

Trapping-detrapping fluctuations in organic space-charge layers

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A trapping-detrapping model is proposed for explaining the current fluctuation behavior in organic semiconductors (polyacenes) operating under *current-injection conditions*. The fraction of ionized traps obtained from the current-voltage characteristics, is related to the relative current noise spectral density at the *trap-filling transition*. The agreement between theory and experiments validates the model and provides an estimate of the concentration and energy level of deep traps. © 2009 American Institute of Physics. [doi:10.1063/1.3271769]

Polymeric as well as small molecular semiconductor electronic products have shown impressive improvements in their performance during recent years. Organic field-effect transistors (FETs) and light-emitting diodes, solar cells, and memories successfully compete with traditional electronic devices when flexibility, large area, low cost, and weight are the main requirements.^{1–3} The injection of charge carriers at molecule-metal interfaces plays a decisive role in the performance of organic semiconductor devices. Defect states drastically alter the injection mechanism, hence their origin and effect on charge transfer across the interface is one of the main investigation issues. Charge carrier trapping-detrapping processes have been indeed recognized as source of current instability and degradation of organic FETs.^{4–14}

Current and voltage noise have been widely exploited as a spectroscopic tool for investigating the role of deep defect states in inorganic insulators and wide-band gap semiconductors operating under current-injection conditions.^{15–20} A comparatively smaller number of works have been addressed to noise in organic devices.^{21–23} Relative current spectral densities obtained on polyacenes have evidenced a striking peaked behavior at voltages corresponding to the trap filling transition (TFT) between Ohmic (Ω) and space charge limited current (SCLC) regimes. This behavior has been interpreted as evidence for continuous percolation between the two regimes, considered as different electronic phases. Accordingly, at the TFT, the clustering of insulating regions should lead to a reduction of the ohmic paths. The overall effect was expected to give a substantial increase of noise in analogy with the increasing of fluctuations near a structural phase transition.²¹ However, a comprehensive quantitative investigation of noise behavior in organic materials is still lacking.

Here, we present a complementary interpretation based on trapping-detrapping processes of injected carriers at the TFT. Accordingly, we carry out a quantitative comparison between theory and experiments, for both transport and noise. The trap filling transition takes place in the range of voltages $V_t - (c+1)V_t$, with V_t the threshold value for the onset of TFT and c a constant whose value depends on the

steepness of the transition. These voltage values correspond to the energy range where the quasi-Fermi level crosses the trap level. In,¹⁵ the relative-noise crossover between Ohmic and SCLC regimes was investigated in the absence of TFT in silicon. Here, that model is generalized by accounting for the presence of the trap-filling region between the Ohmic and SCLC regimes. For a two terminal sample of length L and cross-sectional area A , the expressions of the current-voltage (I - V) characteristics and the spectral density of voltage fluctuations can be written as follows.

$$I_{\Omega} = \frac{e\mu n_o A}{L} V, \quad (1a)$$

$$S_{\Omega}(V, f) = \frac{\alpha_{\Omega}}{A L n_o f} V^2, \quad (1b)$$

where e is the elementary charge, n_o the density and μ the mobility of free thermal carriers, f the frequency and α_{Ω} the Ohmic Hooge parameter. The relative noise power spectral density is

$$\frac{S_{\Omega}(I, f)}{I_{\Omega}^2} = \frac{S_{\Omega}(V, f)}{V^2} = \frac{\alpha_{\Omega}}{f A L n_o}. \quad (2)$$

Equation (2) implies that the relative noise is constant in the Ohmic regime as voltage increases,

$$I_{\text{SCLC}} = \frac{9A\epsilon_0\epsilon_r\mu\Theta}{8L^3} V^2, \quad (3a)$$

$$S_{\text{SCLC}}(V, f) = \frac{\alpha_{\text{SCLC}}}{f} \frac{eL}{5A\epsilon_0\epsilon_r\Theta} V, \quad (3b)$$

where ϵ_r and ϵ_0 are, respectively, the relative dielectric constant of the material and the vacuum permittivity, α_{SCLC} the SCLC Hooge parameter. The product $\mu\Theta$ appearing in Eq. (3a) is usually referred to as *effective mobility* μ_{eff} with Θ given by

$$\Theta = \frac{n}{gn_t} = \frac{n_v}{gn_t} \exp[-E_t/kT], \quad (4)$$

where n and n_t are, respectively, the free and trapped carrier density, g is the trap degeneracy factor, n_v the density of states in the valence band (for n -type transport the density of states in the conduction band n_c should be considered), E_t

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the trap energy level, kT the thermal energy. The relative noise power spectral density is

$$\frac{S_{\text{SCLC}}(f)}{I_{\text{SCLC}}^2} = 4 \frac{S_{\text{SCLC}}(V, f)}{V^2} = \frac{4eL}{5A\epsilon_0\epsilon_r\Theta} \frac{\alpha_{\text{SCLC}}}{f} \frac{1}{V}. \quad (5)$$

Equation (5) implies that the relative noise decreases as $1/V$ in the SCLC regime as voltage increases.

To the purpose of describing the noise at the TFT region, we consider the trapping-detrapping processes as the main source of fluctuations. Following the standard approach within a linear kinetics of trapping processes,¹⁶ the variance of the total number of ionized traps is $\Delta N^2 = N_t u(1-u)$ where N_t is total number of traps in the volume of the device. Hence, the relative noise power spectrum writes

$$\frac{S_{\text{TFT}}(f)}{N_t^2} = \frac{4}{N_t} \frac{\tau}{1 + (2\pi f\tau)^2} u(1-u) \equiv Bu(1-u), \quad (6)$$

where τ is the carrier free time and $u = ALn_t/N_t = 1/\{1 + g \times \exp[(E_t - E_F)/kT]\}$ the fraction of ionized traps. Accordingly, u is a function of the applied voltage through the position of the quasi-Fermi level with respect to the trap energy level. It is worth noting that $u(1-u)$ vanishes at the extremes of the TFT and reaches the maximum value at $u=0.5$, corresponding to half the filling of the total number of traps. The total relative current noise as function of the applied voltage is then given by the sum of three independent contributions as follows:

$$S(f) = \frac{S_I(f)}{I^2} = \frac{S_{\Omega}(f)}{I_{\Omega}^2} + \frac{S_{\text{TFT}}(f)}{I_{\text{TFT}}^2} + \frac{S_{\text{SCLC}}(f)}{I_{\text{SCLC}}^2}, \quad (7)$$

where I_{TFT} is given by the Mark-Helfrich law²⁴

$$I_{\text{TFT}} = AN_v\mu e^{1-l} \left[\frac{\epsilon l}{N_t(l+1)} \right]^l \left(\frac{2l+1}{l+1} \right)^{(l+1)} \frac{V^{l+1}}{L^{2l+1}}. \quad (8)$$

Equation (7) is the major assumption of the present model and is applied to the case of tetracene. To this purpose, the function $u(V)$ is obtained by fitting the I - V characteristics and then introduced in Eq. (6) as described below. The total current I is written as sum of an Ohmic and an SCLC current generator.¹⁴ In correspondence of the TFT regime the relative weight of the two current generators depends on the applied bias through the fraction of filled traps $u(V)$

$$I = I_{\Omega} + u(V)I_{\text{SCLC}}. \quad (9)$$

For the validation of the model, we refer to the set of experiments carried out on polyacenes purified by sublimation, evaporated on glass at 10^{-5} Pa and room temperature. Sandwich structures with Au, Al, and ITO electrodes (namely Au/Pc/ITO, Au/Tc/Al, and Au/Pc/Al) with area $A=0.1$ cm², distant $L=0.40$ – 1.00 μm with $\delta L=0.05$ μm , have been characterized. This large sample set ensures a reliable statistics over the wide variability of chemical and structural properties. Results of I - V and $S_I(f)/I^2$ for a tetracene thin film of length $L=0.65$ μm and cross-sectional area $A=0.1$ cm² are shown. From the values of the Ohmic and SCLC region of I - V characteristics, using Eq. (1a), Eq. (3a), and $\epsilon_r=3.5$, we find $L/(Aen_o\mu)=3 \times 10^{11}$ Ω and $9A\epsilon_0\epsilon_r\mu\Theta/(8L^3)=6 \times 10^{-11}$ A/V². From the SCLC region of the I - V characteristics, the effective mobility $\mu_{\text{eff}}=\Theta\mu=4.7 \times 10^{-10}$ cm²/s V is obtained. From the Ohmic region of the I - V characteristics, $n_o\mu=1.4 \times 10^6$ (mV s)⁻¹ is obtained. Since an indepen-

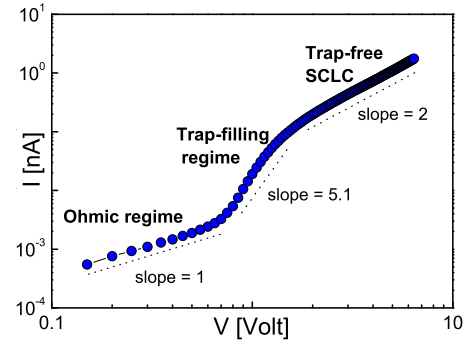


FIG. 1. (Color online) Current voltage characteristics at $T=300$ K for a tetracene thin film of length $L=0.65$ μm and cross-sectional area $A=0.1$ cm². Circles refer to experimental data. (Ref. 21) Dotted lines indicate the Ohmic region at the low voltage, the TFT region between $V=V_t \approx 0.8$ V and $V \approx 2 V_t$ and the SCLC region at the high voltage $V > 2 V_t$. Solid line is obtained by fitting the data by Eq. (9).

dent determination of the Ohmic mobility is not available, we assume that μ ranges between 10^{-3} – 1 cm²/V s, which are reasonable values for low and high quality crystalline materials. Accordingly, by keeping the same level of fit, the values of the parameters related to the mobility can take values in the range $\Theta \approx 10^{-7}$ – 10^{-10} and $n_o=10^7$ – 10^4 cm⁻³. By using Eq. (4) with $n_v=10^{21}$ cm⁻³, $n_t=10^{13}$ cm⁻³, it is $E_t \approx 0.85$ – 1 eV. The values of the function $u(V)$ obtained from the fit of the I - V characteristics (see Fig. 1) are then introduced in Eq. (6) to reproduce the noise behavior at the trap-filling transition. Figure 2 shows the experimental relative current spectral density (circles) and its decomposition in terms of Eq. (7) (dashed lines). The quantity B , fitting the total excess noise in the TFT regime, is given by $B=S_{\text{max}}/0.25=2.8 \times 10^{-10}$ s, where S_{max} is the maximum value of the relative noise. The maximum value of trap concentration compatible with the model used for fitting is $n_t=0.8 \times 10^{13}$ cm⁻³. For this value the carrier free time is $\tau=0.8 \times 10^{-2}$ s. The range of parameter values obtained from the fit are summarized in Table I. As illustrated by Figs. 1 and 2, the theory reproduces quite well both transport and noise behavior at the trap-filling transition. Furthermore, the values of the parameters are compatible with those reported in the literature.¹¹ By taking the values of the power spectral density at $f=20$ Hz, we find $\alpha_{\Omega} \approx 10^{-9}$ – 10^{-12} and

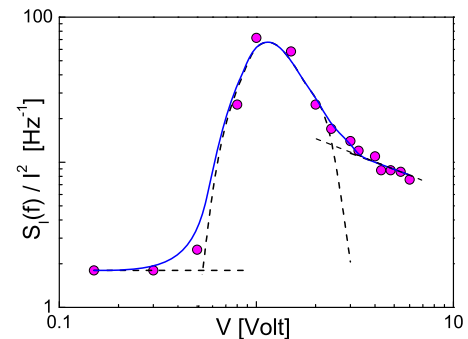


FIG. 2. (Color online) Relative current noise spectral density $S(f)$ at $f=20$ Hz and $T=300$ K vs applied voltage. Circles refer to experimental data. (Ref. 21) Dashed lines represent, respectively: (i) the Ohmic noise component at low voltages, (ii) the trapping-detrapping noise component at intermediate voltages, (iii) the SCLC noise component at high voltage. Solid line is obtained by summing the three noise components according to Eq. (7).

TABLE I. Relevant parameter range for tetracene.

Density of traps	n_t	$\approx 10^{13} \text{ cm}^{-3}$
Valence band state density	n_v	$\approx 10^{21} \text{ cm}^{-3}$
Carrier free time	τ	$\approx 10^{-2} \text{ s}$
Zero-field hole mobility	μ	$\approx 10^{-3} - 1 \text{ cm}^2/(\text{s V})$
Deep trap energy level	E_t	$\approx 0.85 - 1 \text{ eV}$
Effective mobility parameter	Θ	$\approx 10^{-7} - 10^{-10}$
Thermal free carrier concentration	n_0	$\approx 10^7 - 10^4 \text{ cm}^{-3}$
Ohmic Hooe parameter	α_Ω	$\approx (10^{-9} - 10^{-12})$
SCLC Hooe parameter	α_{SCLC}	$\approx (10^{-7} - 10^{-10})$

$\alpha_{\text{SCLC}} \approx 10^{-7} - 10^{-10}$. We remark that the Hooe parameter α_Ω differs from α_{SCLC} to account for the difference in the tetracene medium when going from Ohmic (neutral traps) to SCLC (charged traps) conditions. These values are low when compared with the typical values of about 10^{-3} in most crystalline semiconductors. These low values can be ascribed to the fact that transport takes place in insulators via a microscopic mechanism of hopping type.

In conclusion, by introducing a trapping-detrapping noise contribution associated with the presence of a TFT regime, we have developed a microscopic model which provides a quantitative interpretation of the current voltage and relative current noise in tetracene as function of the applied voltage. The noise mechanism in the TFT region is basically related to the fluctuating occupancy of a single level of traps, which modulates the cross section of the conducting channels and, thus, produces noise. The consistent fit of transport and noise provides a set of parameters (see Table I) of valuable interest for the characterization of the material. We remark that the measured current noise spectrum was found to be more likely to an $1/f$ -sloped rather than Lorentzian, thus, the lifetime estimate should be taken as rather indicative. The broadening of the trap level energy could account for such a spectral difference.^{16,17} Finally, we note that the proposed model can be generalized to the case of several trap levels and hopping transport.

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