Unification of the Hole Transport in Polymeric Field-Effect Transistors and Light-Emitting Diodes

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A systematic study of the hole mobility in hole-only diodes and field-effect transistors based on poly(2-methoxy-5-(3′, 7′-dimethyloctyloxy)-p-phenylene vinylene) and on amorphous poly(3-hexyl thiophene) has been performed as a function of temperature and applied bias. The experimental hole mobilities extracted from both types of devices, although based on a single polymeric semiconductor, can differ by 3 orders of magnitude. We demonstrate that this apparent discrepancy originates from the strong dependence of the hole mobility on the charge carrier density in disordered semiconducting polymers.

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In recent years solution-processible conjugated polymers have had a significant impact in optoelectronic applications such as light-emitting diodes (PLEDs) [1] and metal-insulator-semiconductor field-effect transistors (FETs) [2]. After the discovery of electroluminescence in poly(p-phenylene vinylene) (PPV) and its derivatives, attention has been focused on studying their electrical transport properties [3,4]. One of the most widely studied materials is poly(2-methoxy-5-(3′, 7′-dimethyloctyloxy)-p-phenylene vinylene) (OC_1C_{10}-PPV). It has been demonstrated that the hole current in OC_1C_{10}-PLEDs is space-charge limited (SCL) and that it is governed by hole mobility, μ_h, which is dependent on both the temperature, T, and the applied electric field, E [4]. At low electric fields, and at room temperature, the hole mobility amounts to 5×10^{-7} cm^2/V s [4]. Its field and temperature dependencies are well described by a 3D transport model based on hopping in a correlated Gaussian disordered system [5,6]:

$$\mu = \mu_\infty \exp\left\{ -\left(\frac{3\sigma_{DOS}}{5k_BT}\right)^2 + 00.78\left[\left(\frac{\sigma_{DOS}}{k_BT}\right)^{3/2} - 2\right]\sqrt{\frac{eaE}{\sigma_{DOS}}}\right\}, \quad (1)$$

with μ_∞ the zero-field mobility in the limit $T \to \infty$, σ_{DOS} the width of the Gaussian density of states (DOS), and a the intersite spacing. The hole mobility of OC_1C_{10}-PPV is characterized by a $\sigma_{DOS} = 0.112$ eV and $a = 1.2$–1.4 nm [7].

One of the first and most widely studied solution-processed conjugated polymers in organic field-effect transistors is poly(3-hexyl thiophene) (P3HT) [8]. Typical field-effect mobilities, μ_{FE}, for spin-coated amorphous P3HT films are in the range of 10^{-5}–10^{-4} cm^2/V s, whereas by ordering the polymer in the film the field-effect mobility increased to about 10^{-1} cm^2/V s [9]. The transfer characteristics of amorphous P3HT have been modeled as a function of temperature and gate bias with variable range hopping in an exponential density of states [10]. The value for μ_{FE} at room temperature amounts to 6×10^{-4} cm^2/V s for a gate voltage $V_g = -19$ V.

Apparently, the solution-processible conjugated polymers developed for PLEDs and FETs have fundamentally different properties. The reported hole mobilities differ typically by more than 3 orders of magnitude [4,10]. Theoretically, the field- and temperature-dependent hole mobility in PLED materials is described by hopping in a Gaussian DOS, whereas for FET materials the temperature and gate bias dependencies are described by hopping in an exponential DOS. It has recently been derived that in disordered semiconductors the Einstein relation and, thus, the charge transport properties are dependent on the charge carrier density [11]. However, the dependence of the hole mobility on charge carrier density has not been experimentally addressed so far. In this Letter a unified picture of the hole transport in the two classes of devices is presented. We are able to establish the dependence of the hole mobility in OC_1C_{10}-PPV and P3HT on charge carrier density and to correlate the hole mobility obtained from diodes and field-effect transistors. It is demonstrated that the strong increase of the hole mobility, for both materials, with increasing hole density is responsible for the observed large mobility differences obtained from the hole-only diodes and the field-effect transistors.

Although OC_1C_{10}-PPV and P3HT have often been studied in diodes and field-effect transistors, respectively, the field-effect mobility of OC_1C_{10}-PPV and the hole mobility of P3HT in SCL sandwiched diodes have not yet been determined. In the present study OC_1C_{10}-PPV is used as an active semiconductor in a field-effect transistor, and current density versus voltage (J-V) measurements have been performed on a P3HT-based diode. On top of a highly doped n^{++}-Si substrate (gate electrode) a 200 nm thin film of SiO_2 was thermally grown and used as the gate dielectric. Two gold electrodes were evaporated onto the insulator to form the source and drain contacts. The channel width, W, is 2500 μm, and the channel length, L, typically 10 μm. The transistor is finished by spin coating the OC_1C_{10}-PPV layer from toluene. The transfer characteristics have been measured in the dark, in the linear operating regime of the transistor, by using a drain voltage $V_d = -0.1$ V, which is much smaller than the applied gate voltage (-1 to -20 V). In the diode structures P3HT is spin coated on top of a patterned indium tin oxide bottom electrode used as an anode. The thickness of the polymer layer amounts to 95 nm. As a top electrode an evaporated gold contact is used.

The experimental transfer characteristics of the OC_1C_{10}-PPV FET are presented for the temperature range from 206 to 293 K in Fig. 1. From the transfer characteristics the experimental field-effect mobility is directly calculated by differentiating the channel current I_d with respect to the gate voltage V_g [2]:

$$\mu_{\mathrm{FE}}(V_g) = \frac{\partial I_d}{\partial V_g}\frac{L}{WC_iV_d}. \qquad (2)$$

A field-effect mobility of 4.7×10^{-4} $\mathrm{cm^2/V\,s}$ for OC_1C_{10}-PPV at $V_g = -19$ V at room temperature has been obtained. Surprisingly, this value for the field-effect mobility is approximately 3 orders of magnitude larger than the mobility value determined from hole-only diodes [4].

We establish a relation between the experimental field-effect mobility and the volume charge density in the transistor. The transfer characteristics have been measured in the linear regime using a drain bias much lower than the gate bias. Hence the gradual channel approximation can be applied in which the distribution of charge carriers needs to be described only in the direction perpendicular to the gate dielectric/semiconductor interface, x. Using $C_i = 17$ $\mathrm{nF/cm^2}$ and a dielectric constant of the semiconductor of about 3, the charge carriers at the interface $p(0)$ can be calculated as a function of gate bias [12]. Furthermore, from Eq. (2) the experimental field-effect mobility is also determined as a function of gate bias. In Fig. 2 the resulting dependence of the field-effect mobility [Eq. (2)] on charge carrier density $p(0)$ is presented in the range of 2×10^{17} to 2.9×10^{19} $\mathrm{cm^{-3}}$ (circles) for the OC_1C_{10}-PPV FET. It is observed that in this range the field-effect mobility increases from 1×10^{-5} to 4.7×10^{-4} $\mathrm{cm^2/V\,s}$.

In order to compare the field-effect mobility with that derived from hole-only diodes, the transfer characteristics are measured as a function of temperature and interpreted with the variable range hopping model proposed by Vissenberg and Matters [13]. This hopping percolation model in an exponential density of states yields an expression for the conductivity as a function of the charge carrier density and the temperature. The conductivity can be converted into charge carrier mobility by dividing by ep, where e is the elementary charge and p the charge carrier density:

$$\mu_{\mathrm{FE}}(p) = \frac{\sigma_0}{e}\left(\frac{(T_0/T)^4 \sin(\pi T/T_0)}{(2\alpha)^3 B_c}\right)^{T_0/T} p^{T_0/T-1}, \qquad (3)$$

where σ_0 is a prefactor for the conductivity, α^{-1} is the effective overlap parameter between localized states, T_0 is a measure of the width of the exponential density of

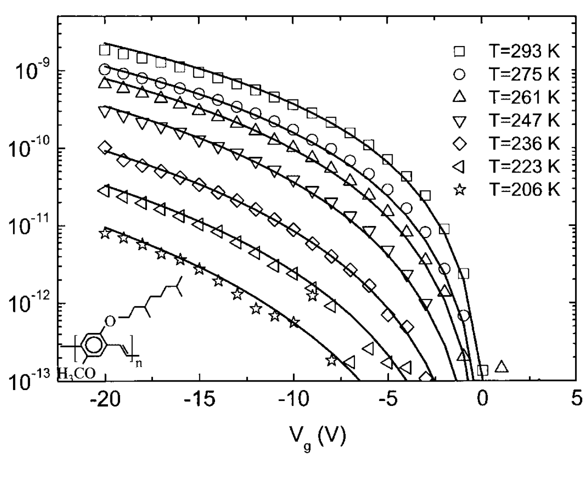

FIG. 1. Drain current vs gate voltage of OC_1C_{10}-PPV field-effect transistor. Solid lines indicate the calculated drain currents. Inset: The chemical structure of OC_1C_{10}-PPV.

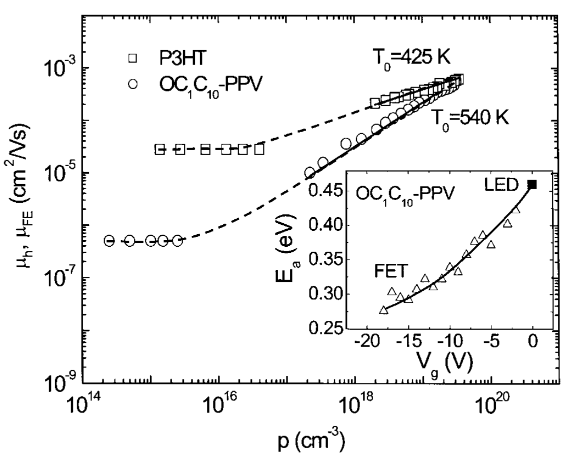

FIG. 2. Mobility as a function of hole density p in a diode and field-effect transistor for P3HT and OC_1C_{10}-PPV [Eq. (2) (symbols) and Eq. (3) (lines)]. The dashed line is a guide to the eye. Inset: The activation energy of the mobility in the OC_1C_{10}-PPV based FET as a function of gate voltage (triangles), together with the activation energy of 0.46 eV as obtained from the diode at low densities (square).

states, and B_c is the critical number for the onset of percolation.

The experimental transfer characteristics can now be described with the variable rate hopping model by using the equation $I_d = WV_d/L \int_0^l ep(x)\mu[p(x)]dx$, where l represents the thickness of the semiconducting film [13]. Using this equation the transfer characteristics could be fitted with a single set of values for the three parameters T_0, σ_0, α^{-1}, namely $T_0 = 540$ K, $\sigma_0 = 3.1 \times 10^7$ S/m, and $\alpha^{-1} = 0.14$ nm (solid lines in Fig. 1). For B_c a value of 2.8 was used [14]. Inserting the obtained T_0, σ_0, and α^{-1} in Eq. (3) provides the calculated power-law dependence $\mu_{FE} \sim p^{T_0/T-1}$, as indicated by the solid line in Fig. 2. This calculated μ_{FE} vs p behavior is in good agreement with the data obtained directly from Eq. (2) (circles), demonstrating that the model is consistent with the experiment. The same analysis has been applied to the transfer characteristics of P3HT-FETs, which could be fitted with $T_0 = 425$ K, $\sigma_0 = 1.6 \times 10^6$ S/m, and $\alpha^{-1} = 0.16$ nm [10]. The resulting μ vs p relation for P3HT as determined directly from $\mu_{FE}(V_g)$ [Eq. (2)] (squares) and from $\mu_{FE}(p)$ [Eq. (3)] (solid line) is also plotted in Fig. 2 in a charge carrier density range of 2×10^{18} to 3.5×10^{19} cm^{-3}. Surprisingly, Fig. 2 shows that when measured at the same high values of charge carrier density per unit volume the field-effect mobility of OC_1C_{10}-PPV is nearly equal to the field-effect mobility of P3HT. Furthermore, the dependence of the field-effect mobility on charge carrier density is stronger for OC_1C_{10}-PPV due to a larger T_0, which is indicative of a larger energetic disorder as compared to P3HT.

In order to determine the hole mobility of P3HT at low carrier densities J-V measurements have been performed for a P3HT-based hole-only diode in a temperature range of 215 to 294 K (see Fig. 3). The current density at room temperature depends quadratically on the applied voltage, which is indicative of space-charge limited transport. The derived hole mobility at room temperature is 2.8×10^{-5} cm^2/V s, which is more than an order of magnitude lower than what is obtained in P3HT FETs (see Fig. 2). The transport model of hopping in a correlated Gaussian disordered system well describes the field and temperature dependence of a P3HT hole-only diode (solid lines in Fig. 3). Using Eq. (1) the width of the Gaussian energy distribution $\sigma_{DOS} = 0.098$ eV has been determined.

In the temperature range 255–294 K the current density of the P3HT diode depends quadratically on the voltage for applied voltages up to 3 V. As a result, the hole mobility is constant for low fields, and thus also independent of the hole density. The lowest charge carrier density in a space-charge limited diode is found at the noninjecting contact and is given by $p_L = 0.75(\varepsilon_0\varepsilon_r V/eL^2)$, where L represents the thickness of the polymer, and $\varepsilon_0\varepsilon_r$ is the permittivity of the polymer [15]. The voltage range applied of 0.1 to 3 V corresponds to hole densities of 1.4×10^{15} to 4.1×10^{16} cm^{-3}. We note that for voltages higher than 3 V (carrier densities

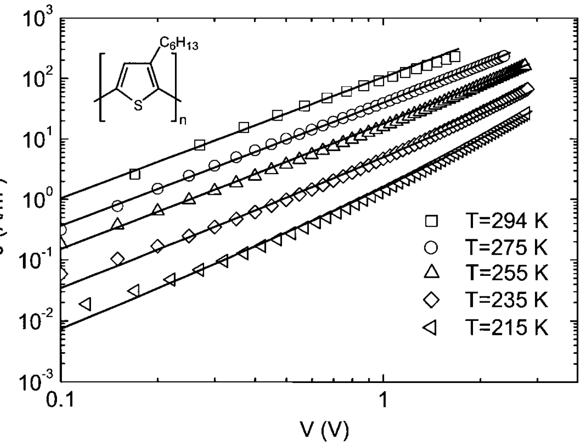

FIG. 3. Temperature dependent current density vs voltage characteristics of a P3HT hole-only diode, with thickness 95 nm and active area 10 mm^2. The solid lines represent the prediction from the space-charged limited model including the field-dependent mobility [Eq. (1)]. Inset: The chemical structure of P3HT.

$>4.1 \times 10^{16}$ cm^{-3}) the carrier density dependence of μ_h cannot be discriminated from the field dependence of μ_h, due to the fact that in a space-charge limited diode both carrier density and field are simultaneously increased. For an OC_1C_{10}-PPV hole-only device with a thickness of 700 nm the mobility of $\mu_h = 5 \times 10^{-7}$ cm^2/V s was constant from an applied voltage of 1 V up to 10 V at room temperature [4], which corresponds to hole densities of 2.5×10^{14} to 2.5×10^{15} cm^{-3}. The experimental mobilities from the hole-only diode measurements and the field-effect mobilities from the transistors are presented together in Fig. 2, for both OC_1C_{10}-PPV and P3HT in the charge carrier density range of 10^{14}–10^{19} cm^{-3}. Combination of the results from the diode and field-effect measurements shows that typically the hole mobility is constant for charge carrier densities $<10^{16}$ cm^{-3} and increases with a power law for densities $>10^{16}$ cm^{-3}. The large differences in mobility values obtained from diodes and FETs, based on a single semiconducting polymer, are direct results of the large differences in charge densities in these devices. It should be noted that in OC_1C_{10}-PPV the optical properties exhibit a significant anisotropy, pointing to a preferential alignment of the chains in the plane of the film [16]. A possible anisotropy in the charge transport properties would obscure a direct comparison between diodes and FETs. A strong indication for the absence of anisotropy is shown in the inset of Fig. 2; the activation energy of the mobility, E_a, which directly reflects the amount of disorder [Eq. (1)], is plotted as a function of gate voltage from -1 to -19 V. Extrapolating towards zero gate voltage yields an E_a of 0.46 eV, exactly equal to the activation energy as obtained from the diode measurements.

The question that remains is whether the mobility description at low carrier densities, using a Gaussian

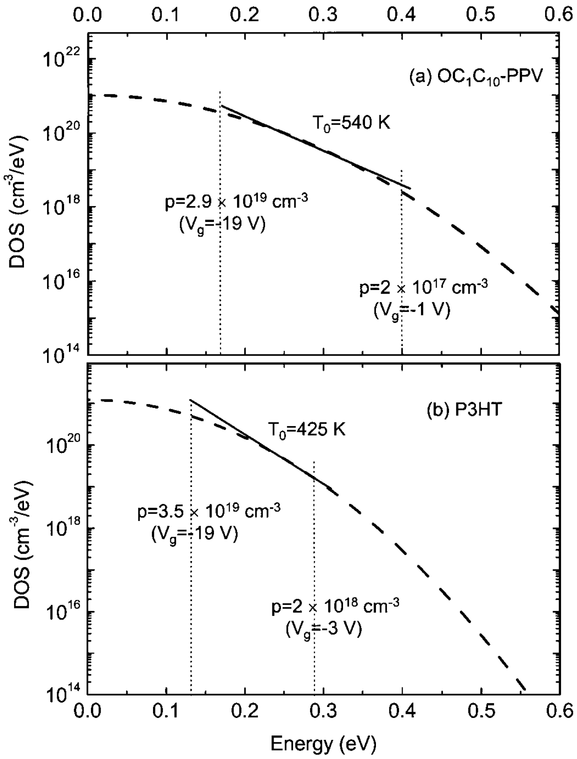

FIG. 4. The Gaussian density of states (DOS), as obtained from the hole-only diode analysis (dashed lines) and the exponential DOS as obtained from the field-effect transistors (solid lines) as a function of energy for (a) OC_1C_{10}-PPV and (b) P3HT. For both semiconductors the exponential density of states is found to be an accurate approximation of the Gaussian density of states, in the energy range in which the transistors operate.

DOS, is fundamentally different from the mobility description at high carrier densities, which employs an exponential DOS. In Figs. 4(a) and 4(b) the obtained Gaussian DOS is plotted as a function of energy for OC_1C_{10}-PPV and P3HT, respectively. For the total number of states per unit volume N_t we have used a value of 3×10^{20} cm^{-3} for both OC_1C_{10}-PPV and P3HT, which corresponds to $1/a^3$ ($a = 1.4$ nm). Additionally, the exponential DOS of OC_1C_{10}-PPV and P3HT as obtained from the FET characteristics are shown, which are described by the characteristic temperature T_0. Both Gaussian and exponential DOS are presented in Fig. 4 in a semilogarithmic plot. For the charge carrier density range in which the OC_1C_{10}-PPV FET operates the Fermi level in the Gaussian, as indicated by the vertical dashed lines, ranges from 0.4 to 0.16 eV with respect to the center of the Gaussian DOS. From Fig. 4(a) it appears that in this energy range the exponential distribution with $T_0 =$ 540 K is a good approximation of the Gaussian DOS with $\sigma_{DOS} = 0.112$ eV. Similar behavior is observed for P3HT in Fig. 4(b), in which the exponential distribution with $T_0 = 425$ K approximates well the Gaussian DOS with $\sigma_{DOS} = 0.098$ eV in the energy range from 0.27 to 0.13 eV. This unifies the two models, in the sense that the exponential DOS accurately describes the Gaussian DOS in the energy range in which the field-effect transistors operate. Consequently, the field, temperature, and density dependencies of the hole mobility in these disordered conjugated polymers are unified in one single charge transport model.

In conclusion, the large mobility differences reported for conjugated polymers used in PLEDs (OC_1C_{10}-PPV) and FETs (P3HT) have been shown to originate from the strong dependence of the mobility on the charge carrier density. The exponential density of states, which consistently describes the field-effect measurements, is shown to be a good approximation of the tail states of the Gaussian in the energy range where the Fermi level is varied.

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