Crossover from one- to two-dimensional space-charge-limited conduction in pentacene single crystals

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We report the crossover from one- to two-dimensional space-charge-limited conduction in pentacene single crystals with planar contacts. The space charge is confined to the in-plane longitudinal direction for \( L/h \leq 15 \), with \( L \) the contact separation and \( h \) the sample thickness. For \( L/h > 250 \), the space charge is dominated by the transverse component of the electric field. © 2006 American Institute of Physics. [DOI: 10.1063/1.2187442]

Small molecule organic crystals can exhibit large electronic mobilities at room temperature if local impurities and extended defects, such as grain boundaries, can be minimized. Thus, single crystals can provide information about the intrinsic electronic transport properties.\(^1\)–\(^6\) Nevertheless, the evaluation of the transport parameters can be difficult because of the charge injection at the interface, or the non-uniform nature of charge carrier density, current density, and electric field under nonohmic conditions. The evaluation of the electronic mobility depends strongly on the correctness of the interdependence between electronic parameters, including mobility, charge density etc., but also on the associated geometry that is used.

In this letter, we analyze the current flow across pentacene single crystals with planar contacts. Our study focuses on the electric field \( E \) pattern for parallel planar contacts with different gap separations \( L \). We discuss the effect of the geometric parameter \( L/h \), with \( h \) the crystal thickness, and the anisotropy of the mobility on the electric field distribution inside the semiconductor. Effects like surface scattering, charge diffusion, surface traps, and surface polarization are neglected. We observe a gradual transition from a one- to two-dimensional (D) space-charge-limited conduction with increasing \( L/h \). This transition has a purely geometrical origin and is determined by the distribution of the electric field inside the crystal.

The charge transport in organic conductors is often limited by the emergence of space charges. There are two limiting geometries to evaluate the conduction in the space-charge-limited current (SCLC) regime. The Mott-Gurney theory\(^8\) describes the current-voltage characteristics for sandwich-type contact geometries [Fig. 1(a)]. This is a 1D theory in which the electric field, as well as the space charge, are confined to the channel. This model gives an expression of the current density \( J \) for the applied voltage \( V \):

\[
J = \frac{9}{8} \Theta \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}. \tag{1}
\]

Here, \( J \) is the current density for the applied voltage \( V \), \( \Theta \) is the trapping factor, \( L \) is the electrodes separation, \( \varepsilon_r \) is the relative dielectric constant of the material, and \( \mu \) is the carrier mobility.

Geurst analyzed theoretically SCLCs in thin semiconductor layers for a gap-structure geometry\(^9\) [Fig. 1(b)]. Here, the thickness of the film is negligible with respect to the separation between the contacts. For this 2D model the longitudinal component of the electric field is responsible for the charge transport and the transversal component, perpendicular to the conduction channel, is determined by the magnitude of the space charge. His analysis leads to an expression in which the value of the current \( I \) depends quadratically on the applied voltage \( V \), and is proportional to the relative dielectric constant of the material, \( \varepsilon_r \), and inversely proportional to the square of \( L \), the distance between the contacts:

\[
I = \frac{2}{\pi} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}. \tag{2}
\]

Zuleeg et al.\(^10\) have introduced the width of the electrodes \( W \), into the expression of Eq. (2). This model improves the approximation of Geurst of infinite long contact length.

Thus, the SCLC at high voltages varies with \( L^{-3} \) in the Mott-Gurney 1D theory [Eq. (1)] and with \( L^{-2} \) in Geurst 2D model [Eq. (2)]. The former was used to estimate the hole mobility in tetracene\(^11\) and rubrene\(^12\) single crystals with parallel plate electrodes. Also, it was applied for analyzing pentacene single crystals\(^3,13\) and tetracyanoquinodimethane (TCNQ)-coronene co-crystals\(^14\) in a gap-type geometry, with a conduction channel length comparable to the thickness of

\[ \text{FIG. 1. Electrode configuration: (a) sandwich-type geometry—side view, (b) gap-type geometry—side view, (c) gap-type geometry—top view (used in this study).} \]
Platelets of high purity pentacene single crystals were grown from double sublimation cleaned powder from Aldrich. Physical vapor transport in a horizontal glass tube under a stream of argon was used. The geometry of the crystals is maximally 4 × 4 mm in plane and thickness typically of 15–20 μm. Pentacene crystallizes in a layered fashion and presents one morphology in the single crystal phase: with space group $P1_{1}$,17,18 We painted silver epoxy contacts parallel on the crystal with a distance varying between 60 μm and 3 mm, limited by the dimensions of the crystals [Fig. 1(c)]. In this geometry, the conduction takes place predominantly along the π-stacking ($c'$) direction. We used a Keithley 237 source measure unit to perform the electrical characterization. All $I$-$V$ curves were taken at room temperature, in darkness and vacuum, to avoid environmental effects.19 For each single crystal of thickness $h$, a voltage $V_{ij}$ was applied across a different pair of electrodes $i$ and $j$ attached to the sample at a distance $L_{ij}$ and the value of the current $I_{ij}$ was measured. The source contact was kept the same to minimize contact effects,7 and the drain was changed.

The $I$-$V$ curves are ohmic at small biases ($I_{Q} \sim V$), and quadratic at high voltages ($I_{SCLC} \sim V^2$). Figure 2 shows the variation of the electrical current $I$ at constant bias voltage for a crystal of $h = 20$ μm thickness and different contact spacings, $L_{ij}$ (60 μm < $L_{ij}$ < 3 mm), in the SCLC regime.

The width of the contacts is approximately $w = 200$ μm. The results are presented as a function of the ratio $L/h$. The inset shows the logarithmic derivative, $d \log I/d \log L$ vs $L/h$, with a value $-3$ corresponding to the 1D conduction, and $-2$ to the 2D model. As it can be observed from this graph, at small $L/h$ ratios the bulk charges are dominant and at high ratios the surface charges determine the conduction. For $L/h \leq 15$, there is a good correspondence between the present experiment that we performed on a crystal with planar contacts and the analytical solution described by Mott-Gurney for devices with parallel plate electrodes ($I \sim L^{-3}$).5 This is due to the fact that at small electrode spacing $L$, the electric field inside the semiconductor is relatively uniform ($E_{\text{long}}$) and parallel to the conduction path. Moreover, when this distance is small, and considering the anisotropy of mobility in pentacene single crystals, the current is confined to the surface of the conductor.20 We demonstrate that the 1D theory [Eq. (1)] has a relatively limited range of validity in case of planar parallel electrodes. It is clear from Fig. 2 that in this geometry the surface contribution becomes gradually dominant as $L/h$ increases. The surface charge density gives rise to the normal component of the electric field ($E_{\text{trans}}$) and the electric field obtains more pronounced 2D characteristics. Thus the 1D space-charge approximation is not valid in this regime and the field distribution within the single crystal must be taken into account.21 The electric field $E$ is no longer uniform inside the crystal. With increasing $L$, the transverse electric field results in $I \sim L^{-a}$, with $a$ ranging from 3 to 2 (see the inset in Fig. 2). We could not reach the $I \sim L^{-2}$ regime, corresponding to Geurst’s analysis [Eq. (2)], as we were limited by the size of the crystals.

In the following we will use the SCLC technique to calculate the value of mobility in pentacene single crystals. We compare the results obtained for the mobility in the a-b plane with the two types of contact geometry described in this study. Because of different bonding and antibonding patterns, the effective mass exhibits different values for the three crystallographic directions.22 This results in a strong anisotropy of the carrier mobility, as is often observed for molecular crystals.1,6 This anisotropy influences the value of the $L/h$ parameter at which the transition between 1D and 2D space charges occurs. We expect that for other molecular crystals the transition from 1D to 2D transport takes place for different geometrical parameters, due to their different mobility anisotropy.

Figure 3 shows the device configurations and current density $J$ vs applied voltage $V$ for pentacene single crystal at room temperature, in vacuum and dark for gap structure contact geometry (○), and sandwich structure configuration (□).
density $J$ versus applied bias $V$ for one pentacene crystal within the $a$-$b$ plane, using sandwich-type and gap-type architectures. The ratio $L/h=25$ in this case sets the system in the intermediate regime, where the conduction is dominated by the 1D space charges. This allows us, in first approximation, to use Eq. (1) to estimate the value of the mobility ($\mu$) for this crystal. At low voltages, the current is ohmic. At higher voltages, the square law dependence of the current with the applied voltage is observed, corresponding to the SCLC regime. Small deviations from the linear and quadratic regimes can be attributed to the nonlinear contribution of Schottky barriers formed at the metal/pentacene interfaces. As the trap-free limit was not reached, $\mu$ cannot be determined, but only the value of the term $\Theta \mu$ can be calculated. The calculation of the mobility with sandwich configuration is straightforward. The device geometry is similar to the one proposed by Montgomery, in which the geometrical factors of the crystal are the values of the components of the resistivity tensor along the three crystallographic directions $x$, $y$, and $z$, corresponding to the isotropic pentacene. We use the Montgomery method to determine the effective thickness ($h_{\text{eff}}$) penetrated by the electric field lines in this configuration. The input for this algorithm are the values of the components of the resistivity tensor along the tree crystallographic directions $x$, $y$, and $z$, and the current flow $I$. This comes from the fact that the current flow is $I=0.33 \text{cm}^2/\text{V s}$. This value should be considered an overestimate of the mobility. The values of mobility obtained with the two geometries agree well, but the intermediate regime, where the conduction is dominated by the 1D space charges should be taken into account. The 1D space charges are predominant in pentacene because of the anisotropy in resistivity.

In conclusion, we report the crossover from 1D to 2D type SCLC conduction in pentacene single crystals with increasing $L/h$ for gap-type contact geometry. For $L/h<15$ the gap-type contact is well approximated by 1D space charges, whereas for $L/h>15$ 2D space charges should be taken into account. The 1D space charges are predominant in pentacene because of the anisotropy in resistivity.