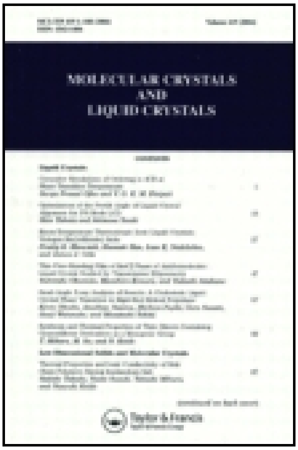

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Anthracene-Based Organic Field-Effect Transistor: Temperature Dependence of the Current-Voltage Characteristics

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We present the characterization of an anthracene single-crystal organic field-effect transistor in the temperature-range of 4.2 to 290 K. We recorded the source-drain current as a function of the applied voltages (source-drain and gate). The measured curves exhibit a superlinear dependence when plotted on a log-log scale with an exponent larger than two, which is typical of a trap-filling regime. At low temperatures, the source-drain current becomes temperature independent and shows a plateau. We estimate a lower bound of the mobility at different temperatures.

1. INTRODUCTION

During the last decades, the electronic properties of organic materials, particularly π-conjugated materials, have attracted much interest [1–6]. On the side of applied research, many promising organic-based devices, covering fully flexible devices for large-area displays, light-emitting devices [7,8] or solar cells have been successfully developed, opening numerous new technological potentialities. However, many basic concepts about electronic transport and charge injection in these materials are still not very well understood, and characterization at nanometer scales is urgently needed.

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The relevant quantity to characterize charge transport at a macroscopic scale is the carrier mobility which represents the ease for charge carriers to move through the material. Various methods have been developed to study this carrier mobility [4]. Among the most popular methods are the time-of-flight (TOF) measurements, electrical characterization in a field-effect transistor (FET) configuration or in a diode configuration, and the time-resolved measurement of microwave conductivity (PR-TRMC) after pulse radiolysis [9,10]. Some of these techniques involve measurements over large areas. Therefore, they are strongly influenced by impurities and defects and they give their best results with materials of high purity and order. Moreover, the mobility is an ensemble parameter. As a consequence, the individual conduction events are completely inaccessible in these measurements.

In a former publication [11], we proposed to study charge transport by means of single-molecule spectroscopy and microscopy at cryogenic temperatures as this technique could ultimately allow us to optically probe displacements of individual charges with a very high accuracy [12]. High-resolution single-molecule spectroscopy in crystalline matrixes requires a “good” fluorescent guest (with both a large absorption cross section and a high fluorescence yield) and a good insertion of the guest into the host lattice, giving rise to a strong and narrow zero-phonon line. Because single-molecule spectroscopy studies require acquisition over extended periods, photo-induced jumps should be minimal. The guest’s zero-phonon line should be very stable, both against photochemistry (photobleaching), which is usually suppressed at cryogenic temperatures, and against spectral diffusion processes, which may obscure the interesting spectral shifts induced by electrical or other dynamic processes. The best results are usually obtained with organic crystal matrices at cryogenic temperatures [13]. We previously showed [14,15] that 7,8,15,16-dibenzoterrylene (DBT) in anthracene (Ac) was a promising system for this purpose.

In organic crystals, the charge carriers have strong interactions with their environment. Their movements generate distortions of the molecules and of the lattice, and change the polarization of the electronic cloud of the surrounding molecules. A movement of the charge carriers will always be accompanied by these perturbations. The strong interaction between the charge carriers and the induced polarization is described by the model of the polaron [16,17].

Organic crystals of small conjugated molecules can be described with a fully filled valence band which consists of the overlapping of the highest occupied molecular orbitals (HOMO) of the individual molecules, and an empty conduction band built on superpositions of the lowest unoccupied molecular orbitals (LUMO). Defects and impurities of the crystal may create some available energy levels in the gap between the HOMO and the LUMO bands, which will act as traps. These traps can be separated into two categories. On the one hand, we have traps with energy levels of the order of a few k_BT, where k_B is the Boltzmann constant and T is the temperature. The detrapping of charges will be thermally activated. For that reason, we will call them shallow traps. On the other hand, some defects or impurities might trap charge carriers at depths much larger than the thermal energy. These traps will be called deep traps. It is clear that the conduction mechanism will not be of the same nature in presence of shallow and/or deep traps. The temperature dependence of the mobility can therefore give crucial information with respect to the processes that are involved in the conduction phenomena.

A FET is a powerful device to study the different processes of charge carrier transport, as it allows one to tune the charge carrier density in a continuous way and therefore to control the working regime of the device via the transverse gate electrode. Several organic crystals have been used as a conducting layer in FET's. Among them are sexithiophene [18], rubrene [19], pentacene [20], tetracene [21,22] and Ac [23]. Thus, the choice of Ac is natural if we consider the single-molecule study that we propose to conduct.

In a FET configuration, essential information about conduction can be obtained via the current-voltage I–V curves, where the current is plotted as a function of the gate-voltage V_g [24] or of the source-drain voltage V_{sd}. From these curves, we can estimate a lower bound of the mobility using the proper formula for the respective regimes of the FET. The temperature dependence of the mobility of Ac-FET's has been studied until 100 K [23]. However, a change of the conduction regime is expected at much lower temperatures (about a few tens of Kelvin).

Herein, we present the properties of an Ac-based FET in the light of the current-voltage characteristics for several temperatures, ranging from 4.2 to 290 K. From these I–V curves, we give a lower bound of the mobility at room and at low temperatures. In Section 2, we describe the experimental setup and procedure. In Section 3, we present the experimental results and discuss their main features. We finally comment on the potentialities of Ac-based FET's for a better understanding of charge carrier transport in molecular crystals.

2. EXPERIMENTAL

Anthracene (Ac; Aldrich, scintillation grade, purity $\geq 99.0\%$) was purified in a home-built zone refiner for about 4000 passes. Single crystals of Ac were then grown by sublimation under a 150 mbar nitrogen atmosphere. Sublimation flakes developed along the (a, b) plane with diameters of a few millimeters and a thickness of a few tens of micrometers. The substrates of the FET structures (Fig. 1) consisted of Si wafers highly p-doped with boron (with a resistivity of 0.001–0.01 Ωcm) with a thermally grown 400 ± 20 nm thick layer of SiO_2. Interdigitated gold electrodes (30 electrodes with 29 gaps, 40 nm thick) with spaces of 5 μm were deposited (by the Fraunhofer-Institut für Mikroelektrische Systeme und Schaltungen, Munich, Germany) on top of the insulator layer by e-beam lithography, with a 12 nm thick layer of TiW. Before contacting the FET structure to the Ac crystal, electrodes were dipped into a solution of 10 mM nitrobenzenethiol in acetonitrile, as this treatment significantly reduces the contact resistance, a crucial parameter for low-temperature measurements [23,25]. The Ac crystals were placed on top of the structures resulting in an optical contact [24]. We believe that van der Waals forces lead to molecular contact between the crystal and the structure. Such a procedure of crystal deposition is different from those frequently used for FETs (e.g., vacuum evaporation), however it has been used in several former works on single-crystal organic transistors based on tetracene [21,26] and Ac crystals [23]. Therefore, we decided to keep to the abbreviation FET also for our single-crystal transistors.

The samples were mounted in a helium bath cryostat and cooled down with liquid nitrogen for temperatures ranging from 290 K to 77 K and liquid helium for lower temperatures (down to 1.4 K).

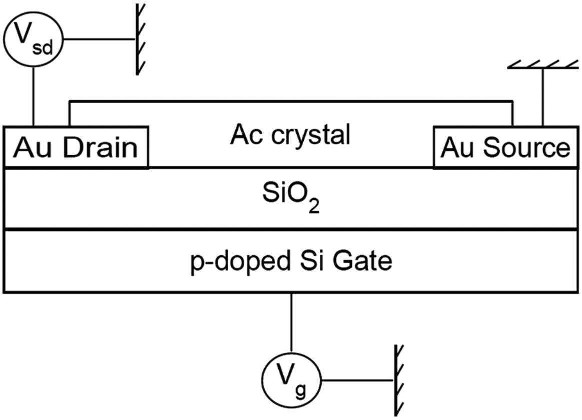

FIGURE 1 Schematic drawing of an Ac FET. Dimensions are discussed in the text.

Source-drain current was detected by means of a home-made ammeter (with several settings of sensitivities, ranging from 0.001 to 0.1 μA) after applying several source-drain and gate voltages. Prior to any measurement and before contacting the Ac crystals, we measured the gate-induced leakage current of the gold electrodes with a more sensitive ammeter (Keithley, Picoammeter 6487). It has been shown [26] that, in order to operate the FET with stability, one requires a leakage current lower than $10^{-9}\,\mathrm{A/cm^2}$. However, our equipment only allows us to measure leakage exceeding $10^{-8}\,\mathrm{A/cm^2}$ and we could not detect any current within our sensitivity. Therefore, we only may conclude that leakage was not exceeding $10^{-8}\,\mathrm{A/cm^2}$.

3. RESULTS AND DISCUSSION

Figure 2 shows a typical plot of log I_{sd} versus log V_{sd} for an Ac-FET at 217 K. The *I–V* curves show a power-law dependence as $I_{\mathrm{sd}} \sim V_{sd}^{n}$. The values of the exponent n range from 6 to 12 for different temperatures, consistent with previous measurements (Mark *et al.* found a value of 12, but mentioned traces of tetracene in the crystal [27], and Aleshin *et al.* obtained values ranging from 6 to 16 [23]). At a given temperature, the exponent is only weakly gate-dependent, slightly decreasing when V_{g} increases. The space-charge limited current (SCLC) theory

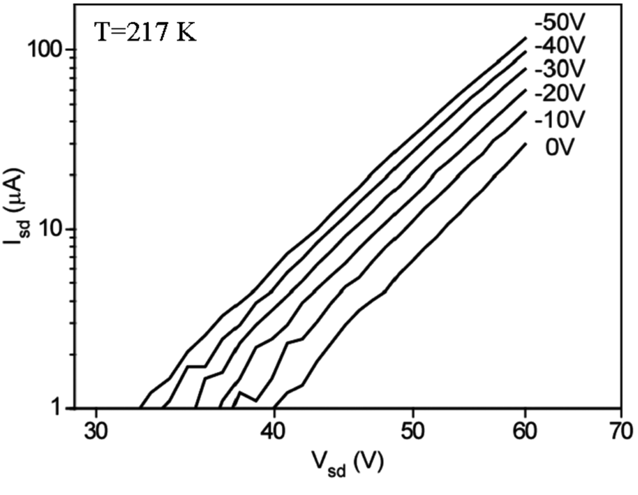

FIGURE 2 I_{sd} as function of V_{sd} for different V_{g} at 217 K, plotted on a log-log scale.

describes transport mechanisms with different regimes [28]. From the Ohmic regime (at low voltages), we pass the rather narrow SCLC regime governed by shallow-traps (where we have a dependence as $I_{\mathrm{sd}} \sim V_{sd}^{n}$, with $n \sim 2$), to the trap-filling limit (where $I_{\mathrm{sd}} \sim V_{sd}^{n}$, with $n \gg 2$). Our measurements exhibit the latter regime of conduction, and the *I–V* curves are superlinear over their entire range.

Ac is an organic crystal with a rather high band gap $E_{\mathrm{g}} \sim 4\,\mathrm{eV}$ [29,30]. The band gap being large, we expect high-purity crystals to act as insulators. Applying a large enough voltage, it is yet possible to pass a current through the crystal if the voltage induces charge injection from the electrodes. It is possible to define an upper bound for the current that can be carried in the regime of space-charge-limited conduction (SCLC). This current corresponds to the maximum amount of charges that can be injected, limited by Coulomb repulsion by the space charge. In the 1 D case, this current can be expressed as [24,28]:

$$I = A\frac{9\varepsilon_r\varepsilon_0\mu h V^2}{8L^3}, \tag{1}$$

where A is the area of the conducting channel, ε_0 is the permittivity of free space, and ε_r the relative dielectric constant of the material (for Ac, $\varepsilon_r = 3.2$), L is the length of the channel, h is a film thickness and V is the applied voltage. This equation, known as the Mott-Gurney law, is directly obtained from the Poisson equation in the 1 D case for a sandwich-type geometry.

However, in a coplanar geometry, a different dependence in gap width is expected, corresponding to a two-dimensional theory [31–33]:

$$I = A\frac{2\varepsilon_r\varepsilon_0\mu V^2}{\pi L^2}. \tag{2}$$

A crossover from one- to two-dimensional SCLC has been measured in pentacene single crystals as a function of the gap width L and of the thickness h of the crystal [34] for increasing ratio L/h. For low values of the ratio L/h (typically lower than 15), the current dependence is well described by the Mott-Gurney law (with a dependence in L^{-3}) while for high values (typically higher than 250), Geurst's model applies (with a dependence in L^{-2}). It is not possible to extrapolate directly the law in case of an Ac crystal from the measurements on pentacene; yet, with a ratio $L/h < 1$, one can assume that the Mott-Gurney regime would be a better approximation as an upper bound of the current.

Various models have been put forward to explain the power law observed in Figure 2. The most popular ones assume either an exponential (or Gaussian) distribution of energy of the trapping states [27,35] or a field dependence of the mobility [36]. The origin of the mobility field enhancement is related either to the Frenkel-Poole process [37] or to hopping through disorder [38].

In the case of an exponential trap energy distribution, we obtain a voltage dependence of the current as $I \propto V^{l+1}$, where $l = T_c/T$ (T_c is a characteristic trap distribution parameter and T is the temperature). From the measured slope at room temperatures, with $V_g = 0\,\mathrm{V}$, we obtain $k_B T_c = 0.3\,\mathrm{eV}$, a value similar to the one found by Mark *et al.* [27]. However, at low temperatures, we expect a tunneling regime, and the law should consequently be temperature independent, as found for a pentacene-based FET [39]. A different law should then be applied.

The upper limit of the current, as defined by Eq. (1), is intrinsic. The presence of traps will just decrease the apparent mobility (as not all charges participate to the detected current). In other words, we obtain a lower bound of the intrinsic mobility of the *mobile* charges from Eq. (1):

$$\mu_{\min} = \frac{8IL^3}{9A\varepsilon_r\varepsilon_0 V^2} \tag{3}$$

We now look at the temperature dependence of the current. Figure 3 shows the temperature dependence of the source-drain current measured for $V_{sd} = 30\,\mathrm{V}$ and $V_g = -50\,\mathrm{V}$ in a temperature range between 6 and 280 K. The curve is plotted on a log-log scale. We can see first a sudden increase of the current when we decrease the temperature. After reaching a peak around 100 K, the current then decreases and around 15 K, it reaches a plateau, where the regime is probably only a tunnel trapping-detrapping mechanism.

We can calculate the lower bound of the mobility (from Eq. (3)) and plot it as a function of temperature. The results are presented in Figure 4.

We first have an increase of the mobility as the temperature decreases. After a peak, the mobility decreases with temperature decrease. Such a non-monotonous temperature dependence of the mobility is usually a good indication for high-quality crystals in presence of shallow traps [21], with $\mu \sim T^{-n} \exp(-E_a/k_B T)$ (where E_a represents an activation energy).

For some samples, we obtained mobility values of $3.5 \cdot 10^{-3}\,\mathrm{cm^2/Vs}$ at 4.2 K, with a maximum around $10^{-2}\,\mathrm{cm^2/Vs}$ at 150 K, for $V_g = -50\,\mathrm{V}$, which is of the same order of magnitude as found in a previous study by Aleshin *et al.* [23].

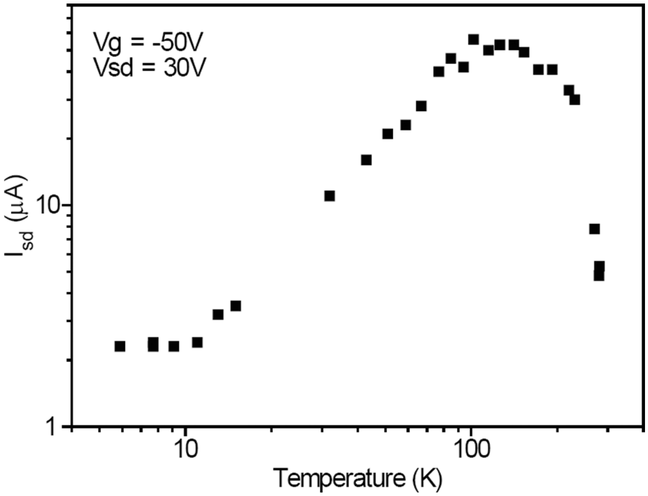

FIGURE 3 I_{sd} versus temperature for $V_{sd} = 30\,V$ an $V_g = -50\,V$, plotted on a log-log scale.

We observed some differences from sample to sample, with variations within one order of magnitude. We always detected a non-monotonous temperature dependence of the mobility, which points to a good quality of the crystals. However, several effects might

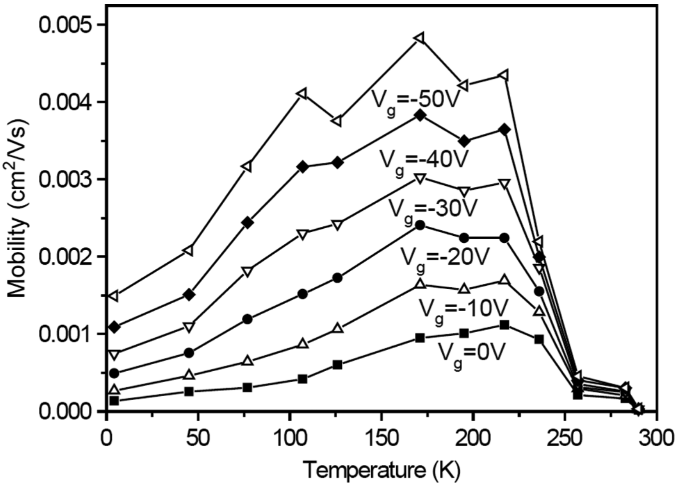

FIGURE 4 Lower bound of the mobility plotted as a function of temperature for different gate voltages. We applied a source-drain voltage $V_{sd} = 60\,V$.

influence the detected current and therefore the mobility. The most likely one can arise from small differences in the quality of the contact at the crystal-electrode interfaces. Note that non-isotropic mobility has been reported in the case of rubrene [40]. In our FET, we did not check the orientation of the crystal. The effect of anisotropy is difficult to estimate. Finally, we have to mention the influence of possible impurities at the surface of the crystal such as anthraquinone, which might also play a role in these differences. It has been shown that the concentration of such derivatives is larger by one order of magnitude on the surface than in the bulk of the tetracene crystals [41]. These oxidized derivatives usually act as deep traps.

Additional measurements are required for a better understanding of the Ac-FET. We propose now to investigate transport phenomena at the nanometer scale via single-molecule spectroscopy.

4. CONCLUSION

We presented the characteristics of our Ac-based FET for several temperatures ranging from 290 to 4.2 K. The I–V curves plotted on a log-log scale are linear with an exponent larger than two which is typical for a trap-filling regime. For high temperatures, the current of our FET increases with a decrease of the temperature, indicating the good quality of the crystals. At low temperatures the current reaches a plateau. This temperature independent process indicates a tunnel conduction regime. We calculated a lower bound of the mobility and plotted it as a function of temperature. We obtained values of $3.5 \cdot 10^{-3}\,\mathrm{cm}^2/\mathrm{Vs}$ at 6 K, with a maximum around $10^{-2}\,\mathrm{cm}^2/\mathrm{Vs}$ at 150 K for some samples. A microscopic study of Ac-based FET could bring new insight into the mechanism of charge carrier transport in this system.

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