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The relevance of correct injection model to simulate electrical properties of organic semiconductors

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ABSTRACT

In this work we demonstrate how a full comprehensive model can be used to understand the electrical behavior of actual organic devices. We address all the aspects which need to be taken into account for realistic simulations of a wide range of device structures and configurations. In particular we stress the relevance of the correct modeling of contact/organic interfaces. The model is applied to perform predictive simulations of organic light-emitting diodes and to deduce how a full experimental characterization of an organic device should be performed in order to completely grasp its electrical behavior.

1. Introduction

Organic electronics is a continuously growing field and in the last decades it has been recognized that organic semiconductors [12] can have an important role in the fabrication of a wide variety of electronic devices. Several applications have been intensively studied and developed, such as *organic light emitting diodes* (OLED) [37], *organic photovoltaics* (OPV) [10], *organic field effect transistors* (OFET) [4]. Research efforts are motivated by the fact that organic devices are cheaper, easier to fabricate and suitable for new applications. Moreover, chemistry offers much control on the tuning of material properties.

From a theoretical point of view, all these kinds of devices require a correct understanding of several aspects: charge injection and transport, energy structure of the organic semiconductors, energy levels alignment at the interface between different materials, the role of trap states, charge recombination and generation. A comprehensive model would be of great help for devices development and optimization. The key problem is to understand the basic mechanisms of charge conduction and injection in organic semiconductors [6]. The conduction model should correctly account for (1) the energy structure of the organic material and (2) the charge transport mechanism. In Section 2 we will review all the relevant theory and explain how we developed an effective drift–diffusion model that can be used to simulate many kinds of device structures within the framework of the finite element method. We will also show how trap states, charge recombination and generation can be straightforwardly inserted in the model.

Charge injection in the organic is a critical issue. Organic semiconductors have large band gaps ($\sim$1.5 to 3.0 eV) – they are almost insulators – and low mobility (10^{-5}–10^{-3} cm^2 V^{-1} s^{-1}, for comparison, silicon mobility is $\sim 10^3$ cm^2 V^{-1} s^{-1} [22]), thus currents in organic devices are essentially injection controlled. It is then very important to correctly model contact interfaces. Metal/organic

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and organic/organic junctions have been intensively studied experimentally [23,9,19,24], but in general those results are not discussed and used in the literature concerning device simulation. In fact in most literature [50,51] all these topics – injection, transport, interfaces, etc. – are treated separately, and a full-comprehensive model is never presented. It is the objective of this article to present such a model and demonstrate how it can be used for realistic simulations of organic devices.

In Section 3 we will illustrate how to model metal/organic interfaces, and in Section 4 we will show how to use the full model to simulate real devices.

In the conclusive section, from the results of our simulations we will deduce how theory and experiment should interact in order to grasp as completely as possible the physics inside a device, and to perform predictive simulations of real devices.

2. Theory

2.1. Conduction in organic semiconductors

We recall the essential aspects of charge transport in organic semiconductors.

2.1.1. Localized states – gaussian DOS

There is a very important difference between organic [12,57] and inorganic semiconductors like Si or GaAs: the latter are covalent solids where the strong bonds between atoms produce a band structure with electron delocalized in the whole solid; in organic materials instead molecules are held together by weak van der Waals forces. The immediately evident consequence of this structure is that organic materials are soft and flexible. As to the electronic structure, weak bonds with negligible superposition of orbitals between molecules imply that electrons remain localized on their respective molecular sites, and their energy spectrum, taking into account polarization effects, is not very different from that one for the gas phase. Because of molecular disorder and random orientation of molecular electric dipoles, energy levels are randomly distributed. Assuming there is no correlation between adjacent sites, the energy distribution (i.e. the *density of states* – DOS) has a gaussian profile. Thus the conduction band is a gaussian centered on the LUMO level, while the valence band is centered on the HOMO (Fig. 1).

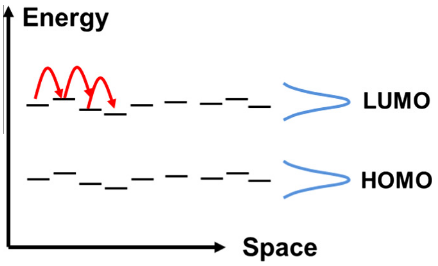

Fig. 1. Conduction and valence bands in organic semiconductors.

This model is commonly referred to as *gaussian disorder model*, GDM [5]. The DOS is given by the expression:

$$g(E,\sigma)dE = \frac{N_0}{\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2}\frac{(E-E_{C,V})^2}{\sigma^2}\right)dE \tag{1}$$

where $E_{C,V}$ indicates the centers of conduction and valence bands, N_0 is the volume density of transport sites and the variance σ is a measure of the band spreading. For commonly used organic materials $\sigma \simeq 0.08 - 0.15$ eV [33,3]; these values are derived from simulations, but as in Ref. [64] it is possible to give an estimate of σ assuming that molecules are arranged on a cubic lattice, and that the molecular dipoles $\mathbf{p}$ are randomly oriented. It can then be shown that:

$$\sigma \simeq \frac{2.35ep}{4\pi\varepsilon a^2} \tag{2}$$

The lattice constant a can be estimated from the molecular density N as $a = N^{-\frac{1}{3}}$. For instance for Alq$_3$ we have $N_{Alq_3} \simeq 1.6 \times 10^{21}$ cm^{-3} [29] and $p_{Alq_3} \simeq 5.3\ D$ [3], then $\sigma_{Alq_3} \simeq 0.13$ eV, in agreement with simulation results.

The density of electrons and holes in transport states can then be calculated using Fermi–Dirac statistics (we indicate with E_{Fn} and E_{Fp} the quasi-fermi levels for electrons and holes respectively; at the equilibrium $E_{Fn}^{eq} = E_{Fp}^{eq} = E_F$):

$$n = \int_{-\infty}^{+\infty} g_n(E,\sigma)\frac{1}{e^{(E-E_{Fn})/k_BT}+1}dE \tag{3}$$

$$p = \int_{-\infty}^{+\infty} g_p(E,\sigma)\left[1-\frac{1}{e^{(E-E_{Fp})/k_BT}+1}\right]dE \tag{4}$$

If we introduce the parameters

$$\xi = \frac{E_{Fn,p}-(E_{C,V}-e\varphi)}{k_BT} \qquad s = \frac{\sigma}{k_BT} \tag{5}$$

then we obtain a function $G(\xi,s)$ such that:

$$n = G(\xi,s) \tag{6}$$

$$p = G(-\xi,s) \tag{7}$$

φ is the electric potential and it has been introduced to take into account the band bending due to the electric field.

As explained in Section 2.2 and Appendix A, we need also the derivative with respect to energy of the densities $n$and p, hence instead of using numerical approximations, we implemented the analytical approximation of the function $G(\xi,s)$ given in Ref. [44].

2.1.2. Miller–Abrahams model

The conduction in organic materials is due to *phonon assisted hopping* of charge carriers between localized states. The hopping rate can be calculated using the theoretical approach first proposed by Miller and Abrahams [35], a model widely discussed in literature [5,57,41,42,13,46]. In the original paper the transition rate from site i to site j is expressed in the form:

When a phonon is absorbed

$$W_{ij} \propto n_{\mathbf{q}}e^{-2\gamma R_{ij}} \tag{8}$$

When a phonon is emitted

$$W_{ij} \propto (n_{\mathbf{q}}+1)e^{-2\gamma R_{ij}} \tag{9}$$