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Intrinsic charge transport properties of an organic single crystal determined using a multiterminal thin-film transistor

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We present an experimental approach to determine the intrinsic field-effect mobility in an organic single crystal as a function of the in-plane crystal-axis direction. Using a multiterminal geometry the experiment also excludes the effects of the contact resistances on the transport properties. We have applied the method to quaterthiophene thin films. At gate voltages above the threshold voltage, the channel conductance varies linearly with the applied gate voltage. The resulting charge carrier mobility is 1.2×10^{-3} cm^2/V s. This value is constant over a period of weeks of continuous operation and does not vary from sample to sample, in contrast to the typically observed lower mobilities of polycrystalline quaterthiophene thin-film transistor devices. These results emphasize the need for well-characterized model systems to study the intrinsic transport properties of organic materials. © *1998 American Institute of Physics.* [S0003-6951(98)01052-3]

Organic semiconducting materials used as active layer in thin film transistors (TFT) have recently received considerable interest.[1–6] In this relatively new research area, further progress requires better materials control for devices together with a more fundamental understanding of their electronic behavior. In the latter area, Torsi *et al.*[1] interpreted their experimental results in terms of the intrinsic transport mechanisms and suggested that the charge carrier transport could be interpreted as a hopping motion of a small molecular polaron as predicted by the Holstein model.

Although these results have been obtained on highly ordered sexithiophene (α-6T) TFTs, large sample to sample variations complicate the interpretation of the results. Despite the formation of molecular crystallites, the active layer itself is polycrystalline. As a consequence, the electrical characteristics are an ensemble average over all the individual single crystallites, with each its specific orientation together with the influences of the grain boundaries and contact resistances.[2,3]

The polaronic nature of the charge carrier together with the *a*-symmetric unit cell of these rod like molecules, require a study of the transport properties as a function of the crystal orientation.[7] Ideally, one would like to measure on a single crystalline TFT, in which the orientation of the crystallite with respect to the drift field is known.

In this letter, we demonstrate a novel experimental approach to measure the mobility of a charge carrier in an organic medium as a function of the in-plane crystal-axis direction. This experiment excludes the effects of grain boundaries and contact resistances on the transport properties, thereby reliably obtaining the field-effect mobility in the organic crystal. The method is applied to quaterthiophene thin films. As a result of this work, we find that the measured mobilities are reproducible and do not vary from sample to sample.

The sample layout is shown in Fig. 1(a). The substrate is a highly doped Si wafer, acting as a gate contact, which is thermally oxidized in a dry atmosphere. The gold contacts are lithographically defined with gap diameters ranging from 3 to 30 μm [see Fig. 1(b)]. A second photoresist layer is deposited to electrically isolate the transistor from neighboring devices. The quaterthiophene oligomer[8] thin film is deposited in the last fabrication step by thermal evaporation in a high vacuum environment (1×10^{-7} mbar). To obtain large crystallites within a polycrystalline thin film, the substrate is held at a temperature of 80 °C during evaporation (rate ~ 0.6 nm/s). With these settings the individual crystallites can grow up to 40 μm in diameter, which is large enough to completely fill one gap, resulting in a single crystal TFT [see Fig. 1(b)]. The orientation and thickness of the crystal within the eight gold electrodes can be obtained by an optical polarization microscopy technique.[9] The method determines the azimuthal orientation of the single crystal, which corresponds to the tilt direction of the molecules with respect to the substrate normal and to the *b* axis of the unit cell [see Figs. 1(b) and 1(c)].

After evaporation the samples are handled in air and measured in an ambient and/or high-vacuum environment. The measurements are done using a Hewlett–Packard 4156A semiconductor parameter analyzer together with an additional home-built module containing four electrometer type voltage probes (input impedance $\sim 10^{14} \Omega$). All measurements are executed in the ''guarded mode'' with triaxial cables in order to minimize leakage currents. With this setup, both the source and drain current together with the potentials of the remaining six terminals can be simultaneously measured.

To determine the charge carrier mobility in a certain crystal direction, the in-plane square conductivity of a crystal is measured as a function of gate voltage in the linear regime,[10] i.e., the applied gate field is much larger than the

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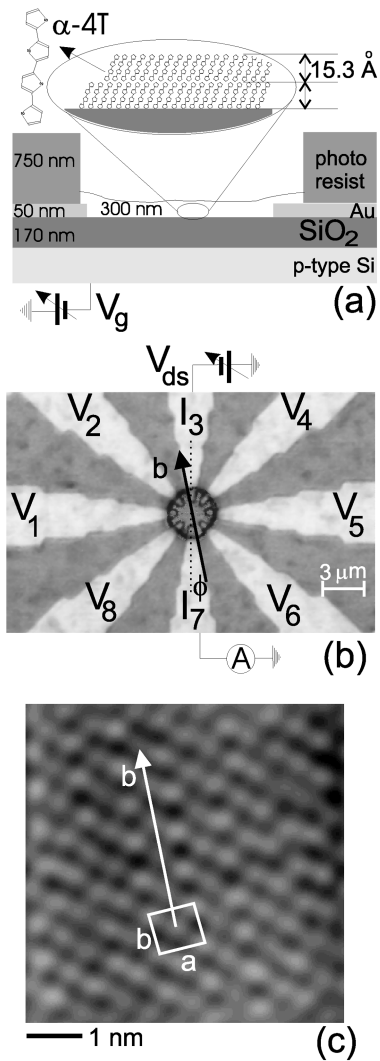
FIG. 1. Multiterminal single crystal quaterthiophene TFT. (a) schematic sample structure. (b) Top view: The single crystal is located at the centre of the eight contacts. On the terminals labeled ''V'' the voltage and ''I'' the current is monitored (c). Molecular resolved AFM image showing the a and b axis of the monoclinic (Ref. 10) unit cell with $a=7.4\pm1$ Å and $b=8.4\pm1$ Å.
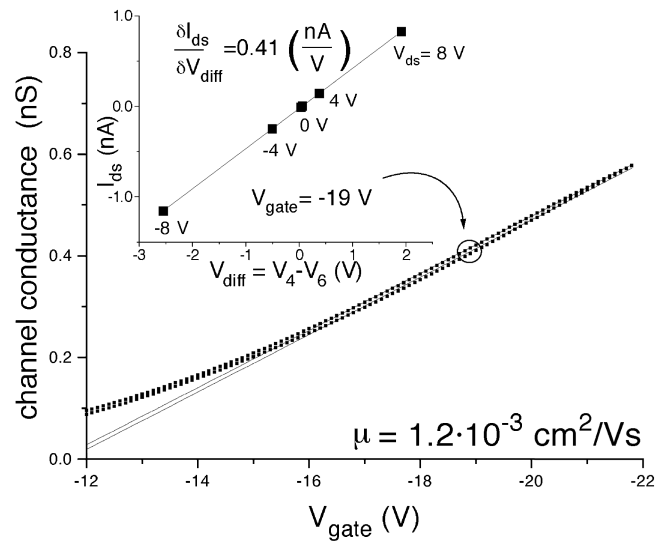

FIG. 2. Two measurements of the channel conductance of a quaterthiophene single crystal as a function of the gate voltage. In the inset the channel current is plotted vs the potential difference V_{diff} between terminals 4 and 6 at a constant gate potential.

in-plane drift field which results in a uniform density of charge carriers in the active channel. The gate voltage is defined with respect to the average potential of the active medium, as is measured by the two additional voltage probes. The multiterminal geometry allows for the conductivity to be probed as a function of the in-plane crystal-axis direction by assigning a different set of terminals as the source and drain terminals.

By applying a source-drain bias, a current will flow and consequently a potential distribution will arise within the single crystal. The channel current in the linear regime $[V_{\mathrm{diff}}\ll(V_g-V_t)]$, after applying a fixed source-drain potential V_{ds} is given by

$$I_{\mathrm{ds}}=G\mu C_i(V_g-V_t)V_{\mathrm{diff}}. \qquad (1)$$

Here C_i is the insulator capacitance, μ the charge carrier mobility, V_t the threshold voltage, V_g the gate voltage, V_{diff} the transverse potential difference observed by the two voltage measuring electrodes and $G(\mu,\phi)$ a correction factor resembling the Z/L ratio for rectangular shaped sample

structures. Due to the structure of the unit cell[11] the mobility should be described by a tensor[7] μ_{ij}, which relates the drift velocity to the applied electric field ($v_i=\mu_{ij}E_j$).

The actual value of G, however, is sample geometry specific and depends not only on the symmetry of the active medium, which is described by the mobility tensor μ_{ij}, but also on the used contact geometry and contact dimensions [see Fig. 1(b)] with respect to the orientation of the crystal (angle ϕ). For a certain in-plane mobility anisotropy μ_{ij}, the correction factor can be numerically calculated, for a specific set of terminals as the measuring pads and for a specific angle ϕ, by solving the continuity relation div $\mathbf{J}=0$ under biased conditions. The resulting correction factor G is then given by the ratio of the calculated conductance ($I_{\mathrm{ds}}/V_{\mathrm{diff}}$) and the assumed square conductance ($\sigma_\square$) of the medium.

A typical measurement result is shown in Fig. 2. At a set gate voltage, the linearity of the channel conductance and the electrical behavior of the source and drain contacts are checked by plotting the channel current versus the observed potential difference V_{diff}, for each applied source drain potentials V_{ds} (see inset Fig. 2). The channel conductance g_D is then calculated by taking the derivative of the channel current with respect to V_{diff}:

$$g_D=\left.\frac{\partial I_{\mathrm{ds}}}{\partial V_{\mathrm{diff}}}\right|_{V_g=\mathrm{const}}=G\mu C_i(V_g-V_t). \qquad (2)$$

Possible leakage currents appear as a general offset in this plot and do not affect the obtained slope and therefore the channel conductance. This procedure applied at every gate potential, results in the channel conductance as a function of gate voltage. The charge carrier mobility is obtained from the slope of the channel conductance versus the applied gate potential.

The electrical characteristics as shown in Fig. 2 are obtained on a single crystalline quaterthiophene TFT with a gap diameter of 5 μm. The measuring geometry with respect to the crystal orientation is shown in Fig. 1(b). At terminals 7 and 3, the source and drain current is measured and the trans-

verse potential difference is probed between contacts 4 and 6. The remaining four terminals are connected to the electrometer probes in order to minimize leakage currents. In this geometry, the conductivity is probed in a direction almost parallel ($\phi \sim 10°$) to the b axis of the unit cell.

In practice, the measurement sequence consists of several gate sweeps ranging from -12 to -22 V in steps of 0.1 V (δV_{step}) for a series of subsequently applied drain voltages (0, -4, -8, 0, $+4$, $+8$ V). In each gate step an amount of charge $\delta Q = C \delta V_{step}$ must be transferred to the gold contacts due to the capacitive coupling with the gate electrode. A delay time of 4 s per gate step is maintained for the system to relax to the equilibrium potential distribution at the new gate potential.

The inset of Fig. 2 demonstrates how the shown channel conductances are obtained. The source-drain current is plotted as a function of the transverse potential difference V_{diff} for all applied drain potentials at a fixed gate potential. The small channel current (few pA) at $V_{diff} = 0$ shows that we can also experimentally exclude leakage currents. From the linear relation we conclude that, although the current injecting contacts have a strong non-ohmic behavior, the medium can indeed be described by one channel conductance g_D. This non-ohmic behavior is demonstrated by the observed small potential difference after applying the source drain potential and the nonlinear increase of V_{diff} with V_{ds}. A voltage drop of 1 to 2 V, depending on the bias conditions of the transistor, is typically observed at the quaterthiophene-gold interface. Note that despite this nonlinearity the channel current is perfectly linear with V_{diff}, which clearly demonstrates the power of the multiterminal technique.

Two independent, hardly distinguishable, measurements of the channel conductance are plotted in Fig. 2 with a time interval of several days. At high gate voltages, a linear increase of the channel conductance is observed, from which the charge carrier mobility and the threshold voltage can be derived [see Eq. (2)]. Assuming an isotropic medium, the correction factor G was calculated to be 2.1, which results in a charge carrier mobility of 1.2×10^{-3} cm²/V s for both measurements. Typically, the reproducibility is within 5% for multiple measurements on one sample with the same contact geometry with only a slight negative shift in the threshold voltage.[12,13] Measurements on several different samples, with a varying orientation of the crystallite with respect to the contact geometry and/or with different pads assigned as the source and drain contacts yield similar plots as is shown in Fig. 2 and result in charge carrier mobilities with a maximal spread of a factor of 2. This might be an indication for the in-plane anisotropy, but additional measurements on one and the same sample need to be done in order to accurately determine the in-plane components of the mobility tensor μ_{ij}. The sample to sample variations of these single crystal thin-film devices are negligible compared to what is generally found for polycrystalline devices,[14] and are therefore believed to be representative for our 4T on SiO₂ TFTs. The mobility value is still low compared to the observed values of the FET structures based on macroscopically grown quaterthiophene single crystals[15] ($\mu = 0.05$ cm²/V s). Clearly, defects and impurities are likely to play a role in this observed difference in the measured field-effect mobilities.

This experiment also shows that the extremely high mobility observed in, i.e., pentacene[3,16] TFTs is not entirely due to increased size of the single crystal domains. Although we measure on a true single crystal, the observed mobility is still three orders of magnitude less than in the pentacene case. This indicates that, next to the size of the crystal domains, the crystal structure together with the electronic structure of the molecules are the main parameters determining the charge carrier mobility.

We have fabricated several single crystal quaterthiophene TFTs with a multiterminal contact geometry, which excludes extrinsic effects such as grain boundaries and contact resistances on the measured mobilities. The single crystal can be described by one channel conductance at every measured gate potential, despite the strong nonlinear behavior of the current injecting contacts. We find a charge carrier mobility of 1.2×10^{-3} cm²/V s. This value is constant over a period of weeks of operation and does not vary from sample to sample, in contrast to the typically observed lower mobilities of polycrystalline quaterthiophene thin-film transistor devices.

[1] L. Torsi, A. Dodabalapur, L. J. Rothberg, A. W. P. Fung, and H. E. Katz, Science **272**, 1462 (1996).

[2] L. Torsi, A. Dodabalapur, L. J. Rothberg, A. W. P. Fung, and H. E. Katz, Phys. Rev. B **5**, 2271 (1998).

[3] S. F. Nelson, Y.-Y. Lin, D. J. Gundlach, and T. N. Jackson, Appl. Phys. Lett. **72**, 1854 (1998).

[4] G. Horowitz, R. Hajlaoui, and P. Delannoy, J. Phys. III **5**, 355 (1995).

[5] K. Waragai, H. Akimichi, S. Hotta, and H. Kano, Phys. Rev. B **52**, 1786 (1995).

[6] A. R. Brown, A. Pomp, C. M. Hart, and D. M. de Leeuw, Science **270**, 972 (1995).

[7] *Organic Molecular Crystals*, edited by E. A. Silinsh V. Càpek (AIP, New York, 1994).

[8] Quaterthiophene material was obtained from Syncom B.V. Groningen, The Netherlands.

[9] J. Vrijmoeth, R. W. Stok, R. Veldman, W. A. Schoonveld, and T. M. Klapwijk, J. Appl. Phys. **83**, 3816 (1998).

[10] A. R. Brown, C. P. Jarret, D. M. De Leeuw, and M. Matters, Synth. Met. **88**, 37 (1997).

[11] W. Porzio, S. Destri, M. Mascherpa, and S. Brückner, Acta Polym. **44**, 266 (1993).

[12] The global threshold voltage shift between two subsequent measurements, of the channel conductance versus gate bias, with identical contact geometries is about 1 V. This shift complicates the determination of the charge carrier mobility since it affects the density of free charge carriers. The nature of the threshold shift is at this moment not exactly known, but there are indications of charge trapping at the SiO₂ gate dielectric interface (See Ref. 13).

[13] W. A. Schoonveld, J. B. Oostinga, J. Vrijmoeth, and T. M. Klapwijk, Proceedings of the International Conference on Science and Technology of Synthetic Metals at Montpellier 1998, to be published in Synthetic Metals.

[14] H. E. Katz, L. Torsi, and A. Dodabalapur, Chem. Mater. **7**, 2235 (1995); R. Hajlaoui, G. Horowitz, F. Garnier, A. Arce-Brouchet, L. Laigre, A. E. kassmi, F. Demanze, and F. Kouki, Adv. Mater. **9**, 389 (1997).

[15] J. H. Schön, Ch. Kloc, R. A. Laudise, and B. Batlogg, Phys. Rev. B **58**, 12952 (1998).

[16] H. E. Katz, A. J. Lovinger, and J. G. Laquindanum, Chem. Mater. **10**, 457 (1998).