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Theoretical analysis of the drift and diffusion of charge carriers in thin layers of organic crystals

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A B S T R A C T

The influence of diffusion on the current shape in the time-of-flight (TOF) experiment under conditions of the quasiequilibrium transport has been considered. An analytical expression for the transient current density has been obtained for the case of the reflecting front electrode. The expression has been found to be in a better agreement with the Monte-Carlo numerical modeling than the usual expression based on the standard convection–diffusion equation. We found an estimate of the minimum layer thickness for a flat plateau appearance on TOF current transients.

1. Introduction

Organic materials have a variety of applications in electronic devices: light-emitting diodes [1], photovoltaic cells [2], memory devices [3], etc. In particular, organic crystals, e.g. pentacene, are considered as perspective materials for field-effect transistors [4]. Theoretical analysis of the hopping drift and diffusion of charge carriers in thin films of a slightly disordered material (a molecular organic crystal at room temperature) has been carried out in this paper. Electron (hole) mobility is the key parameter which defines characteristics of electronic devices. The traditional time-of-flight (TOF) method for mobility measurements is typically applicable only in the films which are thicker than 1 μm (see [5-12]). Attempts to do TOF measurements (by the use of dye generation layers) in thin (about 100 nm) films widely used in organic electronics usually produce highly dispersive current signals [13,14] although non-dispersive signal was reported recently for the sub-micrometer sample [15]. In thin films, the contribution of diffusion to the transport of charge carriers which is usually negligible under TOF conditions can rise significantly. As a result, an adequate choice of boundary conditions becomes important for the theoretical description of the TOF signals.

In this work, the analytical solutions of the convection–diffusion equation (CDE) [16] are compared for two specific types of boundary conditions. The diffusivity D and mobility μ are presumed constant which is true for the case of the quasiequilibrium transport and in particular in materials with a small disorder. One solution described by the Gaussian packet corresponds to the 1D infinite medium (contacts are supposed not to disturb the motion of charge carriers). This solution has been used ubiquitously in TOF analyses under condition of the quasiequilibrium transport [17–20]. Another one obtained in this work applies to a reflecting boundary condition at the front (illuminated) electrode. Additionally, both solutions have been compared with the results of a Monte-Carlo (MC) numerical modeling. It is shown that the latter solution agrees better with the MC-results. An upper limit for the layer thickness allowing the Gaussian description has been found for the typical field strength of 10^7 V/m.

2. Theoretical model and analytic results

The theoretical analysis is based on the 1D convection–diffusion equation [16] for the concentration of charge carriers $n(x, t)$

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} - V\frac{\partial n}{\partial x} \tag{1}$$

where

$$V = \mu F_0 \tag{2}$$

and F_0 is the constant and uniform electric field.

The initial condition corresponds to a surface generation of charge carriers (σ_0 is a surface charge density and L is a layer thickness):

$$n(x, 0) = \sigma_0 \delta(x - L\varepsilon), \quad \varepsilon \to +0. \tag{3}$$

The second boundary condition assumes the counter electrode is not disturbing charge flow:

$$n(+\infty, t) = 0, \tag{4}$$

while the first one could be established in two ways.

One way assumes that the front electrode also does not disturb charge flow

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$$\widetilde{n}(-\infty, t) = 0, \tag{5}$$

which leads to a well-known solution for the concentration in an infinite medium:

$$\widetilde{n}(x, t) = \frac{\sigma_0}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x-Vt)^2}{4Dt}\right]. \tag{6}$$

For the reflecting front electrode [16], it is assumed that

$$\left[Vn(x, t) - D\frac{\partial n(x, t)}{\partial x}\right]\Bigg|_{x=0} = 0. \tag{7}$$

The following analytical solution has been obtained (see Appendix):

$$n(x, t) = \frac{\sigma_0}{\sqrt{4\pi Dt}}\left(2\exp\left[-\frac{(x-Vt)^2}{4Dt}\right] - V\sqrt{\frac{t}{D}}\bullet\exp\left[\frac{Vx}{D}\right]\bullet\sqrt{\pi}\,\mathrm{erfc}\left[\frac{x+Vt}{\sqrt{4Dt}}\right]\right). \tag{8}$$

It is convenient to introduce dimensionless variables:

$$p(z, \tau) = \frac{n(x, t)}{\sigma_0/L}, \quad z = \frac{x}{L}, \quad \tau = \frac{t}{L/V}, \quad b = \frac{D}{VL}, \quad p(z, 0) = \delta(z-\varepsilon), \quad \varepsilon \to +0. \tag{9}$$

Then, solutions (6) and (8) may be written as follows:

$$\widetilde{p}(z, \tau) = \frac{1}{\sqrt{4\pi b\tau}} \exp\left[-\frac{(z-\tau)^2}{4b\tau}\right], \tag{10}$$

$$p(z, \tau) = \frac{1}{\sqrt{4\pi b\tau}}\left(2\exp\left[-\frac{(z-\tau)^2}{4b\tau}\right] - \sqrt{\frac{\tau}{b}}\bullet\exp\left[\frac{z}{b}\right]\bullet\sqrt{\pi}\,\mathrm{erfc}\left[\frac{z+\tau}{\sqrt{4b\tau}}\right]\right). \tag{11}$$

The total current density $j_\Sigma = j_{dr} + j_{diff}$ (the sum of the drift and diffusion components) and its dimensionless expression $Lj_\Sigma/(eV\sigma_0)$ looks like [16]

$$\frac{Lj_\Sigma}{eV\sigma_0} = \int_0^1 p(z, \tau)\mathrm{d}z + b[p(0, \tau) - p(1, \tau)]. \tag{12}$$

Now, dimensionless expressions (10) and (11) were substituted into the integral (12) to give the following results:

$$\frac{L\widetilde{j}_\Sigma}{eV\sigma_0} = \frac{1}{2}\mathrm{erf}\left[\frac{1-\tau}{\sqrt{4b\tau}}\right] + \frac{1}{2}\mathrm{erf}\left[\sqrt{\frac{\tau}{4b}}\right] + \sqrt{\frac{b}{4\pi\tau}}\left(\exp\left[-\frac{\tau}{4b}\right] - \exp\left[-\frac{(1-\tau)^2}{4b\tau}\right]\right), \tag{13}$$

$$\frac{Lj_\Sigma}{eV\sigma_0} = \frac{1}{2}\mathrm{erf}\left[\frac{1-\tau}{\sqrt{4b\tau}}\right] + \frac{1}{2}\mathrm{erf}\left[\sqrt{\frac{\tau}{4b}}\right] + \sqrt{\frac{b}{\pi\tau}}\left(\exp\left[-\frac{\tau}{4b}\right] - \exp\left[-\frac{(1-\tau)^2}{4b\tau}\right]\right). \tag{14}$$

It should be noted that expression (13) coincides with the result obtained earlier in [20]. Expressions (13) and (14) differ by a factor of two in the denominator of the last term. Expressions for the dimensionless drift current density for solutions (10) and (11) look like

$$\frac{L\widetilde{j}_{dr}}{eV\sigma_0} = \frac{1}{2}\mathrm{erf}\left[\frac{1-\tau}{\sqrt{4b\tau}}\right] + \frac{1}{2}\mathrm{erf}\left[\sqrt{\frac{\tau}{4b}}\right], \tag{15}$$

$$\frac{Lj_{dr}}{eV\sigma_0} = \frac{1}{2}\mathrm{erf}\left[\frac{1-\tau}{\sqrt{4b\tau}}\right] + \frac{1}{2} - \frac{1}{2}\exp\left[\frac{1}{b}\right]\bullet\mathrm{erfc}\left[\frac{1+\tau}{\sqrt{4b\tau}}\right]. \tag{16}$$

The difference between expressions (15) and (16) is a direct consequence of the assumption that the front electrode does not disturb charge flow so that carriers spend some time outside the sample (in the region $x < 0$). Expressions for the dimensionless diffusion current density based on solutions (10) and (11) have the following form:

$$\frac{L\widetilde{j}_{diff}}{eV\sigma_0} = \sqrt{\frac{b}{4\pi\tau}}\left(\exp\left[-\frac{\tau}{4b}\right] - \exp\left[-\frac{(1-\tau)^2}{4b\tau}\right]\right), \tag{17}$$

$$\frac{Lj_{diff}}{eV\sigma_0} = \sqrt{\frac{b}{\pi\tau}}\left(\exp\left[-\frac{\tau}{4b}\right] - \exp\left[-\frac{(1-\tau)^2}{4b\tau}\right]\right) - \frac{1}{2}\mathrm{erfc}\left[\sqrt{\frac{\tau}{4b}}\right] + \frac{1}{2}\exp\left[\frac{1}{b}\right]\bullet\mathrm{erfc}\left[\frac{1+\tau}{\sqrt{4b\tau}}\right]. \tag{18}$$

In the practical absence of energy disorder and for a moderate electric field, the Einstein's relation between diffusivity and mobility has the usual form

$$D = \frac{kT}{e}\mu. \tag{19}$$

3. Numerical modeling

We assume that an electron performs random walk on a cubic lattice of localized states (hopping centers). The energy disorder is small, $\sigma/(kT) = 0.1$, where σ is a variance of the Gaussian density of states (DOS). The initial position of an electron corresponds to the coordinate$x = 0$ but then it walks in the presence of the electric field directed against the OX axis. The transversal size of the sample considerably exceeds its thickness (near 1D geometry).

There are no jumps to the region $x < 0$ because the hopping states are absent. The moment the carrier achieves the right boundary means the end of computations in a given test. Tests are repeated no less than 10 000 times for each set of parameters. Hopping rates are given by the well-known Miller-Abraham's formula. The MC algorithm for simulation of random walk has been applied many times in the framework of the Gaussian disorder model [5,21,22]. The concentration of charge carriers was calculated as the number of charge carriers (summation over all tests) which are situated in a small volume $\Delta V = \Delta xYZ$ (Y, Z are the transversal sizes of the sample) during a given small time interval Δt divided by ΔV.

Parameter values used in computations are as follows: $F_0 = 10^7$V/m, $\sigma = 0.0025$eV, $T = 300$K, frequency factor of the Miller-Abraham's formula $\nu_0 = 10^{13}$s^{-1}, lattice constant $a_0 = 1$nm, $2\gamma a_0 = 10$ where γ is the reciprocal localization radius of the wave function. A typical hopping time $t_r = \nu_0^{-1}\bullet\exp[2\gamma a_0] = 2.2$ns.

Also, in our case the diffusivity is equal to

$$D = \frac{a_0^2}{t_r} \tag{20}$$

Then, we find $D = 4.55\bullet10^{-10}$m^2/s, $\mu = 1.76\bullet10^{-8}$m^2/(V•s) and lastly, $V = 0.176$m/s.

4. Calculation results and discussion

Figs. 1 and 2 demonstrate the normalized temporal variation of the total current density with a layer thickness as a parameter (note respective curves are plotted on a semi-logarithmic scale). The normalization unit of current density is 10^{-12} A/m^2.

We see that according to both MC-simulations and an analytical treatment transient currents decrease at short times and in thin layers ($L \leq 40$nm) so that the flat plateau is absent. Qualitatively, the form of these curves resembles that characteristic of the dispersive (highly nonequilibrium) transport. However, the reason for the current decrease at short times should not be associated with this factor as due to the fact that both diffusivity and mobility are constants ostensibly argues against such proposition. The reason, apparently, should be ascribed to the waning influence of diffusion with increasing time as the concentration gradients decrease. Thus, even in the case of the quasiequilibrium transport it seems impossible to produce flat plateaus on TOF current shapes in sufficiently thin films.