Influence of traps on charge transport in organic semiconductors

Ling Li *, Gregor Meller, Hans Kosina

Institute for Microelectronics, TU Vienna, Gusshausstraße 27-29, A-1040 Wien, Austria

Received 12 July 2006; received in revised form 17 December 2006; accepted 18 January 2007

The review of this paper was arranged by Prof. Y. Arakawa

Abstract

The effect of extrinsic traps on the charge transport in organic semiconductors has been investigated. An analytical model describing hopping transport with traps is formulated on the basis of percolation theory. The results show that the presence of a trap distribution with energy offset and width different from that of the intrinsic density of states does not change the basic phenomenology of hopping transport, as revealed by the temperature dependence of the conductivity at high temperature. However the traps may significantly affect the transport at low temperature. The relation between trap concentration and conductivity is discussed. The model predictions are in good agreement with experimental results.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Traps; Conductivity model; Organic semiconductor; Percolation theory

1. Introduction

Over the past 10 years, the interest in organic semiconductors has increased dramatically. Devices such as organic light emitting diodes and organic field effect transistors have been realized [3,4]. In spite of these successful applications, the physical processes underlying the charge transport in organic semiconductors are not well understood. For example, a proper description of the effect of traps on charge transport is still a challenge. Extrinsic localized states differ from the majority of intrinsic hopping states in disordered media in that they require a substantially larger energy to release charge carrier to the intrinsic density of states (DOS). The Columb potential of trapped carriers will influence the charge transport [5]. Borsenberg studied the effect of traps on charge transport using computer simulation [1]. Arikipov has proposed a model for an effective transport energy for deep trap states. However, a direct proof for the existence such as energy in organic semiconductors is not known [8].

In this article we first derive an analytical expression for the trap-dependent conductivity based on the percolation theory. It is assumed that both intrinsic states and extrinsic traps are distributed with an exponential DOS of different widths, and that both distributions are occupied according to Fermi–Dirac statistics. Then we discuss the effect of traps on the conductivity of organic semiconductors. Finally we compare this model with experimental results.

2. Model theory

In organic semiconductors the transport of carriers is governed by hopping between localized states. The conductivity of such a system can be determined using percolation theory. The system is regarded as a random resistor network as proposed by Miller and Abrahams [9,11]. The current is flowing through bonds connecting the sites of such network. The conductance between the site $i$ and $j$ can be described as [12]

$$s_{ij} = \sigma_0 \exp \left( -2z R_{ij} - \frac{|\epsilon_i - \epsilon_F| + |\epsilon_j - \epsilon_F| + |\epsilon_j - \epsilon_i|}{2k_B T} \right).$$

(1)
Here, \( \sigma_0 \) is a prefactor, \( \alpha^{-1} \) is the Bohr radius of the localized wave functions, \( R_{ij} \) denotes the distance between the sites \( i \) and \( j \), and \( \epsilon_i \) is the energy of carriers at site \( i \). According to percolation theory \([12,13]\), the critical conductance value \( s_c \) determines the conductivity of the system when the first infinite cluster occurs \([11]\).

\[
\sigma = \sigma_0 \exp(-s_c).
\] (2)

In order to model the influence of traps in a simple manner, we assume a double exponential function for the DOS.

\[
g(\epsilon) = \frac{N_i}{k_B T_0} \exp \left( \frac{\epsilon}{k_B T_0} \right) \theta(-\epsilon) + \frac{N_d}{k_B T_1} \exp \left( \frac{\epsilon - E_d}{k_B T_1} \right) \theta(E_d - \epsilon).
\] (3)

Here \( N_i \) and \( N_d \) are the concentrations of intrinsic states and traps states, respectively, \( \theta \) is the unit step function, \( T_0 \) and \( T_1 \) are parameters indicating the widths of the intrinsic and the trap state distributions, respectively, and \( E_d \) is Coulomb trap energy \([14]\). Vissenberg and Matters pointed out that they do not expect the results to be qualitatively different for a different choice of \( g(\epsilon) \) \([13]\), as long as \( g(\epsilon) \) increases strongly with \( \epsilon \). Therefore, we assume that transport takes place in the tail of the exponential distribution. The equilibrium distribution of carriers, \( n \), is determined by the Fermi–Dirac distribution as follows

\[
n = \int \frac{g(\epsilon)}{1 + \exp \left( \frac{\epsilon - \mu}{k_B T} \right)} \, d\epsilon = N_i \exp \left( \frac{\mu}{k_B T_0} \right) \frac{\pi T/T_0}{\sin \pi T/T_0} + N_d \exp \left( \frac{\mu - E_d}{k_B T_1} \right) \frac{\pi T/T_1}{\sin \pi T/T_1}.
\] (4)

According to the classical percolation theory \([12]\), at the onset of percolation, the critical number \( B_c \) can be written as

\[
B_c = \frac{N_b}{N_s},
\] (5)

where \( B_c = 2.8 \) for a three-dimensional amorphous system. \( N_b \) and \( N_s \) are, respectively, the density of bonds and the density of sites in this percolation system, which can be calculated as follows \([13,16]\)

\[
N_b = \int \int dR_{ij} \, d\epsilon_i \, d\epsilon_j g(\epsilon_i) g(\epsilon_j) \theta(\epsilon_i - \epsilon_j)\]
(6)

\[
N_s = \int g(\epsilon) \theta(\epsilon - \mu) \theta(\epsilon - E_d).
\] (7)

Here \( R_{ij} \) denotes the distance vector between sites \( i \) and \( j \).

Substituting (4), (6) and (7) into (2), we obtain the expression

\[
B_c = \frac{\pi N_i^2 \psi \exp(2\psi) + \pi N_d^2 \exp(2\gamma) + \frac{1}{2} N_i N_d \exp(\eta + \gamma)(\psi^{-1} + \gamma^{-1})^{-3}}{N_i \exp(\eta) + N_d \exp(\gamma)}.
\] (8)

with

\[
\eta = \frac{E_F + k_B T s_c}{k_B T_0}, \quad \gamma = \frac{E_d - E_d + k_B T s_c}{k_B T_1},
\]

\[
\psi = \frac{T_0}{2\pi T_1}, \quad \zeta = \frac{T_1}{2\pi T_1}.
\]

This equation is obtained under the following conditions:

- the site positions are random,
- the energy barrier for the critical hop is large,
- and the carrier concentration is very low.

The exponent \( s_c \) is obtained by a numerical solution of (8) and the conductivity can be calculated using (2). This model was initially proposed in \([15]\), where a doping level \( E_d \) above the intrinsic level \( E_i \) was assumed. In the present work, we assume a trap level below the intrinsic level to study the effect of extrinsic traps on the conductivity of organic semiconductors.

3. Results and discussion

Figs. 1 and 2 illustrate the temperature dependence of the carrier conductivity for different trap concentrations. The parameters are \( N_i = 10^{23} \text{ cm}^{-3}, E_d = 0.67 \text{ eV}, T_0 = 800 \text{ K}, T_1 = 400 \text{ K}, \alpha = 5 \text{ nm}^{-1} \) and \( \sigma_0 = 1 \times 10^4 \text{ S/cm}. \) Despite the effect of the traps, we can see an almost perfect Arrhenius-type temperature dependence in Fig. 1, with the slope affected by the trap concentration. Increasing the latter, the activation energy decreases. In Fig. 2, \( \log \sigma \) versus \( T^{-2} \) is plotted. The deviation from a straight line occurs at higher temperature, where nearly all carriers occupy the intrinsic states, and the filled extrinsic trap states do not change the trap-free hopping relation \( \sigma \propto T^{-2} \) \([7]\). However, at lower temperature, the carrier distribution will be pinned near the peak of trap DOS \([6]\).

In Fig. 3 we compare the analytical model with experimental data reported in \([1]\). Parameters are the relative
The trap concentration \( c_t = \frac{N_d}{N_t} = 1 \times 10^{-2} \), \( T_0 = 1200 \text{ K} \), \( T_1 = 400 \text{ K} \), \( E_d = -0.15 \text{ eV} \), \( \alpha = 6 \text{ nm}^{-1} \) and \( \sigma_0 = 4.2784 \times 10^8 \text{ S/m} \). The data are for TTA with doping DAT.

The relation between conductivity and \( T_1 \) is shown in Fig. 4. Parameters are \( N_t = 1 \times 10^2 \text{ cm}^{-3} \), \( N_d = 1 \times 19 \text{ cm}^{-3} \), \( T_0 = 1200 \text{ K} \), \( T = 150 \text{ K} \), \( E_d = -0.5 \text{ eV} \), \( \alpha = 3 \text{ nm}^{-1} \) and \( \sigma_0 = 100 \text{ S/m} \). For the exponential trap DOS function of our model, the parameter \( T_1 \) is a characteristic temperature, where \( k_B T_1 \) represents the activation energy [17] and defines the width of the distribution [18]. Fig. 4 confirms that the conductivity decreases with \( T_1 \) almost linearly.

The relation between conductivity and trap concentration is shown in Fig. 5. The parameters are \( N_t = 10^{23} \text{ cm}^{-3} \), \( \alpha = 6 \text{ nm}^{-1} \), \( T_0 = 1000 \text{ K} \), \( T_1 = 500 \text{ K} \), \( E_d = -0.2 \text{ eV} \), the temperature is \( T = 400 \text{ K} \) and \( \sigma_0 = 1 \times 10^4 \text{ S/m} \).

At a critical trap concentration the conductivity has a minimum. This has been verified by experiments [19] and Monte Carlo simulation [2]. The minimum is due to the onset of inter-trap transfer that alleviates thermal detrapping of carriers, which is a necessary step for charge transport [2]. We can also see that a small trap concentration has virtually no effect on the conductivity. At higher trap concentration, however, the activation energy for the conductivity decreases. The traps themselves can serve as an effective hopping transport band, so the effect of traps on the conductivity is significant.
the charge conductivity is qualitatively similar to that caused by a high carrier concentration. It is interesting that such transition has also been observed in thermally stimulated luminescence (TSL) measurements [20].

The relation between the conductivity and the trap energy $E_t$ is shown in Fig. 6. Parameters are $T_0 = 600$ K, $T_1 = 300$ K, $N_i = 1 \times 10^{22}$ cm$^{-3}$, $N_d = 1 \times 10^{19}$ cm$^{-3}$, $\alpha = 4$ nm$^{-1}$, $T = 200$ K and $\sigma_0 = 1 \times 10^4$ S/m. From Fig. 6 we can conclude that the conductivity increases approximately exponentially for $|E_d|$ below a certain critical value and saturates for larger $|E_d|$.

4. Conclusion

An analytical model to describe the effect of traps on the electrical conductivity in organic semiconductors has been derived. This model predicts an Arrhenius-type relationship $\log \sigma \propto T^{-1}$, which implies that the trap-free relationship $\log \sigma \propto T^{-2}$ is not satisfied for higher temperature. Moreover, a minimum of conductivity at low trap concentration, as observed by in experimental data, is also successfully described by this model.

Acknowledgement

Financial support from Austria Science Fund, project P16862-N02, is gratefully acknowledged.

References