Space-Charge-Limited Current Fluctuations in Organic Semiconductors

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Low-frequency current fluctuations are investigated over a bias range covering *Ohmic*, *trap-filling*, and *space-charge-limited current* regimes in polycrystalline polyacenes. The relative current noise power spectral density $S(f)$ is constant in the Ohmic region, steeply increases at the trap-filling transition region, and decreases in the space-charge-limited-current region. The *noise peak* at the *trap-filling transition* is accounted for within a *continuum percolation model*. As the quasi-Fermi level crosses the trap level, intricate insulating paths nucleate within the Ohmic matrix, determining the onset of nonequilibrium conditions at the interface between the insulating and conducting phase. The *noise peak* is written in terms of the free and trapped charge carrier densities.

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Polycrystalline small-weight organic materials, as polyacenes, belong to the class of strongly disordered conductors. The charge carrier transport mainly occurs by variable-range hopping among a system of localized electronic states [1–3], critically depends on the injection from the metal electrode [4–7], and is affected by the presence of deep and shallow traps at the metal-organic interface and in the bulk [8–10]. Compared to inorganic materials, the identification and characterization of defects in organic semiconductors is a more recent issue [11–16]. Defects are often related to chemical impurity, e.g., anthracene as impurity in tetracene/pentacene. A general model, based on density functional calculations of gap states generated by hydrogen or oxygen impurities in a C-H unit valid for small and long chain molecular materials, has been proposed [13]. A metastable defect generation phenomenon driven by bias has been observed by using space-charge-limited current spectroscopy [14]. Long-lived deep traps, located in the grains and evolving with voltage, have been imaged by electric force microscopy [15]. Shallow traps originated by the sliding of pentacene molecules have been recently observed in [16].

Noise studies have been so far addressed to devices performances [17] rather than to carrier dynamics in organic semiconductors. However, current fluctuations can provide information about nonuniform charge distributions and meandering current flow paths arising in the presence of disorder [18–23]. The emergence of disorder determines nonequilibrium conditions at the interface between different phases in systems exhibiting nonlinear response to external fields and threshold behavior to the onset of a steady state. Such systems, e.g., flux lines in disordered superconductors, charge density waves pinned by impurities, phase separation in manganites, charge tunnel in metal dot arrays [23], share the feature that the transition from a weakly disordered state—characterized by steady fluctuations—to a strongly disordered state—characterized by critical fluctuations—is driven by a bias. In this Letter, we report the first study of fluctuations over three transport regimes—*Ohmic*, *trap-filling*, *space-charge-limited*—in polyacenes. We observe that the relative power spectral density $S(f) = S_I(f)/I^2$ [24] is consistent with *steady-state fluctuations* in Ohmic regime. At the trap-filling transition (TFT) between Ohmic and insulating regime, we measure a rapid increase of $S(f)$. Beyond the *threshold voltage* V_T, at the onset of the space-charge-limited regime, $S(f)$ decreases, as expected for steady space-charge-limited current (SCLC) fluctuations. The strong increase of $S(f)$ is discussed within a percolative fluctuations model and is related to the conductor-insulator interface instabilities when the insulating domains increase at the expenses of the conductive ones. The $S(f)$ peak is written in terms of the trapped-to-free charge carrier ratio, directly related to the insulating-conductive phase imbalance. Finally, a mechanism of trap formation due to bias-stress [13–15] accounts for the progressive divergence of $S(f)$ preceding the breakdown.

Pentacene $C_{22}H_{14}$ and tetracene $C_{18}H_{12}$ purified by sublimation have been evaporated on glass at 10^{-5} Pa and room temperature. Sandwich structures with Au, Al, and indium tin oxide (ITO) electrodes, with area $A = 0.1$ cm^2, distant $L = 0.40$–1.00 μm with $\delta L = 0.05$ μm, are investigated. This large set guarantees a reliable statistics over the variations of chemical purity degree and structural homogeneity. Current-voltage I-V curves are shown in Fig. 1 for: (a) Au/Pc/ITO, (b) Au/Tc/Al, (c) Au/Pc/Al. Curve (a) is linear over all the investigated range. Curves (b) and (c) show the typical shape of space-charge-limited current in materials with deep traps. The slope $l = 1$ refers to the Ohmic regime, described by $J_\Omega = q\mu nV/L$. The regions with steep slope, trap-filling regime, correspond to the rapid change undergone by the current as the Fermi level E_F moves through a trap level E_t. The slope $l = 2$, refers to the trap-free space-charge-limited-

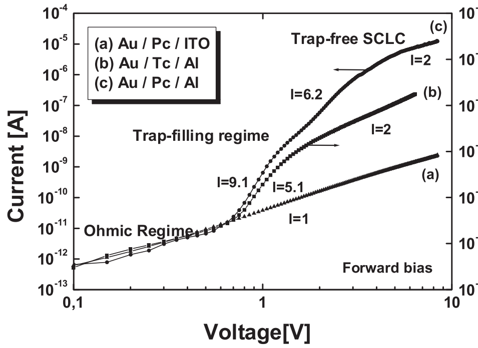

FIG. 1. Current-voltage characteristics for (a) Au/Pc/ITO with $L = 0.85\ \mu$m, (b) Au/Tc/Al with $L = 0.65\ \mu$m, (c) Au/Pc/Al with $L = 0.85\ \mu$m. The geometry is planar with sandwich configuration of the electrodes. Curve (a) is linear over all the investigated voltage range ($l = 1$) and is given in arbitrary units. Curve (b) exhibits the typical SCLC behavior (Ohmic regime $\Rightarrow$ trap-filling transition $\Rightarrow$ SCLC regime). Curve (c) exhibits a more complicated behavior very likely related to deep traps distributed around two different energy levels.

current regime, obeying the Mott-Gurney law $J_{SCLC} = 9\epsilon\epsilon_0\mu\Theta V^2/8L^3$ [1].

Relative current noise power spectra $S(f)$ are shown in Fig. 2 for the Au/Tc/Al sample, respectively, in (a) Ohmic, (b) trap-filling transition, and (c) space-charge-limited current regime, at room temperature, in the dark. The frequency dependence is $f^{-\gamma}$ with $\gamma \approx 1$. The signal is acquired, Fourier transformed, and 50 times averaged over the ranges 1–500 Hz and 500–10^4 Hz. The continuity of the low and high frequency branches ensures the noise stationarity. Roll-off and saturation of $S(f)$ at $f > 1$ kHz are, respectively, due to unavoidable capacitive coupling and circuitry background noise with the low currents ($I < 10^{-10}$ A) and high resistances ($R > 10^4$ MΩ) into play. Therefore, our discussion is limited to the frequency range where the $f^{-\gamma}$ component dominates over the other noise sources. In Fig. 2(a), $S(f)$ does not change with voltage, as expected for uncorrelated resistance fluctuations in nearly ideal Ohmic conditions [18]. Figure 2(b) refers to the trap-filling regime: $S(f)$ sharply increases with V. Figure 2(c) refers to the trap-free SCLC region: $S(f)$ decreases approximately as $1/V$ according to a noise suppression mechanism analogous to that observed in vacuum tubes and inorganic solid-state diodes operating under space-charge-limited conditions [25]. These results are summarized in Fig. 3, where $S(f = 20$ Hz) is plotted over the entire range of voltage for the samples of Fig. 1. The striking feature is the peak exhibited by the relative noise intensity $S(f)$ in the samples undergoing the trap-filling transition. The presence of the peak is the unequivocal signature of nonequilibrium and strong correlation effects causing multiplicative mechanisms of noise generation.

Here we provide an interpretation of the noise results based on a percolation model. In the Ohmic regime, the conductive component almost exclusively consists of thermally excited charge carriers. The deep traps are mostly empty (Ω *phase*). In the space-charge-limited current regime, the transport is dominated by the injected holes controlled by space charge. The deep traps are almost completely filled (SCLC *phase*). In the intermediate voltage region, trap-filling transition, the system can be viewed as a two-components continuum percolative medium [26] characterized by the *competition* between the conductive (Ω) and the insulating (SCLC) phase driven by voltage. The Ohmic phase becomes populated by insulating sites as the voltage increases. The current paths are extremely intricate owing to the inhomogeneous distribution of trapping centers, whose occupancy randomly evolves as the Fermi level moves through the trap level. The system is in a strongly disordered critical state, due to the nucleation of insulating patterns inside the conductive medium. By further voltage increase beyond the threshold V_T, steady-state SCLC fluctuations decreasing with V are observed. The increase of fluctuations, at the TFT transition, is related to the greatly disordered distribution of local fields, compared to the more ordered distribution in Ohmic and SCLC regimes. The competition between repulsive and attractive Coulomb interaction undergone by the carriers moving through oppositely charged sites determines strong correlation effects among the elementary hop instances. The fluctuations of such a system cannot be described as a simple sum of the noise terms related to the Ω and SCLC regions. Let $s_\Omega(f)$ and $s_{SCLC}(f)$ indicate the noise sources characterizing, respectively, the conductive and the insulating elementary sites. An estimate of the noise peak when the percolative regime is approached from the conductive side can be obtained using the relationship [20]:

$$S(f) = s_\Omega(f)\frac{\sum_\alpha i_\alpha^4}{(\sum_\alpha i_\alpha^2)^2}, \quad (1)$$

where $s_\Omega(f)$ and i_α indicate, respectively, the spectral density and the current of each element of the conductive network. The frequency dependence of $S(f)$ is contained in the first factor of Eq. (1). According to the noise models for variable-range hopping [18,19], $s_\Omega(f)$ can be expected to be $f^{-\gamma}$ sloped with $\gamma \approx 1$. In our system, the hop instances are kicked off, respectively, by the thermally activated detrapping (Ω regime) or by the injection (SCLC regime) of a charge carrier. The fluctuation amplitude is determined by the last factor of Eq. (1), that is, related to the conductive volume fraction ϕ by:

$$S \propto \Delta\phi^{-k}, \quad (2)$$

where k is a critical exponent, whose value depends on the structure, composition, and conduction mechanism [27]. The conductive fraction ϕ depends on V. Moreover, ought to a possible mechanism of deep trap formation by bias or

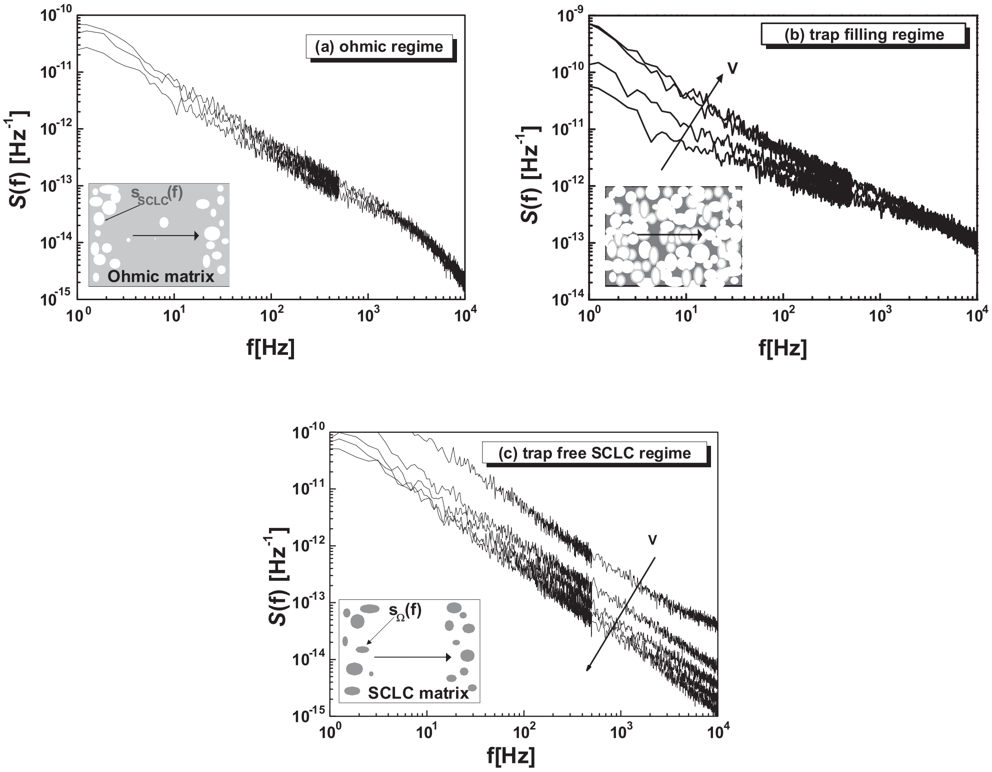

FIG. 2. Relative current noise power spectral density $S(f)$ for the Au/Tc/Al sample. (a) Ohmic regime: $S(f)$ does not vary with V in Ohmic condition (0.3–0.8 V). (b) Trap-filling regime: $S(f)$ sharply increases with V during the trap-filling transition (0.8–2 V). (c) Space-charge-limited current regime: $S(f)$ decreases approximately as $1/V$ (>2 V). The two-phases medium is shown in the insets. The horizontal arrows represent the current direction. The white areas represent filled traps, i.e., insulating sites characterized by $s_{\mathrm{SCLC}}(f)$ noise. The dark areas represent empty traps, i.e., conductive sites characterized by $s_{\Omega}(f)$ noise. (a) The quasi-Fermi level $E_F \ll E_t$, almost all deep traps are empty. Transport is Ohmic. (b) The quasi-Fermi level is moving through the trap level, $E_F \sim E_t$, filling the traps. Tortuous insulating patterns are generated inside the conductive matrix, leading to nonequilibrium condition at the Ohmic-insulating interface and excess fluctuations. (c) The quasi-Fermi level $E_F \gg E_t$, the traps are mostly filled. The system is characterized by steady-state space-charge-limited current fluctuations decreasing with V. Darker areas represent residual conductive sites, shallower tails of Gaussian distributed traps.

thermal stress [12–15], the total density of trap N_t increases. Thus the definition of a universal value of k remains elusive. In our samples, k ranges from 1.1 to 1.8 under strict-sense stationary noise conditions. The change of conductive fraction due to the filling of deep traps can be written as $\Delta\phi \propto (n - n_t)/N_v$, where n and n_t are, respectively, the free and trapped charge carrier density, N_v is the total density of states, coinciding with the molecular density for narrow band materials. Since the relative noise intensity for Ohmic conductors varies as $1/n$, it is convenient to write $\Delta\phi$ as:

$$\Delta\phi \propto \frac{n}{N_v}\left(1 - \frac{n_t}{n}\right). \tag{3}$$

By substitution of Eq. (3) into Eq. (2), it follows that the noise in excess with respect to the Ohmic level is determined by the quantity $(1 - n_t/n)$. It is related to the imbalance between free and trapped carriers and, ultimately, to the departure from the quasiequilibrium Ohmic condition. Assuming for simplicity a discrete trap level, it is $n = N_v \exp[-(E_v - E_F)/kT]$ and $n_t = N_t/\{1 + g^{-1}\exp[-(E_F - E_t)/kT]\} \simeq 2N_t \exp[(E_F - E_t)/kT]$, g being the trap degeneracy factor and the other quantities introduced above. The ratio n_t/n is written:

$$\frac{n_t}{n} = \frac{2N_t \exp[-(E_t - E_v)/kT]}{N_v}. \tag{4}$$

Moreover, the Eq. (4) relates the steep increase of $S(f)$ to that of the current upon trap filling [1,9], providing an independent validation of the proposed noise picture being the conductivity variation proportional to $\Delta\phi^{-\rho}$ within the percolative model. Since $N_v = 4 \times 10^{21}$ cm^{-3}, E_t and N_t typically range between 0.3–0.6 eV and 10^{15}–10^{18} cm^{-3}, the Eq. (4) confirms that a very small density of deep traps may critically affect the fluctuations. The percolation threshold ϕ_c and the onset of breakdown are finally discussed using Eqs. (2)–(4). Nonstationarity and divergence of noise at the trap-filling transition are the precursors of electrical breakdown. Using the Eq. (4), the percolative threshold ϕ_c is reached when $\Delta\phi \Rightarrow 0$, i.e.,

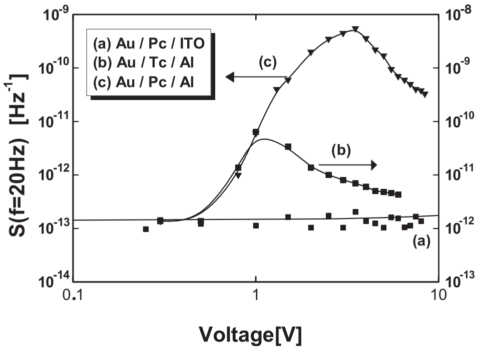

FIG. 3. Log-log plot of the voltage dependence of the relative fluctuation power spectral density at frequency $f = 20$ Hz for (a) Au/Pc/ITO, (b) Au/Tc/Al, (c) Au/Pc/Al. Data (a) are given in arbitrary units, mostly for reference purpose, and correspond to Ohmic behavior over all the voltage range. The *I*-*V* characteristics for the same samples are plotted in Fig. 1.

$2N_t \exp[-(E_t - E_v)/kT] \Rightarrow N_v$. The noise divergence, observed after several bias or thermal cycles, might be caused by the increase of N_t due to the deep trap formation mechanism suggested in [13–15].

In conclusion, we have observed: (i) steady-state fluctuations at low-voltage (Ohmic regime), (ii) critical fluctuations at intermediate voltage (TFT regime), (iii) steady-state fluctuations at high voltage (space-charge-limited-current regime). The $f^{-\gamma}$ shape indicates that the fluctuations result from hops driven by trapping-detrapping processes with a broad range of characteristic times τ, in agreement with [15]. The noise peak, at the TFT transition, has been ascribed to the strong nonequilibrium provoked by the insulating phase nucleating within the conductive one. The noise peak has been estimated within a percolation model of fluctuations: Eq. (3) and (4). These equations have been used to relate the onset of breakdown to the percolation threshold ϕ_c. Finally, it is worthy to remark that: (1) the stochastic processes by which systems with distributed thresholds undergo a transition driven by an external bias [23]; (2) the time-averaged processes underlying space-charge-limited transport—as, for example, the Goodman and Rose law predicted in 1971 and the *seeming simple* 2D planar emission [28]—still represent open fundamental issues. In this Letter, we have shown that a deep insight can be achieved across these two topics studying fluctuations at the voltage-driven transition from Ohmic to insulating phase in space-charge-limited conditions.

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