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Investigation the Dependence of Mobility on Carrier Concentration and Temperature in Organic Semiconductors

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ABSTRACT

The charge carrier mobility is a key performance criteria for organic semiconductors. High-mobility values allow fast device operation as needed for low-cost electronics on large areas with performance meeting market demands. Mobility is conveniently extracted from thin film transistors (TFT) characteristics using the standard gradual channel approximation model. This approach evaluates the mobility of charges during their transport through the high-density accumulation layer at the semiconductor-dielectric interface. This value is therefore directly representative of transistor operation and is a relevant parameter for device integration into circuits. In this paper we have calculated the mobility of an organic semiconductor, one can use percolation theory,. The current flows through the bonds connecting the sites in the network. So far, much attention has been devoted to explain the temperature dependence of the mobility. The model gives a non-Arrhenius-type temperature dependence, which has also been supported by numerical simulations and analytical calculations.

Keywords: Charge carrier mobility; organic semiconductor; amorphous organic materials; percolation theory

INTRODUCTION

Temperature-activated charge transport in disordered organic semiconductors at large carrier concentrations, especially relevant in organic field-effect transistors (OFETs), has been thoroughly considered using a recently developed analytical formalism assuming a Gaussian density-of-states (DOS) distribution and Miller-Abrahams jump rates. We show that this phenomenon is entirely due to the evolution of the occupational DOS profile upon increasing carrier concentration and this mechanism is specific to materials with Gaussian-shaped DOS. The suggested model provides compact analytical relations which can be readily used for the

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evaluation of important material parameters from experimentally accessible data on temperature dependence of the mobility in organic electronic devices. Experimental results on temperature-dependent charge mobility reported before for organic semiconductors by other authors can be well interpreted by using the model presented in this paper.

In high-mobility organic semiconductors and in short channel devices, however, the relative importance of the contact resistance R_c can be such that the standard model is no longer appropriate for mobility extraction. Proper parameter extraction is complicated by the fact that carrier injection from the contact into the semiconductor is often mediated by the gate voltage V_G. When this is not properly taken into account, it leads to serious over-estimation of the mobility. Therefore, a more accurate, yet simple, method is highly desirable for the proper evaluation of μ, the charge carrier mobility in thin films of organic semiconductors in the high-charge density accumulation layer. In this definition, μ characterizes the contact-independent translational motion of charge carriers across the thin film semiconductor material, over distances that may be larger than typical grain size. In this sense, μ encompasses extrinsic barriers to transport such as grain boundaries and therefore does not necessarily correspond to the intrinsic intra-grain charge carrier mobility of the monocrystalline semiconductor. [1]

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There is no general consensus on the mechanism of charge transport in these amorphous organic materials. A complete model of the electrical properties should include a description of the energy distribution of carriers and how the conduction varies as a function of carrier energy. Disorder-induced localized states are also important for the transport, and the essential problem is the relation between temperature, electric field, carrier concentration and the transport properties. Generally, charge transport in disordered materials is described either as hopping between localized states, or as trapping and release from localized states into higher energy mobile states. The degree of structural disorder may change the mechanism even within the same class of polymer. [5]

Because the electronic structure of polymer films is not known exactly, a simplified model has to be assumed. The model assuming that the energy distribution is Gaussian due to the random disorder in the material. The standard deviation of Gaussian is around 0.1 eV and increases with increasing disorder of the material. To simplify the calculations, an electronic structure comprising an exponential tail in the bandgap is often used as well. [6, 7]

In this chapter, we present three different models to describe the carrier concentration dependence of the mobility, the temperature and electric field dependence, and a unified mobility model that can explain the temperature, electric field and carrier concentration characteristics together. [8]

Recently it has been realized that the carrier concentration plays an important role for the mobility. Experiments show that for a hole-only diode and a FET fabricated from the same conjugated polymer, the mobility could differ up to three orders of the magnitude [9]. This difference can only be explained by taking into account the dependence of mobility on the carrier concentration. This problem with the concept of a transport energy E_t, but there is no direct proof for the existence of such transport energy in organic systems. In this work we will focus on explain the discrepancy of mobilities measured in OLEDs and OFETs. [10,11]

In this section, an analytical mobility model with a Gaussian DOS function has been obtained. It can explain the relation between the mobility and carrier concentration. Results are in good agreement with experimental data.

CALCULATION AND MODEL

To calculate the mobility of an organic semiconductor, one can use percolation theory,. The current flows through the bonds connecting the sites in the network. The conductance between the states m and m' can be described as

$$Z_{mm'}^{-1} = Z_0^{-1} \exp(-2\alpha(R_m - R_{m'})) \exp \left(-\frac{(E_m - E_F) + (E_{m'} - E_F) + E_m}{2k_B T} \right) \qquad (1)$$

Where Z_0^{-1} is a prefactor, α^{-1} is the Bohr radius of the localized wave functions, T is the temperature, R_m and E_m denote the position and energy of site m. In theory the value of $Z_{mm'}$ is determined by the threshold or critical conductance Z_c, at which the first infinite cluster will form, given by the relation

$$\sigma = \sigma_0 Z_c^{-1}. \qquad (2)$$

Here σ_0 is a prefactor. To describe the field-effect mobility in organic semiconductors .

$$g(E) = \frac{N_t}{k_B T_0} \exp\left(\frac{E}{k_B T_0}\right) \qquad (E \leq 0) \qquad (3)$$

N_t is the number of states per unit volume and T_0 specifies the width of the exponential distribution. Connecting Equation (2) and Equation (3), the conductivity can be described as [12,13].

$$\sigma(\delta,T) = \sigma_0 \left(\frac{\pi \delta N_t (T_0/T)^3}{(2\alpha)^3 B_c \Gamma(1 - T_0/T) \Gamma(1 + T_0/T)} \right)^{T_0/T}. \tag{4}$$

Here B_c is the critical number of bonds per site and δ is the fraction of occupied states, defined as

$$\delta \cong \exp\left(\frac{\epsilon_F}{k_B T_0} \right) \Gamma(1 - T/T_0) \Gamma(1 + T/T_0), \tag{5}$$

Γ is the gamma function. Then an expression for the mobility as a function of the carrier concentration n can be obtained.

$$\mu(n,T) = \frac{\sigma_0}{q} \left(\frac{(T_0/T)^4 \sin(\pi T/T_0)}{(2\alpha)^3 B_c} \right)^{T_0/T} n^{T_0/T-1}. \tag{6}$$

However, this expression cannot account for the carrier concentration independent mobility when the carrier concentration is very low (LED regime). To overcome this problem, we derive another mobility model assuming a Gaussian DOS and VRH theory. In this model, the DOS function is given as [14,15].

$$g(E) = \frac{N_t}{\sqrt{\pi} k_B T_\sigma} \exp\left[-\left(\frac{E}{k_B T_\sigma} \right)^2 \right]. \tag{7}$$

Here E is the energy measured relative to the center of the DOS and T_σ indicates the width of the DOS. The value of the Fermi energy E_F can be determined by the equation for the carrier concentration n.

$$n = \int_{-\infty}^{\infty} \frac{g(E)dE}{1 + \exp((E - E_F)/k_B T)}. \tag{8}$$

At low concentration, the exponential function is large compared to one (the nondegenerate case) [16], and we obtain the Fermi energy as

$$E_F = -\frac{k_B T_\sigma^2}{4T} + k_B T \ln \delta. \tag{9}$$

According to percolation theory [17,18], at the onset of percolation, the critical number B_c can be written as

$$B_c = \frac{N_b}{N_s}. \tag{10}$$

$B_c = 2.8$ for a three-dimensional amorphous system, N_b and N_s are, respectively, the density of bonds and density of sites in a percolation system, which can be calculated as [19,20]

$$N_b = \int d\mathbf{R}_{ij} dE_i dE_j g(E_i) g(E_j) \theta(s_c - s_{ij}) \tag{11}$$

and

$$N_s = \int dE g(E) \theta(s_c k_B T - |E - E_F|). \tag{12}$$

Here R_{ij} denotes the distance vector between sites i and j, s_c is the exponent of the conductance given by the relation $\sigma = \sigma_0 e^{-s_c}$ [21,22] and θ is step function. Substituting (10) and Equation (11) into Equation (12), we obtain a new percolation criterion for an organic system as

$$B_c \approx \frac{2N_t(\sqrt{2}+1)\sqrt{\pi}}{(2\alpha T/T_\sigma)^3} \left(\frac{E_F + k_B T s_c}{k_B T_\sigma} \right)^2 \exp\left(-\left[\frac{E_F + k_B T s_c}{k_B T_\sigma} \right]^2 \right) \tag{13}$$

This equation has to be solved for s_c and an expression for mobility can be obtained. [23]

$$\mu = \frac{\sigma_0}{qN_t} \exp\left(\eta\right), \qquad (14)$$

where

$$\eta = -\frac{T_\sigma}{T}\sqrt{-W\left[-\frac{B_c\left(2\alpha T/T_\sigma\right)^3}{2\pi N_t\left(1+\sqrt{2}\right)}\right]} - \frac{T_\sigma^2}{4T^2} \qquad (15)$$

W is the Lambert function [24]. Equation (15) is obtained assuming: that the site positions are random, the energy barrier for the critical hop is large and the charge carrier concentration is very low.

RESULTS AND DISCUSSION

So far, much attention has been devoted to explain the temperature dependence of the mobility .As shown in Fig 1, the model gives a non-Arrhenius-type temperature dependence, which has also been supported by numerical simulations and analytical calculations. The model shows good agreement for a value $C \approx 0.71$.

In Fig. 2, the mobility is plotted. When plotted in this way, there exists the regime with a linear relation between μ and $T^{-1/3}$. This indicates that the variable-range hopping effect has to be taken into account.

The degenerate limit of organic semiconductors has been studied in [17]. In Fig 3 (a) we show the Fermi energy for Boltzmann and Fermi-Dirac distributions assuming some typical values of the parameter T_σ / T as 1.5, 3.5 and 6.0 [21]. Fig 3 (b) is a comparison especially for the higher carrier occupation regime. The analytical result Equation (7) agrees well with the numerically calculated result for decreasing carrier occupation and increasing T_σ / T . Therefore, for the LED regime with low charge carrier concentration, Equation (7) is a good approximation of the solution of Equation (6).

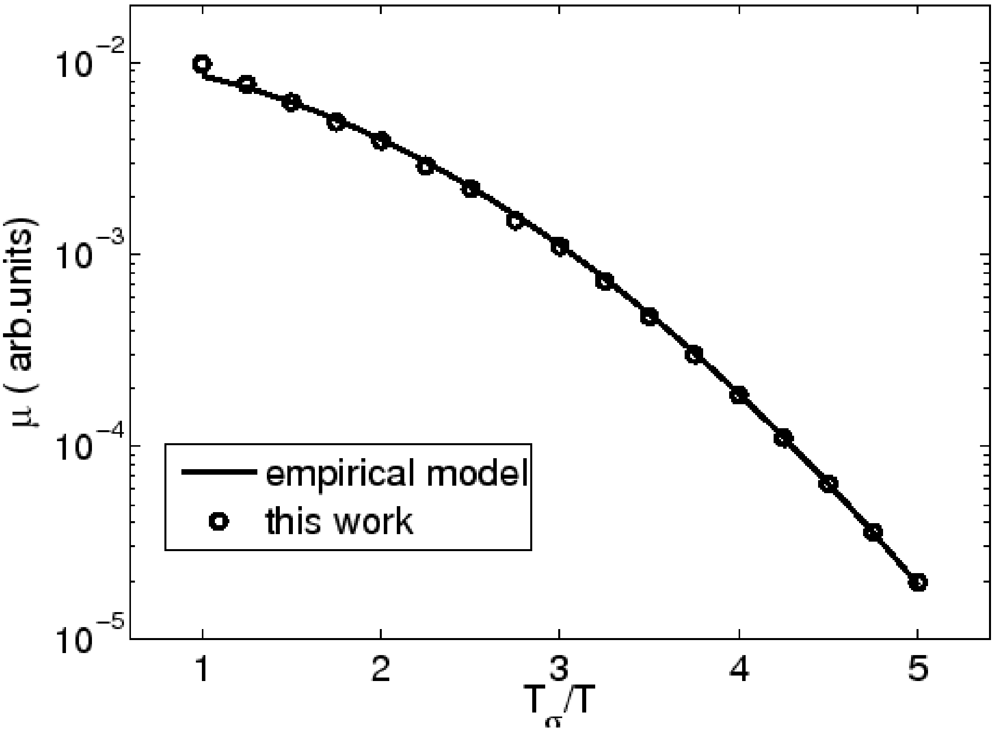


Fig. 1. Comparison between the analytical model and empirical model for different temperature.

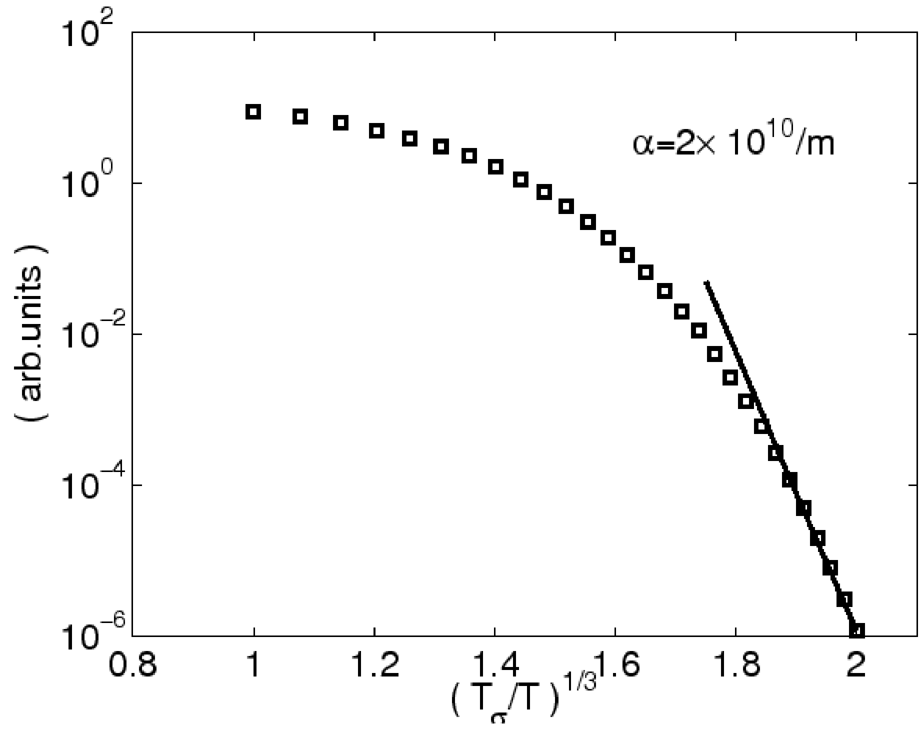
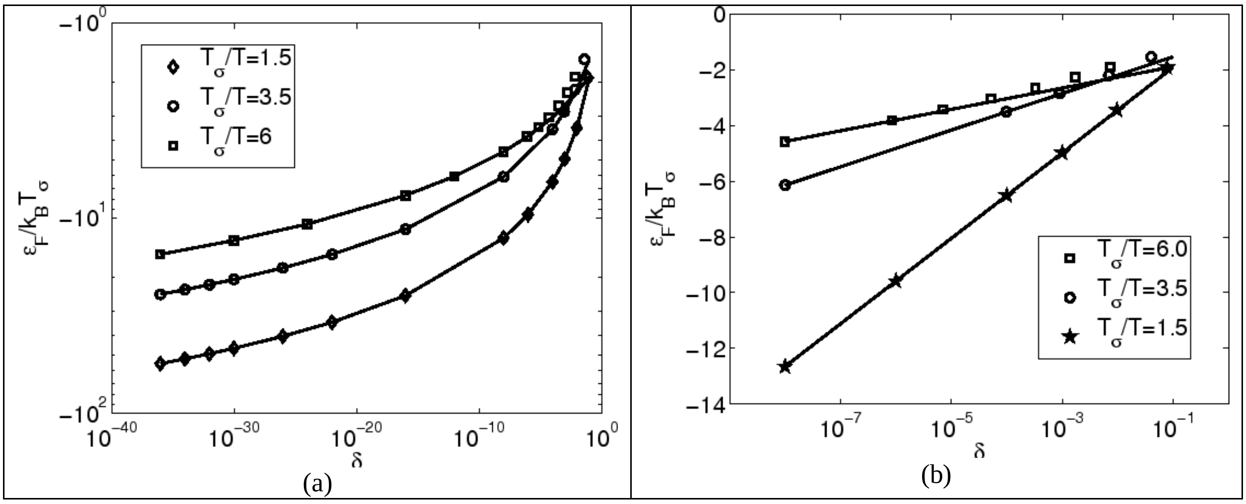


Fig. 2. The mobility as a function of for different α.



(a)

(b)

Fig. 3. Fermi-energy as a function of the carrier occupation probability. The symbols represent Fermi-Dirac and the solid lines Boltzmann represent statistics. Panel (a) shows the case of carrier occupation between 10^{-40} and 1. Panel (b) shows the case of carrier occupation bigger than 10^{-10}.

The mobility as a function of the carrier concentration is presented in Fig 4, where T_σ/T is in the range $1.5-9$, corresponding to some typical values for organic semiconductors. The mobility stays constant until a certain threshold value of the carrier occupation. Above this threshold, the mobility can increase about four orders of magnitude at $T_\sigma/T=9$. These effects have also been observed experimentally.

However, (9) is valid only in the LED regime with very low carrier concentration. As it is difficult to get an analytical expression for the mobility at higher carrier concentration, we use Equation (4) as the mobility model for the higher carrier concentration. The combined model can explain the experimental data in [19],as shown in Fig. 5.

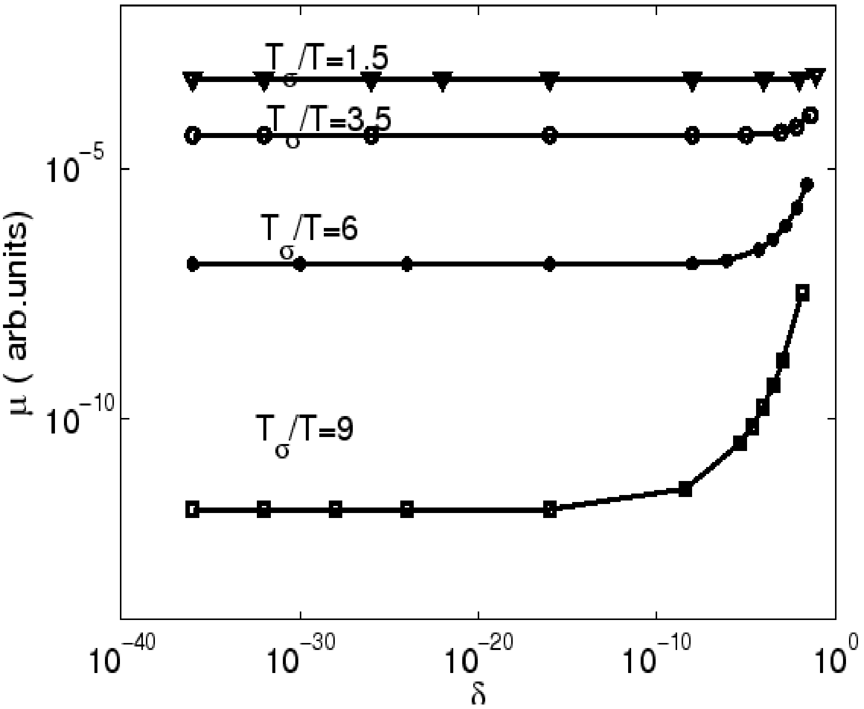


Fig. 4. The calculated mobility versus carrier occupation at different temperature.

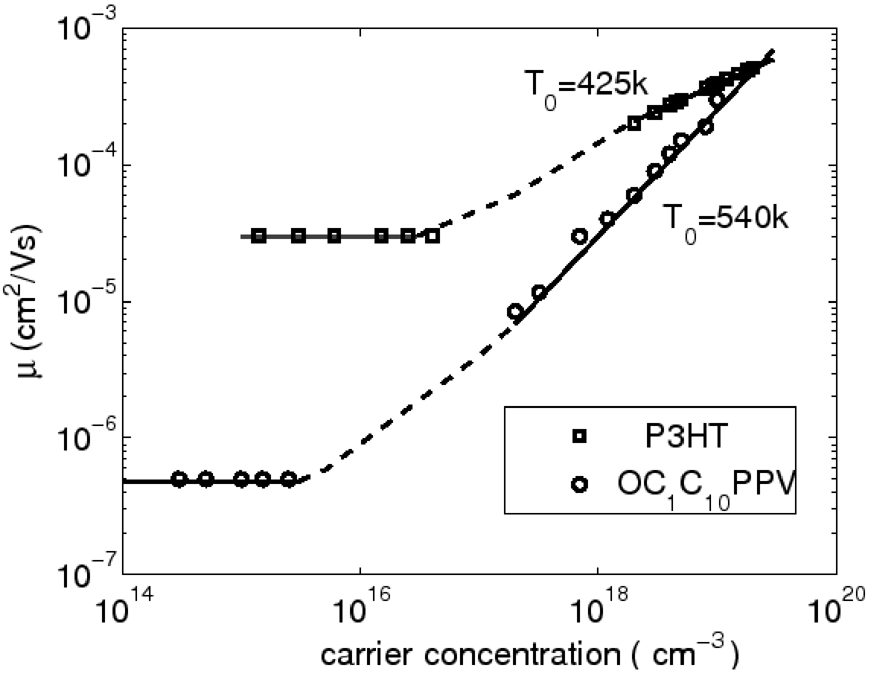


Fig. 5. Comparison between calculation and typical experimental results.

The curves results plotted in Figure 3 and Figure 4 show that the increment of mobility increases with charge carriers density for both the lower and higher densities for all the temperatures specified here. However, at temperature T=235 K the mobility is independent of density in the low density region in a narrow range between 10^{14} to $4\times10^{14}\,\mathrm{cm}^{-3}$. The reason for the increment of mobility with charge carriers density in a disordered Gaussian energy system is connected to the filling of the deep states due to, as described above, the impact that the density has on Fermi-energy, and also on the localization length. When the density increases the deep states are filled and the Fermi-energy are lifted up. Increasing charge carriers density can, also, increase the localization length. These lead to an increment of the average hopping rate of a charge carrier, which in turn leads to the increment of a charge carrier mobility. This means that mobility variation with the density presupposes the presence of deep states (or states with lower energies) and because of this the variation of mobility with density is more pronounced when, for the disorder energy, the energy distribution width (σ) is more or the temperature is less. Our simulation results found in the higher density region has similarity with the results demonstrated experimentally. However, the results we got for the lower density region, though similar with the numerical results reported in, are at variance with the general conclusion made in which says that mobility is independent of density in the low density region. The variation shown with the experimental results is due to the fact that the effects of electric field and density were not separated in the experiment. The effect of density on mobility, particularly, in the low density region can be compromised with that of the electric field which is visible when we examine the curves for two different electric fields shown in Figure 3 and Figure 4. The charge carriers density dependence on mobility is more vivid in Figure 4 where the electric field is F=0.05×σ/σeb than in Figure 3 where F=0.1×σ/σeb. The value of the electric field used in these experiments was close to the latter and because of this the influence of the charge carriers is suppressed.

REFERENCES

[1] C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, Plastic Solar Cells, Adv. Funct. Mater., 11 (2001) 15.

[2] F. C. Krebs, Fabrication and processing of polymer solar cells: A review of printing and coating techniques, Sol. Energy Mater. Sol. Cells, 93 (2009) 394-412.

[3] G. Li, R. Zhu, and Y. Yang, Polymer solar cells, Nature Photon., 6 (2012) 153161.

[4] H. Hoppe and N. S. Sariciftci, Organic solar cells: An overview, J. Mater. Res., 19 (2004)19241945.

[5] M. K. Wei, C. W. Lin, C. C. Yang, Y. W. Kiang, J. H. Lee, H. Y. Lin, Emission characteristics of organic light-emitting diodes and organic thin-films with planar and corrugated structures, Int. J. Mol. Sci., 11 (2010) 1527-1545.

[6] S. Kappaun, C. Slugovc, E. J. W. List, Phosphorescent organic light-emitting devices: Working principle and iridium based emitter materials, Int. J. Mol. Sci., 9 (2008) 1527-1547.

[7] C. Liang, Y. Wang, D. Li, X. Ji, F. Zhang, Z. He, Modeling and simulation of bulk heterojunction polymer solar cells, Sol. Energy Mater. Sol. Cells, 127 (2014) 67–86.

[8] T. Tromholt, M. Manceau, M. Helgesen, J. E. Carle, F. C. Krebs, Degradation of semiconducting

polymers by concentrated sunlight, Sol. Energy Mater. Sol. Cells, 95 (2011) 1308.

[9] Y. Zhou, J. Pei, Q. Dong, X. Sun, Y. Liu, W. Tian, Donor- Acceptor Molecule as the Acceptor for Polymer-Based Bulk Heterojunction Solar Cells, J. Phys. Chem. C, 113 (2009) 7882.

[10] D. Rezzonico, B. Perucco, E. Knapp, R. Hausermann, N. A. Reinke, F. Muller, B. Ruhstaller, Numerical analysis of exciton dynamics in organic light-emitting devices and solar cells, J. of Photonics for Energy, 1 (2011) 011005-1.

[11] J. D. Kotlarski, L. J. A. Koster, P. W. M. Blom, M. Lenes, and L. H. Slooff, Combined optical and electrical modeling of polymer:fullerene bulk heterojunction solar cells, J. Appl. Phys. 103 (2008) 084502.

[12] A. H. Fallahpour, A. Gagliardi, F. Santoni, D. Gentilini, A. Zampetti, M. Auf der Maur, and A. Di Carlo Modeling and simulation of energetically disordered organic solar cells, J. Appl. Phys., 103(2014) 184502.

[13] L. J. A. Koster, E. C. P. Smits, V. D. Mihailetchi, P. W. M. Blom, Device model for the operation of polymer/fullerene bulk heterojunction solar cells, Phys. Rev. B, 72 (2005) 085205.

[14] A.Mahmoudloo, Transient Trap-Limited Field Dependence charge carrier transport in organic semiconductors for time of flight configuration, Journal of Optoelectronical Nanostructures, 6.3. (2021)

[15] J. Nelson, J. J. Kwiatkowski, J. Kirkpatrick, and J. M. Frost, Modeling charge transport in organic photovoltaic materials, Acc. Chem. Res., 42 (2009) 1768.

[16] F. F. Stelzl, Uli Wurfel, Modeling the influence of doping on the performance of bulk heterojunction organic solar cells: One-dimensional effective semiconductor versus two-dimensional onor/acceptor model, Phys. Rev. B., 86 (2012) 075315.

[17] B. Ray and M. A. Alam, Random vs regularized OPV: Limits of performance gain of organic bulk heterojunction solar cells by morphology engineering, Sol. Energy Mater. Sol. Cells, 99 (2012) 204.

[18] M. Pfeiffer , K. Leo, X. Zhou, J.S. Huang, M. Hofmann, A. Werner, J. Blochwitz-Nimoth, Doped organic semiconductors: Physics and application in light emitting diodes, Organic Elec. 4 (2003) 89103.

[19] B. A. Gregg, Transport in Charged Defect-Rich p-Conjugated Polymers, J. Phys. Chem. C, 113 (2009) 5899.

[20] B. A. Gregg, Charged defects in soft semiconductors and their influence on organic photovoltaics, Soft Matter., 5 (2009) 2985

[21] A. Nollau, M. Pfeiffer, T. Fritz, K. Leo, Controlled n-type doping of a molecular organic semiconductor: naphthalenetetracarboxylic dianhydride (NTCDA) doped with bis (ethylenedithio)- tetrathiafulvalene (BEDT-TTF), J. Appl. Phys., 87 (2000) 4340-4343.

[22] A. Veysel Tunc, A. De Sio, D. Riedel, F. Deschler, E. Da Como, J. Parisi, E. von Hauff, Molecular doping of low-bandgap-polymer: fullerene solar cells: Effects on transport and solar cells, Org. Electron., 13 (2012) 290.

[23] B. Maennig, M. Pfeiffer, A. Nollau, X. Zhou, K. Leo, P. Simon, Controlled p-type doping of polycrystalline and amorphous organic layers: Self-consistent description of conductivity and field-effect mobility by a microscopic

percolation model, Phys. Rev. B, 64 (2001) 195208.

[24] V. A. Trukhanov, V. V. Bruevich, and D. Y. Paraschuk, Effect of doping on performance of organic solar cells, Phys. Rev. B, 84 (2011) 205318.

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بررسی وابستگی تحرک پذیری به چگالی حاملین بار و دما در نیم رساناهای آلی

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چکیده

تحرک پذیری حاملین بار معیار کلیدی برای عملکرد نیمه هادی های آلی است. تحرک پذیری بالا امکان عملکرد سریع دستگاه را در صورت نیاز برای وسایل الکترونیکی کم‌هزینه در مناطق بزرگ با عملکردی که نیازهای بازار را برآورده می‌کند، می‌سازد. تحرک پذیری ، از ویژگی های ترانزیستورهای لایه نازک (TFT) با استفاده از مدل تقریب کانال تدریجی استاندارد استخراج می شود. رویکرد تحرک پذیری بارها را در طول ترابرد آنها از طریق لایه تجمعی با چگالی بالا در رابط نیم رسانا–دی الکتریک ارزیابی می کند. بنابراین، اندازه تحرک پذیری مستقیماً نماینده عملکرد ترانزیستور است و یک پارامتر مرتبط برای ادغام دستگاه در مدارها است. برای محاسبه تحرک پذیری یک نیم رسانای آلی، می توان از نظریه نفوذ استفاده کرد. جریان از طریق پیوندهایی که سایت ها را در شبکه به هم وصل می کنند جریان می یابد. تا کنون، توجه زیادی به توضیح وابستگی دمایی تحرک پذیری اختصاص داده شده است. این مدل یک وابستگی دمایی غیر از نوع آهارانیوس را ارائه می دهد که توسط شبیه سازی های عددی و محاسبات تحلیلی نیز پشتیبانی شده است.

کلید واژه‌ها: تحرک پذیری حاملین بار؛ نیم رساناهای آلی؛ مواد آلی آمورف؛ تئوری نفوذ

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