Diffusion-enhanced hole transport in thin polymer light-emitting diodes

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The transport of holes in polymer light-emitting diodes (PLEDs) based on poly(2-methoxy, 5-(2′ ethyl-hexyloxy)-*p*-phenylene vinylene) (MEH-PPV) is investigated as a function of layer thickness. For thicknesses smaller than 100 nm, the current in these thin PLEDs is strongly enhanced as compared to the expected space-charge limited (SCL) current. Applying the standard SCL model to measurements on a PLED with a thickness of only 40 nm results in an apparent increase of the hole mobility of a factor of 40. We show that this strong increase of the hole transport properties in these thin devices originates from the presence of an Ohmic hole contact. For Fermi-level alignment, holes diffuse from the contact into the MEH-PPV, forming an accumulation layer with a width of a few tens of nanometers. Due to the density dependence of the mobility, the hole transport in this accumulation region is strongly enhanced. For the analysis of thin PLEDs, it is therefore essential that both drift and diffusion of charge carriers are taken into account.

After the discovery of electroluminescence in conjugated polymers in 1990,[1] attention has been focused on charge transport properties of poly(*p*-phenylene vinylene) (PPV) and its derivatives. It has been demonstrated that the hole transport in polymer LEDs based on poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-*p*-phenylene vinylene) (OC$_1$C$_{10}$-PPV) is space-charge limited (SCL) with a hole mobility μ_h of 5×10^{-11} m^2/V s at low voltages at room temperature.[2] The enhancement of the SCL current at higher voltages was initially attributed to the electric field dependence of the mobility,[3] originating from the lowering of the hopping barriers in the direction of the applied electric field.[4] However, recently, the dependence of the hole mobility on the charge carrier density in PPV derivatives has also been investigated by a combined study on field-effect transistors (FETs) and polymeric diodes.[5] The combined results show that the hole mobility is constant for charge carrier densities $<10^{22}$ m^{-3} and increases with a power law for densities $>10^{22}$ m^{-3}. Its density dependence can be approximated by the empirical relation

$$\mu_h(p,T) = \mu_h(0,T) + \frac{\sigma_0}{e} \left(\frac{\left(\frac{T_0}{T}\right)^4 \sin\left(\pi \frac{T}{T_0}\right)}{(2\alpha)^3 B_c} \right)^{T_0/T} p^{T_0/T-1}.$$

(1)

In this equation, $\mu_h(0,T)$ is the hole mobility at low densities obtained from the quadratic SCL current, σ_0 is a conductivity prefactor, α^{-1} is the effective overlap parameter between localized states, T_0 is a measure of the width of the exponential density of states, and B_c is the critical number of the onset of percolation. The parameters σ_0, α^{-1}, and T_0 are all experimentally obtained from the temperature dependence of the transfer characteristics of the FET.[5]

In the space-charge limited regime, the carrier density and electric field are simultaneously increased upon application of a voltage. Since the mobility depends on both the field and density, an important question is which of the two dependencies enhances the charge transport at higher voltages. It has

been demonstrated that at room temperature the enhancement of the mobility at higher voltages is totally due to the increase of the carrier density.[6] The dominance of the carrier density on mobility at room temperature was further confirmed by the investigation of the thickness dependence of SCL devices in the 200–900 nm range.[7] Thus, in contrast to earlier assumptions[3] the field dependence of the mobility does not play a role at room temperature. However, at lower temperatures the field dependence of the mobility becomes increasingly more important. These experiments revealed that for a complete description of the charge transport in conjugated polymers, a model that incorporates both the effect of carrier density and electric field on the mobility is required. Such a transport model has recently been developed.[8]

In the classical model for SCL conduction, there are two important requisites: The first is the presence of an Ohmic contact, such that the electric field at the injecting contact is close to zero. Furthermore, the amount of injected charges scales linearly with the applied voltage. As a result, it is assumed that at zero bias there is no net charge present in the device, whereas upon application of a voltage charges are injected into the device, thereby forming a space-charge region. However, when an Ohmic contact is applied to a semiconductor, a charge accumulation region is formed close to the contact in order to align the Fermi level, with a typical width of 10–20 nm,[9] as schematically indicated in Fig. 1. As a result, for very thin layers approaching the thickness of the accumulation layer(s), this diffusion driven charge accumulation leads to a considerable amount of net background charges in the device. In regular semiconductors, the presence of this additional background charge will mainly show up at low voltages as an Ohmic current that depends linearly on the applied voltage. At higher voltages, the number of injected charges will exceed the background charge and the standard SCL current is observed. Conjugated polymers as the PPV derivatives studied here, however, are strongly disordered semiconductors in which the charge transport is described as hopping in a Gaussian density of states (DOS). The width of the Gaussian DOS reflects the amount of ener-
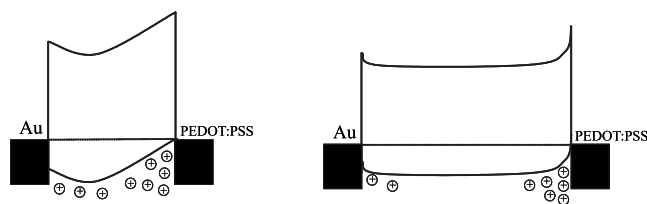
FIG. 1. Schematic representation of the band diagram of a thin and thick PPV-based hole-only device. The PPV film is sandwiched between an Ohmic PEDOT:PSS contact and a Au contact. Also indicated are the hole accumulation regions close to the contacts.

getic disorder in the organic semiconductor.[4] The resulting strong dependence of the mobility on carrier density will amplify the effect of an additional background density on the charge transport. In studies performed on SCL currents in conjugated polymers so far, diffusion of charge carriers from the contacts into the device was not taken into account. Consequently, the formation of an accumulation region with high carrier density close to the contact was ignored. An important question is now whether the omission of this effect is relevant in the analysis of the charge transport in these materials. From Fig. 1, it is evident that for very thick layers, where the contacts fill only a small fraction of the device, the influence of these extrinsic charge carriers is expected to be small. In the present study, we demonstrate that for devices with thicknesses smaller than 100 nm the mobility in PPV-based SCL devices is significantly enhanced due to the presence of charge carriers that have diffused in from the Ohmic contacts. For devices as thin as 40 nm, the enhancement of the mobility is even more than an order of magnitude. As a result, SCL current measurements on these thin devices are not representative for the intrinsic carrier transport, but lead to a strong overestimation of the intrinsic mobility due to the presence of extrinsic carriers.

In order to study the effect of carrier accumulation at an Ohmic hole contact, hole-only diodes were fabricated from poly(2-methoxy,5-(2′-ethyl-hexoxy)-p-phenylene vinylene) (MEH-PPV) with different layer thicknesses. Hole-only diodes from this MEH-PPV are prepared as follows: On top of a glass substrate, a transparent electrode, indium tin oxide, has been patterned to form the hole injecting electrode. As a first step, an anode of a hole-conducting layer of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) is spin coated. Then, on top of the PEDOT:PSS, MEH-PPV films ranging in thickness from 40 to 320 nm have been spin coated from toluene solution. The device was finished by thermal evaporation of 100 nm of gold (Au) through a shadow mask. The hole-only diodes have been measured under controlled N_2 atmosphere. The electrical measurements have been performed using a Keithley 2400 source meter.

In Fig. 2, the current density-voltage (J-V) measurements are presented for MEH-PPV hole-only diodes with thicknesses L of 40 and 318 nm. The applied voltage is corrected for the built-in voltage V_{bi} of 0.4 V, resulting from the work function difference between PEDOT:PSS and the evaporated Au electrode. Corrected with this built-in voltage, the J-V curves show a quadratic behavior at a low (<1 V) effective voltage (V-V_{bi}) for all thicknesses. For thick devices, a large
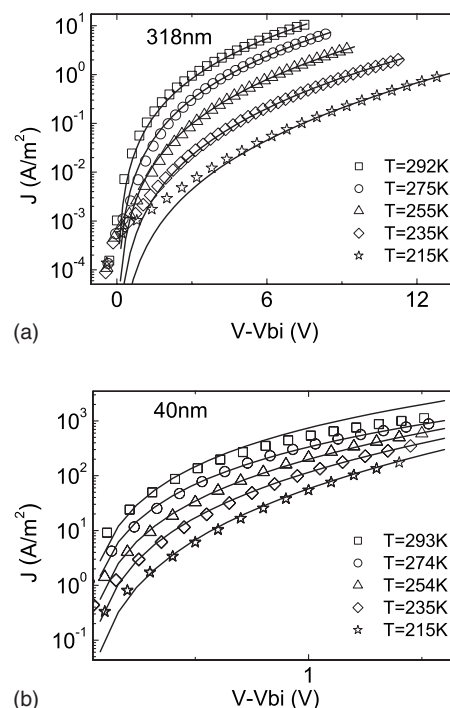

FIG. 2. Temperature dependent J-V characteristics of MEH-PPV hole-only diodes (empty symbols) with polymer thicknesses L of (a) 318 nm and (b) 40 nm. The solid lines represent the fits with the SCL model without taking into account diffusion of charge carriers.

voltage range is measured and the exact choice of V_{bi} is not critical. Also shown are fits with a SCLC model that assumes that at $V=0$ V there are no charge carriers present in the device. In order to fit the J-V at higher voltages, a density and field dependent mobility has been taken into account.[8] For the device with a thickness of 318 nm, a low-density mobility $\mu_h(0,T)$ [Eq. (1)] was found to be 3.0 $\times 10^{-11}$ m^2/V s at room temperature, which is in agreement with earlier reported values.[10] However, for the 40 nm device, a room temperature mobility was found to be 8.7 $\times 10^{-10}$ m^2/V s. Apparently, the mobility seems to increase by more than an order of magnitude when going from a thick (318 nm) to a thin (40 nm) device. In order to study this mobility increase in more detail, devices with a series of different thicknesses have been measured and modeled. In Fig. 3, the room temperature mobility μ_h as obtained from the SCLC model is shown as a function of MEH-PPV layer thickness.

Figure 3 shows that with decreasing layer thickness the mobility gradually starts to increase, with an especially strong increase for thicknesses below 100 nm.

In order to investigate whether this mobility increase originates from the diffusion of charge carriers from the contacts into the device, we have to calculate the charge carrier profiles at $V=0$. The amount of charge carriers in the devices will strongly depend on the boundary condition that is used for the injecting contact, located at $x=L$. From earlier measurements on MEH-PPV, it is known that the width of the Gaussian DOS typically amounts to 0.1−0.11 eV.[10] Furthermore, the middle of the highest occupied molecular orbital
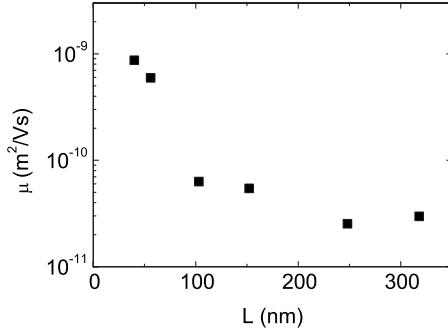
FIG. 3. Distribution of the room temperature mobility $\mu_h(0,300\ \text{K})$ as a function of the MEH-PPV layer thickness.

(HOMO) is located at around 5.35 eV below the vacuum level.[11] Together with the work function of PEDOT:PSS of 5.0 eV, as measured by a Kelvin probe, this gives a hole density of $5 \times 10^{23}\ \text{m}^{-3}$ at the injecting PEDOT:PSS/MEH-PPV interface, as shown in Fig. 4. For the Au contact (x =0), a value of $1 \times 10^{15}\ \text{m}^{-3}$ was used, which was derived from the increase of the injection barrier with V_{bi}, but the calculations are not sensitive to the choice on this boundary.

It should be noted that the work function of PEDOT:PSS might be modified due to interface dipoles when brought into contact with organic semiconductors such as pentacene.[12] On the other hand, electrochemical modification of the PEDOT work function in PPV-based solar cells showed that the open-circuit voltage exactly followed the behavior as expected from the PEDOT work function.[13] This shows that the PE-DOT work function is not pinned in this system, which supports our estimate of the hole density at the interface. We use a recently developed drift-diffusion model to calculate the distribution of holes $p(x)$ as a function of distance x in the device.[14] The injecting contact is taken at $x=L$. The inset of Fig. 5 shows the hole distribution for the device with a thickness of 40 nm. The hole density nearly exponentially decreases as a function from the injecting contact. In order to quantify the amount of charge that flows into a device to equilibrate the Fermi level, we will use the average charge density ρ_{av} that is calculated from the distribution of $p(x)$, given by
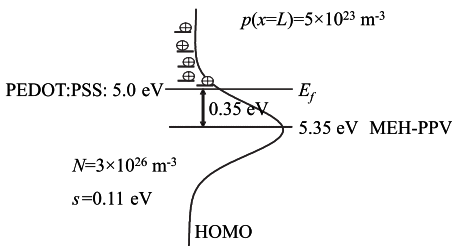

FIG. 4. Boundary condition at the injecting PEDOT:PSS/MEH-PPV contact ($x=L$). For the total number of sites in the Gaussian DOS with a width of $\sigma=0.11$ eV, a value N of $3 \times 10^{26}\ \text{m}^{-3}$ was used.[5]
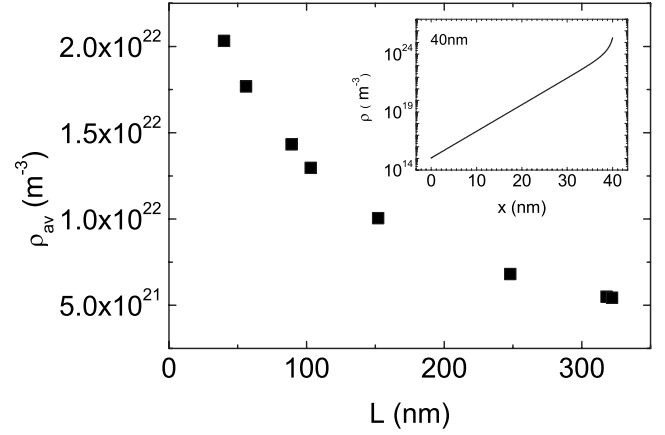

FIG. 5. Numerically calculated distribution of the average hole density ρ_{av} as a function of polymer layer thicknesses L at zero bias ($V=0$ V).

$$\rho_{av} = \frac{\int_0^L p(x)dx}{L}. \qquad (2)$$

In Fig. 5, the increase of ρ_{av} is shown for decreasing device thickness. It typically increases from $5 \times 10^{21}\ \text{m}^{-3}$ for the 318 nm device to $2 \times 10^{22}\ \text{m}^{-3}$ for the 40 nm device.

As a next step, we calculate the J-V characteristics at room temperature, combining the presence of charge carrier accumulation regions close to the contact with the density dependence of the hole mobility, as given by Eq. (1). From temperature dependent field-effect measurements, the mobility parameters T_0, σ_0, and α^{-1} have been obtained; T_0 =540 K, $\sigma_0=3.1 \times 10^7$ S/m, and $\alpha^{-1}=0.14$ nm.[5] For B_c, a value of 2.8 was used.[15] In Fig. 6, the experimental J-V measurements for the MEH-PPV hole-only diodes with different thicknesses are shown (symbols). The solid lines represent the calculated J-V characteristics, taking drift and diffusion and the density dependent mobility into account. All
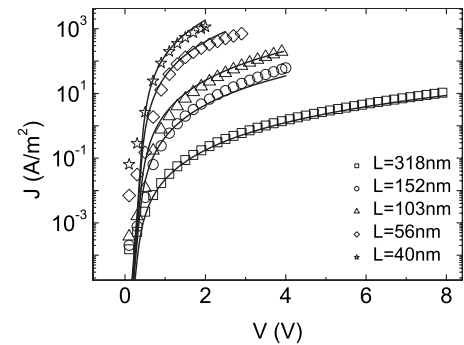

FIG. 6. J-V characteristics of MEH-PPV hole-only diodes (empty symbols) with different thicknesses L of the polymer. The solid lines represent the calculations from a drift-diffusion SCL model that takes into account the presence of holes at zero bias due to diffusion from the Ohmic contact, combined with a density dependent mobility [Eq. (1)].

thicknesses can be described using the above-mentioned parameters for the density dependence of $\mu_h(p,T)$ and a $\mu_h(0,300\ \text{K})$ of $1.25 \times 10^{-11}\ \text{m}^2/\text{V s}$. This demonstrates that, indeed, the diffusion of charge carriers from the contacts into the polymer is responsible for the apparent increase of the charge carrier mobility. Even for the thick device of 318 nm, a low-density mobility of $3.0 \times 11^{-11}\ \text{m}^2/\text{V s}$ was obtained from the standard SCL model, whereas an analysis of the complete thickness dependence including diffusion leads to an intrinsic mobility of $1.25 \times 10^{-11}\ \text{m}^2/\text{V s}$ for MEH-PPV. These results show that extrinsic carriers that diffuse in from Ohmic contacts clearly influence the results of charge transport studies in these materials.

A decreasing mobility with increasing layer thickness has also been observed in transient measurements on PPV.[16] On short time scales the hole transport is dispersive, and for thin layers the holes do not relax to the deeper sites of the density of states giving rise to faster transit times. In that case, a systematic decrease of the transient "mobility" was observed, from layers of 100 nm down to 460 nm. Even for 460 nm layers, this transient mobility was still a factor of 3 above the measured dc mobility as obtained from $J\text{-}V$ measurements. In our dc $J\text{-}V$ measurements, where the contribution of fast and slow carriers are integrated in time, the mobility is already close to the intrinsic value at thicknesses >200 nm, as shown in Fig. 3. As a result, we do not expect that relaxation effects play a large role in the interpretation of our data.

It has been demonstrated that the mobility-density relation can be directly obtained from the $J\text{-}V$ characteristics.[6] The SCL current, with a density dependent mobility according to Eq. (1) through a device with thickness L, could be accurately approximated by $J = 0.8 e p_{av} \mu_a(p_{av}) E_{av}$, where $E_{av} = V/L$, p_{av} is the average density in the device given by $p_{av} = 1.5(\varepsilon_0 \varepsilon_r V/eL^2)$,[17] and $\mu_h(p_{av})$ is the mobility at density p_{av}. Using an experimental $J\text{-}V$ characteristic, E_{av} and p_{av} can be directly calculated for every applied voltage, V, and the corresponding J then directly gives the mobility μ_{av} using $\mu_{av}(p_{av}) = J/(0.8 e p_{av} E_{av})$. The resulting $\mu_{av} \sim p_{av}$ relation then showed a consistent correspondence with the field-effect mobilities from FET measurements.[6] However, in the case of thin devices, it appears that this approximation has to be corrected for the average amount of carriers ρ_{av0} that are
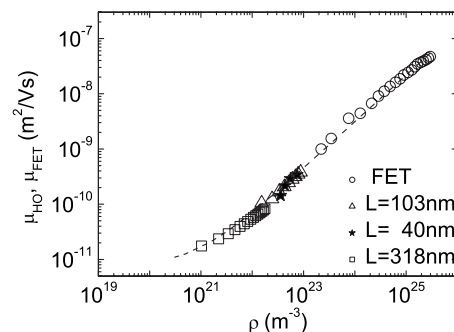

FIG. 7. Hole mobility as function of hole density in a hole-only diode field-effect transistor for MEH-PPV (symbols). The dashed line is calculated using Eq. (2).

already present in the device at $V = 0$ V, given by

$$J = 0.8e(\rho_{av0} + p_{av})\mu(\rho_{av0} + p_{av})E_{av}. \qquad (3)$$

For the different thicknesses, the ρ_{av0} is used from the numerical calculations, as shown in Fig. 5. In Fig. 7, the obtained $\mu_{av}(p_{av})$ relation is shown for devices with a layer thickness of 40, 103, and 318 nm, together with the mobilities obtained from field-effect measurements on MEH-PPV. Due to the high carrier concentrations in the thin devices, the "gap" between the hole-only diode data and the FET data has been closed, in contrast to earlier reported results on thicker samples.[6] Figure 7 then shows the full experimentally determined mobility vs density relation for MEH-PPV.

In conclusion, we demonstrate that the mobility as obtained from space-charge limited polymeric diodes is enhanced by diffusion of charge carriers from an Ohmic contact into the device. For devices of only 40 nm thickness, the mobility value is enhanced by more than 1 order of magnitude. The apparent increase of the mobility is described by a combination of a drift-diffusion model with a density dependent mobility. Omission of diffusion, as is done in the standard SCLC model, leads to an overestimation of the intrinsic charge carrier mobility in thin polymer light-emitting diodes.

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