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Electric Field Confinement Effect on Charge Transport in Organic Field-Effect Transistors

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While it is known that the charge-carrier mobility in organic semiconductors is only weakly dependent on the electric field at low fields, the experimental mobility in organic field-effect transistors using silylethynyl-substituted pentacene is found to be surprisingly field dependent at low source-drain fields. Corroborated by scanning Kelvin probe measurements, we explain this observation by the severe difference between local conductivities within grains and at grain boundaries. Redistribution of accumulated charges creates very strong local lateral fields in the latter regions. We further confirm this picture by verifying that the charge mobility in channels having no grain boundaries, made from the same organic semiconductor, is not significantly field dependent. We show that our model allows us to quantitatively model the source-drain field dependence of the mobility in polycrystalline organic transistors.

Organic semiconductor films offer a huge potential for the emerging flexible large-area electronics because they allow for a low cost device fabrication and a low-temperature processing of semiconductor layers compatible with flexible plastic substrates [1,2]. In typical amorphous or polycrystalline films the charge carriers move much more slowly than in perfect molecular crystals because they hop among localized states that are distributed in space and energy. The charge-carrier mobility (μ) is thus a critical parameter for the operating speed of a device, notably, in an organic field-effect transistor (OFET).

In high-quality organic single crystals μ is normally independent of electric field at room temperature [3,4]. It is well established that in disordered organic semiconductors μ increases with electric field in a Poole-Frenkel fashion, $\ln\mu \propto F^{1/2}$ [5,6]. This is a consequence of thermally activated hopping within a manifold of states commonly described by a Gaussian density-of-states (DOS) distribution [5]. The applied electric field tilts the DOS and thus lowers the average barrier height for energetic uphill jumps in the field direction. The initial Gaussian disorder model [5] predicts the $\ln\mu \propto F^{1/2}$ dependence yet for a rather high electric field only [5]. Subsequent work [7,8] showed that by introducing spatial correlation of the energies of transport, experimentally observed Poole-Frenkel-type dependence at lower fields is recovered.

Another important advancement of the disorder formalism [9–13] relates to the space charge existing in OFETs and organic diodes. In an OFET the current is confined to a very thin conductive layer and a sizable fraction of the DOS distribution is occupied, and charge transport occurs by hopping from states at the Fermi level to the transport energy. Pasveer, Coehoorn, and co-workers [9,10] predict from extensive simulations using the extended Gaussian disorder model that μ increases with both the carrier density (c) and the electric field (F). This model was also corroborated by analytic theories, first formulated for a zero-field limit [11,12] and recently extended for arbitrary electric fields [13]. Recently, Bouhassoune *et al.* [14] also included the effect of spatial energy correlations [extended correlated disorder model (ECDM)].

All previous versions of the disorder model predict that μ should saturate at fields $\lesssim 10^4$ V/cm. For instance, the ECDM approach [14] predicts the electric field dependent OFET mobility just for the range $0.25 < (eaF/\sigma)^{1/2} < 1.0$, where σ is the width of the DOS, a is average intersite distance, and e is the elementary charge. For representative parameters for a disordered solid, viz., $\sigma = 70$ meV, $a = 0.7$ nm, and $c = 10^{-3}$ (where $c = n/N$ is the relative carrier concentration with respect to the concentration of localized states N), it translates into electric fields $6.25 \times 10^4 < F < 10^6$ V/cm. This is at variance with experiments on OFET to be described below. This observation calls for another extension of the disorder model. It is based upon the notion that the electric field is not necessarily homogenous—as is usually tacitly assumed—but it can be inhomogeneous. This notion will be corroborated by scanning Kelvin probe microscopy (SKPM) of the active layer of an OFET based on 6,13-bis(tri-isopropyl-silylethynyl) pentacene (TIPS-PEN) during device

operation. We show that the morphology of the layer has an immediate impact on charge transport properties: strong local fields result in lateral-field dependence of OFET mobility in TIPS-PEN, while no such dependence was observed in channels where electric field was homogenous. Ink-jet printable TIPS-PEN was chosen as the model material in the present work since our previous studies have shown that pure TIPS-PEN films feature crystallite grains with dimensions compatible with the spatial resolution of SKPM, and have indicated that this material allows for the manipulation of film morphology within a transistor channel from multiple grains separated by grain boundaries (GB) to a single grain [15].

TIPS-PEN was synthesized according to the literature [16] and used as the functional semiconductor layer in bottom-contact–bottom-gate OFETs fabricated by ink-jet printing (details of the ink-jet process and device structure were described in Ref. [15]). Two types of TIPS-PEN films were prepared: (i) pure TIPS-PEN forming irregular shaped crystalline deposit with multiple-grain morphology within a transistor channel (namely "channel with GB"), and (ii) TIPS-PEN blended with polystyrene (PS) (weight ratio 2/1) that features much larger TIPS-PEN crystallites with more homogenous film morphology throughout transistor channels. The films were checked by cross-polarized optical microscope to assure that in the latter case a large crystallite of TIPS-PEN covers the whole transistor channel under investigation (namely "channel without GB").

Transistors were characterized with an Agilent 4155C semiconductor parameter analyzer at room temperature in inert atmosphere. The average charge (Q) in a transistor channel can be expressed in the linear regime as [17]

$$Q = C_i\left(V_G - \frac{V_D}{2} - V_{\text{th}}\right), \qquad (1)$$

where V_G and V_D are the source-gate and the source-drain voltage, respectively, C_i is the capacitance per unit area of the gate dielectric, and V_{th} is the threshold voltage. μ in this study was obtained from output characteristics (I_{SD} versus V_D plots) at a constant Q in the channel. Constant Q was assured by sweeping the gate voltage (V_G) at half of the rate for V_D sweeping [according to Eq. (1)]; i.e., V_D swept from 0 to -20 V with -0.5 V/step, meanwhile V_G swept from -10 to -20 V with -0.25 V/step (see Sec. 1 of the Supplemental Material [18]). Then according to a modified metal-oxide-semiconductor field-effect transistor equation [17,19,20], the average mobility $\mu(V_D)$ can be determined in the linear regime as (see Sec. 2 of the Supplemental Material [18])

$$\mu(V_D) = \frac{L}{WC_i(V_G - \frac{V_D}{2} - V_{\text{th}})}\left(\frac{\partial I_{SD}}{\partial V_D}\right)\left(\frac{\partial V_D}{\partial V_{D\,\text{channel}}}\right), \quad (2)$$

where L and W are the channel length (20 μm) and width (≈ 1.7 mm), respectively. And $V_{D\,\text{channel}}$ is the actual voltage drop within the channel region by subtracting the drops

at the edges of source and drain contacts, measured by SKPM at different applied V_D and the corresponding V_G assuring a constant Q in the channel.

Local surface potential distributions along the transistor channel for both pure TIPS-PEN and blend films were measured by using SKPM under device operation parametric in different V_G, using a Veeco Dimension 3100 with a NanoScope IVa controller operating in the lift mode. The accuracy of our SKPM measurements is comparable to earlier reports on working organic transistors with buried source and drain contacts (i.e., bottom contact) [21–23]. Note that applicability of SKPM for evaluation of lateral-field distribution in organic devices has already been demonstrated [24].

Figure 1 (symbols) shows OFET mobility as a function of lateral electric field in two types of TIPS-PEN channels with and without GB (circles and squares, respectively), calculated from the experimentally obtained output characteristics using Eq. (2) in the linear regime with constant channel charges. The extracted μ in the TIPS-PEN PS blend was higher than that of the pure TIPS-PEN, in agreement with previous studies [15], probably due to improved film morphology [25], and/or due to a purification process by the blended polymer during solidification [26]. Surprisingly, the field dependences of mobility in the
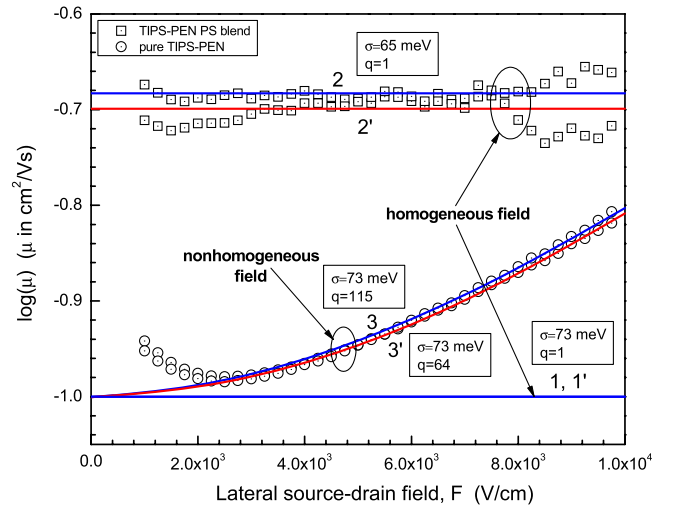
FIG. 1 (color online). Lateral-field dependences of the OFET mobility measured in TIPS-PEN channel with GB (circles) and without GB (squares) at $T = 300$ K. Charge mobilities calculated assuming homogenous electric field ($q = 1$) for $\sigma = 65$ meV and $\sigma = 73$ meV within Pasveer-Coehoorn model (curves 2 and 1, respectively, in blue) and by Fishchuk model (curves 2' and 1', respectively, in red). Other parameters used are $a = 0.7$ nm, $c = 10^{-3}$, and the ratio $a/b = 10$ and 5 for Pasveer-Coehoorn and Fishchuk models, respectively. The best-fit curve for the channel with GB calculated assuming strong local electric fields accounted for by the field magnification parameter $q = 115$ within Pasveer-Coehoorn model (curve 3, in blue) and by $q = 64$ within Fishchuk model (curve 3', in red). Note that curves 1 and 1' coincide.

above two types of channels are found to differ drastically. In the TIPS-PEN channel with GB (circles in Fig. 1), μ increases with lateral electric field, while μ is virtually field independent in TIPS-PEN channels without GB (squares in Fig. 1). Such a trend was very well reproducible in all TIPS-PEN-based samples (pure versus blend) we examined. A slightly negative field dependence of μ was observed in the pure TIPS-PEN channels with GB at $F < 2 \times 10^3$ V/cm; however, the appearance of this behavior was sample dependent and we temporally ascribe it to the possible influence of contact resistance at very low V_D, and this effect will not be discussed hereafter.

To explain our observations, we first tried to fit the experimental field-dependent mobility (Fig. 1) with the Pasveer-Coehoorn model [9,10]. Most of the material parameters used for calculation were taken from experiments, viz., carrier concentration experimentally estimated as $c = 10^{-3}$, $a = 0.7$ nm taken as a typical intermolecular distance for pentacene [27], $a/b = 10$ used according to Ref. [9] (b is the localization radius of a charge carrier); for TIPS-PEN channels with GB the energetic disorder parameter $\sigma = 73$ meV was estimated from experimentally measured Meyer-Neldel temperature (T_{MN}) (not shown here) according to the method described recently [28], while for the blended TIPS-PEN channels $\sigma = 65$ meV was used as fitted parameter, the prefactor mobility μ_0 was chosen to match the zero-field mobility value. Note that activation energy (energetic disorder) for the OFET mobility in TIPS-PEN films was found to depend significantly on the fabrication procedure [29]. Mobilities calculated according to Refs. [9,10] under the premise of homogenous lateral electric field are shown by solid blue curves 1 and 2 in Fig. 1, and they evidence that the original Pasveer-Coehoorn model predicts no field dependence at such low fields and reasonable material parameters. This model can quantitatively describe well just the flat field dependence of μ observed in TIPS-PEN blend channels without GB, but it clearly fails to describe the data for pure TIPS-PEN channels with GB (circles in Fig. 1).

Next, the mobilities in the relevant lateral electric field range were calculated by the Fishchuk analytic model [13] for the same set of material parameters and assuming homogenous electric field (curves $1'$ and $2'$ in Fig. 1). These calculation results are quite similar to those obtained by the Pasveer-Coehoorn model (cf. curves 1 and 2 in Fig. 1) and similarly fail to fit the experimental data for TIPS-PEN channels with GB (circles in Fig. 1).

Thus, the established hopping charge transport models assuming homogenous electric field are unable to provide a quantitative description of the increasing OFET mobility in TIPS-PEN in the range of low lateral electric fields relevant for experiments. To solve the puzzle, we propose that in multiple-grain channels the OFET mobility is controlled not by the lateral field averaged over the transistor channel (as conventionally assumed), but rather by the much

stronger effective local electric fields generated in such inhomogeneous media. This is supported by measuring the surface electrostatic potential distributions along transistor channels by SKPM during device operation at applied lateral voltage $V_D = -5$ V and varying source-gate voltage V_G on the same TIPS-PEN samples as used for charge transport measurements in Fig. 1. Typical potential profiles obtained in the channel containing GB and that without GB are shown in Figs. 2(a) and 2(b), respectively. Both types of TIPS-PEN films show typical smooth parabolic potential profiles from source to drain electrodes (Fig. 2) in studied channels when devices are in the "off state" (before V_G reaches V_{th}), but abrupt potential drops occur within the channel of TIPS-PEN with GB [shown by the red arrows in Fig. 2(a)] when the device is in the "on state," i.e., upon charge accumulation near the gate electrode.

The electrostatic field profile in Fig. 3 (lower panel) clearly reveals several sharp peaks (see Sec. 3 of the Supplemental Material [18]). Note that these peaks could in reality be much bigger because of the limited spatial
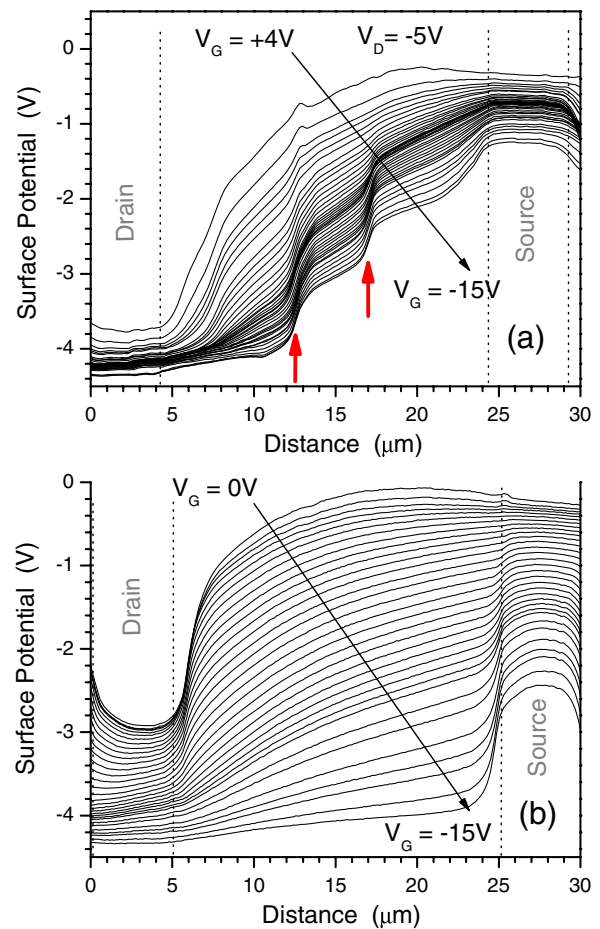

FIG. 2 (color online). Surface potential profiles of pure TIPS-PEN (a) and the TIPS-PEN PS blend (b) measured by SKPM in the active layer of OFET devices at $V_D = -5$ V and for different V_G voltages. Positions of GB are indicated by red arrows in (a).
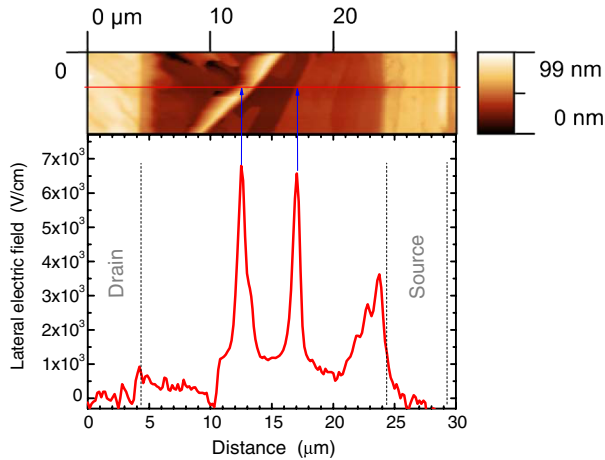
FIG. 3 (color online). Lower panel: Distribution of lateral electric field calculated from the surface potential distribution from Fig. 2(a) at $V_D = -5$ V and $V_G = -15$ V in pure TIPS-PEN channel. Positions of GB are indicated by arrows. Upper panel: Corresponding AFM topography image of the studied channel. The red horizontal line in the upper panel depicts the position where the cross section of the SKPM scan in Fig. 2(a) was taken.

resolution of SKPM [30]. These spikes in the field distribution correlate with the locations of GB revealed by atomic force microscope (AFM) topography image (cf. lower and upper panels in Fig. 3). The TIPS-PEN blend channel devoid of GB (indicated by AFM and cross-polarized optical micrographs) shows rather smooth surface potential profiles within the transistor channel irrespective of whether transistor is in the *on* or *off* state [Fig. 2(b)].

Strong inhomogeneity of the lateral electric field in the conductive channel can be rationalized in terms of electrostatic screening due to different local conductivities within grains and at GB. GB are known to limit charge transport in polycrystalline films by establishing major potential barriers [22,31–33] between their more-ordered domains. In such cases the OFET conductive channel can be considered as a series of resistors whose resistance is controlled by the "microscopic" charge mobility. In the off state the lateral field is homogenous because the dielectric constant is virtually isotropic. Therefore, μ is isotropic. Upon applying a gate voltage to a channel with GB, charges (holes) start to accumulate in the channel, and instantaneously the density of accumulated holes within an individual grain is redistributed along the external lateral field (source to drain) direction: at one side of the grain it generates a locally increased hole concentration, and at the other side a reduced (or close to locally "depleted") hole density. This creates an internal lateral electric field within the individual grain which compensates the applied external field. Note that this "charge-redistribution" effect stems from the mobile (not trapped) holes inside grains induced by V_G voltage, therefore here termed as a charge

accumulation (rather than trapping) process at the grain boundary. This effect generates high local field between the grains (i.e., at the GB), while the field inside the grains is screened. This would translate into an inhomogeneity of the lateral electric field. As long as the spatial extension of GB is much smaller than the average size of more-ordered grains, the local fields could be much stronger than the average applied field.

The concept of inhomogeneous local fields can describe quantitatively the experimentally observed lateral-field dependence of the OFET mobility by slightly modifying either the Pasveer-Coehoorn model or the Fishchuk model. The barrier heights due to GB are subject to distribution over the film; therefore, taking into account a huge variety of percolative passes present between the long source and drain electrodes, the charge transport in average could be considered as that occurring in an effectively random disordered system even though charge carriers may experience just a few crossings over GB in a particular percolative pass. Since the actual ratio between the local field at the GB and the averaged field is not amenable to analytical treatment, we will introduce a phenomenological field magnification parameter $q \gg 1$ as a fitting parameter. Evidently that employment of the q parameter just results in renormalization of the electric field F used in our calculations.

Figure 1 demonstrates that the experimental results on the field dependence of μ in TIPS-PEN channels with GB (Fig. 1, circles) can be well fitted using $q = 64$ and $q = 115$ for the Fishchuk (Fig. 1, red curve 3') and the Pasveer-Coehoorn (Fig. 1, blue curve 3) models, respectively, using the same $\sigma = 73$ meV. The flat lateral-field dependence observed in channels without GB (Fig. 1, squares) is also well described by our model, assuming the absence of strong local fields ($q = 1$) in the homogenous film using a smaller energetic disorder parameter $\sigma = 65$ meV.

In conclusion, by disentangling the effect of lateral field from carrier density, we have observed an unexpected field dependence of the charge-carrier mobility in an organic field-effect transistor at low electric fields. It is a signature of a phenomenon that could be termed as the electric field confinement effect in a grainy organic film, and this concept can quantitatively describe the experimentally observed lateral-field dependence of the OFET mobility with modified hopping transport models. It originates from a lateral redistribution of accumulated (gate-induced) mobile charges by the applied source-drain voltage, at the grain boundaries. It gives rise to strong local electric field and is relevant for organic films with inhomogeneous morphology caused by, e.g., sample annealing in order to improve charge transport, and for chemically doped organic polycrystalline films.

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