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# **1. Introduction**

This document reports on the visit of me to Bologna in the month July 2002 during which several subjects were studied, ranging from BDT and tetracene films grown by molecular deposition to tetracene fibers, grown in solution. For the characterization of these materials, a dedicated program was written in LabVIEW that can measure the electrical parameters of field-effect transistors (FETs) in continuous-wave and pulsed mode.

# **2. BDT**

High mobilities have been reported for FETs based on the thiophene oligomer BDT (see Figure 1) [1]. Encouraged by these reports, BDT was also gown and deposited by us. During my visit, new BDT devices were grown with old (recycled) substrates. The substrates that



 $\varepsilon/d = 43.2 \ \mu\text{F/m}^2$ ). All device parameters are summarized in Table 1. The BDT is

deposited in the Edwards Auto 306

vacuum-sublimation chamber and the IV characteristics were measured in situ. The

reproduction of earlier results, namely

poor FET devices, with the main characteristics of small field effects and

resulted

in

а

Figure 1: The BDT molecule.

measurements

were used were of the Bangor type, namely with circular interdigitated gold source and drain electrodes and a silicon bottom gate separated by an insulating layer of SiO<sub>2</sub>. In the schematic picture below:  $L = 23.2 \,\mu\text{m}$ ,  $W = 23.5 \,\text{cm}$ ,  $d = 800 \,\text{nm}$  (*Cox* =

first



Figure 2: Structure of an FET.

absence of saturation.

A summary of the IV characteristics:

- No saturation.
- Strong hysteresis.
- Low mobility  $(10^{-4} 10^{-3} \text{ cm}^2/\text{Vs})$  compared to literature.
- Device degradation (electrode deterioration).

These are now discussed in detail:

#### No saturation



**Figure 3**: *IV curve,*  $Vg = 1 V (b80_iv7)$  showing absence of saturation.

Hysteresis



**Figure 4**: *IV curves for Vds scanning upwards, 0 to -100 V (red, top) and downwards, -100 to 0 V (green, bottom) (b82iv03 and b82iv04 respectively) and averaged (blue, middle). Vg = 30 V.* 

**Low mobility** (small field effect)



**Figure 5:** Transfer curves. Left: at Vds =  $-1 V (b80\_g5)$ . Mobility:  $6.5 10^{-5} cm^2/Vs$ . Right: at Vds = -100 V, assuming saturation (b80\\_g6). Mobility:  $8.8 10^{-4} cm^2/Vs$ .

**Device degradation**. Due to electron migration, the electrodes degrade during operation. This is similar to effects observed by Sirringhaus *et al.* [1]. Because of this, we cannot recycle our devices and we have to be careful when calculating the mobility; the effective channel width can be much smaller than the designed channel width. To avoid this, it is always better to used pulsed measurements or at least measure as fast as possible. Note: these effects probably only occur when measuring the devices in air (In Faro Henrik didn't see degradation, September 2002)



**Figure 6**: Unused electrode set (left) and used device (right) from the same plate after cleaning with acetone. (Note the images have been inverted; the electrodes are the dark spots). Clearly electron migration has take place during operation (in both source and drain). Before cleaning with acetone, there were dark spots in the BDT material on an around the electrodes.





**Figure 7**: *IV curves for the 90-nm tetracene films measured in situ for various gate-voltages ranging from 0 V to -40 V.* 

A tetracene film was grown on top of a large rectangular Faro FET structure (see Table 1 for the device parameters) in the Edwards growth chamber. Growth rate: 0.013 nm/s, substrate temperature: RT, crucible temperature: 118 °C. Pressure: 2.0x10<sup>-6</sup> mbar. Total thickness 91 nm. The device shows clear saturation effects, see Figure 7, but in the saturation region the current is linearly proportional to the gate voltage instead of the conventional quadratic.

Note also that the turning point going from the linear region to the saturation region is nearly

independent of the gate (-4 V). In theory, however, this turning point is Vg-Vt and hence should depend linearly on Vg. This is very peculiar and is as if the gate voltage does not reach the channel, but is absorbed by the interface somehow. In that case, the as-measured mobility would be much lower than the real mobility. As a rough estimate, we're losing a factor 20.

The scans of Figure 7 were taken the day after preparing the films. The first measurements, directly after deposition had much larger currents (up to 80 nA for -40 V on the gate, see Figure 9a); the device is degrading rapidly whilst scanning. The curves of



Figure 7 were reproducible after two days relaxing in vacuum. The mobility drops from  $1.0 \times 10^{-5}$  cm<sup>2</sup>/Vs to  $3.9 \times 10^{-7}$  cm<sup>2</sup>/Vs in this time, compare Figure 9a and Figure 9c.



**Figure 9**: a (*left*): Original transfer curve in saturation (Vds = -40 V). The dashed line gives a fit to the data yielding a mobility of approximately  $1.0x10^{-5}$  cm<sup>2</sup>/Vs. b (center): Transfer curves in the linear region for various drain-source voltages (0 to -14 V in steps of 1 V) After Vds = -5 V, the curves become independent of the voltage, as it is entering the saturation region. c (right): Transfer curves in saturation for various drain-source voltages (-25 to -30 V, step 1 V). These curves are not depending any longer on the drain-source voltage, indicating that we are fully in the saturation region. The dashed line gives a fit with a threshold voltage of 3.2 V and a mobility of  $3.9x10^{-7}$  cm<sup>2</sup>/Vs.

Table 1: Device parameters of Faro (Bangor) FET structures.

parameter	circular	small rectangular	large rectangular
L	23.2 µm	25 µm	25 µm
W	235 mm	58.5 mm	108 mm
$C_{ox}$	$43.2 \mu\text{F/m}^2$	$43.2 \mu\text{F/m}^2$	$43.2 \mu\text{F/m}^2$

## 4. Tetracene fibers

Tetracene fibers with macroscopic dimensions (up to a millimeter) were grown in solution. Devices were prepared using the drop-cast technique of placing a drop of solution on top of an FET structure (small rectangular FETs, see Table 1) and letting the solvent evaporate. The highest currents were obtained in a device with a large coverage of fibers. See for example Figure 10. Note the magnitude of the currents, which is much larger than in similar structures covered by films (see section 2), even though the coverage is orders of magnitude smaller (some % at best).



**Figure 10**: Drop-cast experiment (Pulsed, ton = 0.1 s, toff = 2.0 s, see section 5, start always at 0 V). (-5 V, -450 nA; bottom curve): First measurement.

(-10 V, -275 nA): Second measurement (immediately after 1<sup>st</sup>).

(-10 V, -40 nA; top curve): Third measurement.

(-10 V, -75 nA): Fourth measurement after 20 minutes delay (recovering!).

Image on the right: detail of the device (inverted and contrast enhanced). Picture taken after the measurements.

Comments on the measurements:

- Note the transition voltage going from the linear to the saturation region in Figure 10, about -4 V, which is exactly equal to the transition voltage in the tetracene film (see Figure 7). This seems to be a material parameter, therefore.
- No field effect was observed for the fibers, although the curves themselves show saturation and hence FET behavior.
- It seems that the fibers prefer to orient with an angle of about 30° with the electrodes.



**Figure 11**: Fifth drop cast experiment. Left: first IV curve at Vg = 0 V (solid red) and one measured much later (green dashed). Middle: Set of stable IV curves for various gate voltages (from 0 V to 16 V), measured after about an hour of measuring curves. No field effect is observed. Lowest curve (first of the set) is the same as dashed curve in left picture. Pulsed mode. Picture on the right: detail of the device.



Figure 12: Results of first drop cast experiment and the microscopic picture.



Figure 13: Drop-cast experiment 3,4. No currents were observed in this device, which was measured after putting it several hours in air and nitrogen.

A single fiber (see Figure 14) was connected and submitted to an electrical study. This fiber did not conduct at all (the currents were the same currents as measured in opencircuit, some nA's for 50 V). In view of the measurements above on multi-fiber devices, the expected currents are below the noise level, though, and we cannot exclude a high conductivity.

This fiber was a single crystal, as evidenced by the polarization of light homogeneously over the entire length of the fiber.



**Figure 14**: Single crystal of tetracene placed on top of an FET structure (visible are also the contact pads of a circular FET) before and after contacting with silver paint. The size of the crystal is approximately  $600 \ \mu m$  (long axis). Images were inverted for better visibility. The hairy object in the right picture was mechanically removed before the measurements.

## 5. Bologna FET software



The Bologna FET software was modified to include pulse-mode measurements. There are two basic parameters to a pulse:  $t_{on}$  and  $t_{off}$  which mean the time the voltage is "on" and the time which it is "off " (or is at bias level, which is programmed to be 0 in the current version). Note that these two states should *each* be long enough to accommodate the default delay (which depends on the measurement range, see Table 3 and Keithley

Figure 15: Pulse timing diagram.

command "W") and the measurement time, which in its turn depends on the integration time (from 416  $\mu$ s for noisy, low precision curves, up to 20 ms for high precision measurements, see Keithley command "S"). Disabling the default delay

would allow for shorter pulses, at the cost of inaccurate readings (not allowing for settling of the current). For that reason this option

has not been implemented in the program, which automatically sets the default-delay option. The program also automatically adjusts the pulse length when too short for default delay and integration time. Therefore, theoretically, it should not be possible that the error 'Pulse Time Not Met'' appears in the display of the Keithley (for this, the 27 ms of Table 2 had to be increased to 28 ms).



The fastest measurement can be made with a

measurement time of 1 ms and a range of 100  $\mu$ A or larger, in which case the pulse can be as short as 1 ms.

The lowest noise measurements are made with a measurement time of 28 ms. Always use this range for normal measurements. The noise is orders smaller.

Note that in CW mode the program only uses the 'off-time" parameter, which is now called the 'interval time"; it is the time between setting the new voltage and giving a trigger to measure the current. The 'on-time" parameter is ignored.

 Table 2: Measurement times as depending on the integration
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 time
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Integration Time	Resolution	Measure Time
416 µs	4-digit	1 ms
4.0 ms	5-digit	5 ms
$16.67 \text{ ms}^1$	5-digit	23 ms
$20 \text{ ms}^2$	5-digit	$28 \text{ ms}^{3,4}$

1: 60 Hz power supply only

2: 50 Hz power supply only

3: preferred setting

4: 1 ms longer than according to manual!

**Table 3:** Default delay as a function of measurement range.

I-Measure	Default
Range	Delay
1 nA	360 ms
10 nA	75 ms
100 nA	20 ms
1 μΑ	5 ms
10 µA	2 ms
100 µA	0
1 mA	0
10 mA	0
100 mA	0

(These tables are Table 3-9 on p. 3-83 and 3-12 on page 3-86 of the Keithley 236 Operator's manual)



Figure 17: Interface to the Bologna-FET program written in LabVIEW.

In pulsed mode, the auto measurement and source range are not allowed. The program automatically corrects for this by changing the ranges when pulse mode is selected. The user has to make sure the ranges are correct.

Note that the timing diagrams shown in the figures also include the overhead time, the time it takes to set-up each point, including communication time and processing time. This should be of the order of 100 ms per data point (see section 3.7 of the Keithley Operator's Manual, KOM): The IEEE communicates at 5000 characters per second. A typical command string is of the form Q3,1,1,100,1XH0X (say 20 characters) the reply will be about 80 characters, totaling 100 characters, or 20 ms communication time. Executing the commands takes about (see Table 3.8 of KOM) 50 ms. Since it is very difficult to calculate this and since it is not very useful information, it is ignored in the program. Note, however, that the scans take longer than programmed (by about n/10 s, with n the number of data points) and the voltage stays a little longer at each point (at bias level in pulsed mode and at last voltage in CW).

Note also the option to change the output file type. In MatLab type, also the relevant scanning parameters are saved on lines starting with % - for instance the comment line and the sample name are added to the files - and at the end some MatLab instructions are added. MatLab can directly process these files. Any spreadsheet program, like Excel, can also read them, so I advise to use this format.

Finally, note the button 'keep' in the status panel (Press this button when you want to keep the voltages at the end of the scan) and an LED for when the current went into overload during the scan.

Things still to change in the program

- Automatic checking if the source range is adequate for the programmed *Vds* range.



Note: (discovered later, while measuring tetracene fiber) sometimes the current jumps to its limits. This is an <u>artifact</u>; measuring the same curve with a higher scale does not reproduce the current jump. Very strange.



Result of the first pulsed measurement:



**Figure 18**: Left: Open-circuit curves in CW (red, solid) and pulsed (green, dashed) mode. Right: 300 M $\Omega$  curves in CW and pulsed mode. The green curve is the difference (100x).

# 6. References

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- [3] BDT: Matters, Synth. Met. 102, 998 (1999).
- [4] FETs: G. Horowitz, Adv. Mater. 10, 365 (1998).