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Carrier concentration dependence of the mobility in organic semiconductors

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Abstract

Charge transport in organic materials as a function of carrier concentration is investigated. An analytical model of the concentration dependent mobility based on the variable hopping range theory is formulated. This model is applied to analyze the discrepancy between the experimental mobilities extracted from FETs and LEDs. The result shows that an exponential density of states (DOS) is a good approximation of the tail states for describing the charge transport in FETs. When applied to the low carrier concentration regime, for example to the LEDs regime, a Gaussian DOS should be assumed.

1. Introduction

Organic semiconductors have witnessed a considerable development in recent years, mainly pushed by commercial display applications based on LEDs [1,2] whose cost and performance are potentially better compared with more conventional solutions. At the same time, interest has also grown for organic thin film transistors (TFTs) [3]. However, the main obstacle to further application of organic transistors is the poor mobility which can be several order of magnitudes smaller than that of conventional semiconductors. Another problem is the lack of knowledge of the microscopic charge transport mechanisms [4]. However, understanding the carrier transport properties in these organic materials is of crucial importance to design and synthesize better materials and to improve device performance.

In organic semiconductors, intramolecular interactions are mainly covalent, but intermolecular interactions are due to much weaker van der Waals and London forces. As a result, the transport bands in organic crystals are much narrower than those of their inorganic counterparts, and the band structure is easily disrupted by disorder in such systems. This disorder causes the formation of localized states in the energy gap. In order to enable a current through the device, charge carriers trapped at the localized states need to escape from these sites. Such a conduction process is entirely determined by the tunneling transitions of carriers between the localized states, provided that the electronic wave functions of the localized states have sufficient overlap. This theory was originally given by Mconwell [5] and Mott [6]. A more systematic theory called variable range hopping (VRH) was introduced by Mott in 1968 [7]. The transport properties of organic semiconductors can be well described by VRH theory [8–10]. The central transport quantity is the mobility μ of the charge carriers and most of the work related to the mobility is on the temperature and electric field dependence. Recently, it has been realized that the carrier concentration also 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 [11]. This difference can only be explained by taking into account the dependence of mobility on the carrier concentration. Rubel et al. [10] analyzed this problem with the concept of a transport energy ϵ_t, but there is no direct proof for the existence of such transport energy in organic systems. In this paper, we will focus on extending the percolation model based on VRH theory by Vissenberg [12] to explain the discrepancy of measured mobilities in OLEDs and OFETs. 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.

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2. Theory

To calculate the mobility of an organic semiconductor, one can use percolation theory, regarding such system as a random resistor network (network of Miller and Abrahams) [4,13]. The current flows through the bonds connecting sites in the network. The conductance between the states m and m' can be described as

$$Z_{mm'}^{-1} = Z_0^{-1} \exp(-2\alpha|R_m - R_{m'}|) \exp\left(-\frac{|\epsilon_m - \epsilon_F| + |\epsilon_{m'} - \epsilon_F| + |\epsilon_{m'} - \epsilon_m|}{2k_B T}\right).$$

where Z_0^{-1} is a prefactor, α^{-1} the Bohr radius of the localized wave functions and R_m and ϵ_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

$$\sigma = \sigma_0 Z_c^{-1}. \tag{1}$$

Here, σ_0 is a prefactor. To describe the field-effect mobility in organic transistors, Vissenberg assumed an exponential density of localized states [12].

$$g(\epsilon) = \frac{N_t}{k_B T_0} \exp\left(\frac{\epsilon}{k_b T_0}\right) \quad (\epsilon \le 0) \tag{2}$$

where N_t is the number of states per unit volume and T_0 specifies the width of the exponential distribution. Connecting (1) and (2), conductivity can be described as [12]

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

Here, δ is the fraction of occupied states, and B_c is the critical number of bonds per site. Then an expression for the mobility as a function of the carrier concentration n can be obtained.

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

Here, e is the elementary charge. However, this expression can not account for the carrier concentration independent mobility when the carrier concentration is very low (LED regime). To overcome this problem, we derive a new mobility model assuming a Gaussian DOS [4] and VRH theory. In this model, the DOS function is given as

$$g(\epsilon) = \frac{N_t}{\sqrt{\pi} k_B T_\sigma} \exp\left[-\left(\frac{\epsilon}{k_B T_\sigma}\right)^2\right]. \tag{5}$$

It is slightly different from [4], where ϵ 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 ϵ_F can be determined by the equation for the carrier concentration n.

$$n = \int_{-\infty}^{\infty} \frac{g(\epsilon)\, d\epsilon}{1 + \exp((\epsilon - \epsilon_F)/k_B T)}. \tag{6}$$

At low n, the exponential function is large compared to one (the non-degenerate case) [14], and we obtain the Fermi energy as

$$\epsilon_F = -\frac{k_B T_\sigma^2}{4T} + k_B T \ln \delta. \tag{7}$$

According to percolation theory [15], at the onset of percolation, the critical number B_c can be written as

$$B_c = \frac{N_b}{N_s}. \tag{8}$$

where $B_c = 2.8$ 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 [16,12]

$$N_b = \int d\mathbf{R}_{ij}\, d\epsilon_i\, d\epsilon_j g(\epsilon_i) g(\epsilon_j) \theta(s_c - s_{ij})$$

and

$$N_s = \int d\epsilon g(\epsilon) \theta(s_c k_B T - |\epsilon - \epsilon_F|).$$

Here, $\mathbf{R_{ij}}$ denotes the distance vector between sites i and j, s_c the exponent of the conductance given by the relation $\sigma = \sigma_0 e^{-s_c}$ [17] and θ is step function. Substituting (5) and (7) into (8), we obtain a new percolation criterion for an organic system as

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

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

$$\mu = \frac{\sigma_0}{e N_t} \exp(\eta) \tag{9}$$

where

$$\eta = -\frac{T_\sigma}{T} \sqrt{-W\left[-\frac{B_c (2\alpha T/T_\sigma)^3}{2\pi N_t (1 + \sqrt{2})}\right]} - \frac{T_\sigma^2}{4T^2} \tag{10}$$

where W is the Lambert function [18]. Eq. (9) 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.

3. Results and discussions

So far, much attention has been devoted to explain the temperature dependence of the mobility [19,20]. As shown in Fig. 1, the model (9) gives a non-Arrhenius-type temperature dependence of the form $\mu \propto \exp(-(C\sigma/k_B T)^2)$, which has also been supported by numerical simulations [21] and analytical calculations [22]. The model (9) shows good agreement for a value $C \approx 0.71$. This value is close to $C \approx 0.69$ given in ref. [23] and

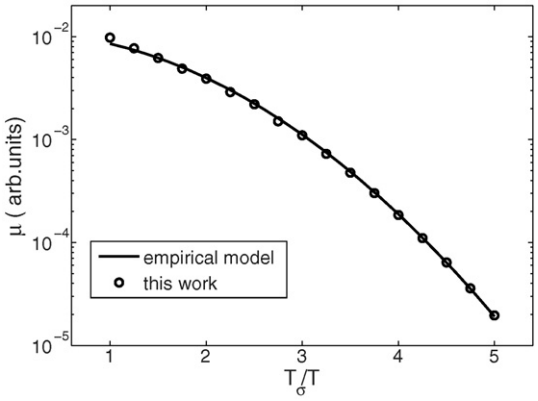

Fig. 1. Comparison between this work and the empirical model $\mu \approx \exp(-(C\sigma/k_B T)^2)$ for different temperature.

0.64 in ref. [22]. In Fig. 2, the mobility is plotted as a function of $(T_\sigma/T)^{1/3}$. When plotted in this way, there exists a regime with a linear behavior between μ and $T^{-1/3}$. This indicates that the variable-range hopping effect has to be taken into account [24,25].

To obtain (7), a Boltzmann distribution function has been used. The degenerate limit of organic semiconductors has been studied in [26,27]. In Fig. 3(a) we show the Fermi energy for Boltzmann and Fermi-Dirac distribution assuming some typical values of the parameter T_σ/T as 1.5, 3.5 and 6.0 [19], Fig. 3(b) is a comparison especially for the higher carrier occupation regime. The analytical result (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, (7) is a good approximation of the solution of (6).

The mobility as a function of the carrier concentration is presented in Fig. 4, where T_σ/T is in the range 1.5–9.0, 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 been observed in the experimental work [11,28].

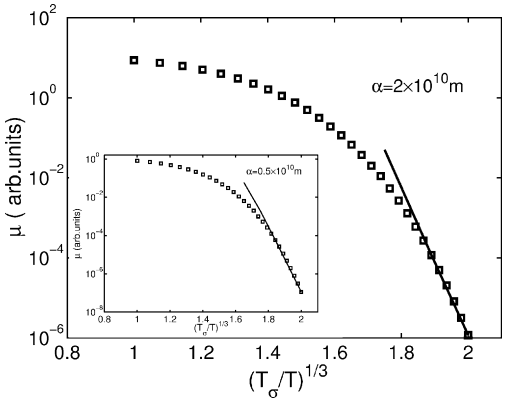

Fig. 2. The mobility as a function of $(T_\sigma/T)^{1/3}$ at different α.

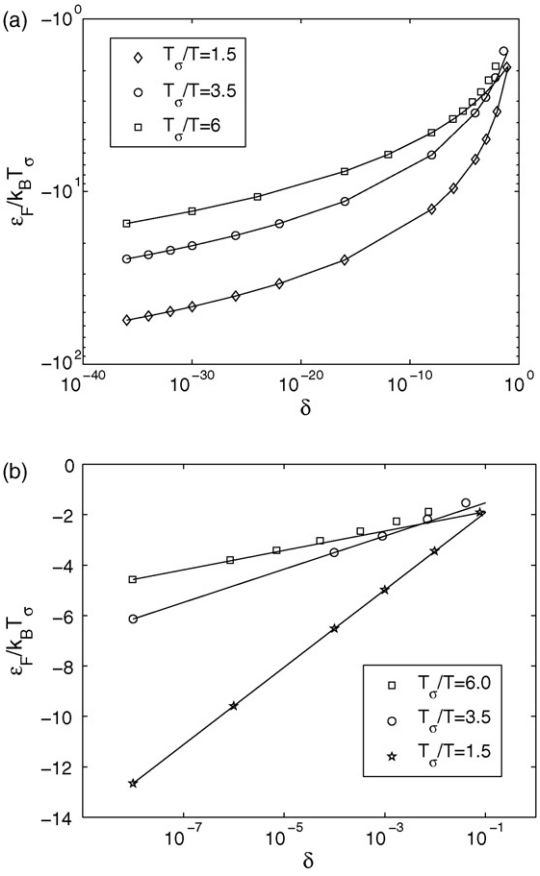

Fig. 3. Fermi-energy as a function of the occupation probability. The symbols represent Fermi-Dirac distribution and the solid lines Boltzmann distribution. (a) Shows the case of carrier occupation between 10^{-40} and 1 and (b) shows the case of carrier occupation bigger than 10^{-10}.

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 (4) as the mobility model for the higher carrier concentration. The combined model can explain the experimental data in [28,11], as shown in Fig. 5.

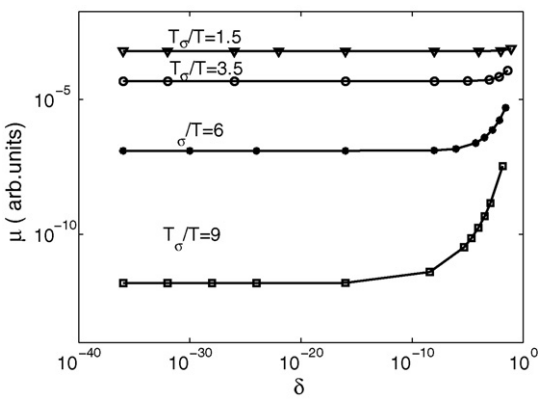

Fig. 4. The calculated mobility vs. carrier occupation at different temperature.

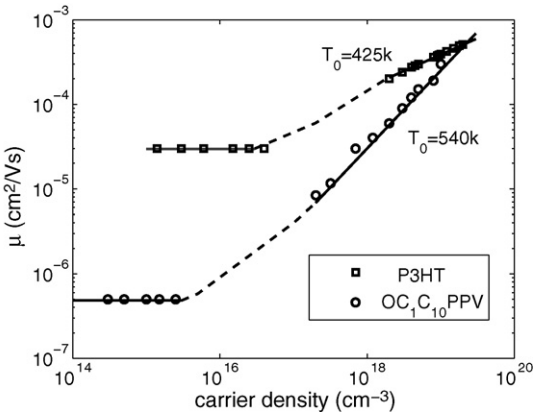

Fig. 5. Comparison between calculation and typical experimental results [11].

4. Conclusion

An analytical mobility model has been obtained on the basis of variable range hopping theory. This model can explain the relation between mobility and carrier concentration, especially the mobility's independence of the carrier concentration in the LED regime. We can conclude that a Gaussian density of states function is a better description for the low carrier concentration regime than an exponential one. The model also gives non-Arrhenius temperature characteristics.

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References

[1] A.B. Walker, A. Kambili, S.J. Martin, J. Phys.: Condens. Matter 14 (2002) 9825–9876.
[2] N.C. Greenham, S.C. Moratti, D.D.C. Bradley, R.H. Friend, A.B. Holmers, Nature 365 (1993) 628–630.
[3] C.J. Drury, C.M.J. Mustaers, C.M. Hart, M. Matters, D.M.de. Leeuw, Appl. Phys. Lett. 73 (1998) 108.
[4] H. Bassler, Phys. Stat. Sol. (b) 175 (1993) 15–56.
[5] E. Mconwell, Phys. Rev. 103 (1) (1956) 51–61.
[6] N.F. Mott, J. Phys. 34 (1956) 1356.
[7] N.F. Mott, J. Non-Cryst. Solids 1 (1968) 1.
[8] B. Maennig, M. Pfeiffer, A. Nollau, K. Leo, Phys. Rev. B 64 (2001) 1952081–1952089.
[9] C. Godet, J. Non-Cryst. Solids 299 (2002) 333–338.
[10] O. Rubel, S.D. Baranovskii, P. Thomas, Phys. Rev. B 69 (2004) 0142061–0142065.
[11] C. Tanase, E.J. Meijer, P.W.M. Blom, D.M. de Leeuw, Phys. Rev. Lett. 91 (2003) 216601–216604.
[12] M.C.J.M. Vissenberg, M. Matters, Phys. Rev. B 57 (1998) 12964–12967.
[13] A. Miller, E. Abrahams, Phys. Rev. 120 (1960) 744–755.
[14] I.P. Zvyagin, A.V. Plyukhin, Mos. Univ. Phys. Bull. 45 (1990) 84–88.
[15] V.A. Mbegaokar, B.I. Halperin, J.S. Langer, Phys. Rev. B 4 (1971) 2612.
[16] P.N. Butcher, Linear and Nonlinear Electron Transport in Solids, Plenum, New York, USA.
[17] M. Sahimi, Applications of Percolation Theory, Taylor Francis, London, UK, 1994.
[18] R.M. Corless, G.H. Gonner, D.E.G. Hare, Adv. Commun. Math. 5 (1996) 329–359.
[19] P.M. Borsenberger, E.H. Magin, M.V. der Auweraer, F.C. de Schryver, Phys. Status Solidi B 175 (1993) 15.
[20] C. Godet, Philos. Mag. Lett. 83 (2003) 691–698.
[21] G. Schonherr, H. Bassler, M. Silver, Philos. Mag. B 44 (1981) 369.
[22] B. Movaghar, M. Grunewald, H. Bassler, D. Wurtz, Phys. Rev. B 33 (1986) 5545–5554.
[23] H. Bassler, Hopping and Related Phenomena: Advances in Disordered Semiconductors, World Scientific, Sigapore, 1990.
[24] S. Boutiche, http://hal.ccsd.cnrs.fr/docs/00/03/00/41/PDF/, 2001, pp. 1–10.
[25] K. Horiuchi, S. Uchinobu, A. Hashii, Appl. Phys. Lett. 85 (2004) 1987–1989.
[26] G. Paasch, P.H. Nguyen, S.L. Drechsler, Syn. Met. 97 (1998) 255–265.
[27] Y. Preezant, Y. Roichman, N. Tessler, J. Phys.: Condens. Matter 14 (2002) 9913–9924.
[28] C. Tanase, P.W.M. Blom, D.M. de Leeuw, D. Leeuw, Phys. Stat. Sol. (a) 201 (2004) 1236–1245.