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Electric potential mapping by thickness variation: A new method for model-free mobility determination in organic semiconductor thin films ☆

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ABSTRACT

Charge transport, with charge carrier mobility as main parameter, is one of the fundamental properties of semiconductors. In disordered systems like most organic semiconductors, the effective mobility is a function of the electric field, the charge carrier density, and temperature. Transport is often investigated in a space-charge limited current (SCLC) regime in thin film single carrier devices, where an electric current is driven in the direction perpendicular to the surface. Direct evaluation of the current–voltage characteristics, however, is problematic, because parasitic contributions from injection or extraction barriers can falsify results.

Here, we present a novel measurement and evaluation technique for key transport parameters. First, it allows for the direct determination of the potential profile in single carrier devices. It is obtained from a series of steady-state current–voltage measurements from devices with varying thickness ("electric *p*otential *m*apping by thickness variation", POEM). Second, the data can be evaluated to obtain the effective charge carrier mobility $\mu(F,n)$ as a function of the electric field F and the charge carrier density n. Single carrier transport is achieved by sandwiching the organic material under investigation between equally doped layers, i.e. p-i-p (resp. n-i-n) devices for hole (electron) transport investigations. The POEM concept is validated using drift-diffusion simulation data. It is furthermore experimentally applied to small molecular organic semiconductors, where the hole transport in a blend of zinc phthalocyanine (ZnPc) and C_{60} is characterized. In the measured range of $F \approx (1–5) \times 10^5$ V/cm and hole densities of approx. $(1–5) \times 10^{16}\ \text{cm}^{-3}$, the hole mobility is found to be in the range of $(10^{-7}–10^{-5})\ \text{cm}^2/\text{V s}$, comprising a pronounced field activation with an activation constant of $0.01\ \sqrt{\text{cm/V}}$. A dependence of the mobility on the charge carrier density in the given range is not observed.

The POEM approach does not require a given mobility function as input, i.e. it constitutes a model-free determination of the effective mobility $\mu(F,n)$. It is especially suitable for semiconductors which require complex mobility models, like hopping or trap-dominated transport in disordered systems, and relatively low mobilities, like e.g. neat or mixed organic semiconductors.

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1. Introduction

Organic semiconductors attract scientific and commercial attention, because they are expected to complement classic inorganic electronics on several fields, including photovoltaics, displays, illumination, sensors, and other electronics [1–8]. Charge carrier transport in the active organic semiconductors is one of the key parameters for device design, understanding, and material evaluation. Its characterization is an ongoing challenge, particularly as the number of materials potentially suitable for organic electronics is large and steadily being extended. Device understanding and design – including simulations on several levels of detail [9–11] – rely on accurate material and transport parameters, with the charge carrier mobility being one of the key parameters [12–15]. Efficient characterization of new materials accelerates the development and understanding of new and optimized materials and devices.

The available transport characterization methods include organic field effect transistors (OFET) [16], time of flight (TOF) measurements [17], charge extraction with linear increasing voltage (CELIV) [18] and its extensions [19–21], and space-charge limited current (SCLC) measurements. All methods have their specific features and issues, considering the device geometry which should be the same as for the targeted application, the charge carrier density and field strength, which should be in the relevant range, the required quantity of material for sample preparation, a sophisticated measurement set-up, and/or evaluation steps which are based on stronger or weaker assumptions. For a more detailed overview see Ref. [22].

Our aim is to characterize electron and hole transport separately in thin layers of intrinsic or blend organic semiconductors in the direction perpendicular to the surface and at charge carrier densities, field strengths, and current densities relevant for applications like organic photovoltaics (OPV) or organic light emitting diodes (OLEDs). The characterization is done in a stacked device geometry and with a measurement technique as simple as steady-state current–voltage characteristics. The steps of the evaluation are kept transparent and simple, and are based only on plausible basic assumptions. They are model-free with respect to the transport theory, i.e. it is not necessary to compare the measured characteristics to the result of a model-based calculated characteristic to obtain the mobility. This way, unbiased access is gained to the investigated properties, which is especially the charge carrier mobility.

In the following, the idea for the transport characterization through "electric *pot*ential *m*apping by thickness variation" (POEM) is outlined on the level of an ideal single-carrier device disregarding contacts. This is followed by a short section about the general rules for device design, taking non-ideal contacts and their implications for the validity of the POEM theory into account. To proof the principle of the evaluation method, an established drift-diffusion simulation tool is used to create *j*–*V* data in a controlled manner, employing several mobility models. The mobility as a function of field and charge density is calculated from these simulated *j*–*V* curves, successfully reconstructing the mobility functions used for the simulations. Finally, we investigate the hole transport in a ZnPc:C_{60} blend layer. The hole mobility is determined experimentally, showing a strong field activation and no resolvable charge density dependence in the investigated range.

2. Theory

We analyze charge carrier transport in a thin symmetric semiconductor layer when a mono-polar – i.e. electron-only or hole-only – electric current is driven perpendicular to the layer surface. Transport is regarded as a one-dimensional problem along the spatial variable *x* in the direction of current, i.e. perpendicular to the thin film surface area. The thickness d_i of the device corresponds to the channel length and the device area *A* to the channel cross-section area.

2.1. Space-charge limited current

At low current density, we observe an Ohmic current–voltage (*j*–*V*) characteristic which can be understood by the fact that the current is mainly carried by the thermal equilibrium charge carrier density. When increasing the current density *j*, the charge carrier density *n* within the semiconductor is increased by additionally injected charges and the current density increases beyond the Ohmic behavior. This situation is characterized by a space-charge density distribution decreasing in the direction of current and commonly referred to as space-charge limited current (SCLC). The current density *j* is independent of *x*, and according to the drift transport equation

$$j = e\,n\,\mu F \tag{1}$$

the electric field $F(x)$ is reciprocal to the charge carrier density $n(x)$ and increasing from a very small value at the injection contact towards the extraction contact. The charge carrier mobility is denoted by μ and the elementary charge by *e*. Throughout this work, the charge carrier density is interpreted as the quantity including all mobile and immobile, i.e. free and – if applicable – trapped charge carriers $n = n^{\text{free}} + n^{\text{trapped}}$, and the mobility is regarded as the effective mobility of all these charge carriers, following Eq. (1).

In the theoretical case of a constant charge carrier mobility μ independent of electric field and charge carrier density, and assuming trap-free transport, the electric field has a square-root shape $F(x) \propto \sqrt{x}$ and the *j*–*V* characteristics in this case follow the Mott–Gurney law [23, Section 5]

$$j = \frac{9}{8}\,\varepsilon\varepsilon_0\,\mu\,\frac{V^2}{d_i^3} \tag{2}$$

where ε is the relative permittivity of the semiconductor and ε_0 is the vacuum permittivity.

In the case of a field activated mobility according to

$$\mu = \mu_0 \exp\left(\gamma\sqrt{F}\right) \tag{3}$$

where γ is the field enhancement factor, the *j*–*V* characteristics can be approximated according to Murgatroyd [24], [25, Section 6.4] by