and corresponding current transients in the time of flight technique (a – small charge differential TOF, b – high light intensity integral TOF)

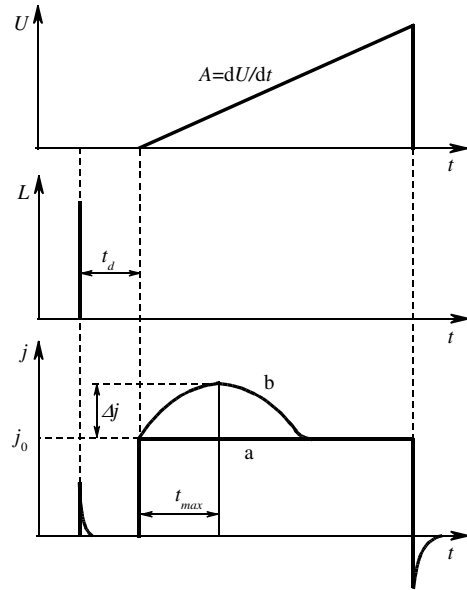


Fig. 2. Voltage, light pulses and corresponding current transients in the CELIV technique (a – no light excitation, b – with light excitation)



In Fig. 3 a Schematic voltage pulse and current response in DoI current transient technique is shown. 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 the beginning the current transient is governed by the displacement current of the external  $RC$  circuit with a characteristic time constant  $\tau_{RC}$ . After  $\tau_{RC}$  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.

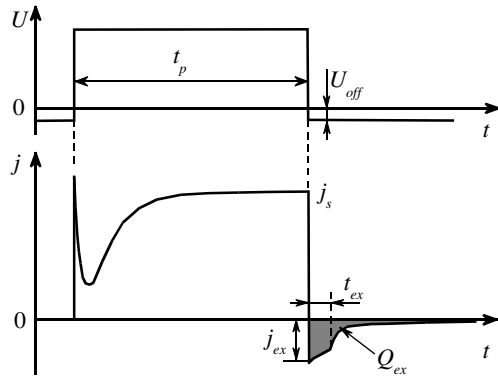


Fig. 3. Schematic voltage pulse and current response in DoI current transient technique.

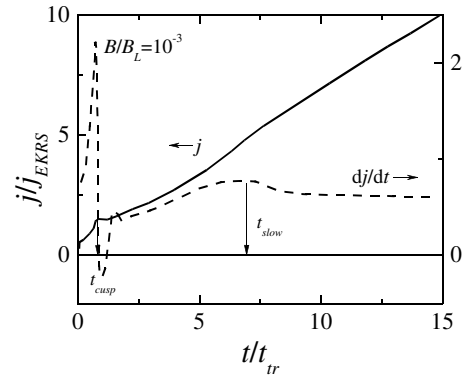


Fig. 4. Initial DoI current transient (solid line) and the time derivative (dashed line) of the current showing  $t_{slow}$ , the transit time of the slower carrier.

Fig. 4 shows how,  $\mu$  and  $B$  of charge carriers can be estimated from the specific points of

DoI transient [6]  $\mu_n + \mu_p = 0.8 \frac{d^2}{U t_{cusp}}$ . The mobility of slower charge carrier's

$\mu_{slow} = 0.8 \frac{d^2}{U t_{slow}}$  and bimolecular recombination coefficient  $B = \frac{\ln 3}{2} \frac{e(\mu_n + \mu_p)U}{j_s t_{1/2} d}$  can be estimated.

## Charge carrier transport and recombination

One of the most important features, which limits efficiency solar cells is recombination of charge carriers. In organic materials the low charge carrier mobility is caused by short, comparing to Coulomb radius, hopping distance, which causes decreased photo-generation quantum efficiency (Onsager–type) and bimolecular charge carriers recombination (Langevin–type).

### Organic semiconductors

For the investigation of charge carrier's transport and recombination properties in organic semiconductors, the 1.9  $\mu\text{m}$  thick sample was used.

In Fig. 5 I–V dependence of double injection current is shown. It is clearly seen that when  $U < 1$  V the current through sample was limited by contact barrier. When  $U > 1$  V the current density follows  $j \propto U^{3/2}$  law, showing that plasma injection into semiconductor in case of the bimolecular recombination is taking place[7].

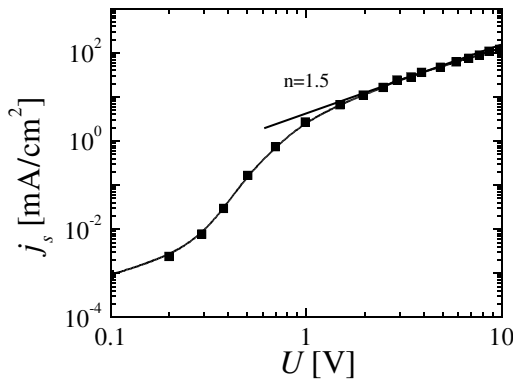


Fig. 5. Current-voltage dependence of the organic semiconductor .

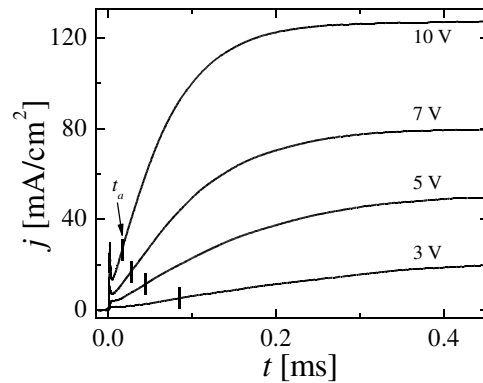


Fig. 6. Experimentally measured DoI current transients in organic semiconductor for different applied square-voltage pulse.

Typical DoI current transients and ambipolar transit time  $t_a$  in organic semiconductor are shown in Fig. 6. After the ambipolar carrier transit time (clearly seen as a peak in the time derivative of the current) the current grows until it achieves the saturation value. The higher the external electric field the faster current saturates.

From the experimental transients, we calculated  $\mu_a$  and  $B / B_L$  as shown in Fig. 7. The

ambipolar mobility and bimolecular recombination coefficient weakly depends on the applied electric field.

We have also measured the temperature dependencies (Fig. 8) of  $\mu_a$  and  $B/B_L$  using DoI transients and  $\mu_{fast}$ ,  $\tau_\sigma$  using CELIV techniques. The solid star shows bimolecular recombination coefficient value estimated from TOF and open star was measured from photo-CELIV techniques.

The experimentally estimated  $B/B_L$  in this sample demonstrates, that bimolecular recombination is reduced compared to Langevin recombination and is in good agreement with photo-CELIV and TOF results. The estimated values of reduced bimolecular recombination coefficient shows that the probability for an electron and hole to meet and recombine is greatly reduced and suggest that electron and hole pathways are different.

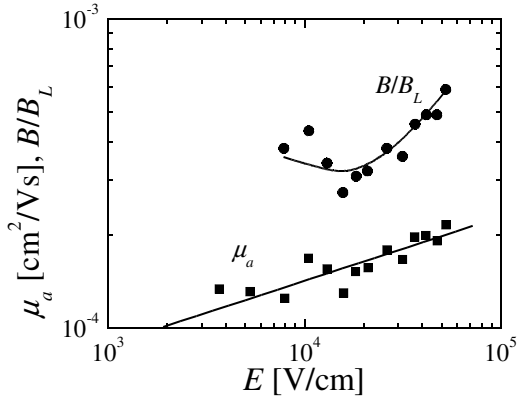


Fig. 7. The estimated  $B/B_L$  (circles) and ambipolar mobility (squares) measured as a function of external electric field.

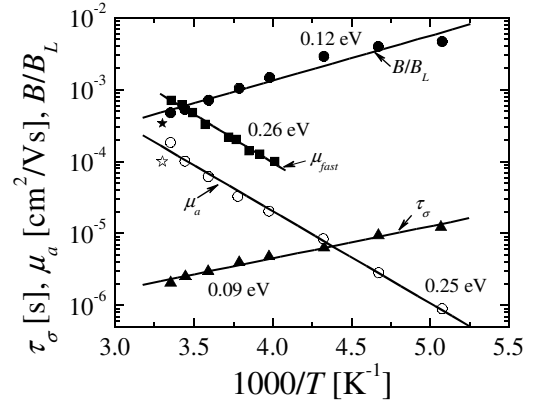


Fig. 8. Dielectric relaxation time  $\tau_\sigma$ ,  $\mu_a$  and  $B/B_L$  experimentally measured as function of temperature.

We found that the activation energy for bimolecular recombination is smaller than for the Langevin recombination by 0.12 eV. According to Adriaenssens and Arkhipov, when electrons and holes are moving through different pathways caused by the random potential, a decrease of the bimolecular recombination as  $B \propto B_L \exp\left(\frac{\Delta}{kT}\right)$ , where  $\Delta$  is the average height of the recombination barrier is expected. This predicts that the  $B/B_L$  ratio must decrease with decreasing temperature. However, our measurements demonstrate the opposite dependence. The much higher activation energy of the electron and hole drift mobilities ( $\Delta_\mu = 0.25$  eV) compared to that of the conductivity ( $\Delta_\sigma = 0.09$  eV) suggests trap-free hopping mobility ( $\Delta_\mu \approx \Delta_\sigma$ ) of the

Langevin recombination. However, even in this case, the barrier  $\Delta$  should be higher than 0.2 eV to explain the observed  $B / B_L = 5 \times 10^{-4}$  at  $T = 300$  K, inconsistent with our data. Thus, we think, that the bimolecular recombination is partly caused by tunnelling through the polymer-PCBM interface.

### Organic isolators

For investigation of charge carrier transport and recombination properties in organic isolators the 1.4  $\mu\text{m}$  and 2.6  $\mu\text{m}$  thick samples were used.

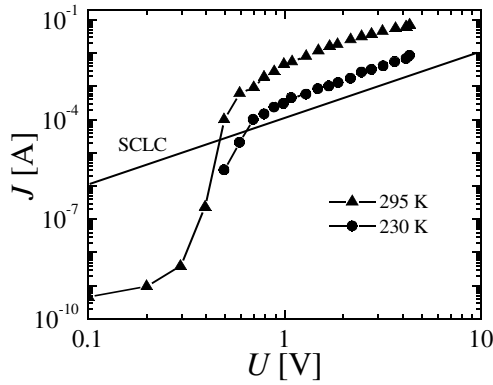


Fig. 9. Current-voltage characteristics measured at room temperature (circles) and at 230 K (triangles). The straight lines show the calculated SCLC using the obtained mobility  $\mu \approx 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  ( $d = 1.4 \mu\text{m}$ ).

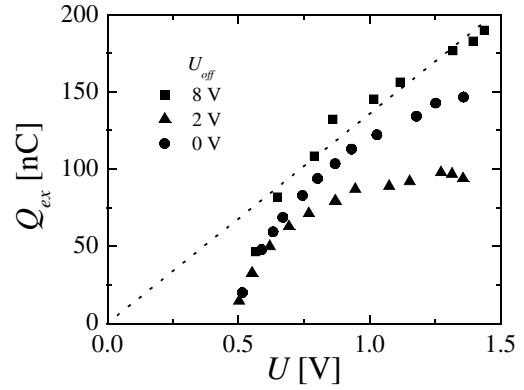


Fig. 10. The extracted charge as a function of applied external voltage measured for different offset voltages ( $d = 1.4 \mu\text{m}$ ). The dotted line shows the theoretical linear dependence of the extracted charge on the applied voltage.

In Fig. 9 the current as a function of voltage for two temperatures is shown. At very low voltages the current is diffusion driven as has been observed in similar films, whereas at high voltages the current is proportional to the voltage squared  $j \propto U^2$ . The experimentally measured current values are much higher than the calculated (room temperature) SCLC values. The straight lines show the calculated SCLC using the obtained mobility  $\mu \approx 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ . The fact, that  $j \propto U^2$ , shows that double injection of plasma is active and that the DoI current is limited by bimolecular carrier recombination [7]. Since the DoI current is much higher than the SCLC, the bimolecular charge-carrier recombination is strongly reduced compared to the Langevin type,  $B / B_L \gg 1$ .

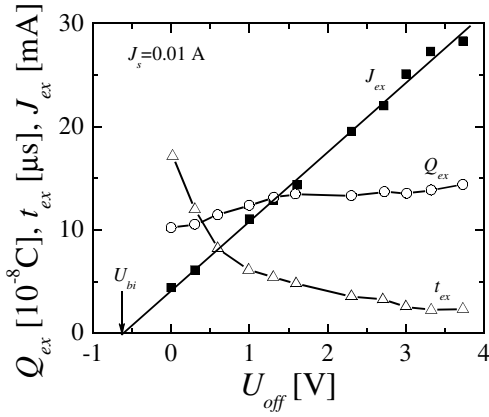


Fig. 11. The extracted charge, extraction time and extraction current shown as a function of applied offset voltage at a constant DoI current of 0.01 A ( $d = 1.4 \mu\text{m}$ ).

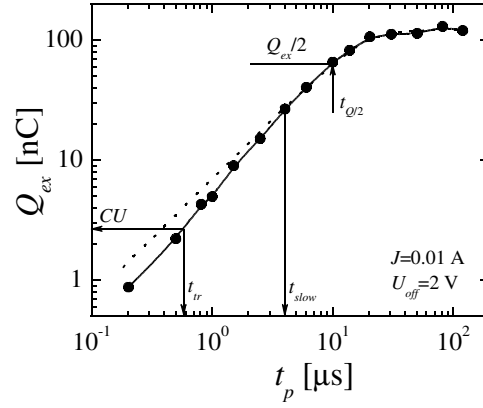


Fig. 12. Extracted charge as a function of injecting voltage pulse duration ( $d = 1.4 \mu\text{m}$ ).

In order to study the amount of charge carriers that are extracted from the sample or recombines, 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. 10.

In the case, when DoI current is limited by the bimolecular recombination into an insulator, the extracted charge is directly proportional to the applied voltage  $Q_{ex} \propto U$  ( $j \propto U^2$ ,  $j \propto Qv$  and  $v \propto U$  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. 10. The reason is that it takes a longer time to extract all of the carriers, giving more time for the 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. 11. As it can be seen, 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 without recombination.

The extraction time  $t_{ex}$  decreases as a function of offset voltage, because at higher offset

voltages, the 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 it is found to be  $U_{bi} = 0.65$  V.

The extracted charge as a function of injecting voltage pulse duration  $t_p$  is shown in Fig. 12. The extracted charge  $Q_{ex} \gg CU$  confirms that the bimolecular recombination coefficient is reduced in comparison with the Langevin-type recombination coefficient. For the short pulse duration the extracted charge follows near to linear dependence, whereas for the long pulse durations, the extracted charge saturates due to the charge-carrier recombination. Since most of the injected charge is extracted from the sample, we can calculate  $B = 2.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at an electric field  $E = 10^4 \text{ V cm}^{-1}$ . The sum of both carrier mobilities ( $\mu_n + \mu_p$ ) is estimated from

the time when the injected charge equals  $CU$ :  $t_p \approx \frac{d^2}{(\mu_n + \mu_p)U}$ . Moreover, the mobility of slower charge carriers, is estimated by using the time when the extracted charge starts to follow

the equation  $Q_{ex}(t_p) = \int_{t_p}^{\infty} J_{ex}(t) dt = Q_s \tanh\left(\frac{B Q_s t_p}{e d}\right)$ .

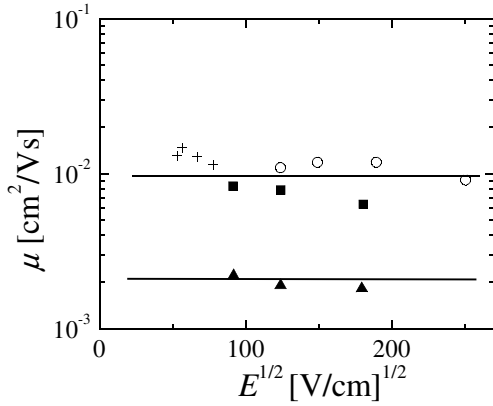


Fig. 13. Comparison of the measured charge-carrier mobility as a function of electric field:  $\mu_n$  using CELIV (crosses),  $\mu_n$  using TOF (circles),  $\mu_n + \mu_p$  using DoI (squares), slower carrier mobility  $\mu_p$  using DoI (triangles) ( $d = 1.4 \mu\text{m}$ ).

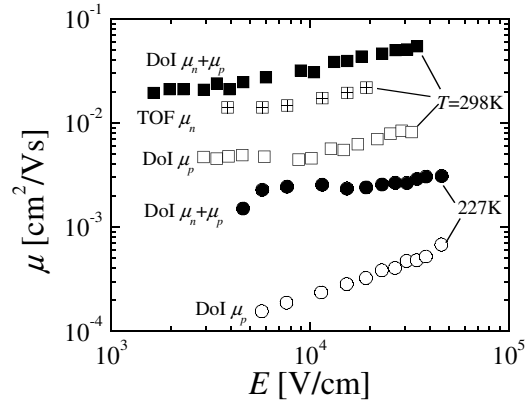


Fig. 14. The electric field dependence of carrier mobility at different temperatures, determined by TOF and DoI transient techniques ( $d = 2.6 \mu\text{m}$ ).

In Fig. 13 the obtained results of both the slowest mobility and sum of the mobilities are

compared to the measured electron mobility using TOF and to the mobility of the faster carriers obtained using CELIV. The dependencies of  $\mu_n$  and  $\mu_p$  on electric field estimated from DoI transient and TOF experiments are compared in Fig. 14. The very good agreement between the three independent techniques shows that the faster carriers are electrons and the holes are slower. The estimation of the hole mobility is only approximate, because in photo-CELIV two extraction maximums corresponding to different carriers are not observed, which shows that the carrier mobility ratio is not large.

In Fig. 15 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 with light intensity. By

using  $B = \frac{edS}{t_e Q}$  we can directly calculate  $B = 3.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  using the saturated extracted charge  $Q$  and extraction time  $t_{ex}$  as shown in Fig. 15.

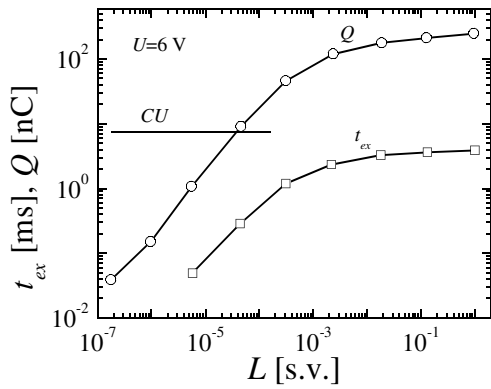


Fig. 15. The extracted charge and the extraction time as a function of laser light intensity measured using integral TOF mode ( $d = 1.4 \mu\text{m}$ ).

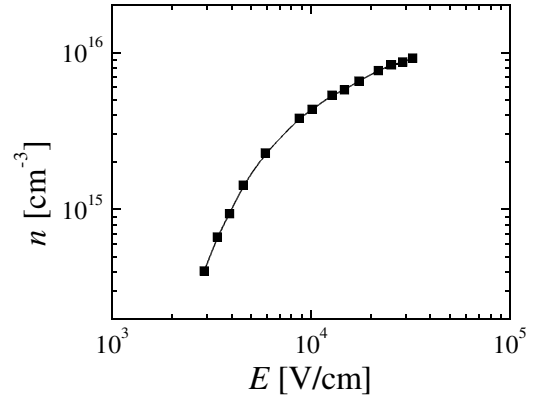


Fig. 16. The electric field dependence of charge carrier density ( $d = 2.6 \mu\text{m}$ ).

In Fig. 16 the electric field dependence of charge carrier density, estimated from current–voltage characteristic is shown. Using transient photovoltage and transient optical absorption spectroscopy techniques, it was estimated that  $B$  is dependent on charge carrier density (see Fig. 17), similarly to the case of Auger recombination:  $B = \gamma n$ , where  $\gamma$  is the Auger-type recombination coefficient. In the case of Auger-type recombination DoI  $n \propto U^{2/3}$  and after

photogeneration by short pulse of light, charge carrier density relaxation has to follow

$$n = \left( \frac{1}{n_0^2} + \frac{\gamma t}{2} \right)^{-\frac{1}{2}} .$$

Using photo-CELIV technique, the experimentally measured charge carrier

recombination transient fits well  $t^{-1/2}$  law (see Fig. 18), which confirms that experimentally obtained bimolecular recombination increase with electric field is caused by  $B$  dependence on charge carrier density, as in case of Auger-type recombination.

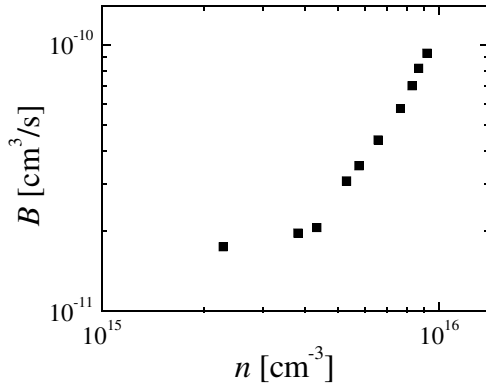


Fig. 17. The charge carrier density dependence of bimolecular recombination coefficient ( $d = 2.6 \mu\text{m}$ ).

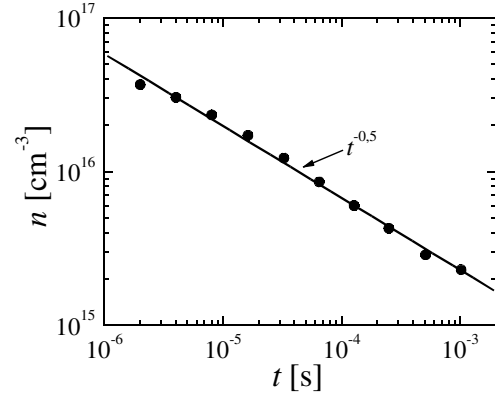


Fig. 18. Photogenerated charge carrier density as a function of time measured using photo-CELIV. The line corresponds the  $t^{-1/2}$  dependence ( $d = 2.6 \mu\text{m}$ ).

The mobility and bimolecular recombination coefficient of charge carriers were investigated, by using double injection current transient technique and compared to mobility and bimolecular recombination coefficient values obtained using TOF and CELIV techniques. The bimolecular recombination coefficient is strongly reduced compared to Langevin recombination and depends on the density of charge carriers.

## Charge carrier transport and recombination in annealed and non-annealed organic solar cells

For investigation of charge carrier transport and recombination properties in annealed and non-annealed organic solar cells, the non-annealed 270 nm thick sample was used while the annealed sample thickness were 284 nm and 1.4  $\mu\text{m}$ .

External quantum efficiency (EQE) as a function of light wavelength is shown in Fig. 19.



The external quantum efficiency in the annealed devices resembles to the typical shape for RR-P3HT/PCBM organic solar cells, whereas the maximum value of EQE at strongly absorbed light is approximately 5 times larger than one in non-annealed films, showing that the recombination in non-annealed samples is much stronger compared to annealed.

In order to estimate the difference between the charge carrier generation, transport and recombination the external quantum efficiency as a function of external electric field has been measured in both types of the samples (Fig. 20). Low light intensity of the strongly absorbed wavelength has been used for photogeneration. At zero applied external voltage the charge carrier photogeneration and extraction to the contacts proceeds at the built-in potential of the solar cell. For annealed solar cell the quantum efficiency rapidly increases with applied electric field and finally saturates to a value close to 90 %, leading to a conclusion that the charge carrier photogeneration and extraction efficiencies are close to unity. However, the external quantum efficiency in non-annealed sample demonstrates stronger electric field dependence without a clear saturation. Like in pure  $\pi$ -conjugated polymers the free carrier generation is strongly dependent on the electric field, where high electric fields are required for efficient carrier dissociation from an exciton. This demonstrates that the charge carrier generation process originates from Coulombically bounded charge carriers pairs.

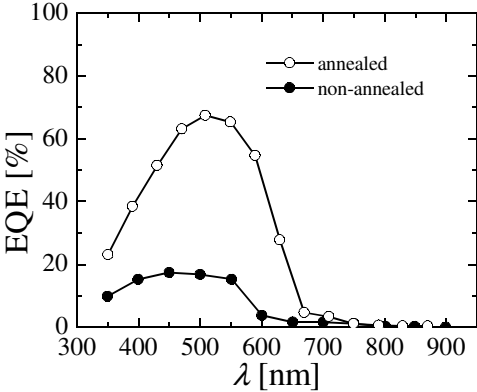


Fig. 19. The external quantum efficiency as a function of light wavelength.

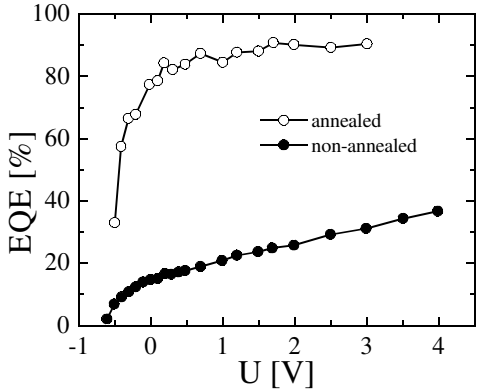


Fig. 20. The external quantum efficiency as a function of applied voltage.

Since we have shown that the charge carrier generation and extraction can be highly efficient already at close to built-in voltages in annealed devices. It is worthwhile to study the difference of carrier recombination for both types of the films (see Fig. 19). We have experimentally measured stationary dark current-voltage characteristics which are shown in

Fig. 21, the experimentally measured current (solid line) is compared with the calculated space charge limited current (dash lines). The mobility of faster charge carriers is used to calculate the SCLC current. At built in electric fields, the faster carrier's mobility in annealed films  $\mu \approx 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  and the mobility in non-annealed films  $\mu \approx 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ . The experimentally measured current values in annealed and non-annealed films differs by orders of magnitude at the same electric field as seen in Fig. 21. Moreover, the current value exceeds SCLC in the annealed films, whereas in the non-annealed films the current is much less than SCLC and approaches SCLC only at very high voltages. The reason for such a high currents in annealed devices is the presence of reduced bimolecular charge carrier recombination. The presence of DoI current in annealed films confirms that the electron and hole injection is not limited by the contact, but by the carrier recombination in the bulk of the film [7].

Since the injection currents do not directly reveal the dynamics of the charge carrier transport and recombination, we have used high light intensity TOF technique to study the charge carrier recombination directly in both types of films. In Fig. 22 the extracted charge  $Q_e$  normalized to  $CU$  and extraction time  $t_e$  as a function of light intensity are shown. At low intensities of light the extracted charge follows linear dependence in both films with the following saturation due to the presence of bimolecular carrier recombination at highest intensities (hundreds of  $\text{mJ}/\text{cm}^2$ ). For the annealed films the maximum extracted charge exceeds  $CU$  value up to 20 times, whereas for non-annealed films the extracted charge exceeds the  $CU$  value about 5 times. Moreover, the development of extraction time to more than 5 times in the annealed films is seen when compared with to non-annealed samples. Using absolute values of the extracted charge and the extraction time at highest intensities we can directly calculate [8] the bimolecular carrier recombination  $B/B_L = 10^{-4}$  in annealed films. The exact estimation of recombination coefficient in non-annealed films using TOF technique is difficult, because the measurements were performed on thin films where it is possible to extract charge up to 7 times more than  $CU$  at very high intensities even in case of Langevin-type recombination.

The extraction transients of injected charge for both annealed and non-annealed films are shown in Fig. 23. By integrating the current over time during extraction we obtain the total extracted charge and compare it to the charge stored on the contacts  $CU$ . By comparing DoI current transients at the same low (2 mA) and high (10 mA) injection currents, it is clearly seen that in non-annealed films the extracted charge stays almost the same and it is independent on the injection current level. Moreover, the value of extracted charge in this case is equal to  $CU$  which again confirms the presence of Langevin-type carrier bimolecular recombination in these

films. In the case of the annealed films, the extracted charge exceeds  $CU$  value more than 10 times and saturates as a function of injection current, demonstrating the presence of reduced bimolecular carrier recombination. The bimolecular carrier recombination coefficient is then directly estimated using the experimentally measured extraction time  $B / B_L = 10^{-4}$ .

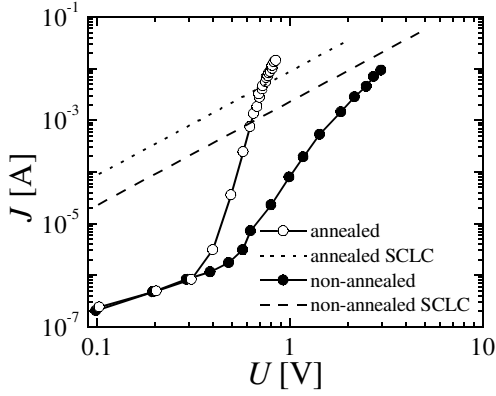


Fig. 21. Stationary current-voltage dependencies. Points are denoting experimentally measured data, and lines are calculated space charge limited current value using carrier mobility obtained from time-of-flight technique.

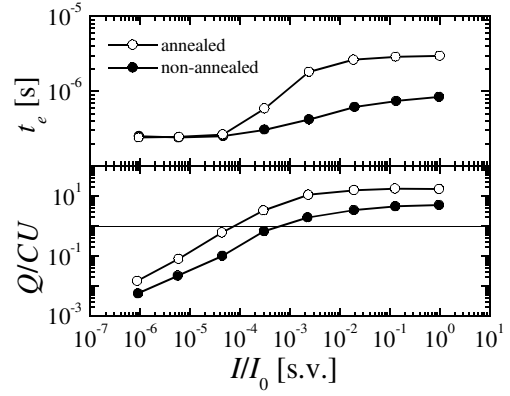


Fig. 22. Extracted charge normalized to  $CU$  and extraction time shown as a function of light intensity.

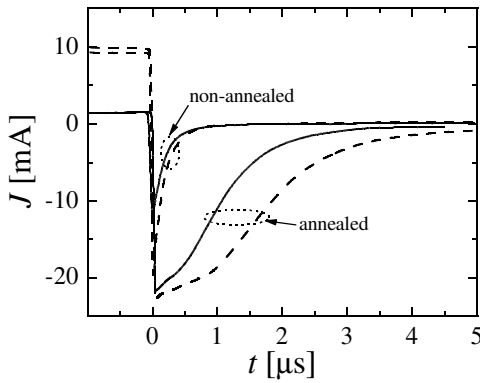


Fig. 23. Double injection current transients and the extraction of injected plasma.

The experimentally measured capacitances as a function of applied voltage for both annealed and non-annealed samples using the capacitance bridge in Fig. 24 are shown. The capacitance of non-annealed sample do not depend on the applied voltage at room temperature

and corresponds to the geometrical capacitance value of the sample. However, as is seen from Fig. 24, the capacitance of the annealed sample depends on the applied voltage at room temperature, but not at low temperatures. The capacitance of the sample at room temperature is approximately two times higher than the value at 272 K and approaches the geometrical capacitance value at low temperatures. The small differences in capacitances between annealed and non-annealed samples at low temperatures are caused by slight differences in sample thicknesses and contact areas.

The capacitance and bulk conductivity as a function of applied voltage (in reverse bias) are shown in Fig. 25. The annealed 1.4  $\mu\text{m}$  thick sample was measured with the capacitance bridge at various temperatures. The sample conductivity is determined by equilibrium charge carriers when reverse bias is applied, and slightly decreases when a reverse voltage increases due to extraction of the equilibrium charge carriers.

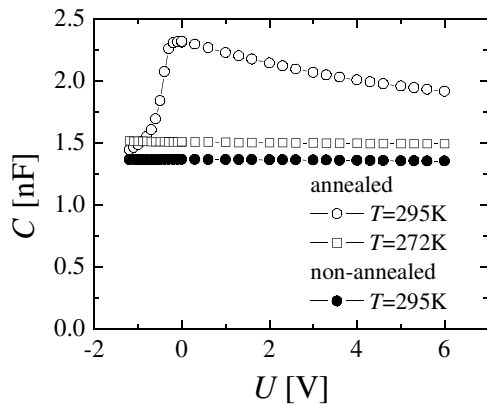


Fig. 24. The experimentally measured sample capacitance as a function of applied reverse bias voltage for annealed and non-annealed samples. The annealed sample thickness was 284 nm with a contact area of 12  $\text{mm}^2$ , while the non-annealed sample thickness was 270 nm with a contact area of 10.5  $\text{mm}^2$ .

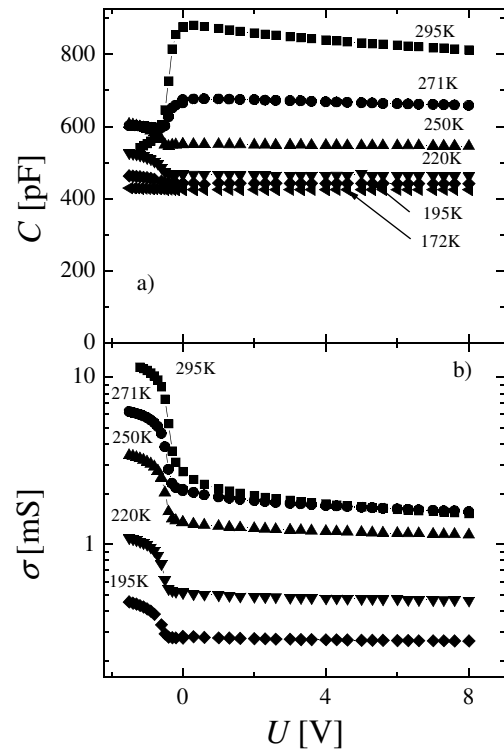


Fig. 25. Measured capacitance (a) and conductivity (b) as a function of applied reverse bias voltage at various temperatures for the 1.4  $\mu\text{m}$  thick annealed sample.

The similar capacitance values as a function of voltage at various temperatures has previously been observed [9][10][11]. Parisi [9] explained this behaviour as charge trapping. However, the double injection current transients do not show any signs of injected charge carriers trapping in these bulk-heterojunction solar cells (see Fig. 26). We have shown that the bulk-heterojunction solar cells shows an increase of capacitance after annealing, caused by RR-P3HT and PCBM phase separation and formation of conducting PCBM nanostructures.

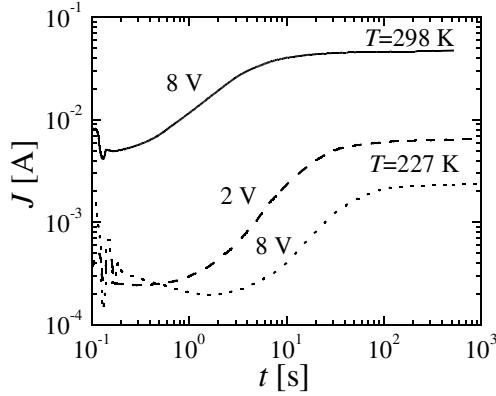


Fig. 26. Double injection current transients in RR-P3HT/PCBM blend at different temperatures and voltages.

In conclusion, we have measured the charge carrier transport and recombination in annealed and non-annealed RR-P3HT/PCBM bulk-heterojunction solar cells using various electrical techniques. It has been demonstrated that the nanomorphology of the bulk-heterojunction solar cells is very important in terms of efficiency, carrier transport and recombination. The presence of double injection current with reduced Langevin-type bimolecular carrier recombination was observed, whereas SCLC dominates the non-annealed solar cells. High light intensity TOF technique and double injection current transients confirm the presence of reduced bimolecular recombination and allows us to measure directly the value of recombination coefficient from the current transients. The external quantum efficiency was found to be electric field dependent only in non-annealed low efficiency solar cells, which lead to a conclusion that Onsager-type electric field assisted charge carrier generation in these films. The electron mobility (faster carriers) is improved by an order of magnitude in annealed solar cells. These effects can be attributed to a certain beneficial nanostructure of polymer and PCBM in bulk-heterojunction solar cells.

## TiO<sub>2</sub>/RR-P3HT interface influence to charge carrier photo generation and recombination

The heterojunction of TiO<sub>2</sub> with organic materials are potential structures for photovoltaic applications [12][13][14]. TiO<sub>2</sub> is a good electron accepting material and the organic material has to be a good transporting material for holes. The TiO<sub>2</sub>/polymer interface plays decisive role in dissociation of photogenerated excitons to free charge carriers. Thus, the aim of this study was to investigate the influence of TiO<sub>2</sub>/RR-P3HT interface on photogenerated exciton separation and charge carrier recombination.

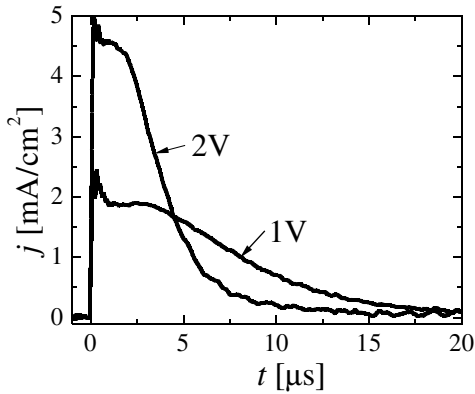


Fig. 27. Transients of TOF current at different voltages for electrodes made of porous TiO<sub>2</sub> films.

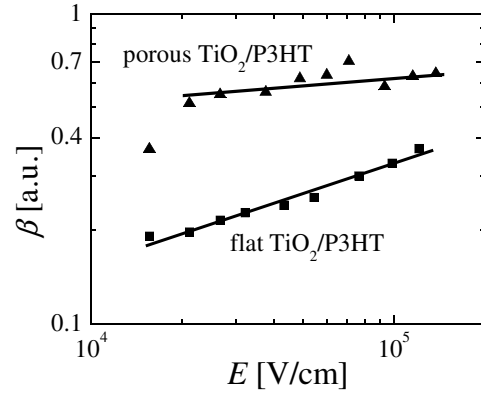


Fig. 28. Dependencies of charge carrier photogeneration efficiencies on the electric field for porous and flat TiO<sub>2</sub> film structures.

In Fig. 27, the current transients of the small charge drift are shown, where the visible kinks correspond to transit time of charge carriers through the interelectrode distance. These behaviours shows, that the charge carriers are generated at the interface. Contrarily, as in the bulk photogeneration case, we should see continuous decrease of current. The hole mobility  $\mu_h=10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  was calculated from  $t_{tr}$ , and was insignificantly dependent on electric field. In porous TiO<sub>2</sub> films the photogeneration efficiency was higher than in flat TiO<sub>2</sub> ones. The photogeneration efficiency dependence on the electric field is shown in Fig. 28, from which it follows that in the porous TiO<sub>2</sub> films the photogeneration efficiency dependence on the electric field is weaker than one in the flat TiO<sub>2</sub>. The latter result together with higher value of photogeneration efficiency indicates that the higher efficiency of charge carrier separation in porous structures is due to the larger surface of the interface.

Charge carriers reservoir created by short light pulse is extracted during time  $t_e$ , which is determined as a difference of half times of saturated on light intensity and small charge current transients. For monomolecular recombination  $t_e \sim \ln L$ . In case of bimolecular or trimolecular recombination  $t_e \sim L$  and saturates at high light intensities. In the case of Langevin recombination, typical for organic materials,  $t_e$  approaches zero [15], if the charge carrier recombination is reduced compared to the Langevin one, then  $t_e \gg t_{tr}$ . The recombination mechanism can be estimated from the  $t_e$  dependencies on the extraction current  $j_e$ . In the case of bimolecular recombination  $t_e \sim j_e^{-1/2}$ , while in the case of trimolecular one  $t_e \sim j_e^{-2/3}$ . Experimentally, the magnitude of extraction current could be varied by changing the loading resistor. As follows from Fig. 29, the fitting of  $t_e$  experimental results confirm trimolecular (Auger – type) recombination for both flat and porous  $\text{TiO}_2$  with similar values of recombination coefficient calculated. This type of recombination was also observed in PCBM / P3HT blends.

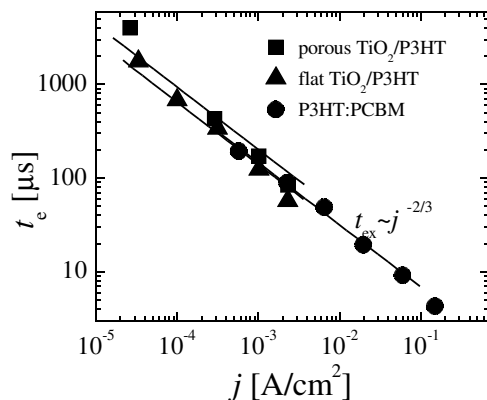


Fig. 29. Dependencies of extraction time on the density of extraction current

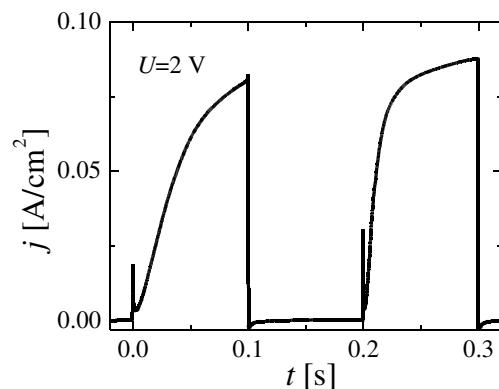


Fig. 30. Double injection current transients for porous  $\text{TiO}_2$  film structures

Another independent possibility to test the recombination is to use the double injection current transients [16]. In the case of Langevin recombination, injected charge carriers fully recombine in the interelectrode distance, the observed forward injection current is similar to space charge limited current transient where the sum of both charge carrier mobilities predetermine the spike of transit time. In the case of reduced bimolecular recombination, after the transit time of slower charge carriers, the current increases and, due to recombination, saturates. Such an increase of current can be seen in Fig. 30. The second forward current pulse demonstrates the faster increase of the current, which is caused by the filling of deep trapping states during first current pulse and decreased trapping probability for the following charge

carriers. Charge carriers are trapped in the vicinity of the interface, because in pure RR-P3HT films the trapping of charge carriers is not observed. The electron mobility in RR-P3HT ( $\mu_n \sim 10^{-7} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) was estimated from the spike of the DoI transient, and the density of trapped states  $n_t \sim 10^{18} \text{ cm}^{-3}$  was calculated from the difference of delay time between the first and second pulses of the forward current.

From the experimental results it was concluded that the photogenerated charge carriers are separated in the vicinity of  $\text{TiO}_2 / \text{RR-P3HT}$  interface. In structures with porous  $\text{TiO}_2$  films the charge carrier photogeneration efficiency weaker depends on the electric field than in structures with flat  $\text{TiO}_2$  films. The charge carriers recombination is of trimolecular type and the value of the recombination coefficient for structures with porous and flat  $\text{TiO}_2$  films are almost the same. The deep charge carrier trapping at interface of structures with porous  $\text{TiO}_2$  films was observed.

## Conclusions

1. After annealing changes in morphology of organic materials are observed, which increase the quantum efficiency, charge carriers mobility, and decrease charge carriers recombination.
2. The bimolecular charge carrier recombination coefficient is reduced compared with Langevin recombination coefficient in bulk heterojunction RR-P3HT/PCBM solar cells.
3. The higher photogeneration efficiency and deep trapping of the charge carriers at interface of the structures with porous  $\text{TiO}_2$  films were observed. Trimolecular charge carriers recombination was observed in porous and flat  $\text{TiO}_2/\text{RR-P3HT}$  structures.

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- [S1] G. Sliaužys, G. Juška, K. Genevičius, G. Juška, J. H. Smått, M. Lindén, R. Österbacka, „TiO<sub>2</sub>-PHT interface influence to charge carrier photo generation and recombination“, *SPIE Proceedings* **7142**, 71420K (2008).
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- [S9] G. Juška, K. Genevičius, N. Nekrašas, G. Sliaužys, G. Dennler, "Trimolecular Recombination in P3HT:PCBM Bulk Heterojunction Organic Solar Cells ", *Applied Physics Letters* **93**, 143303 (2008).
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- [T1] G. Sliaužys, G. Juška, K. Genevičius, G. Juška, J. H. Smått, M. Lindén, R. Österbacka, „TiO<sub>2</sub>-PHT interface influence to charge carrier photo generation and recombination“, AOMD-6, 24 - 27 August 2008, Riga, Latvia.
- [T2] G. Juška, K. Genevičius, N. Nekrašas, G. Sliaužys, G. Dennler, “Charge carrier recombination in PCBM / RR-P3HT solar cells”, Excitonic Solar Cell Conference 2008, 9 - 12 September 2008, Warwick, United Kingdom.
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## Reziomė

Sparčiai besivystančiame pasaulyje nuolat didėja energijos poreikis. Neatsinaujinančių energijos išteklių kiekis vis mažėja, todėl vis labiau domimasi alternatyviais ir atsinaujinančiais energijos šaltiniais. Saulės energetika yra labai perspektyvi sritis, kadangi saulės šviesa verčiama tiesiogiai į elektros energiją. 1954 metais buvo pademonstruotas pirmas saulės elementas pagamintas iš silicio. Šiuolaikinių kristalinio silicio saulės elementų efektyvumas siekia 20 %, tačiau tokių saulės elementų gamybos kaina didelė. Dėl šios priežasties ieškoma naujų medžiagų ir technologijų, kurios leistų sumažinti gamybos kainas. Viena alternatyva yra iš organinių medžiagų pagaminti saulės elementai. Nors šie elementai nusileidžia savo efektyvumu kristalinio silicio saulės elementams, tačiau jų gamybos technologija yra labai paprasta, todėl vis didėja susidomėjimas tokiais saulės elementais.

Yra apskaičiuota, jog gerai parinkus organines medžiagas ir eliminavus visus krūvio pernašos bei rekombinacijos nuostolius organinių saulės elementų efektyvumas gali siekti 10 % [5], o tandeminių – net 15 % [17]. Todėl labai svarbu iširti krūvio pernašos ir rekombinacijos savybes organiniuose saulės elementuose, iširti organinių ir neorganinių medžiagų sandūros įtaką krūvininkų fotogeneracijai ir rekombinacijai bei pritaikyti naujus matavimo metodus šių savybių tyrimams.

Šiame darbe buvo pirmą kartą išmatuoti ir tarpusavyje palyginti krūvininkų pernašos ir rekombinacijos parametrai trimis skirtingais matavimo metodais, įvertinta atkaitinimo įtaka krūvininkų pernašos ir rekombinacijos savybėms bei išmatuota krūvininkų prilipimo įtaka organiniams saulės elementams. Be to, pritaikytas dvigubos injekcijos metodas organinių medžiagų tyrimams, kuris leidžia išmatuoti dreifinio judrio bei kvadratinės rekombinacijos priklausomybes nuo elektrinio lauko stiprio bei įvertinti krūvininkų prilipimo lygmenų tankį.

Atlikus eksperimentinius matavimus nustatyta, kad saulės elementuose su tūrine RR-P3HT / PCBM heterosandūra rekombinacija yra tūkstantį kartų mažesnė lyginant su Lanževano rekombinacija. Kvadratinės krūvininkų rekombinacijos koeficientas didėja didinant elektrinio lauko stiprį, krūvininkų tankį arba mažinant temperatūrą. Krūvininkų prilipimas nestebimas. Po atkaitinimo saulės elementų efektyvumas padidėja, kadangi padidėja kvantinis efektyvumas, padidėja dreifinis judris, o sumažėja kvadratinė krūvininkų rekombinacija. Saulės elementuose su titano oksido ir polimero sandūra didesnis kvantinis efektyvumas bei krūvininkų prilipimas stebimas bandiniuose su porėtu titano oksido sluoksniu. Trimolekulinė krūvininkų rekombinacija stebima bandiniuose su porėtu ir plokščiu TiO<sub>2</sub> sluoksniu.

## **CURRICULUM VITAE**

Gytis Sliaužys was born in Širvintos, Lithuania on April 9, 1977.

### **Education:**

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