ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 16, No. 1. 2010

Impact of Carrier Traps on Charge Transport in the Composites of Poly(3-Hexylthiophene) an Fullerene Derivative for Organic Photovoltaics

Vaidotas KAŽUKAUSKAS*, Mindaugas PRANAITIS, Andrius ARLAUSKAS

Semiconductor Physics Department, Institute of Materials Science and Applied Research of Vilnius University, Saulėtekio 9, bldg.3, LT-10222 Vilnius, Lithuania

Received 18 March 2009; accepted 08 September 2009

We have investigated impact of carrier trapping on charge transport in blends of poly(3-hexylthiophene) (P3HT) with the fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) that are important for the development of organic Solar cells. The devices with quantum efficiency of 3.7 % fabricated in the inverted layer sequence were analysed. We demonstrate that, though the fill factor of their Current-Voltage characteristics is as high as 68 %, carrier trapping is effectively involved in the transport phenomena. The evaluated trapping state activation energy is about 0.18 eV and their density is up to $(10^{20} \div 7\times10^{21})$ cm^{-3}. At such high densities these states presumably act as transport states, limiting carrier mobility.

Keywords: organic solar cells, inverted layer sequence, efficiency, carrier trapping, mobility.

INTRODUCTION

In photovoltaic organic material engineering and device development carrier transport properties are of primary importance as they are directly related with macroscopic material parameters determining device functionality and efficiency. Charge carrier mobility is one of the main factors limiting carrier transport in highly disordered organic materials [1, 2]. On the other hand, mobility is often limited by severe carrier trapping, resulting in an imbalance of different carrier flows. This problem has to be addressed by specific technological measures. Evidence of the charge trapping effects depending on the applied bias to the poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene (MDMO-PPV) and methano-fullerene[6,6]-phenyl C_{61}-butyric acid methyl ester ([60] PCBM) bulk-heterojunction solar cells was proven in [3]. Carrier trapping was evidenced not only in organic devices and blends [2 – 5], but in single layer samples as well [6], evidencing that carrier trapping is an internal feature of organic materials. Therefore fundamental investigations of complex carrier transport phenomena are practically important task. In this paper carrier transport and trapping effects are analyzed in blends of P3HT with PCBM that are of particular importance for the development of organic Solar cells.

EXPERIMENTAL

We had investigated P3HT:PCBM organic bulk-heterojunction structures (Fig. 1). Solar cell devices were produced in the inverted layer sequence, which was demonstrated to have some practical advantages as compared to the conventional device setup [7].

Device layout is described in [7]. The devices were fabricated on cleaned floatglass. First an Al layer of 80 nm was thermally evaporated, then a Ti layer of 20 nm was evaporated by electron-beam heating both in high vacuum.

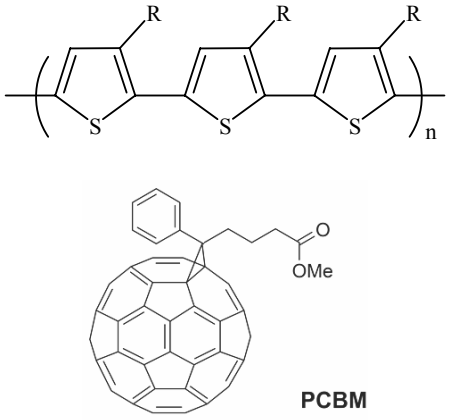

Fig. 1. Structures of the blend constituents P3HT (R = C_6H_{13}) and PCBM

The Ti forms the electron contact, while the Al layer is needed to assure a high sheet conductance of the electrode. After that the photoactive layer was spincoated at 1000 rpm from tetralin solution (~ 2 % wt.) with a ratio of 6 : 5 wt. P3HT:PCBM (P3HT 4002 electronic grade synthesized by Rieke Metals, and PCBM synthesized by Nano-C). The layer thickness was about 200 nm or 350 nm. As a hole contact Poly(3,4-ethylenedioxythiophene) poly(styrenesul-fonate) (PEDOT:PSS) was spincoated on top (Baytron F CPP105D) with a layer thickness of 200 nm. To support the sheet conductance of the PEDOT:PSS layer a gold grid was evaporated on top with a finger width of 100 μm and a distance between the fingers of 500 μm. After the preparation the samples have been annealed for 10 min at 100 °C to improve the efficiency as proposed by Padinger et al. [8].

Current-Voltage (IV) characterization was used to investigate carrier injection properties. Carrier traps were analyzed by the Thermally Stimulated Current (TSC) spectroscopy [6], and Carrier mobility measurements were performed by the CELIV (Charge Extraction by Linearly Increasing Voltage) method [9].

* Corresponding author. Tel.: +370-5-2366035; fax.: +370-5-2366003.
E-mail address: *vaidotas.kazukauskas@ff.vu.lt* (V. Kažukauskas)

The experimental results were analyzed numerically by taking into account mobility variation according to the Gaussian Disorder Model (GDM) approximation [10] as well as carrier thermal generation from traps [11, 12]. Such complex analysis had enabled not only evaluation of the trap parameters, but it had also demonstrated a clear coincidence of the results given by both methods, evidencing that carrier trapping is a decisive factor, giving their mobility behaviour.

RESULTS AND DISCUSSION

IV characteristics and photovoltaic efficiency

To test the quality of the devices IV curves were measured under illumination by AM 1.5 spectrum light with 100 mW/cm² incident power density as presented in Fig. 2.

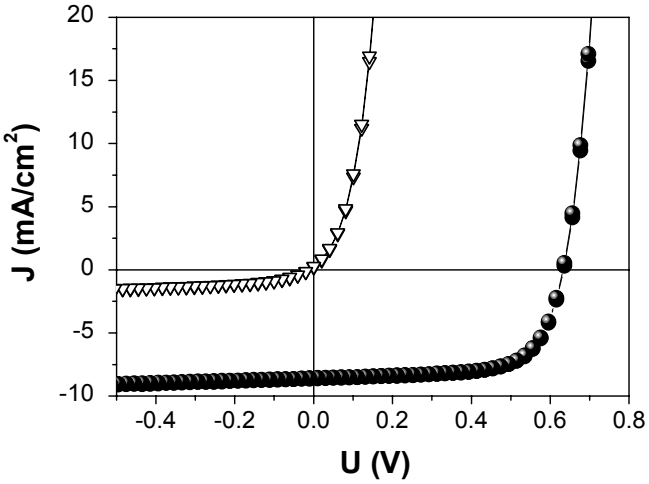

Fig. 2. Current-voltage dependencies in the dark (triangles) and under illumination by AM 1.5 spectrum light with 100 mW/cm² power density (dots)

In the tested devices a solar efficiency of (3.7 ±0.2) % was reached. The high fill factor of 68 %, the open circuit voltage of 634 mV and the short circuit current of 8.6 mA/cm^2 demonstrate significant improvement of the device parameters as compared to the first devices produced in this layout [7]. Moreover the high fill factor evidences that transport problems are of minor importance. Nevertheless to have a clearer insight, we had investigated carrier transport properties in more detail as described below.

Thermally stimulated current spectra

The experimental TSC spectra are presented in Figs. 3 for two devices fabricated on the same glass substrate. Notably, though the devices were produced simultaneously, their current spectra do not coincide quantitatively, indicating that even small variations in technological process might result in significant deviations of device properties.

Nevertheless, upon subtraction of the dark current from the TSCs obtained after the light excitation, a qualitative coincidence of the results is clearly seen. In both cases characteristic maxima appear in the TSC curves, though they are different. Appearance of the current maxima cannot be explained by carrier mobility behaviour within the GDM model, which foresees only mobility increase with temperature.

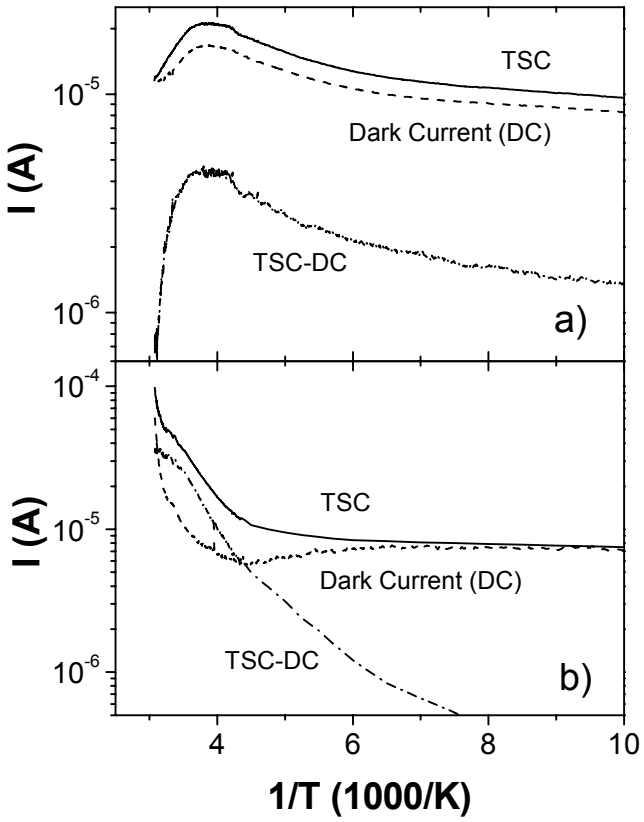

Fig. 3. Experimental TSC spectra of two devices fabricated on the same glass substrate measured after the light excitation (solid curves), dark currents (dashed curves) and their differences (dashed-dotted curves)

Though in systems with two perfectly blocking electrodes current maxima can appear when all carriers become extracted from the device as their mobility grows with the temperature [13]. This is because the number of carriers is limited in the sample volume and their injection from the blocking contacts is impossible. In such case maxima positions should demonstrate an expressed dependence on the heating rate and applied electric field [13], but we did not observe such behavior. Moreover in our samples current growth took place after the maxima were passed, indicating that the TSC maxima were caused by the emptying of the traps.

Therefore the obtained resulting curves were modelled by taking into account the carrier mobility increase and thermal generation of carriers from trap states as it was described in detail in [6]. The results for the same samples, as shown in Figs. 3, are presented in Figs. 4. The thermal activation energy values of the traps were coinciding well within the range of experimental errors: they were equal (0.18 ±0.02) eV in all samples. The density of traps was evaluated by integrating the current dependence over time. It was found to range between 10^{20} cm^{-3} to some 10^{21} cm^{-3}. Such high density of traps implies that they could take active part in carrier transport, acting as transport states and mediating carrier hopping. Qualitatively similar effect called impurity band transport is well known in crystalline semiconductors. Characteristically in samples of lower

conductivity trap density was also significantly lower [4, 6], confirming qualitatively the above conclusion. The coinciding activation energy of the traps in different samples and their high density imply that they are most probably not caused by some dopants, e. g., oxygen, but are rather related to material structure itself.

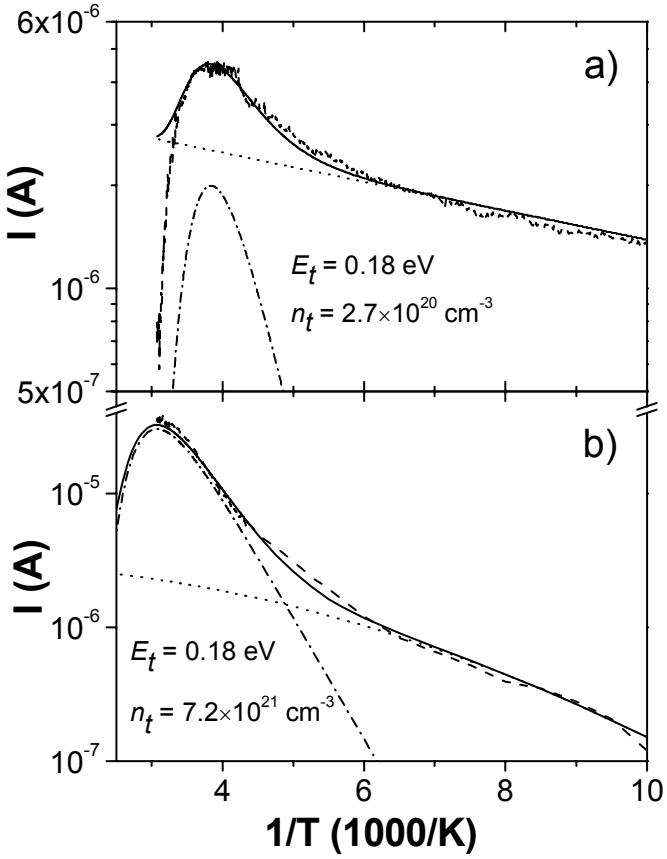

Fig. 4. Experimental curves (dashed curves) and their modelling (solid curves) by taking into account carrier mobility variation (dotted lines) and thermal generation of carriers (dash-dotted curves) in two samples (a and b)

Carrier mobility dependencies

Carrier mobility data could be compared by two different methods: TSCs and direct mobility measurements, presented in Fig. 5. In GDM charge transport in disordered organic conductors is supposed to proceed by means of hopping in a Gaussian site-energy distribution, reflecting the energetic spread in the charge transporting levels of chain segments due to fluctuation in conjugation lengths and structural disorder [9]:

$$\mu(F,T) = \mu_\infty \exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right] \exp\left\{C\left[\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right]\sqrt{F}\right\}. \quad (1)$$

This equation was derived from Monte-Carlo simulations of the hopping processes of charge carriers in a material with energetic (σ) and positional disorder (Σ) described by Gaussian distribution functions. μ_∞ is the high temperature limit of the mobility and C is a specific parameter that is obtained from the simulations as $C = 2.9\times10^{-4}$ (cm/V)$^{1/2}$. Fitting of the TSCs by GDM, shown in Figs. 4 by dotted lines, have given the following values: the positional disorder parameter Σ was equal to 4.5, and the parameter of energetic disorder σ ranged from 0.028 eV to 0.042 eV. The high-temperature mobility limit μ_∞ was found to be $(1.5\div1.9)\times10^{-3}$ cm^2/Vs, meanwhile coefficient C was $(4.5\div6)\times10^{-4}$ (cm/V)$^{1/2}$.

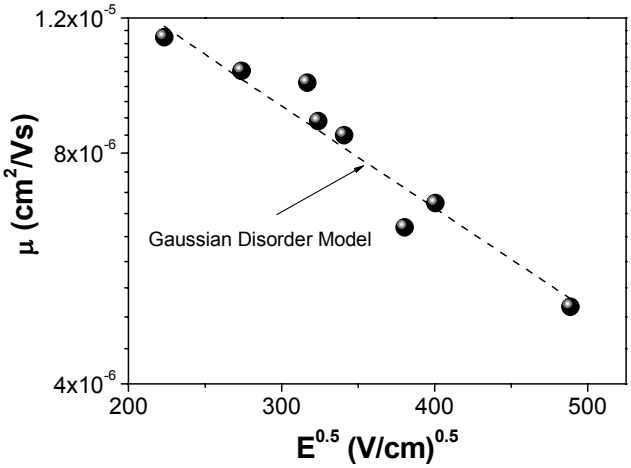

Fig. 5. Mobility dependence versus applied electric field strength and its fitting by the Gaussian Disorder Model.

The so-called negative mobility behaviour was observed in Fig. 5. Such behaviour is usually observed in materials in which carrier transport is governed by the positional disorder, rather than the energetic one. Similar behaviour was many times observed in different disordered materials as, e. g., molecularly doped polymers, molecular glasses, etc. In polymers, the negative mobility behaviour was first evidenced by the CELIV method in P3HT in [14] and P3OT in [15]. The prevailing role of positional disorder is quite logical in the investigated Solar cells with bulk heterojunction structure. The experimentally measured dependence in Fig. 5 was also fitted by the GDM with the following fitting parameters: $\Sigma = 4.5$, $\sigma = 0.045$ eV, $\mu_\infty = 9.5\times10^{-4}$ cm^2/Vs, $C = 1.8\times10^{-4}$ (cm/V)$^{1/2}$. It can be seen that the fitting parameters of the experimental data obtained by completely different methods coincide quite well. This evidences that carrier trapping is a decisive factor, giving their mobility behaviour.

SUMMARY AND CONCLUSIONS

We have investigated carrier transport and trapping in blends of 6 : 5 wt. P3HT:PCBM that are important for the development of organic Solar cells. The devices with the inverted layer sequence and solar efficiency of 3.7 % were analysed. We demonstrate that, though the fill factor of the IV characteristics is as high as 68 %, carrier trapping is effectively involved in the transport phenomena. The evaluated trapping state activation energy is about 0.18 eV and their density is up to $(10^{20}\div7\times10^{21})$ cm^{-3}. At such high density these states may probably act as transport states, limiting carrier mobility. The results were analyzed by taking into account mobility variation according to the Gaussian disorder model as well as carrier thermal generation from traps. The mobility parameters obtained by both methods demonstrate good coincidence.

Acknowledgments

The work was performed as a part of FP6 project OrgaPVNet. The samples of solar cells were kindly provided by M. Glatthaar, and A. Hinsch (Fraunhofer Institute for Solar Energy, Freiburg, Germany).

REFERENCES

1. **Kim, Y., Cook, S., Tuladhar, S. M., Choulis, S. A., Nelson, J., Durrant, J. R., Bradley, D. D. C., Giles, M., Mcculloch, I., Ha, C. S., Ree, M.** A Strong Regioregularity Effect in Self-Organizing Conjugated Polymer Films and High-Efficiency Polythiophene: Fullerene Solar Cells *Nature Materials* 5 (3) 2006: pp. 197 – 203.
2. **Pacios, R., Chatten, A. J., Kawano, K., Durrant, J. R., Bradley, D. D. C., Nelson, J.** Effects of Photo-Oxidation on the Performance of Poly[2-Methoxy-5-(3',7'-Dimethyloctyloxy)-1,4-Phenylene Vinylene]:[6,6]-Phenyl C-61-Butyric Acid Methyl Ester Solar Cells *Advanced Functional Materials* 16 (16) 2006: pp. 2117 – 2126.
3. **Offermans, T., Meskers, S. C. J., Janssen, R. A. J.** Electro-Optical Studies on MDMO-PPV:PCBM Bulk-Heterojunction Solar Cells on the Millisecond Time Scale: Trapped Carriers *Organic Electronics* 7 2006: pp 213 – 221.
4. **Kažukauskas, V., Čyras, V., Pranaitis, M., Apostoluk, A., Rocha, L., Sicot, L., Raimond, P., Sentein, C.** Influence of Polar Molecular Chain Orientation on Optical and Carrier Transport Properties of Polymer Blends *Organic Electronics* 8 2007: pp. 21 – 28.
5. **Renaud, C., Huang, C. H., Zemmouri, M., Le Rendu, P., Nguyen, T. P.** Study of Traps in Polydiacetylene Based Devices Using TSC Technique *The European Physical Journal - Applied Physics* 36 2006: pp. 215 – 218.
6. **Kažukauskas, V.** Investigation of Carrier Transport and Trapping by Oxygen-Related Defects in MEH-PPV Diodes *Semiconductor Science and Technology* 19 (12) 2004: pp. 1373 – 1380.
7. **Glatthaar, M., Niggemann, M., Zimmermann, B., Lewer, P., Riede, M., Hinsch, A., Luther, J.** Organic Solar Cells Using Inverted Layer Sequence *Thin Solid Films* 491 (1 – 2) 2005: pp. 298 – 300.
8. **Padinger, F., Rittberger, R. S., Sariciftci, N. S.** Effects of Postproduction Treatment on Plastic Solar Cells *Advanced Functional Materials* 13 (1) 2003: pp. 85 – 88.
9. **Juška, G., Arlauskas, K., Viliūnas, M., Kočka, J.** Extraction Current Transients: New Method of Study of Charge Transport in Microcrystalline Silicon *Physical Review Letters* 84 (21) 2000: pp. 4946 – 4949.
10. **Baessler, H.** Charge Transport in Disordered Organic Photoconductors. A Monte Carlo Simulation Study *Physica Status Solidi (b)* 175 (1) 1993: pp. 15 – 56.
11. **Simmons, J. G., Taylor, G. W.** High-Field Isothermal Currents and Thermally Stimulated Currents in Insulators Having Discrete Trapping Levels *Physical Review* B 5 1972: pp. 1619 – 1629.
12. **Kavaliauskienė, G., Kažukauskas, V., Rinkevičius, V., Storasta, J., Vaitkus, J. V., Bates, R., O'Shea, V., Smith, K. M.** Thermally Stimulated Currents in Semi-Insulating GaAs Schottky Diodes and Their Simulation *Applied Physics A* 69 1999:pp. 415 – 420.
13. **Chen, I.** Theory of Thermally Stimulated Current in Hopping Systems *Journal of Applied Physics* 47 1976: pp. 2988 – 2993.
14. **Mozer, A. J., Sariciftci, N. S., Pivrikas, A., Österbacka, R., Juška, G., Brassat, L., Bässler, H.** Charge Carrier Mobility in Regioregular Poly(3-Hexylthiophene) Probed by Transient Conductivity Techniques: A Comparative Study *Physical Review B* 71 (3) 2005: pp. 035214 (9 pages).
15. **Kažukauskas, V., Pranaitis, M., Sicot, L., Kajzar, F.** Negative Mobility Dependence in Different Regioregular Polythiophenes Revealed by the Charge Extraction by Linearly Increasing Voltage Method *Molecular Crystals and Liquid Crystals* 447 2006: pp. 459 – 471.