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Electron traps in semiconducting polymers: Exponential versus Gaussian trap distribution

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The low electron currents in poly(dialkoxy-*p*-phenylene vinylene) (PPV) derivatives and their steep voltage dependence are generally explained by trap-limited conduction in the presence of an exponential trap distribution. Here we demonstrate that the electron transport of several PPV derivatives can also be well described with a trap distribution that is Gaussianly distributed within the band gap. In contrast to the exponential distribution the trap-limited electron currents can now be modeled using the same Gaussian trap distribution for the various PPV derivatives.

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I. INTRODUCTION

Semiconducting polymers have received considerable attention due to their potential use in polymer light-emitting diodes^{1,2} (PLEDs), solar cells,³ and field-effect transistors⁴ (FETs). Especially for PLEDs, a balanced electron and hole transport is important for optimal device performance. Poly(dialkoxy-*p*-phenylene vinylene) (PPV) derivatives have been used as a model system for studying the charge transport in conjugated polymers.⁵ The hole current in PPV is space-charge limited with a mobility depending on both the electric field and charge-carrier density. Initially, in FETs the density dependence has been described using the Vissenberg and Matters expression, originating from hopping in an exponential density of states (DOS).⁶ This description has been used to unify the charge transport in FETs and LEDs.⁷ Later, a description for the mobility incorporating both the density and field dependence was obtained, based on charge-carrier hopping within a Gaussian DOS.⁸ The fact that both models provide a consistent description of the diode current-voltage (*J*-*V*) curves originates from the fact that the section of the Gaussian DOS that is being filled during a *J*-*V* scan may also be approximated by an exponential, or vice versa.⁷

II. THEORY

The electron current in most conjugated polymer diodes is observed to be strongly reduced as compared to the hole current.⁹ Moreover, steeper voltage dependence and stronger layer-thickness dependence are observed. This characteristic is generally explained by a trap-limited electron current (TLC), with an exponential distribution of trap states in the band gap according to

$$D_t(E) = \frac{N_t}{kT_t} \exp\left[-\frac{(E_c - E)}{kT_t}\right], \quad (1)$$

with N_t the total concentration of electron traps, T_t a characteristic temperature specifying the decay of the exponential distribution, and $E_c - E$ the energy below the lowest unoccupied molecular orbital (LUMO) of the polymer.^{10,11}

Neglecting diffusion, the current can then be expressed analytically as¹²

$$J = N_c q \mu \left(\frac{\varepsilon_0 \varepsilon_r}{q N_t}\right)^r \left(\frac{2r+1}{r+1}\right)^{r+1} \left(\frac{r}{r+1}\right)^r \frac{V^{r+1}}{L^{2r+1}}, \quad (2)$$

with q the elementary charge, $\varepsilon_0 \varepsilon_r$ the dielectric constant, μ the trap-free mobility, V the applied voltage, L the sample thickness, and $r = T_t/T$. From Eq. (2), the trap temperature T_t can be directly estimated from the thickness and voltage scaling of the electron transport. However, since the charge transport in conjugated polymers is generally described by hopping in a Gaussian DOS that is broadened due to disorder,¹³ it would be obvious that the broadening of the trap states is also described by a *Gaussian* distribution, centered at a depth E_t below the LUMO, according to

$$D_t(E) = \frac{N_t}{\sqrt{2\pi}\sigma_t} \exp\left[-\frac{[E - (E_c - E_t)]^2}{2\sigma_t^2}\right], \quad (3)$$

with σ_t the width of the distribution and $E_c - E_t$ the trap energy. However, the applicability of a model based on a TLC in the presence of Gaussian-distribution trap states has not been investigated so far. In literature, a number of approximations have been reported for a TLC with Gaussian trap states, but these are only valid in a limited voltage regime.¹⁴ Hwang and Kao obtained a description for the case of a shallow Gaussian trap, given by¹⁵

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \theta \frac{V^2}{L^3}. \quad (4)$$

Equation (4) is essentially the expression for trap-free space-charge-limited current (SCLC) given by the Mott-Gurney square law¹⁶ scaled with a factor θ given by

$$\theta = \frac{N_c}{N_t} \exp\left[-\frac{E_t}{kT} - \frac{1}{2} \left(\frac{\sigma_t}{kT}\right)^2\right], \quad (5)$$

with N_c the effective density of states in the LUMO. For a narrow trap distribution, Eq. (5) reduces to the expression for a single discrete trap level.¹⁷ In the derivation of Eq. (5) it is assumed that only the tail of the Gaussian is filled and it is therefore only valid when the Fermi energy lies below the center of the trap DOS (shallow trap). For the case where the Fermi energy is above the center of the trap DOS, defined

as a deep Gaussian trap, another approximation was obtained by Nešpůrek and Smejtek¹⁸ and later by Hwang and Kao.¹⁵ Remarkably, in this case the obtained approximation for the current-voltage characteristic is equal to Eq. (2), but now with the exponent r given by

$$r' = \sqrt{1 + 2\pi \left(\frac{\sigma_t}{4kT} \right)^2} \quad (6)$$

and involving an effective trap density N'_t according to

$$N'_t = \frac{N_t}{2} \exp[E_t/r'kT]. \quad (7)$$

Both approximations for the case of a Gaussian trap distribution are essentially the equations for an exponential trap DOS and a single discrete trap level. This means that the current-voltage characteristics of the trap-limited transport in the presence of a Gaussian trap distribution can be approximated by a single discrete trap level at low trap occupancies, meaning low voltages, and an exponential trap distribution level at high occupancies and thus high voltages.

However, in the approximations leading to Eqs. (2) (shallow traps) and (4) (deep traps) several assumptions and simplifications are made. For instance, in all cases diffusion is neglected and a constant mobility is assumed. More importantly, these approximations are only valid in the range where the free-carrier density is much smaller than the density of trapped charges ($n \ll n_t$). For a more accurate description of the trap-limited current a numerical device model has to be used, which includes diffusion and allows for the use of a density- and field-dependent mobility. In such a device model only the free charges contribute to the current, while both free and trapped carriers influence the electric field via the Poisson equation. To numerically calculate the trap-limited current it is therefore required to separate the total carrier density into free and trapped carriers. This relation can be calculated by assuming local thermal equilibrium.¹⁹ The occupancy of the trap distribution is then calculated using Fermi-Dirac statistics. While the occupancy of an exponential trap distribution or a single-level trap can be relatively easily calculated analytically, the occupancy of a Gaussian trap distribution, given by the product of the trap DOS and the Fermi-Dirac function is not straightforward. Only very recently an accurate approximation of the Gauss-Fermi integral was reported by Paasch and Scheinert.²⁰ In this study we have used their approximation to evaluate the effect of Gaussianly distributed traps on the transport and compare it with the approximations of exponentially distributed traps and a discrete level trap. We demonstrate that the numerical device model including Gaussian traps well describes the temperature-dependent electron transport in three PPV derivatives. As a result the trap-limited currents in PPV, previously described with an exponential trap distribution, can also be explained with the Gaussian trap model.

III. ANALYSIS

As stated above, the calculation of trap-limited currents requires a separation of the total carrier density into free (n) and trapped (n_t) carriers. For a single trap level the relation is simply linear $n_t \propto n$, whereas for an exponential distribution

FIG. 1. (Color online) Dependence of n_t on n for a Gaussian, exponential, and single-level trap distribution at room temperature. The total trap density is $N_t = 1 \times 10^{24} \text{ m}^{-3}$, $E_t = 0.2 \text{ eV}$, and $\sigma_t = 0.10 \text{ eV}$. The effective density in the LUMO N_c is set at $3 \times 10^{26} \text{ m}^{-3}$. The parameters for the single level and the exponential are chosen such that Eqs. (2) and (4) should give a correct description. For the exponential trap DOS N'_t and T_t are given by Eqs. (6) and (7) as $N'_t = 1.9 \times 10^{25} \text{ m}^{-3}$ and $T_t = 785 \text{ K}$. The effective trap depth for the single-level trap is $E_t = 0.40 \text{ eV}$. The inset shows a schematic representation of a discrete single-level trap, an exponential distribution, and a Gaussian distribution.

of traps, n and n_t are related via a power law given by $n_t \propto n^{1/r}$, with $r = T_t/T$. More generally, a dependence of the form $n_t \propto n^{1/r}$ leads to $J \propto V^{r+1}/L^{2r+1}$ [giving $J \propto V^2/L^3$ for a single trap level ($r = 1$)]. Figure 1 shows the approximation between n and n_t as obtained by Paasch and Scheinert for a Gaussian distribution, as well as the relations for the exponential and single trap level distribution. The trap parameters for the latter two are calculated using Eqs. (5)–(7), such that Eqs. (2) and (4) are valid approximations of the trap-limited current for the case of a Gaussian trap DOS. It can be observed from Fig. 1 that the $n_t(n)$ relation of the Gaussian trap DOS asymptotically reaches a slope equal to 1 in the log-log plot for small densities, which corresponds to the behavior of a discrete trap level. Accordingly, the current in this low-density regime will have a slope of 2 and the current density can then be well approximated with Eq. (4). The exponential trap distribution gives a constant and smaller slope of the $n_t(n)$ dependence (higher r), leading to stronger voltage and thickness dependence. However, the $n_t(n)$ relation for the Gaussian trap DOS does not have a constant slope. In the low trap density limit, the slope equals 1, and when the Gaussian is filled up further, the slope of $n_t(n)$ changes. It can therefore be expected that the slope of the J - V characteristics in a log-log plot is not constant but depends on the part of the Gaussian trap DOS being filled during a voltage sweep.

As a next step, we have implemented the Gaussian trap distribution of trap states in a numerical drift-diffusion model.²¹ To evaluate the charge transport in the presence of a Gaussian trap distribution we simulate a number of metal-semiconductor-metal sandwich devices, using a mobility of $1 \times 10^{-11} \text{ m}^2/\text{V s}$, and symmetric Ohmic contacts ($V_{bi} = 0$).

FIG. 2. (Color online) Simulated J - V plots for $L = 300$ nm, $N_t = 2 \times 10^{23}$ m $^{-3}$, $E_t = 0.4$ eV, and varying values of σ_t . The prediction from Eq. (4) is shown for $\sigma_t = 0.05$ eV.

To keep the calculations as transparent as possible we have chosen to perform these simulations with a constant mobility, so that the effects of the trap parameters can be independently distinguished from the influence of a field- or density-dependent mobility. Since the single-level trap can be regarded as a limiting case of the Gaussian distribution with $\sigma_t = 0$, it is interesting to compare the calculated currents for varying values of σ_t (Fig. 2). The trap-limited current in the case of a single discrete trap level can be described by a quadratic behavior up to the trap-filled limit given by $V_{\text{TFL}} = q N_t L^2 / 2 \epsilon_0 \epsilon_r$.²² At this point the traps are completely filled and all additional injected carriers contribute to the transport, causing a rapid increase of the current towards the trap-free SCLC. For the Gaussian trap distribution, this change is more gradual due to the broadness of the trap distribution and for a broad distribution (large σ_t), this transition region becomes indiscernible from the rest of the J - V characteristic. Furthermore, for the broader trap distributions the quadratic part can also no longer be discerned at low voltages. The range where the current is quadratic depends on the trap density, the sample thickness, and the width of the Gaussian distribution. Equation (4) is therefore only applicable to thick devices with a high trap density and a narrow trap distribution.

An interesting feature can be seen in Fig. 2. All the calculated J - V curves cross at $V \approx 24$ V. At this bias, the Fermi level passes through the middle of the Gaussian trap distribution and exactly half of the traps are occupied, independently of the width of the Gaussian distribution. Analogous to the calculation of the trap-filled limit, this voltage can be calculated as

$$V_{\text{half}} = \frac{q L^2}{4 \epsilon_0 \epsilon_r} (N_t - n_{t0}), \quad (8)$$

with n_{t0} the density of trapped electrons in the absence of applied voltage.

In Fig. 3 the dependence of the J - V curve on the trap depth is depicted. It follows that a deeper trap results in steeper J - V . As the voltage passes $V_{\text{half}} = 50$ V, the Gaussian trap distribution gradually fills up, and the density of free electrons

FIG. 3. (Color online) Simulated J - V curves for $L = 300$ nm, $N_t = 4 \times 10^{23}$ m $^{-3}$, $\sigma_t = 0.2$ eV, and varying trap depths. Also shown is approximation equation (2) for the case of $E_t = 0.3$ eV, with r' and N'_t given by Eqs. (6) and (7).

increases rapidly so that it surpasses the density of trapped electrons. The current then eventually becomes limited by the trap-free SCLC. For deeper trap levels, the trap-limited current is lower, so the transition towards the trap-free SCLC is steeper. It should be noted that this behavior is fundamentally different as compared to an exponential distribution of traps. In the latter case the slope of the J - V curve is only determined by $r = T_t/T$, and is independent of the trap depth. As is clear from Figs. 2 and 3 the slope of the J - V curve for Gaussian traps is both dependent on the shape of the distribution (σ_t) as well on the trap depth ($E_c - E_t$). The approximation according to Eq. (2) is also shown in Fig. 3 for $E_t = 0.3$ eV. It is clear that Eq. (2) gives a poor description of the numerically calculated J - V 's as expected from the different dependence of n_t in Fig. 1 and as was previously shown by Paasch and Scheinert.²³ The slope of the J - V differs significantly, while the currents start to deviate beyond V_{half} . This is due to a critical simplification made in the derivation of Eq. (2). The concentration of free carriers is assumed to be small compared to the concentration of trapped carriers. In effect this implies that it is assumed that the Gaussian is never filled up beyond the center. Accordingly, in Eq. (2) the trap distribution is never filled up completely, and n_t eventually exceeds the total trap density N_t , while in the numerical simulation the concentration of trapped electrons asymptotically approaches N_t .

Equations (2) and (4), as well as the simulations shown in Figs. 2 and 3, are derived and carried out using the band transport formalism, based on Boltzmann statistics for the density of free charges. However, as mentioned before, the charge transport in organic semiconductors is generally described by hopping in a Gaussian DOS, in which case Boltzmann statistics are not valid. Assuming that only the tail of the Gaussian LUMO is filled, the density of free electrons is given by the nondegenerate limit.²⁴ This equation has the same functional form as the Boltzmann approximation, only shifted by a temperature-dependent factor $\sigma^2_{\text{LUMO}}/kT$. This makes it possible to take into account the Gaussian distribution of the

FIG. 4. Temperature dependence of the electron current for three PPV derivatives. The lines are numerical fits incorporating a Gaussian trap with trap parameters for (a) OC₁C₁₀-PPV: $N_t = 1.3 \times 10^{23} \text{ m}^{-3}$, $\sigma_t = 0.10 \text{ eV}$; (b) MEH-PPV: $N_t = 1.1 \times 10^{23} \text{ m}^{-3}$, $\sigma_t = 0.10 \text{ eV}$; and (c) NRS-PPV: $N_t = 1.1 \times 10^{23} \text{ m}^{-3}$, $\sigma_t = 0.10 \text{ eV}$.

LUMO by introducing an effective trap depth, analogous to the correction for the case of an exponential trap distribution.²⁵ Incorporating the effect of energetic disorder for the mobile carriers into the model leads to an effective trap depth,

$$E_{t,\text{eff}} = E_{t,\text{abs}} - \frac{\sigma_{\text{LUMO}}^2}{2kT}. \quad (9)$$

By plotting $E_{t,\text{eff}}$ against $1/kT$, the absolute trap depth $E_{t,\text{abs}}$ and the width of the Gaussian of the LUMO σ_{LUMO} can be obtained.

IV. EXPERIMENTAL RESULTS

Having evaluated the transport in the presence of a Gaussian trap distribution we apply the model to electron-transport measurements of three PPV derivatives: poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene] (OC₁C₁₀-PPV), poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV), and poly[{2-[4-(3',7'-dimethyloctyloxy-phenyl)]}-co-{2-methoxy-5-(3',7'-dimethyloctyloxy)}-1,4-phenylene vinylene] (NRS-PPV). The electron transport was measured using sandwich-type devices with an aluminum bottom contact functioning as a hole-blocking anode.¹⁰ The PPV layers were spincoated from a toluene solution in a nitrogen environment. The anode and cathode were evaporated using a shadow mask at a pressure of $\sim 10^{-6}$ mbar. The cathode consisted of a 5 nm barium layer capped with a 100 nm aluminum layer.

For MEH-PPV it has been recently demonstrated by Zhang *et al.* that the electron transport is consistently described by the concept of free electrons in combination with deep traps.²⁶ The free-electron mobility was shown to be equal to the mobility of free holes by deactivating the electron traps through *n*-type doping. As a result the dependencies of the mobility on electric field and density are known.²⁷ As shown in Fig. 4 the electron transport of the three polymers can be well described with a broad Gaussian trap with parameters $\sigma_t = 0.1 \text{ eV}$ and $N_t = 1.1 \times 10^{23} \text{ m}^{-3}$ (MEH-PPV and NRS-PPV) and $N_t = 1.3 \times 10^{23} \text{ m}^{-3}$ for OC₁C₁₀-PPV. Figure 5 shows the dependence of $E_{t,\text{eff}}$ on temperature. For all three polymers the dependence can be well described by Eq. (9) with $\sigma_{\text{LUMO}} = 0.13 \text{ eV}$ for OC₁C₁₀-PPV, $\sigma_{\text{LUMO}} = 0.12 \text{ eV}$ for

FIG. 5. (Color online) Dependence of the effective trap depth $E_{t,\text{eff}}$ on temperature. The lines are fits of Eq. (9) with $E_{t,\text{abs}} = 0.71 \text{ eV}$ and $\sigma_{\text{LUMO}} = 0.13 \text{ eV}$ for OC₁C₁₀-PPV, $E_{t,\text{abs}} = 0.69 \text{ eV}$ and $\sigma_{\text{LUMO}} = 0.12 \text{ eV}$ for MEH-PPV, and $E_{t,\text{abs}} = 0.82 \text{ eV}$ and $\sigma_{\text{LUMO}} = 0.14 \text{ eV}$ for NRS-PPV. The inset shows a schematic representation of the Gaussian LUMO and trap DOS. The trap density is exaggerated for clarity.

MEH-PPV, and $\sigma_{\text{LUMO}} = 0.14$ eV for NRS-PPV. These values of the width of the Gaussian DOS are in good agreement with previous reported values for these polymers.^{8,28,29} The absolute trap depth amounts to ~ 0.7 eV for OC1C10-PPV and MEH-PPV, respectively, and to 0.82 eV for NRS-PPV. Remarkably, the trap-limited electron transport for the three PPV derivatives can be described with one and the same trap distribution: A total amount of traps of $N_t \approx 1.0 \times 10^{23} \text{ m}^{-3}$, Gaussianly distributed with a width of $\sigma_t = 0.1$ eV and with its center located 0.7–0.8 eV below the LUMO. The electron transport of these materials has been previously described with the exponential trap model.²⁵ That this is also possible can be understood from Fig. 1: During a J - V scan, only a part of the trap DOS is being filled up, which can alternatively be approximated by an exponential trap DOS. However, for each PPV derivative the trap parameters N_t and T_t had to be adjusted individually to get agreement with experiment. When the traps in PPV have a common physical origin, i.e., an oxygen-related defect, it is far more realistic that the trap-limited currents in the various PPV derivatives can be described with a single (Gaussian) trap distribution.

V. CONCLUSIONS

In conclusion, we have investigated the trap-limited current in disordered semiconductor diodes for the case of a Gaussian trap distribution. The Gaussian trap distribution was implemented in a numerical drift-diffusion model for device simulation and the numerical results were compared to previously reported analytical approximations for shallow and deep traps. We show that the Gaussian trap model can be used to describe the temperature-dependent electron transport in three PPV derivatives. These experimental data, which had previously been described using an exponential trap distribution, can also be explained with the Gaussian trap model using the same trap distribution for the three derivatives.

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