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# Space-charge limited current in regioregular poly-3-hexyl-thiophene

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Temperature dependent current–voltage characteristics of an organic diode based on a thin film of regioregular poly-3-hexyl-thiophene (P3HT) are compared with results of a theoretical model assuming space-charge limited currents with a density of states (DOS), nonmonotonous in energy. This DOS was deduced from experiments utilizing the method of thermally stimulated currents. Both, experiments and theory result in an almost power-law dependence of  $j \propto V^m$ , where the exponent  $m$  increases with decreasing temperature assuming a value of  $m=2$  at room temperature. This effect can be accounted for by filling of deep traps at lower temperatures. Transport of charge carriers in P3HT seems to be limited by hopping in disordered regions rather than by the transport via extended states within crystalline grains. © 2003 American Institute of Physics.

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## I. INTRODUCTION

Highly regioregular poly-3-hexyl-thiophene (P3HT) is well known as one of the most promising materials for applications in organic field-effect transistors (OFETs). Field-effect mobilities on the order of  $0.1 \text{ cm}^2/\text{Vs}$  have been reported,<sup>1</sup> which are comparable to those of amorphous silicon. The origin of such high mobilities is the high molecular order and hence the global alignment of molecules in the charge transport channel. The highest mobilities are achieved if the molecules resume a preferential orientation such that the direction of intermolecular  $\pi$ – $\pi$  stacking occurs parallel to the OFET substrate.<sup>2</sup> Field-effect mobility of P3HT increases by 4 orders of magnitude (from  $10^{-5}$  to  $0.1 \text{ cm}^2/\text{Vs}$ ) with an increase of the degree of regioregularity.<sup>2</sup>

The field-effect mobility of regioregular P3HT is strongly influenced by the self organization of the polymer chains near the gate oxide, which coincides with the surface of the OFET substrate in case of a bottom gate configuration. It has been demonstrated that due to self organization charge transport is no longer dominated by the amorphous regions of the polymer film but is reflecting the transport properties of ordered, crystalline polymer domains of lamellar type.<sup>1</sup> Interchain coupling in these lamellas is sufficiently strong so that the charge carriers cannot be considered to be confined to a single chain, rather, they exhibit quasi two-dimensional characteristics in OFET applications.<sup>2–4</sup> The situation is more complicated and less investigated considering the bulk mobility in the P3HT film when sandwiched between two electrodes.<sup>5,6</sup> Bulk mobilities are typically several orders of magnitude less than field-effect mobilities<sup>6</sup> due to the absence of near-surface effects. The microstructure is complex consisting of microcrystalline grains with a typical size of 10 nm embedded into a more disordered, amorphous matrix.<sup>2,7</sup>

Transport in such two-phase systems is limited by the amorphous regions and not by the crystalline grains. Therefore the carrier mobility at least for samples with a thickness much larger than the grain size is small and values are on the order of  $10^{-5}$ – $10^{-6} \text{ cm}^2/\text{Vs}$ .<sup>2</sup> However the situation is not so obvious on a length scale of 100 nm, which resembles a typical thickness of a light-emitting diode.<sup>8</sup> In this case the crystalline grain size cannot be considered small compared to sample thickness. Consequently the mobility strongly decreases with the increase of drift distance.<sup>5</sup>

Transport in organic systems is generally described by the model based on hopping between point-like localized states, which are disordered in space and energy,<sup>9,10</sup> but the restrictions of this concept for the case if transport occurs via extended states within microregions, as in the conjugated polymers, was also discussed in the literature.<sup>11</sup> However, the self-consistent hopping theory of space-charge limited current (SCLC), accounting for the filling of localized states was not applied to polycrystalline organic diodes. On the other hand, the concept of a “transport level”<sup>12,13</sup> allows the description of hopping transport to be reduced to a multiple-trapping (MT) formalism. Such formalism was applied previously in a theoretical analysis of SCLC in organic materials with a Gaussian density of states (DOS).<sup>14,15</sup> It was demonstrated that current–voltage ( $I$ – $V$ ) characteristics of single-layer organic diodes are sufficiently affected by the spatial-dependent filling of traps in the SCLC regime.

In this article results of experimental investigations of the structure, DOS, and temperature dependence of SCLC in single-layer diodes based on regioregular P3HT are presented. The DOS of P3HT, which was estimated from the method of thermally stimulated currents, exhibits nonmonotonous character with the presence of an additional energy distribution of deep states, similar to results for other organics.<sup>11,16</sup> The increase of SCLC with applied voltage becomes considerably steeper with a decrease of temperature from 300 to 80 K.  $I$ – $V$  characteristics were modeled by the use of MT formalism assuming nonmonotonous DOS in en-

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ergy. It will be shown that accounting for of the progressive filling of deep states can explain the faster increase of the SCLC with voltage. It is demonstrated that the slope of the  $I$ - $V$  characteristics and its dependence on temperature better describes the experimental results assuming the presence of deep states in the DOS. The physical nature of charge transport in thin polycrystalline films and guidelines for its further experimental and theoretical analysis are discussed.

## II. EXPERIMENT

Glass substrates, covered with 100 nm indium-tin-oxide (ITO) (MERCK KGaA) were used for device fabrication. The ITO was first photolithographically patterned, cleaned in a detergent solution, and washed with de-ionized water. To improve the ITO surface the sample was exposed for 30 min to an ozone atmosphere (UVP100 PR-100). Immediately after the washing the substrate was transferred into an oxygen and water free, nitrogen flooded glovebox where a polymer solution (1 wt. %) from commercially available regioregular P3HT (Aldrich) dissolved in chloroform (99.8% purity) was spin coated on the substrate using an angular velocity of 1000 rpm for 30 s. This resulted in a layer thickness of 120 nm determined by a DekTak surface profilometer. The sample was then transferred to an evaporation chamber without exposure to ambient air where 100 nm aluminum was deposited at a base pressure of  $10^{-6}$  mbar through a shadow mask using a deposition rate of 1 nm/s resulting in an active area of the diode of  $0.1 \text{ cm}^2$ .

For electrical measurements the device was transferred into an Oxford cryostat without exposure to air. The cryostat setup is equipped with two independent heating elements to control the cryostat wall and the sample holder independently. Liquid nitrogen was used for cooling and helium as an exchange gas to guarantee thermal equilibrium inside the cryostat system. An electrometer (Keithley 6517A) was connected to the sample and used simultaneously as voltage source and current measurement unit. For temperature dependent  $I$ - $V$  characteristics the sample was cooled down in the dark and measured using 0.02 V steps with a delay time of 1 s. After each measurement the device was heated up to room temperature to release any charges that have been trapped during the  $I$ - $V$  cycle. Injection of holes from the ITO electrode is assumed to be of ohmic nature due to a low energetic barrier.<sup>17</sup>

Thermally stimulated current (TSC) experiments were performed as described by von Malm *et al.*<sup>16</sup> The sample was initially cooled to 80 or 4 K in the dark, followed by an optical trap filling by exposure to light at a wavelength of  $\lambda=400 \text{ nm}$  for 300 s. Generated holes and electrons are trapped in states, which are deep enough not to release thermally during experimental times. After trap filling the temperature of the sample is increased linearly with a rate of 10 K/min resulting in a detrapping of charge carriers with increasing temperature. The resulting thermally stimulated currents are detected with the electrometer, mentioned above.

For x-ray diffraction (XRD) measurements a diffractometer (Seifert 3003 PTS) was used in Bragg Brentano geometry. To achieve sufficient diffraction volume a drop casted

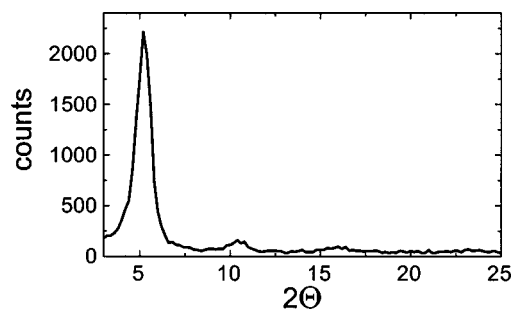


FIG. 1. X-ray diffraction pattern of a thin film of regioregular P3HT cast from chloroform solution on a glass substrate.

polymer film with a thickness of a few hundred nanometres was prepared on a silicon (100) wafer.

## III. EXPERIMENTAL RESULTS

### A. X-ray diffraction results

The XRD pattern of a casted P3HT film is shown in Fig. 1 and displays a diffraction peak around  $5.2^\circ$  which is known to correspond to a well organized lamellar structures for this material. For an estimation of the crystallite size the well known Scherer equation<sup>18</sup> was used correlating the diffraction peak full width at half maximum  $\beta_{1/2}$  with the crystal size of the grain

$$\beta_{1/2} = k_s \lambda / l \cos \Theta,$$

where  $k_s=0.94$  is the Scherer constant,  $\Theta$  is the diffraction angle, and  $\lambda$  the wavelength of the radiation crystalline grain used. With  $1^\circ$  a grain size of  $l=8 \text{ nm}$  was estimated. This is in good agreement with published values.<sup>7,19</sup>

### B. Thermally stimulated current (TSC) results

The TSC signals of two different batches are displayed in Fig. 2. The solid line resembles the TSC signal of the devices, from which the  $I$ - $V$  characteristics (Fig. 3) were taken. This sample was trap filled at 80 K and subsequent measurement shows two main current peaks, a narrow peak

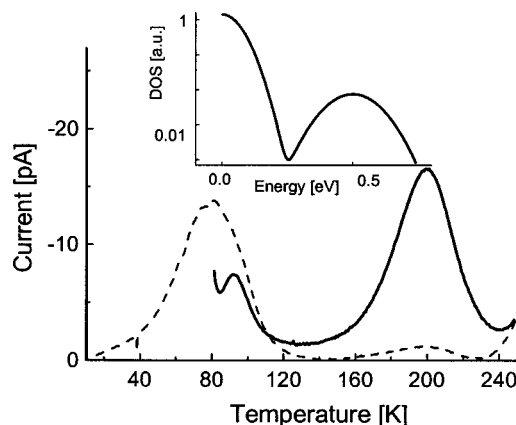


FIG. 2. TSC signals from a thin film of P3HT sandwiched between an ITO and aluminum electrode for the case of temperature of trap filling 77 K (solid line) and 4 K (dashed line). Inset shows the energy dependencies of the DOS.

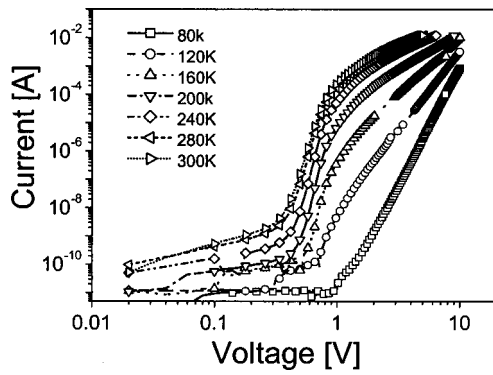


FIG. 3. Current–voltage characteristics of a P3HT diode sandwiched between ITO and aluminum electrodes at different temperatures as indicated.

with a maximum at 93 K, and a much broader peak at 200 K. It is likely that the appearance of the broad current peak around 195 K resembles a distribution of traps comparable to the case of  $\text{Alq}_3$ .<sup>20</sup> The TSC peak is clearly separated from the low temperature peak at 93 K. Therefore, it can be considered as a separate band in the DOS. In order to get more information on the peak at 93 K, measurements were carried out by trap filling at liquid helium temperature. Despite the different amplitudes of the TSC currents the main features remain the same. One recognizes that the peak at 93 K is only the tail of the TSC peak of the helium-temperature illuminated sample. Therefore at least two separate bands have to be considered in the DOS. For the DOS resembling shallow trapped carriers it is still open if it consists only of tail states of the transport related Gaussian DOS (TDOS) or resembles an independent DOS band.<sup>9</sup> In both cases the low-temperature TSC peak can be interpreted as generated by emptying of shallow traps subsequent to trap filling at the lowest utilized temperature, e.g., 77 K for the solid line and 4 K for the dashed line in Fig. 2. This process is significant in both cases due to occurrence of tunneling jumps of charge carriers downward in energy.<sup>11</sup> However, in the former case release of charge carriers is a much faster process due to an additional contribution of thermal activation. This may explain the different amount of charge stored in each of the two peaks for both charging conditions. However, both measurements yield the same position of the high-temperature TSC peak, which corresponds to deep traps. Qualitatively one has to conclude from the form of the TSC signal that the DOS is composed out of two or three bands.

### C. Current–voltage characteristics

The  $I$ – $V$  characteristics of P3HT measured at temperature from 80 to 300 K are displayed in Fig. 3 and exhibit a transition from an  $I \propto V$  law at low voltages of  $V \ll 1$  V to an approximately power-law dependence  $I \propto V^m$  at high voltages, where  $m$  is found to be temperature dependent ranging from  $m = 2.5$  at  $T = 300$  K to  $m \approx 8.3$  at  $T = 80$  K. These two regions at  $I$ – $V$  characteristics are separated by an intermediate region of a faster increase of the current at  $V \approx 0.3$ – $1$  V, which probably can be interpreted as the transition from an ohmic to an SCLC behavior in the presence of traps.<sup>21</sup> At this point it seems to be reasonable to assume that

the same traps are involved that generate the high-temperature maximum of the TSC signal at 195 K. It should be mentioned that the relatively high ohmic current at low voltages is most probably caused by a vast amount of impurities in the utilized materials.

## IV. THEORY

In polymers and other classes of amorphous organic semiconductors charge transport occurs mainly via hopping.<sup>9,10</sup> On the other hand, the transport via extended states is dominant in organic crystals.<sup>22</sup> Drift and diffusion of extended carriers are, however, controlled by trapping-and-release processes as can be described by the MT model. This model can be directly applied to a description of a transport through the polycrystalline layer of P3HT, providing that traps are associated with the sharp boundaries between grains. However, it has been reported that microcrystalline domains in P3HT do not exhibit sharp boundaries and that they are rather being embedded into an amorphous matrix.<sup>2</sup> Therefore charge transport has to be limited by the most difficult hopping processes in the amorphous regions. However, the formalism of MT can be employed also in this case by the use of the concept of effective transport level.<sup>11–13</sup> This level is virtually equivalent to the mobility edge in the MT model. Hence, all states can be qualitatively separated as conductive or trap states. Recently, the MT approach in the presence of SCLC was applied for the theoretical description of  $I$ – $V$  characteristics for an organic material with Gaussian DOS.<sup>15</sup> In this article we apply the same formalism in order to investigate the influence of an additional band of deeper traps on the  $I$ – $V$  characteristic of organic diode under variable temperature. The band of deep traps is also assumed to be Gaussian in energy. The energetic position of this “mobility edge” is combined here with the position of the peak of the TDOS, as in Ref. 15. This assumption is qualitatively approved because: (i) the energetic position of the transport energy has a weak temperature dependence and is located near of the peak of the TDOS<sup>12,13</sup> and (ii) the density of traps in a deep band is assumed to be small enough in order not to disturb the transport energy. Possible restriction of this approach to the hopping transport will be discussed below.

The total spatial density of charge carriers,  $p(x)$ , is the sum of densities of carriers in the conductive states and in the trap states,  $p_c(x)$  and  $p_t(x)$ , respectively. The current density  $j$  is proportional to the density of carriers in the conductive states

$$j = e \mu_0 F(x) p_c(x), \quad (1)$$

where the spatial distribution of the electric field  $F(x)$  is governed by the total density of carriers through the Poisson equation

$$\frac{dF(x)}{dx} = \frac{e}{\epsilon \epsilon_0} [p_c(x) + p_t(x)], \quad (2)$$

where  $e$  is the elementary charge and  $\mu_0$  is the mobility of charge carriers in the conductive states. The density of

trapped carriers is determined under thermal equilibrium conditions by the DOS function  $g(E)$  and the Fermi–Dirac occupation probability function

$$p_t(x) = \int_0^\infty \frac{dE g(E)}{1 + \exp\left[-\frac{E - E_F(x)}{kT}\right]}, \quad (3)$$

where  $E$  is the energy of the charge carriers where  $E=0$  corresponds to the mobility edge,  $T$  the temperature, and  $k$  the Boltzmann constant. The local quasi-Fermi level is governed by the current density and the coordinate-dependent electric field<sup>15</sup>

$$E_F(x) = kT \ln[e \nu_0 \tau_0 \mu_0 N F(x) / j], \quad (4)$$

where  $N$  is the spatial density of traps,  $\nu_0$  is the attempt-to-escape frequency, and  $\tau_0$  is the lifetime of charge carriers in conductive states. It should be noted that the right-hand side of Eq. (2) depends on coordinate  $x$  only via the field strength  $F(x)$ , see Eqs. (1) and (3). Hence, one can separate the variables in Eq. (2) and obtain the dependence  $F(x)$  in implicit form after integration

$$x = \epsilon \epsilon_0 \mu_0 \int_0^F \frac{dF' F'}{j + e \mu_0 F' p_t(F')}, \quad (5)$$

by the use of Eq. (1) and the well-known SCLC boundary condition of  $F(0) = 0$ .<sup>21</sup> The condition of constant applied voltage  $V$  on the polymer layer of the thickness  $L$

$$V = \int_0^L dx F(x), \quad (6)$$

yield the voltage  $V$  for a given current density  $j$  after numerical integration in Eqs. (3)–(5) and hence the current–voltage characteristic of the polymer diode.

## V. DISCUSSION AND COMPARISON WITH EXPERIMENT

$I$ – $V$  characteristics at low voltages,  $V \leq 0.3$  V exhibit an ohmic dependence,  $I \propto V$ , (see Fig. 3). However, it is hard to interpret this dependence in the framework of a conventional model of ohmic conductivity.<sup>21</sup> Indeed, the estimation of the density of intrinsic (thermally generated) carriers resulting from equality of ohmic and SCL currents yield  $N_{\text{cond}} \cong 2 \epsilon \epsilon_0 V_0 / e L^2 \approx 0.6 \times 10^{16} \text{ cm}^{-3}$  at  $V_0 = 0.3$  V. The respective average distance between neighbor charges is  $N_{\text{cond}}^{-1/3} \cong 70$  nm and hence is comparable to the thickness of the P3HT layer of  $L = 125$  nm. Therefore the Coulombic fluctuations of electric field induced by the individual charges should be accounted for. Hence, the macroscopic model, which is described above, is not applicable to the description of charge transport in the low-voltage limit. Therefore, the present investigation will be focused on the case of moderate and high voltages meaning  $V \geq 0.3$  V.

A concrete form of the DOS function  $g(E)$  has to be defined in order to perform numerical calculations. The ubiquitous form for the DOS in organic semiconductors is a single Gaussian function from here on called the TDOS.<sup>9</sup> The results of recent TSC and TSL measurements (see, for example, Refs. 13 and 16), as well as TSC results of this

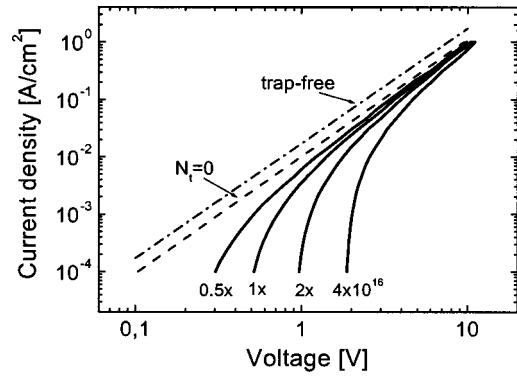


FIG. 4. Current–voltage characteristics of a P3HT-based diode calculated from Eqs. (3)–(7) (solid lines) as a function of the density of deep traps  $N_t$  in  $\text{cm}^{-3}$ , as indicated in the figure. Dot-dashed line shows the  $I \propto V^2$  law for the trap free case where all carriers exhibit the same mobility and the dashed line the case of a Gaussian transport band with  $N_t = 0$ . All other parameters are:  $L = 125$  nm,  $T = 300$  K,  $E_t = 0.5$  eV,  $N = 10^{18} \text{ cm}^{-3}$ ,  $\nu_0 = 10^{12} \text{ s}^{-1}$ ,  $\sigma = 0.05$  eV,  $\sigma_t = 0.08$  eV,  $\mu_0 = 10^{-4} \text{ cm}^2/\text{V s}$ , and  $\epsilon = 3$ .

work (see Fig. 2) suggest, however, the existence of at least one additional band of trapping states which is shifted to lower energies relative to the TDOS. Therefore a superposition of two Gaussian peaks is assumed as the total DOS energy distribution

$$g(E) = \sqrt{\frac{2(N - N_t)}{\pi}} \frac{1}{\sigma} \exp\left(-\frac{E^2}{2\sigma^2}\right) + \frac{N_t}{\sqrt{2\pi}\sigma_t} \times \exp\left(-\frac{(E - E_t)^2}{2\sigma_t^2}\right) \quad E > 0, \quad (7)$$

where  $E_t$  denotes the average trap energy,  $\sigma_t$  the width of the trap distribution,  $N$  the total density of states, and  $N_t$  the total number of traps in the deep band, assumed to be much smaller than  $N$ . This assumption is deduced from TSC results.<sup>16,20</sup>

Typical current–voltage characteristics as a function of density of deep states  $N_t$  is shown in Fig. 4 (solid lines). Three regimes can be distinguished in the  $j(V)$  dependence. The high-voltage limit is described by the trap-free Mott–Gurney law  $j_{\text{free}} = (9/8) \epsilon \epsilon_0 \mu_0 V^2 / L^3$  shown as the dot-dashed line in the Fig. 4. In this limit all traps are filled and therefore no reduction of the mobility has to be taken into account. In the low-voltage limit, which is not shown in Fig. 4, one observes a  $j \propto V^2$  dependence again, but the current is reduced by the factor  $\theta \ll 1$  due to the fact that all traps are involved in the transport which reduces the free mobility  $\mu_0$  to the effective mobility  $\mu_{\text{eff}} = \mu_0 \theta$  and therefore directly reduces the current.<sup>20</sup> At intermediate voltages the current increases faster than the  $V^2$  dependence due to progressive filling of traps. This phenomenon was reported for an exponential and monoenergetic DOS by Lampert and Mark<sup>21</sup> and for the case of a Gaussian DOS by Kao and Hwang<sup>14</sup> and recently by Arkhipov *et al.*<sup>15</sup> The current controlled by the single Gaussian distribution ( $N_t = 0$ , see the dashed lines) is close to the trap-free case for the used parameter set but not equal, again a consequence of the nonfilled states of the DOS modifying the mobility. For  $N_t \neq 0$  the currents increase

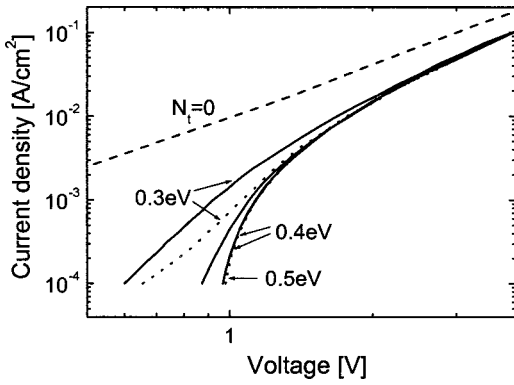


FIG. 5. Current–voltage characteristics of a P3HT-based diode calculated from Eqs. (3)–(7) (solid lines) as a function of the mean energy of the deep traps  $E_t$ , as indicated in the figure for  $N_t=2 \times 10^{16} \text{ cm}^{-3}$ . All other parameters are the same as in Fig. 4. Dashed and dotted lines are calculated for the cases of  $N_t=0$  and  $\sigma_t=0$ , respectively.  $I(V)$  characteristics with  $\sigma_t \neq 0$  and  $\sigma_t=0$  practically coincide for the case of the deepest trap level of  $E_t=0.5 \text{ eV}$ .

faster than those of the TDOS alone whereby the region of most pronounced increase shifts towards higher voltages with increasing  $N_t$ .

In Fig. 5 the dependence on trap depth is displayed. One recognizes that at intermittent voltages the slope of the current becomes smaller with decreasing trap depth  $E_t$ . To indicate the difference to a monoenergetic trap distribution,  $j(V)$  is calculated using a single discrete trap level at the average energy  $E_t$  and density  $N_t$ . The result is added to Fig. 5 as dotted lines. It can be seen that the slope of the  $j(V)$  curve in case of the trap distributions exhibits a smaller slope than for the respective monoenergetic distributions (dotted lines). Therefore it can be deduced that the width of the distribution has a significant influence on the shape of the  $j(V)$  curve as long as the trap states are actively contributing to the transport. If the traps are energetically too deep, however, there will be no dependence on the shape of the deep band of the DOS, which under the present condition is almost reached for  $E_t=0.5 \text{ eV}$ . To underline the importance of the width of the DOS on the  $I-V$  characteristics,  $j(V)$  has been calculated for different widths of the DOS for two different trap densities. The results are displayed in Fig. 6. For the case where the voltage is high enough, the  $j(V)$  dependences exhibit almost an “apparent” power law dependence with a mean exponent considerably larger than two and increasing for increasing trap concentrations.

After having considered the general behavior of the present model, it will now be applied to the temperature dependent  $I-V$  characteristics of P3HT. The result of calculations using Eqs. (3)–(7) is in qualitative agreement with experimental data for voltages  $V \geq 0.3 \text{ V}$  as can be seen in Figs. 7(a) and 7(b). Results of the same calculations but assuming the absence of the deep trap band in the DOS, i.e.,  $N_t=0$ , are shown by the lines without symbols in Fig. 7(b) for comparison. For voltages higher than 1 V both the calculations and measurements yield almost power-law dependences of type  $j(V) \propto V^m$ , where the exponent  $m$  increases with decreasing temperature. In both cases the slope of the power-law dependence is increasing with decreasing tem-

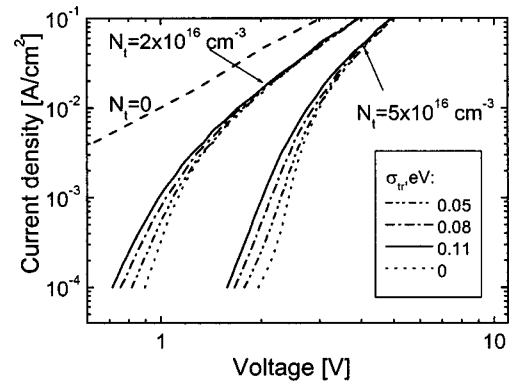


FIG. 6. Current–voltage characteristics of a P3HT-based diode calculated from Eqs. (3)–(7), as a function of the energetic variance of deep traps  $\sigma_t$ , at a fixed average energy of  $E_t=0.35 \text{ eV}$  for two different values of trap density  $N_t$ , indicated in the figure. All other parameters are the same as in Fig. 4.

perature. This effect is well known for the case of a single Gaussian DOS for the limit of sufficiently high voltages, meaning that the majority of traps are deeper in energy than the local quasi-Fermi level. Under these approximations the analytic solution is<sup>14</sup>

$$j(V) \propto V^{m'} \quad \text{with} \quad m' = \left( 1 + \frac{2\pi\sigma_t^2}{16k_B^2 T^2} \right)^{1/2}. \quad (8)$$

Arkhipov *et al.*<sup>15</sup> generalized the model by Kao<sup>14</sup> including a spatial dependence of filling of the TDOS. In both cases the  $j(V)$  dependence can be considered as an approximate power law if the applied voltages exceeds a certain value, e.g., in the present case for voltages exceeding approximately 1.0 V.

Concerning temperature dependence, the experimentally determined exponent varies from  $m=2.5$  at  $T=300 \text{ K}$  to  $m=8.3$  at  $T=80 \text{ K}$  and increases faster than predicted for a single Gaussian TDOS, namely a change from  $m=2.2$  to 4.5. The temperature dependence of  $m$  can be better described assuming a DOS with the band of deep traps [see Eq. (7)],

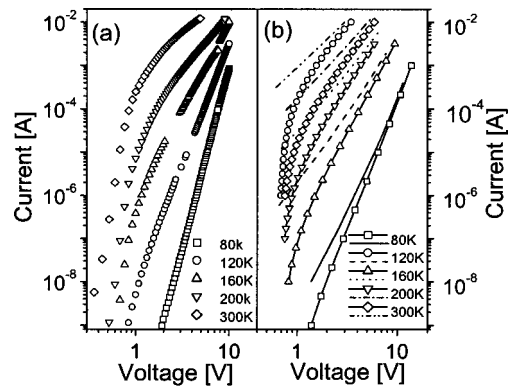


FIG. 7. Comparison of temperature dependence of current–voltage characteristics of a P3HT-based diode: experimental (a); theoretical calculated from Eqs. (3)–(7), assuming  $N_t=1.5 \times 10^{16} \text{ cm}^{-3}$  (symbols) (b), and theoretical results for  $N_t=0$  (lines) (c). Temperature values utilized for the theoretical calculations are the same as used for the experiments and are indicated ( $\tau_0\nu_0=1$ ,  $\sigma=0.055 \text{ eV}$ ,  $\mu_0=10^{-3} \text{ cm}^2/\text{V s}$ , other parameters are the same as in Fig. 4).

namely  $2.7 < m < 5.7$ . The density of deep traps,  $N_t = 1.5 \times 10^{16} \text{ cm}^{-3}$ , was taken in order to provide the filling of these states and respective fast increase of current at the applied voltages between 0.5 and 1 eV in accordance with the experiment. This value was estimated as the low limit for the density of deep traps from previous fractional TSC measurements.<sup>16,20</sup> The other parameters of the DOS, namely  $E_t = 0.5 \text{ eV}$ ,  $\sigma = 0.055 \text{ eV}$ , and  $\sigma_t = 0.08 \text{ eV}$  are also in the qualitative agreement with previous TSC measurements<sup>16,20</sup> for the case of other hole-transporting materials, as well as with TSC measurements of this work. The low total density of states,  $N = 10^{18} \text{ cm}^{-3}$ , which was used in these calculations, may seem to be puzzling, because: (i) it is much smaller than the density of molecular states, which is typically on the order of  $10^{21} \text{ cm}^{-3}$ , and (ii) the transport energy is assumed to be the energy of the upper peak of the DOS and hence the density of traps should be comparable with the total DOS. This apparent contradiction could be explained, considering the structure of the conjugated polymer P3HT. It is generally believed that the charge transport in conjugated polymers is controlled by hopping between segments of a polymer chain, separated from each other by topological defects.<sup>11</sup> The length of segments is subject to random variation in the amorphous media. The typical value of 6–8 nm has to be considered as a typical distance between traps and hence its density is 3 orders of magnitude smaller than the density of molecules. The low value of the mobility of “free carriers,”  $\mu_0 = 10^{-3} \text{ cm}^2/\text{Vs}$ , which is much smaller than the lower limit for the mobility in extended states, is in agreement with the assumption that the rate-limiting step for the transport is a tunneling jump between segments. The other parameter, which is specific for the MT formalism, namely the product  $\tau_0 \nu_0$ , seems to be of the order of unity because both values  $\nu_0$  and  $\tau_0^{-1}$  are controlled by tunneling. As shown above the MT formalism yields the qualitative description of  $I-V$  characteristics for this case. An application of this formalism is approved because the temperature dependence of the transport energy is known to be much weaker than the temperature dependence of energetic distribution of trapped charge carriers. However, the mentioned effect has to be accounted for in order to achieve quantitative agreement with the experiment. Further improvement could be achieved also by a more rigorous experimental determination of the energetic profile of the DOS, especially in the region of shallow states. In addition, temperature depend injection may be influential and affect the theoretical results. Therefore no attempt was made to quantitatively fit the data.

## VI. CONCLUSIONS

Temperature dependence of current–voltage characteristics of a polymer diode, based on regioregular P3HT, could be qualitatively described on the base of MT formalism in the SCLC regime assuming besides the usual energy distribution of shallow traps an additional Gaussian band of deep traps centered at the energy  $E_t \approx 0.5 \text{ eV}$ . It is concluded that

the transport of charge carriers in the polymer film of the thickness of about 100 nm seems to be limited by hopping between the conjugated segments of the polymer chain in disordered regions of P3HT. To attain quantitative agreement with the experimental  $I-V$  characteristics at different temperatures, however, further improvement of the theoretical models is required. Such models have to be formulated in a self-consistent way, solely in terms of hopping parameters. Thereby the interpretation of TSC data have to be improved, in order to account for the release-trapping processes in shallow states and hence provide more detailed information about the DOS. The dependences of the  $I-V$  characteristics on the film thickness, in addition to the dependence on temperature, is also advisable to clarify the energy distribution of shallow localized states for charge carriers.

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