



# Electrical Measurements of Organic Semiconductors

P. Stallinga

Gdańsk, January 2001

Introducing Faro

Organic Semiconductors

Electrical Measurements

DLTS

Interface states

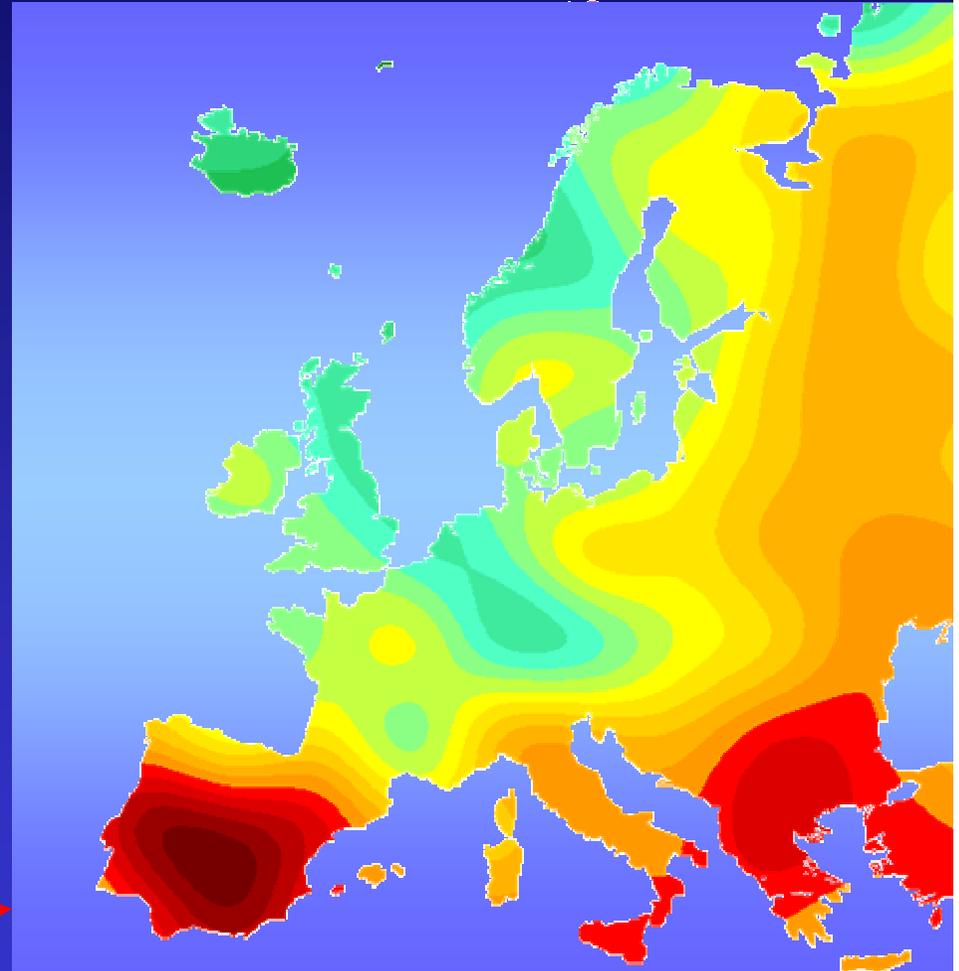
Field Effect Transistors

## Introducing Faro

# Geography



Universidade do Algarve  
Faro, Portugal

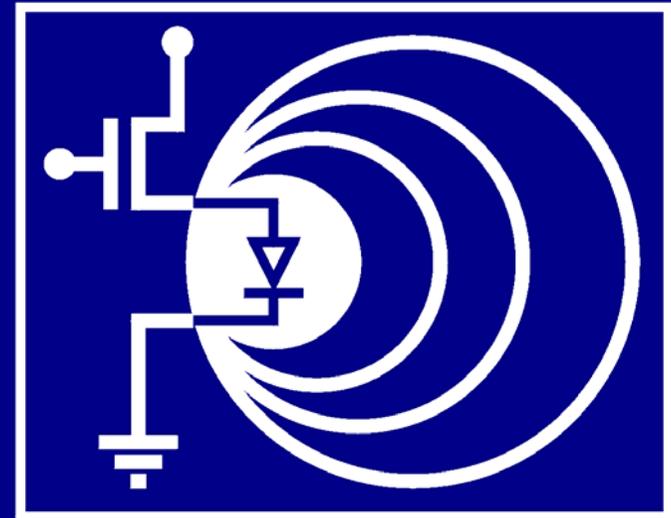


# OptoEl



<http://www.ualg.pt/fct/adeec/optoel>

**OPTO-ELECTRONICS**



**UNIVERSIDADE DO ALGARVE**

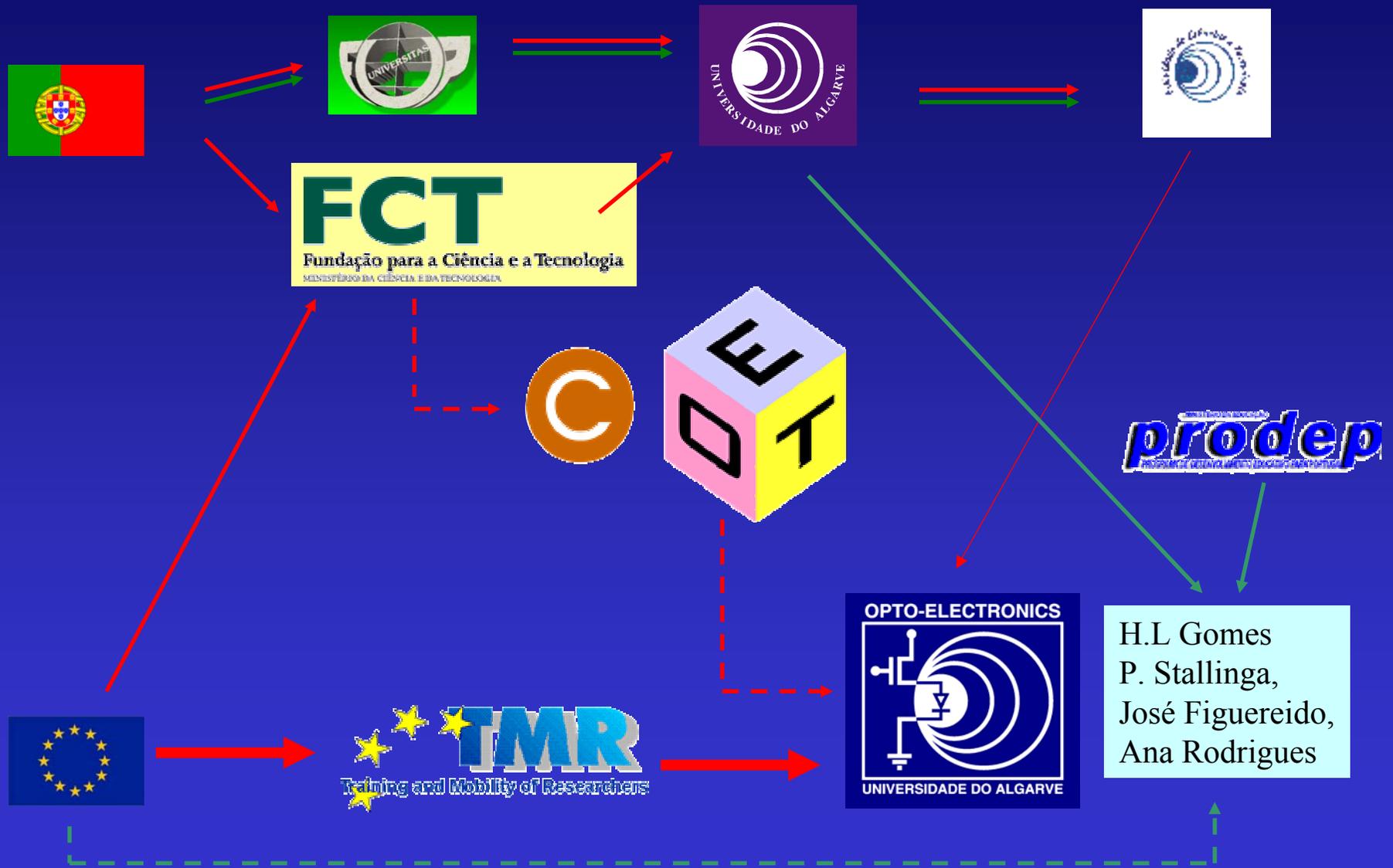
# CEOT

Centro de Electrónica, Opto-electrónica e Telecomunicações



Center for Electronics, Opto-electronics and Telecommunications

# Funding



## Projects in which OptoEl is involved:

- SELOA (European TMR project): organic electronics
- BioFET: measuring living cells with organic based FETs
- TNT: designing sensors for detecting landmines
- MONA-LISA (European RTD project): single-molecule organic FETs
- bilateral project with Bologna: electronics based on BDT

Madrid



STM, AFM

Uni Wuppertal



Device structures  
(nanotechnology)

Uni Wuerzburg



Device structures  
(stamping)

CNR, Bologna



Material deposition  
AFM, EL, PL

Optoel, Faro



Device structures  
Electrical measurements

Philips Eindhoven



Device Characterization

**MONA-LISA (Molecular  
Nanostructures made by  
Lithography and their  
Scaling Aspects)**

Study of organic  
materials in nano-scale  
devices.

Ultimately: single  
molecule electronics

Why? Organics have low  
mobility due to disorder.  
Single molecule has high  
order, hence high  $\mu$ .

## Organic Semiconductors

- They are **cheap** to make
  - No high purity required (no clean rooms, etc)
  - No extreme conditions required ( $T$ ,  $p$ )
- **Taylor-made**: Infinite number of possibilities  
bandgap engineering
- Optical efficiency high in **complete color range**
- **Flexible**. Imagine the roll-up screen you are looking at now. It could be the display of the future.

## Disadvantages:

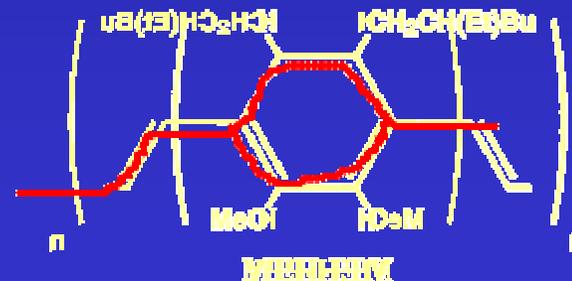
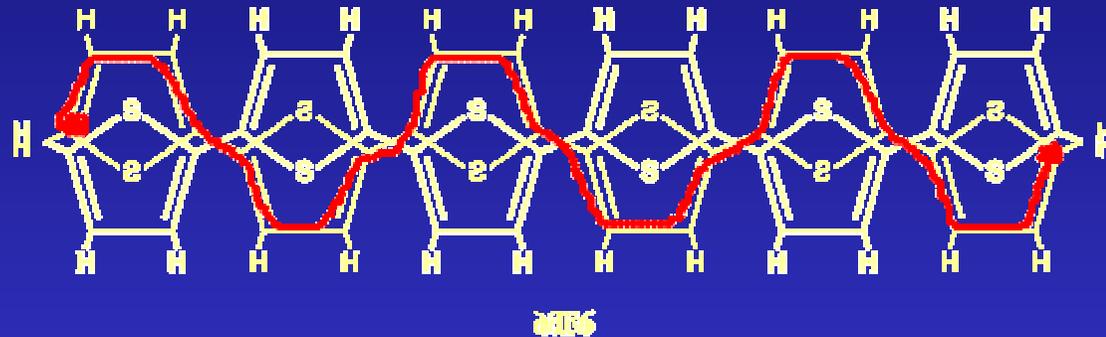
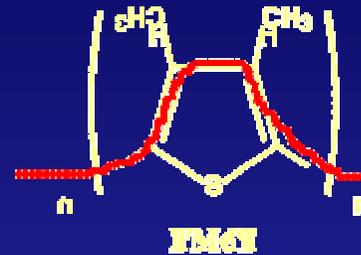
- Most unstable in air (so far!)
- Slow (low  $\mu$ )! Forget application of fast electronics.

## Applications:

LEDs, displays (background ill.), solar cells, tagging ...

# Examples

MONA-LISA



Conjugated polymers have paths with alternating single and double bonds

# “Plastics are conductors ?!”

- Every semiconducting polymer has a “backbone” of under-coordinated carbon atoms



- 4<sup>th</sup> electron is in weak  $p_z$ - $p_z$  bonds. Loosely bound  $\rightarrow$  metal
- Jahn-Teller deformation of backbone: creation of alternating single and double bonds



- This causes opening of a band gap  
 $\rightarrow$  semiconductor
- band gap  $\pm 2.5$  eV
- wide band gap  $\frac{1}{2}$  con

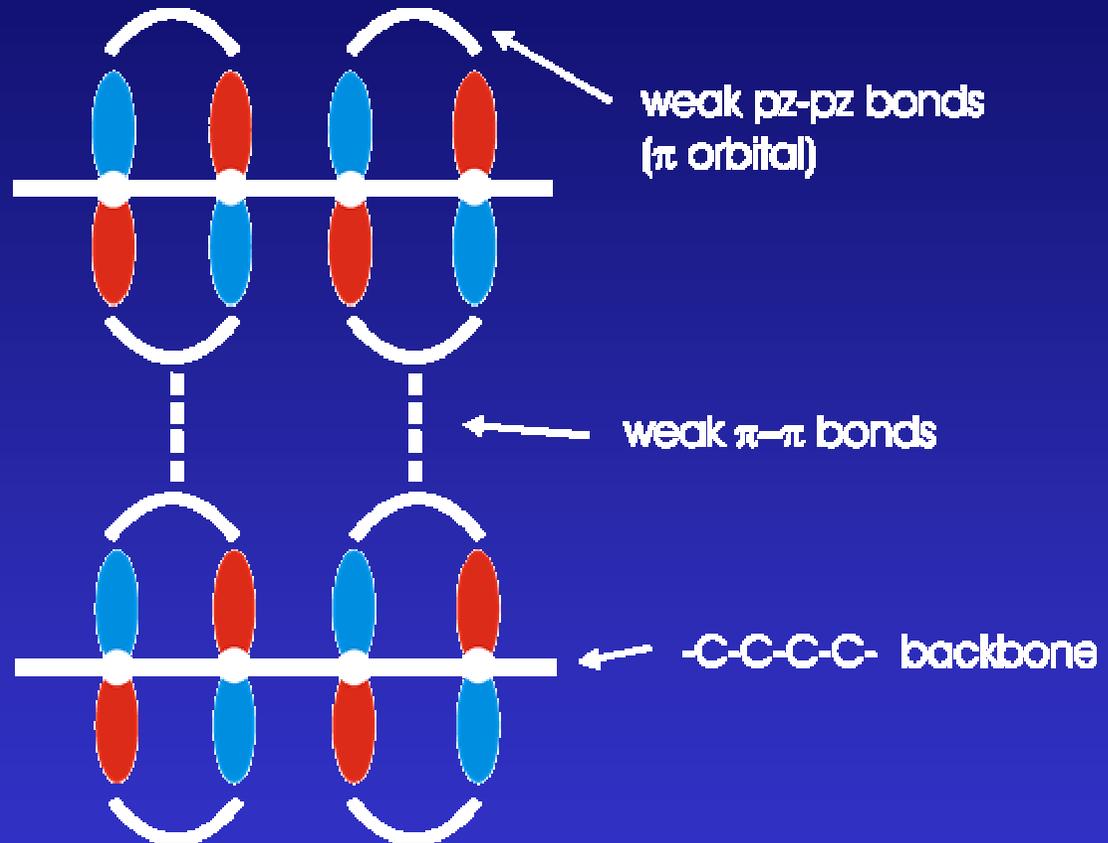
Material	Band gap
SiO <sub>2</sub>	>10 eV
C (diamond)	5.47 eV
GaN	3.36 eV
Polymers	2.5 eV
GaAs	1.42 eV
Si	1.12 eV
Ge	0.66 eV

# 3D conduction

Conduction along backbone is easy

Conduction from chain to chain is Difficult. Hopping Conduction

Two activation energies for conduction



The **stacking of the molecules** is very important!

Best 3D conductivity achieved by vacuum deposition

## Electrical measurements

Note: a survey of electrical measurement techniques is available at our internet pages:  
<http://www.ualg.pt/fct/adeec/optoel/theory>

## Devices:

- **bulk**
- **Schottky barrier**
- **pn-junction**
- **FETs**

## Techniques:

- **current-voltage (DC)**
- **capacitance, conductance (AC)**
- **admittance spectroscopy**
- **Transient techniques:**
  - **capacitance transients**
  - **DLTS**
  - **TSC**

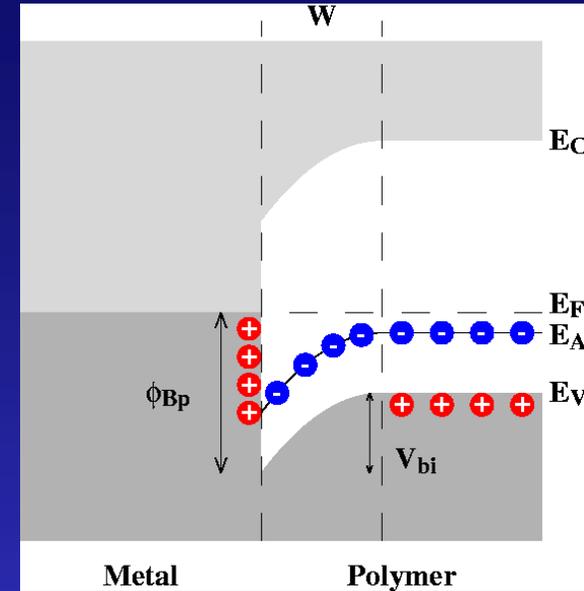
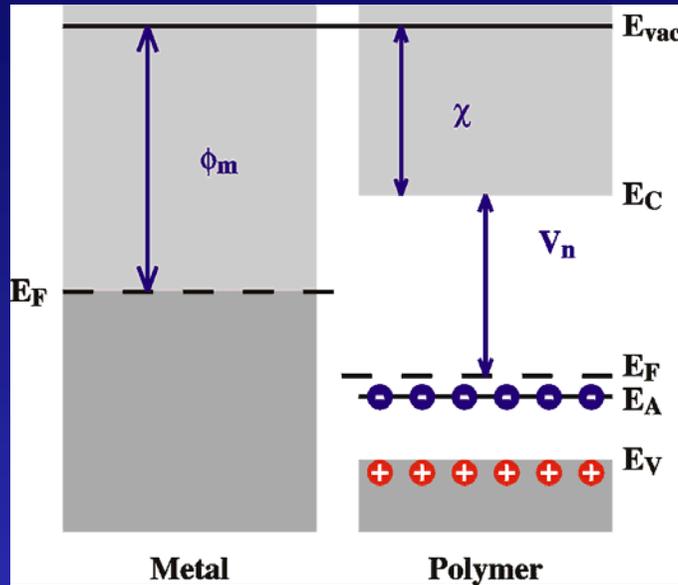
## Information:

- **conduction model**
- **carrier type**
- **carrier mobility**
- **shallow levels**
  - **position**
  - **density**
- **deep levels**
  - **position**
  - **density**
- **dielectric constant**
- **barrier height**



Each of these techniques are standard characterization techniques for classical semiconductors (Si, GaAs, GaN, etc), but care has to be taken to apply them to organic materials!

# Schottky barrier



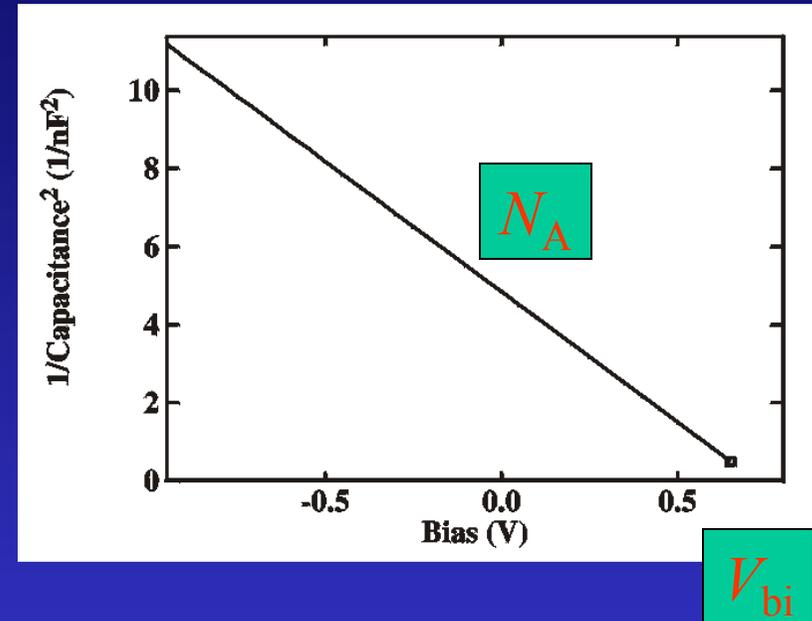
- metal and  $\frac{1}{2}$ con have different **Fermi level**
- electrons will flow from metal to  $\frac{1}{2}$ con
- build-up of **(space) charge Q** (uncompensated ionized acceptors)
- causes electric field and voltage drop (band bending,  $V_{bi}$ )
- over a range **W** (depletion width)

$$V_{bi} = \chi + V_n - \phi_m$$

# Schottky barrier: Capacitance

$$C = A \sqrt{q \epsilon N_A / 2(V_{bi} - V)}$$

$$C^{-2} = 2(V_{bi} - V) / A^2 q \epsilon N_A$$



- slope reveals  $N_A$
- extrapolation reveals  $V_{bi}$

# Schottky barrier: Admittance spectroscopy

## Spectra

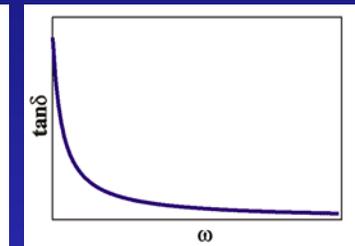
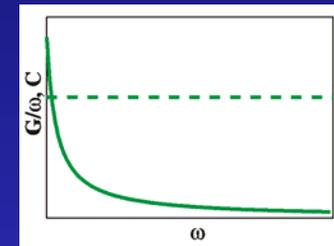
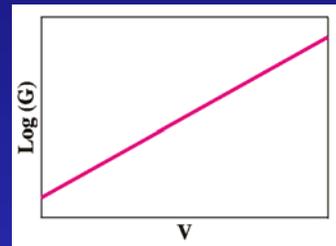
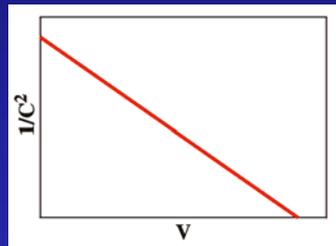
$C^{-2}-V$

$\text{Log}(G)-V$

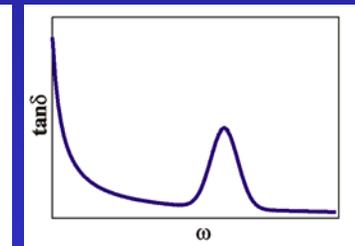
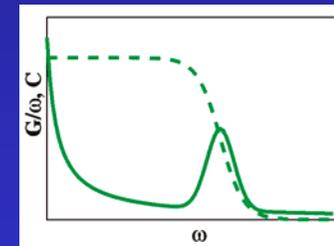
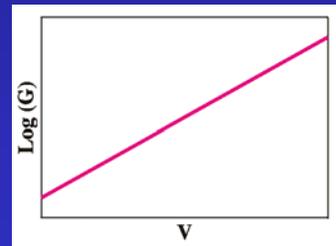
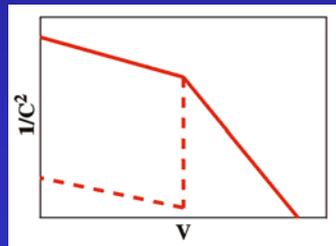
$C, G/\omega-\omega$

$\tan\delta-\omega$

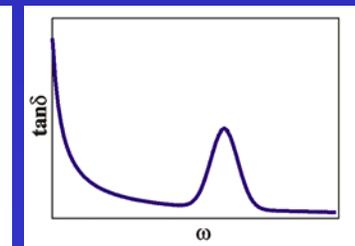
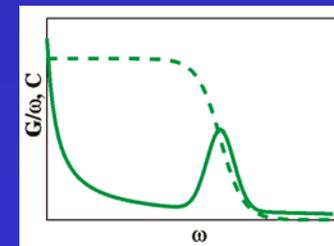
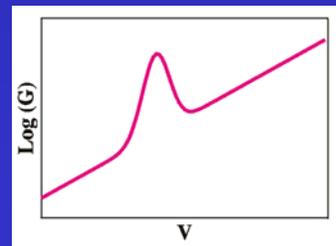
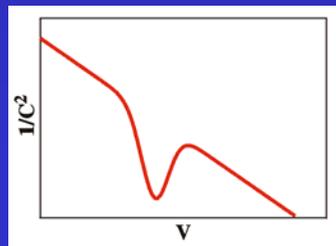
shallow  
homogeneous



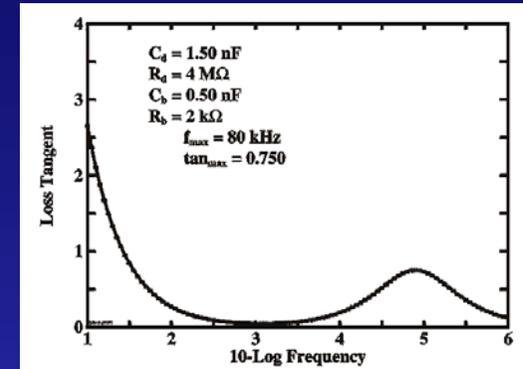
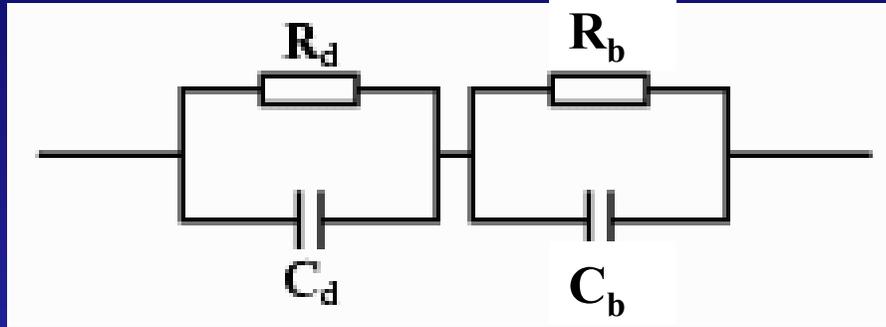
+ deep  
homogeneous



+ interface



# Schottky barrier: Admittance spectroscopy



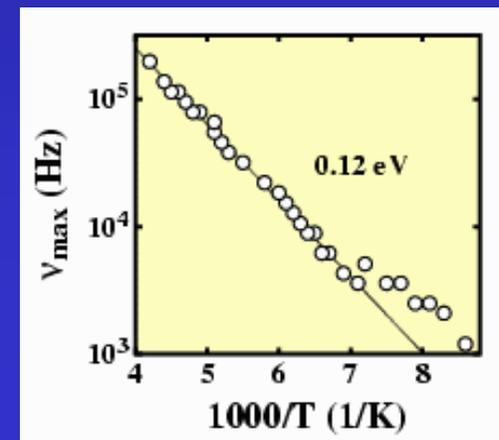
Maximum at

$$1/\omega_{\text{max}} = R_b C_b(C_b + C_d)$$

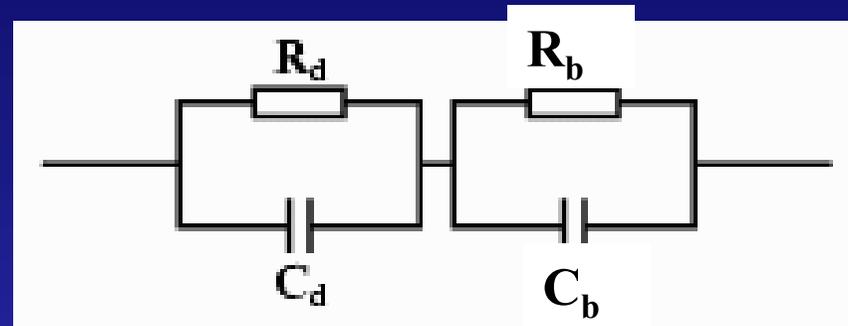
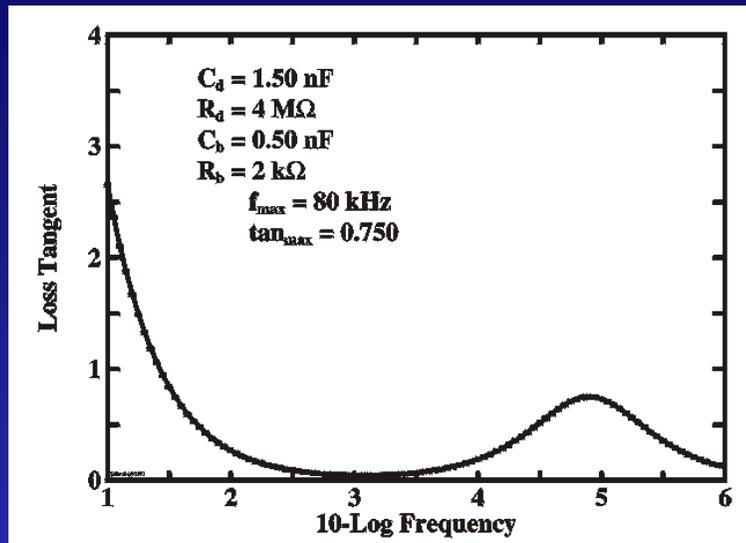
$$R_b \sim \exp(-E_a/kT)$$

We can determine the **bulk activation energy** from the  $\tan\delta$  data

example



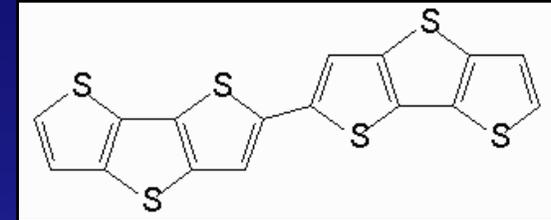
# Schottky barrier: Admittance spectroscopy



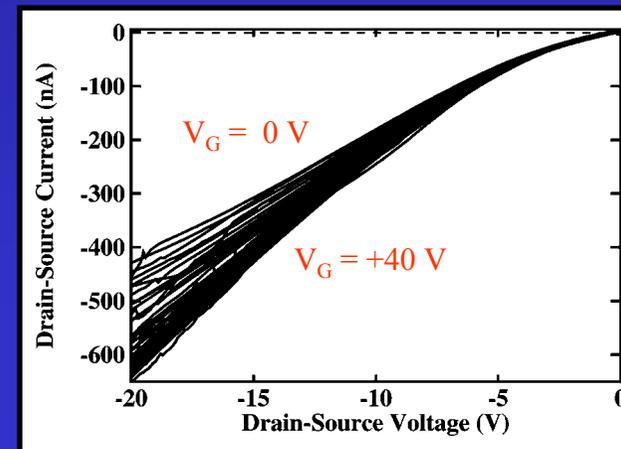
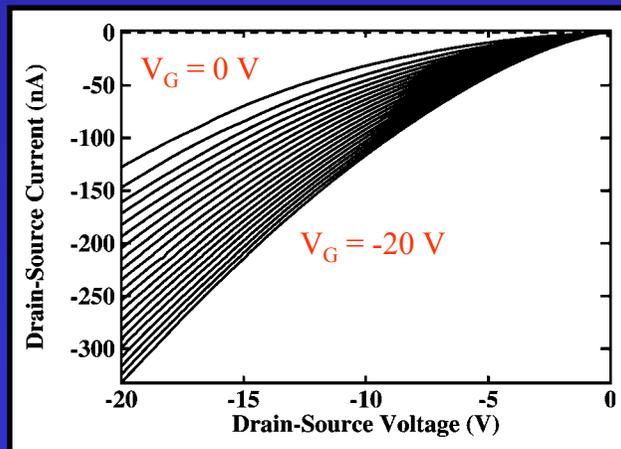
Measuring above  $\omega_{\text{max}}$  will give no information about the interface  $C_d, R_d$  !

Most commercial equipment works at 1 MHz. Most organic materials cut around 10 kHz.

## BDT, the “light emitting FET”



For a light-emitting FET we need to be able to inject both electrons and holes; the device has to be **ambipolar**. BDT has shown to have this behavior.



DLTS

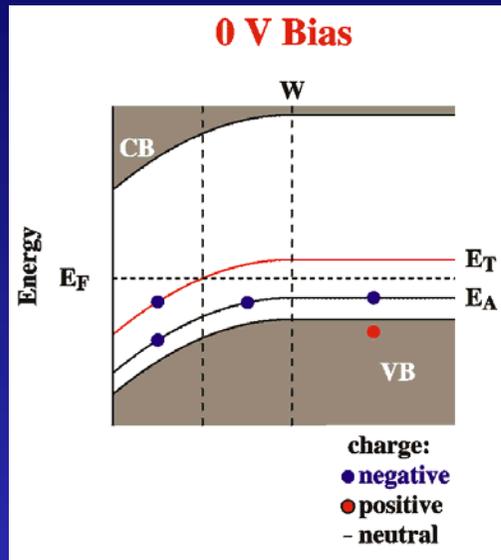
DLTS: “Change the bias and let’s look how the capacitance evolves over time”

- Capacitance depends on **bias** (remember, something like  $C \sim 1/V^{1/2}$ )
- A new **depletion width** has to be reached. At the end:

$$C = \epsilon A/W$$

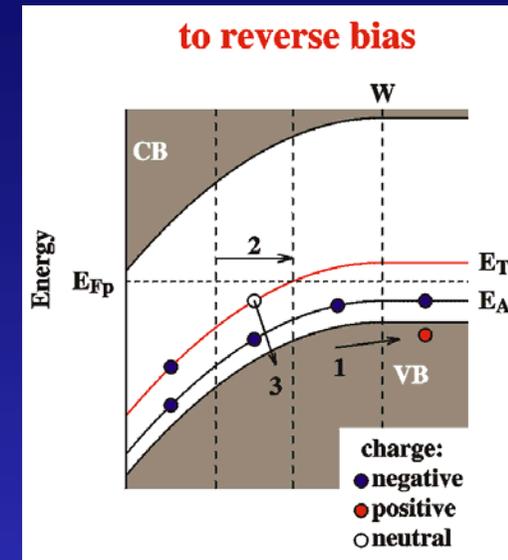
- For **shallow levels**: response is immediate. Limited only by speed at which free carriers can move out ( $\mu_p$ ).
- For **deep levels**: the charges have to come off there first.

# Deep-level transient-spectroscopy

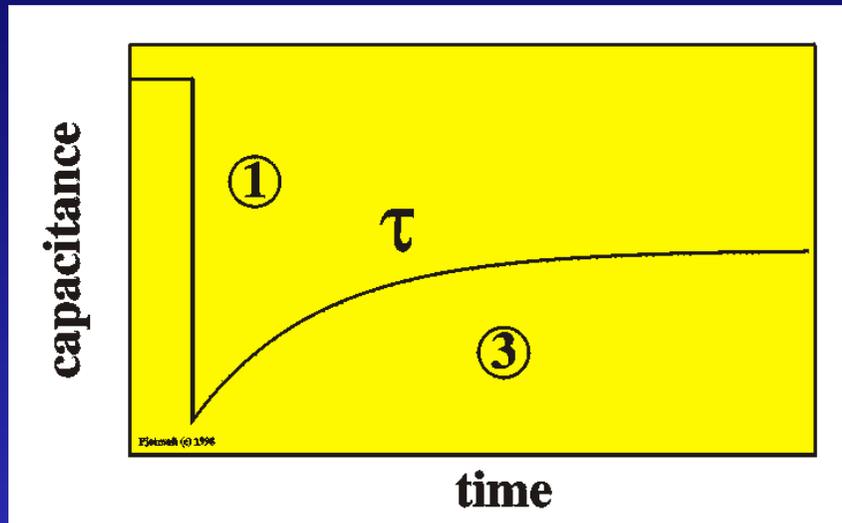


Change

bias



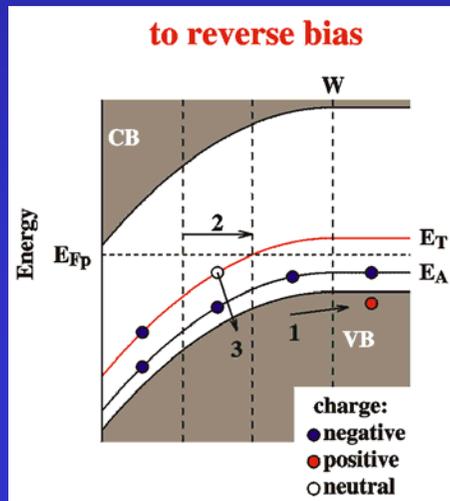
1. **Free holes** move out of interface region. Immediate increase of  $W$  ( $C \downarrow$ )
2. This creates a region where the deep levels are **off-equilibrium**
3. Charges are **slowly emitted** from the deep levels there
  - higher space-charge density
  - less depletion width is needed to reach condition  $\int f f_0^W \rho(x) d^2x = V_{bb}$
4.  **$W$  slowly shrinks** again a little. Increased capacitance



Summary:

- 1) Free carriers move out
- 2) Region off-equilibrium
- 3) Deep levels empty

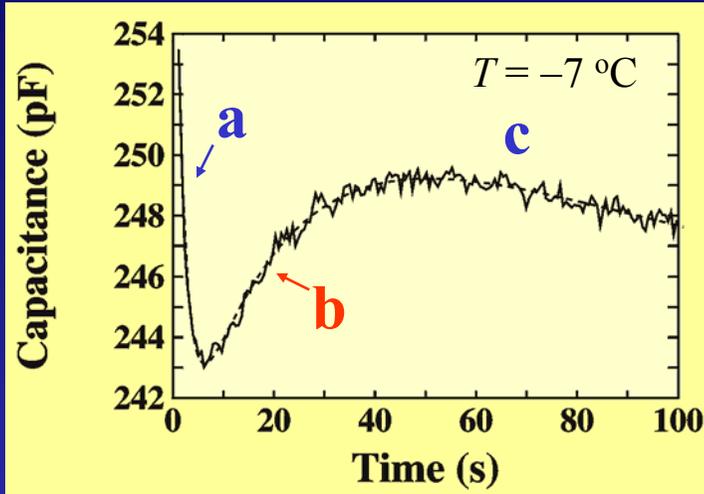
$$1/\tau = e_p = \gamma T^2 \sigma \exp(-E_a/kT)$$



Monitoring  $\tau$  over temperature  
will give us  $E_a$

Very sensitive and very accurate!

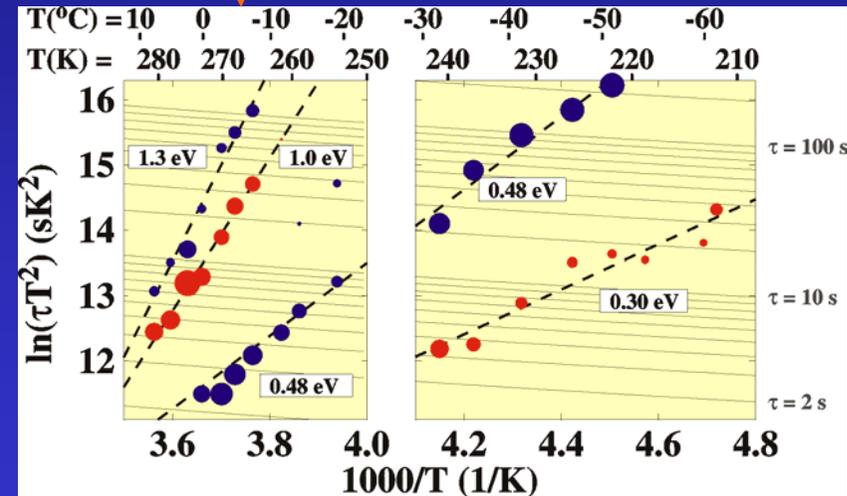
# Deep-level transient-spectroscopy



## MEH-PPV on Silicon

- 2 minority traps: a, c
- 1 majority trap: b

$$1/\tau = e_p = \gamma T^2 \sigma \exp(-E_a/kT)$$



First successful “DLTS” experiment in an organic semiconductor

P. Stallinga *et al.* J. Appl. Phys. **89**, 1713 (2001)

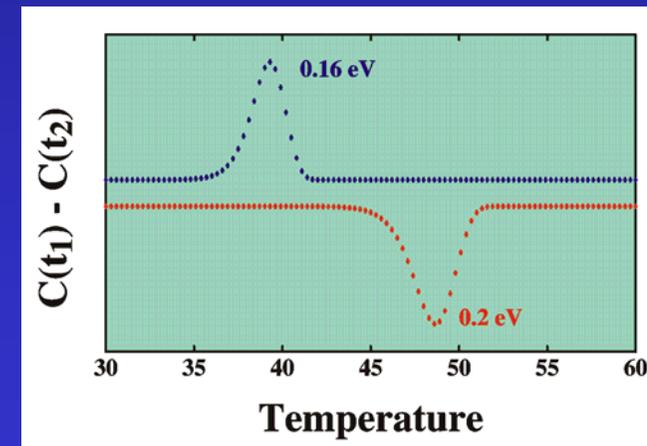
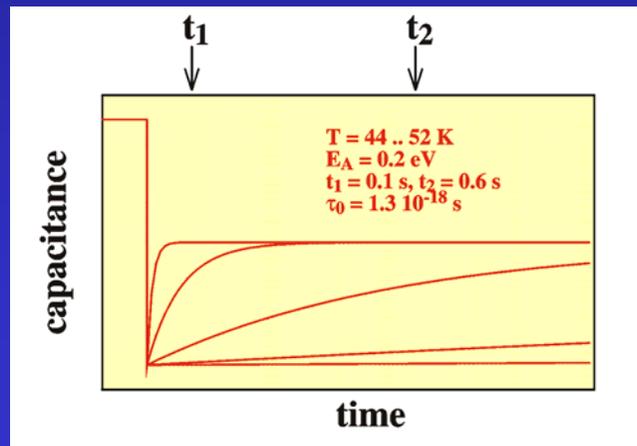
## Standard DLTS procedure:

- Of the entire set of data, take only two points, at  $t_1$  and  $t_2$
- The DLTS signal is then  $S = C(t_1) - C(t_2)$

For low-T:  $\tau = \infty$ ,  $C(t_1) = C(t_2)$ :  $S = 0$

For high-T:  $\tau = 0$ ,  $C(t_1) = C(t_2)$ :  $S = 0$

Maximum when:  $\tau_0 T^{-2} \exp(E_a/kT) = (t_2 - t_1) / [\ln(t_1/t_2)]$



... not followed (don't throw away data)

## DLTS is

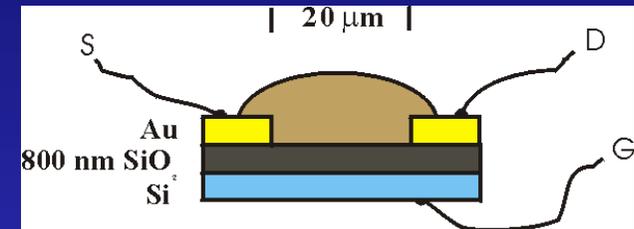
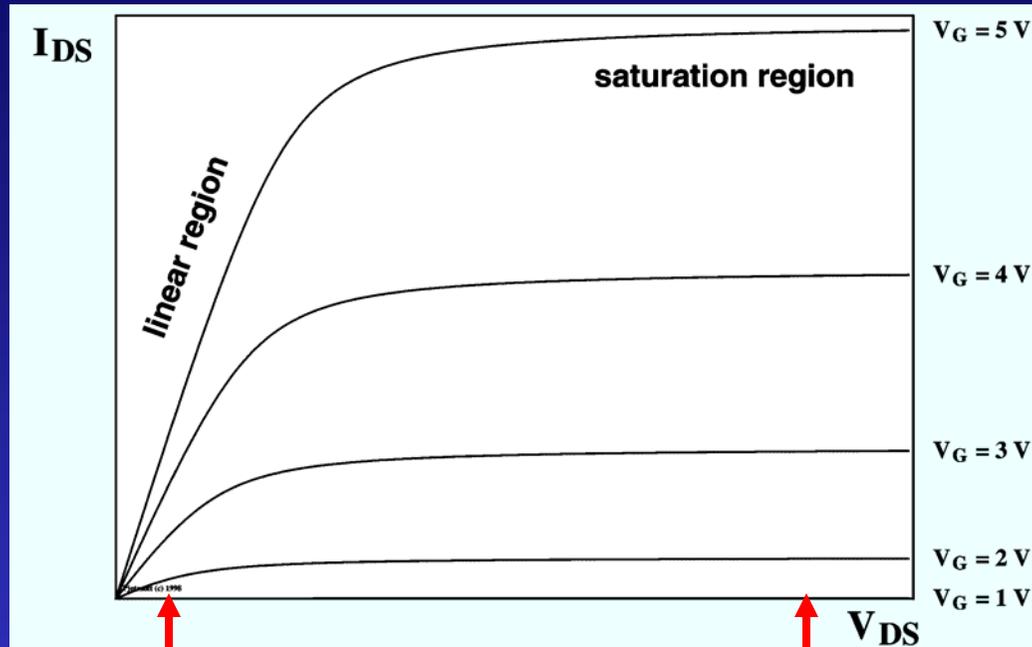
- very easy to perform. “Walk-away” measurements
- sensitive
- reliable data with accurate energy determination
- “Fingerprint” spectra of defects
- able to determine density of defects.  $\Delta C/C = N_T/2(N_A - N_D)$

## Problems for organic semiconductors

- cut-off frequency (10 kHz)
- deep levels – slow transients ( $T=300$  K,  $\tau=1$  min)
- condition  $N_T \ll N_A$  not true in most cases (transients non exponential)

## Field Effect Transistors

# Field Effect Transistors



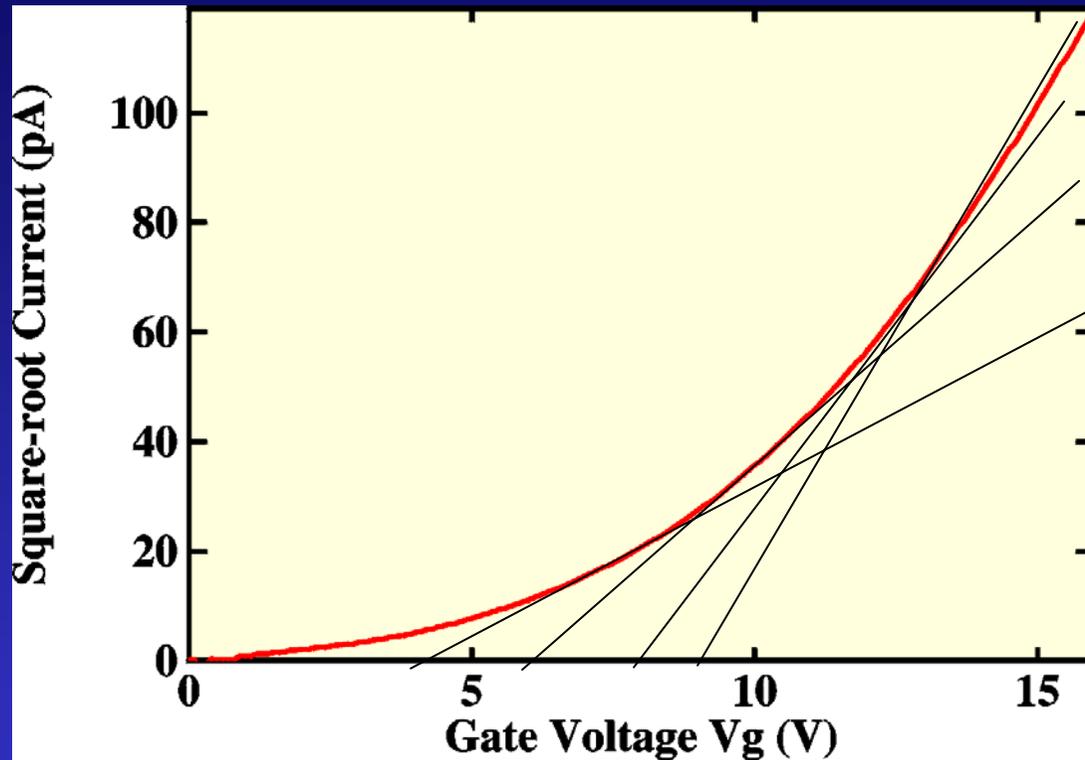
FET in linear region:

$$I_{DS} = \frac{Z}{L} \mu_p C_i (V_G - V_T) V_D$$

FET in saturation region:

$$I_{DS} = \frac{mZ}{L} \mu_p C_i (V_G - V_T)^2$$

# FET: sexi-thiophene ( $\alpha$ T6)

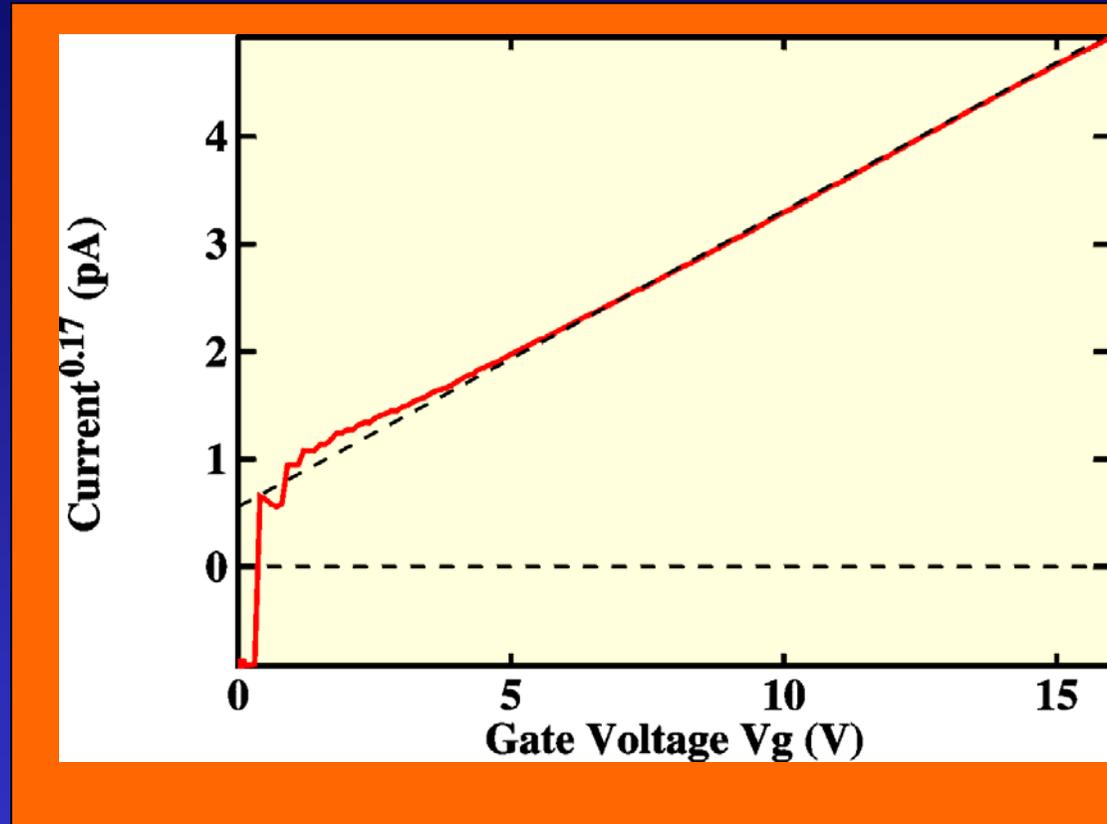


$\alpha$ T6

Mobility changes as function of gate voltage

# $\alpha$ T6 transfer curve

SAT:

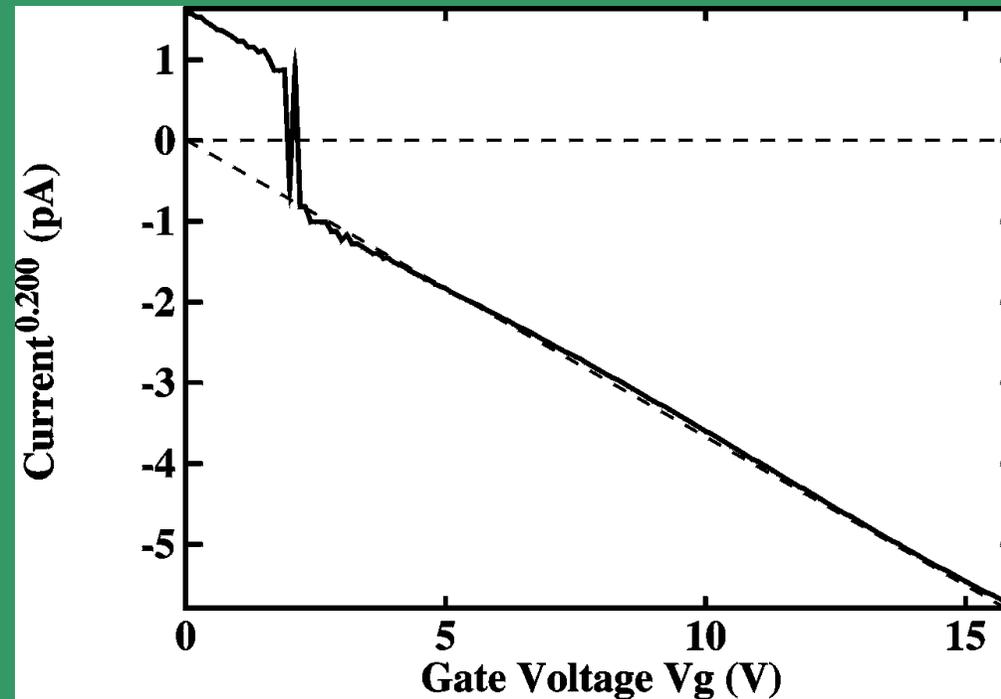


Perfect straight line when plotted as 6<sup>th</sup>-root of current vs. Vg

$$I_{ds} \sim (V_g - V_t)^6$$

# $\alpha$ T6 transfer curve

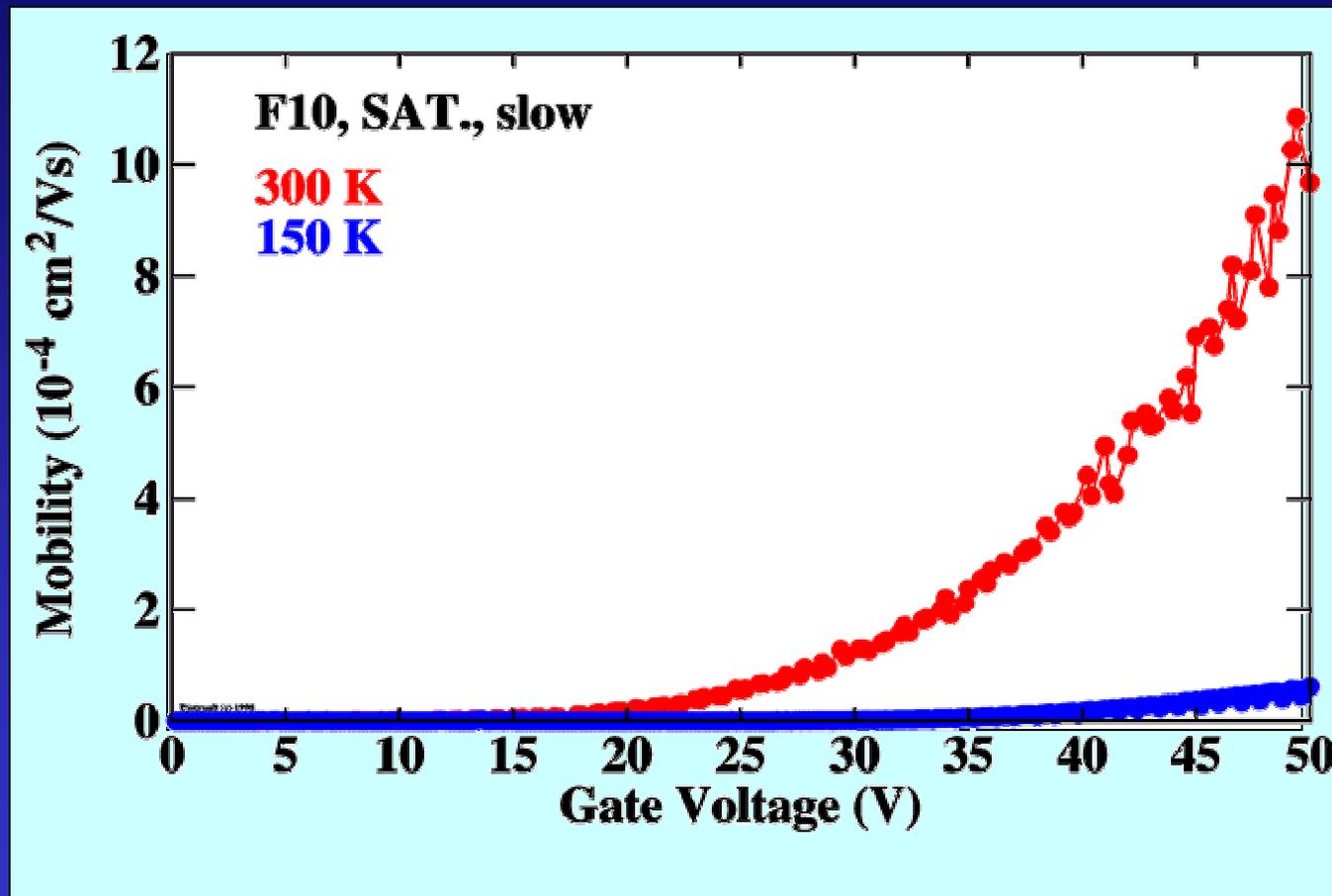
LIN:



Plotted as 5<sup>th</sup>-root. Consistent with saturation-region data

$$I_{ds} \sim V_{ds} (V_g - V_t)^5$$

# Mobility



Gate-voltage-dependent mobility up to  $1 \times 10^{-3} \text{ cm}^2/\text{Vs}$

# Variable Range Hopping



PHYSICAL REVIEW B

VOLUME 57, NUMBER 20

15 MAY 1998-II

## Theory of the field-effect mobility in amorphous organic transistors

M. C. J. M. Vissenberg\*

*Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands  
and Instituut-Lorentz, University of Leiden, 2300 RA Leiden, The Netherlands*

M. Matters†

*Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands  
(Received 13 January 1998)*

The field-effect mobility in an organic thin-film transistor is studied theoretically. From a percolation model of hopping between localized states and a transistor model an analytic expression for the field-effect mobility is obtained. The theory is applied to describe the experiments by Brown *et al.* [Synth. Met. **88**, 37 (1997)] on solution-processed amorphous organic transistors, made from a polymer (polythiethylene vinylene) and from a small molecule (pentacene). Good agreement is obtained, with respect to both the gate voltage and the temperature dependence of the mobility. [S0163-1829(98)01320-4]

Gate-voltage dependent  
mobility predicted and  
measured before

Variable-range hopping

JOURNAL OF APPLIED PHYSICS

VOLUME 85, NUMBER 6

15 MARCH 1999

## Gate voltage dependent mobility of oligothiophene field-effect transistors

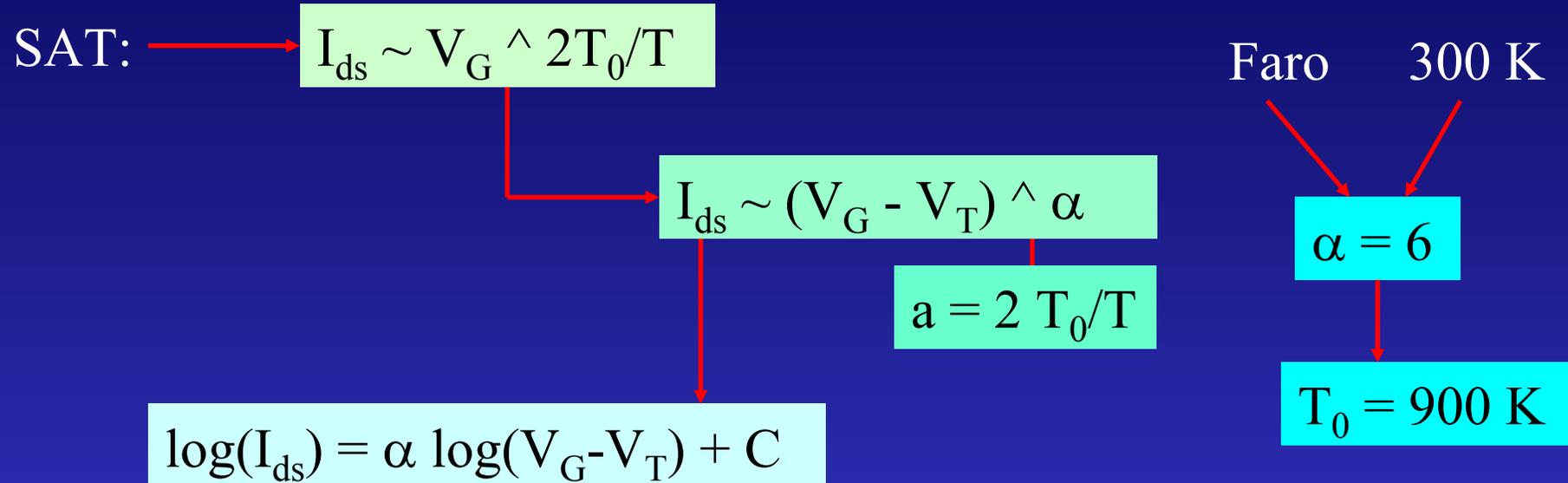
Gilles Horowitz,<sup>(\*)</sup> Riadh Hajjaoui, Denis Fichou, and Ahmed El Kassmi

*Laboratoire des Matériaux Moléculaires, CNRS, 2 rue Henry-Dunant, 94320 Thiais, France*

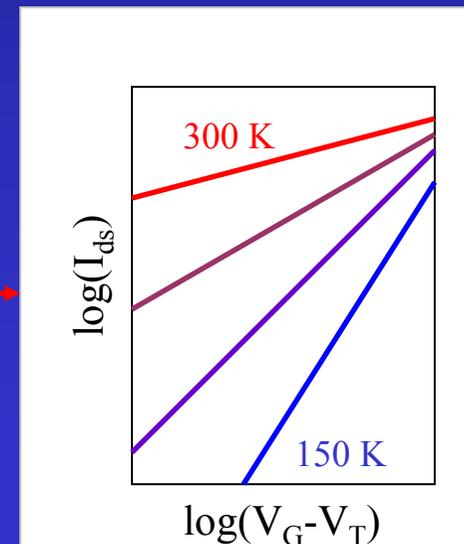
(Received 5 May 1998; accepted for publication 8 December 1998)

Organic field-effect transistors, in which the active semiconductor is made of oligothiophenes of various lengths, have been fabricated and characterized. A method is developed to estimate the field-effect mobility  $\mu$  corrected for the contact series resistance. The mobility is found to increase by a factor of nearly 100 from quaterthiophene (4T) to octithiophene (8T). More importantly,  $\mu$  increases quasilinearly with gate voltage. The origin of this gate bias dependence is discussed. One explanation could be the presence of traps that limit charge transport. Alternatively, the gate-voltage dependence is tentatively attributed to a dependence of the mobility with the concentration of carriers in the accumulation layer. © 1999 American Institute of Physics.  
[S0021-8979(99)02506-2]

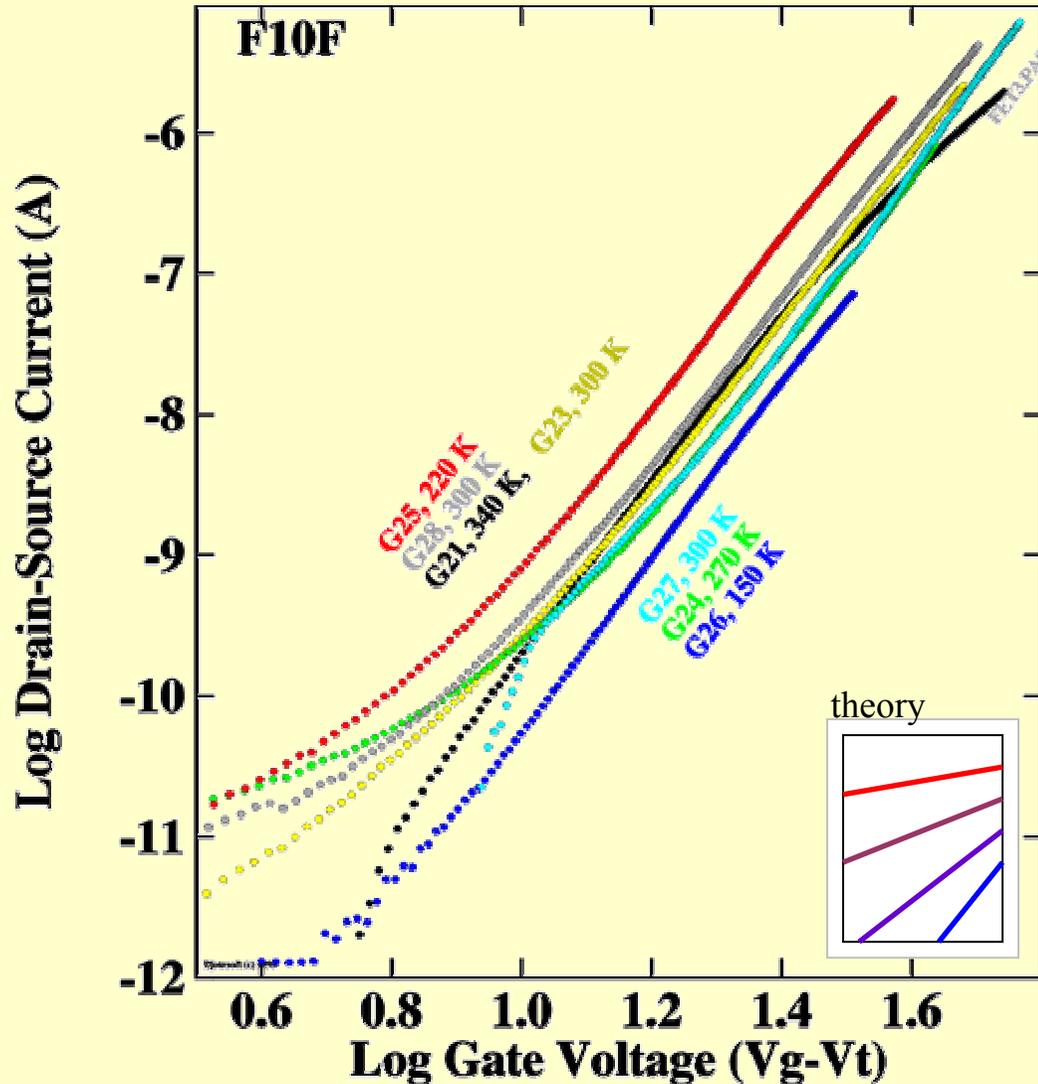
# Variable Range Hopping



Prediction



# VRH vs. experiment $\alpha T6$



Each line represents a transfer curve at a different temperature

VRH

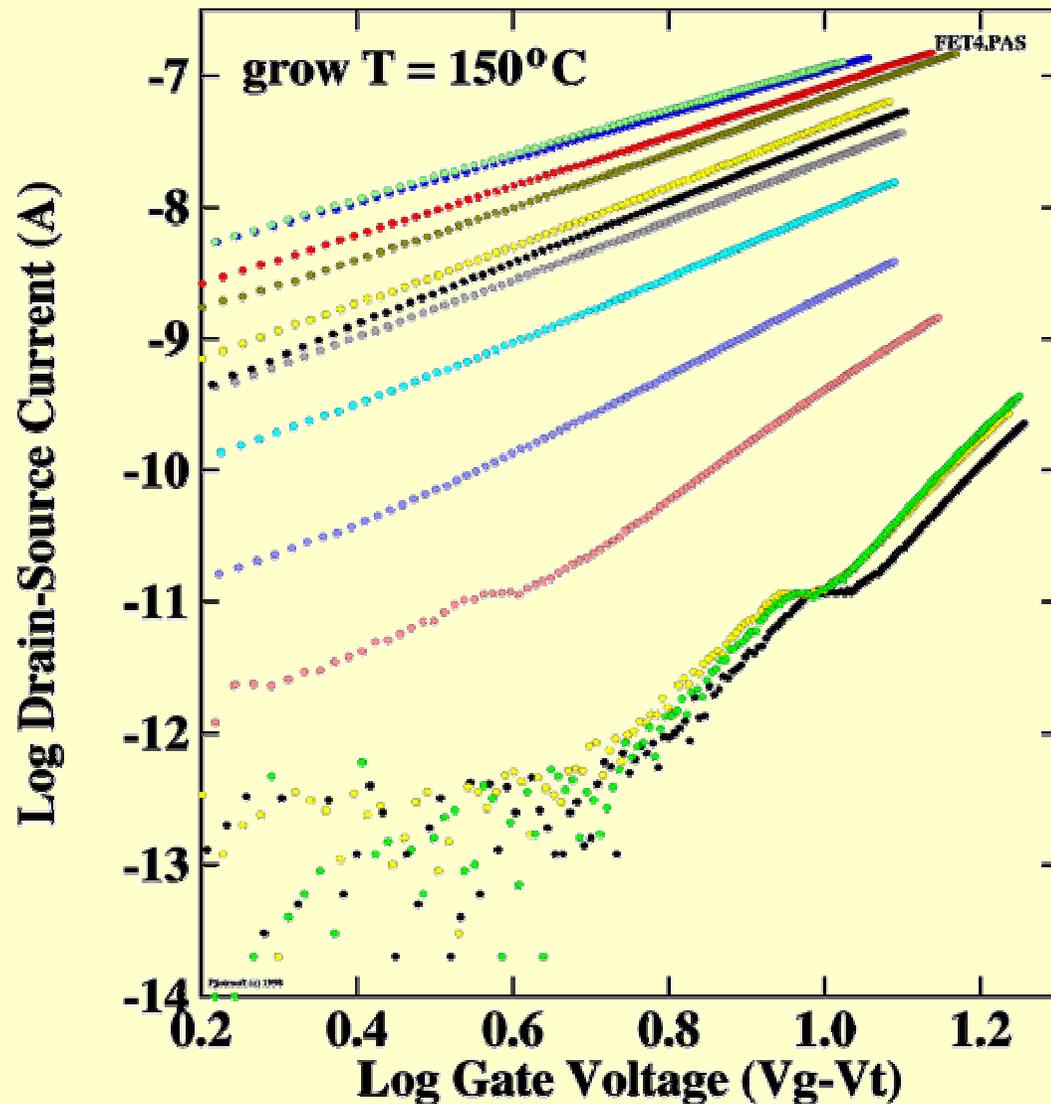
$$\alpha = 2 T_0/T$$

Slopes 'a'  
independent of  
temperature!

Failure of VRH  
theory!

Tunneling  
conduction?

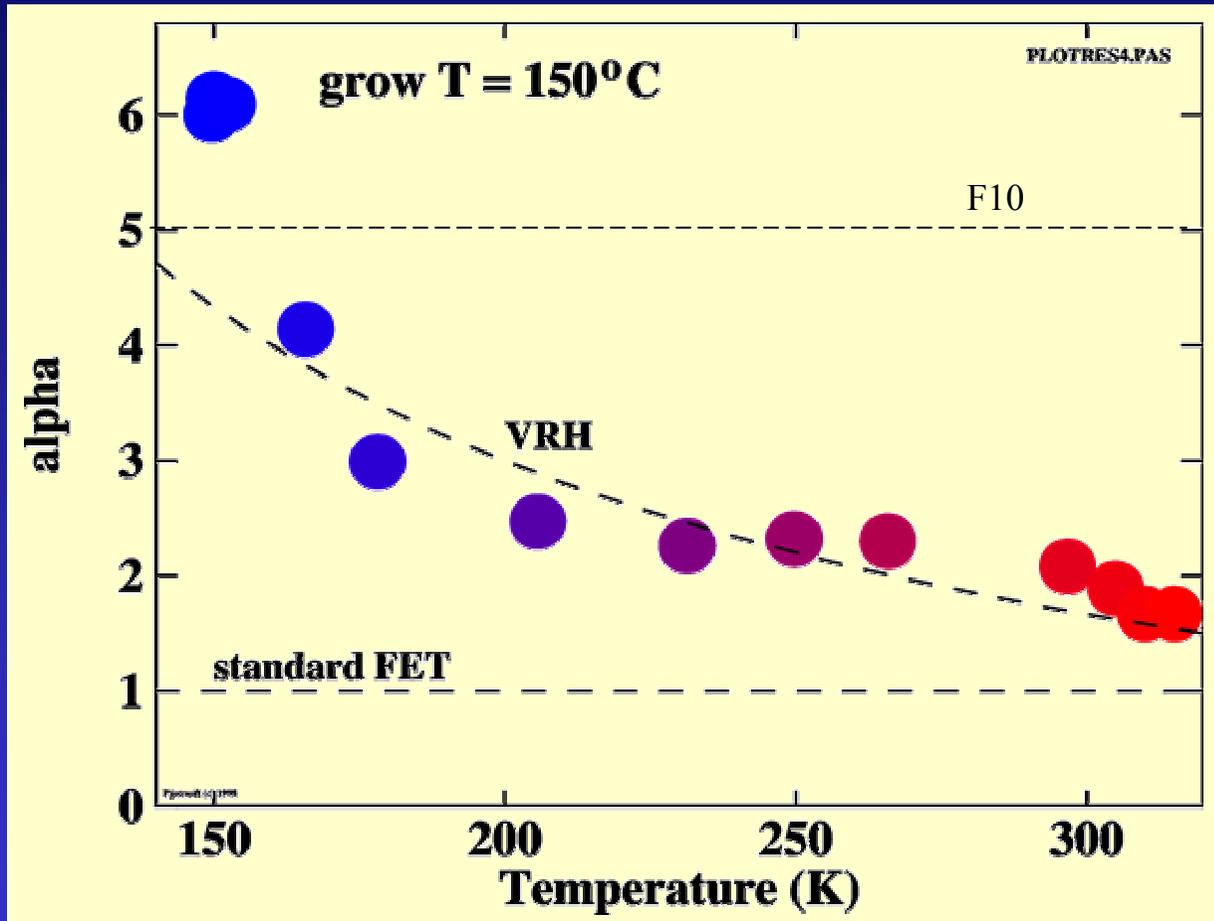
# VRH vs. experiment



In a sample with better morphology

Slopes ' $\alpha$ ' depend on temperature!

VRH works?

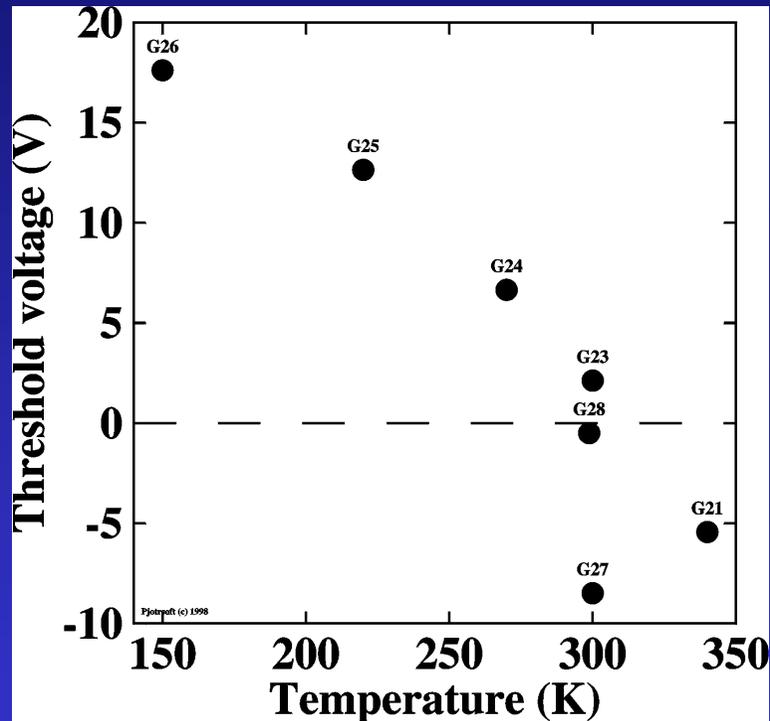


Each dot represents the value of the slope in a transfer curve at a different temperature (of previous page)

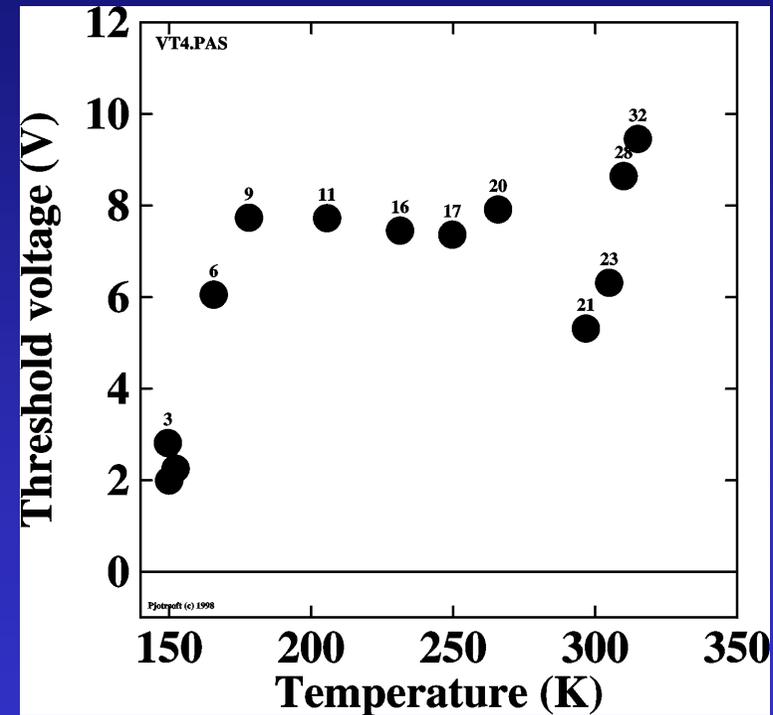
Slopes ' $\alpha$ ' not well predicted by VRH

# Threshold voltage

## Sample F10



## Sample X20



Impurity levels freeze out in F10 and not in X20

# T6 - FET mobility conclusions

Bad morphology

Failure of VRH theory

$V_T$  shows huge number of traps

Better morphology

Hints of VRH theory

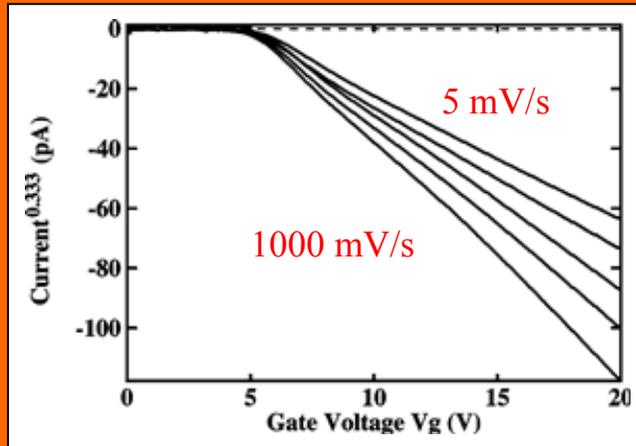
$V_T$  shows smaller number of traps

Good morphology

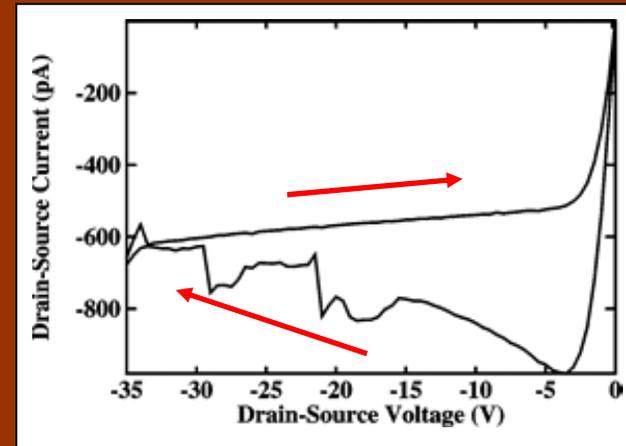
Standard FET theory

$V_T$  shows nearly no traps

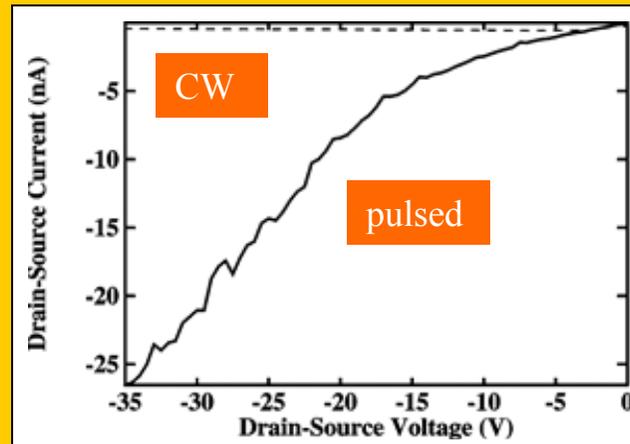
# Other FET measurements



Scanning speed

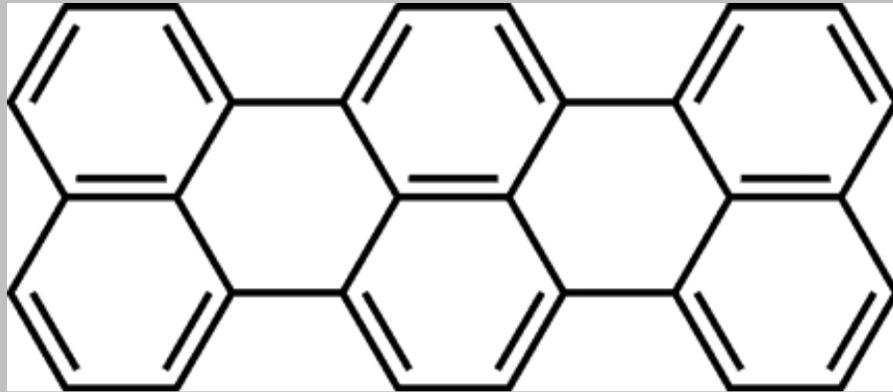


Hysteresis

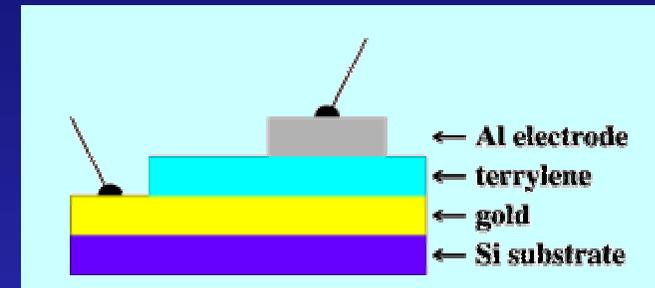


Pulsed / CW

Interface states



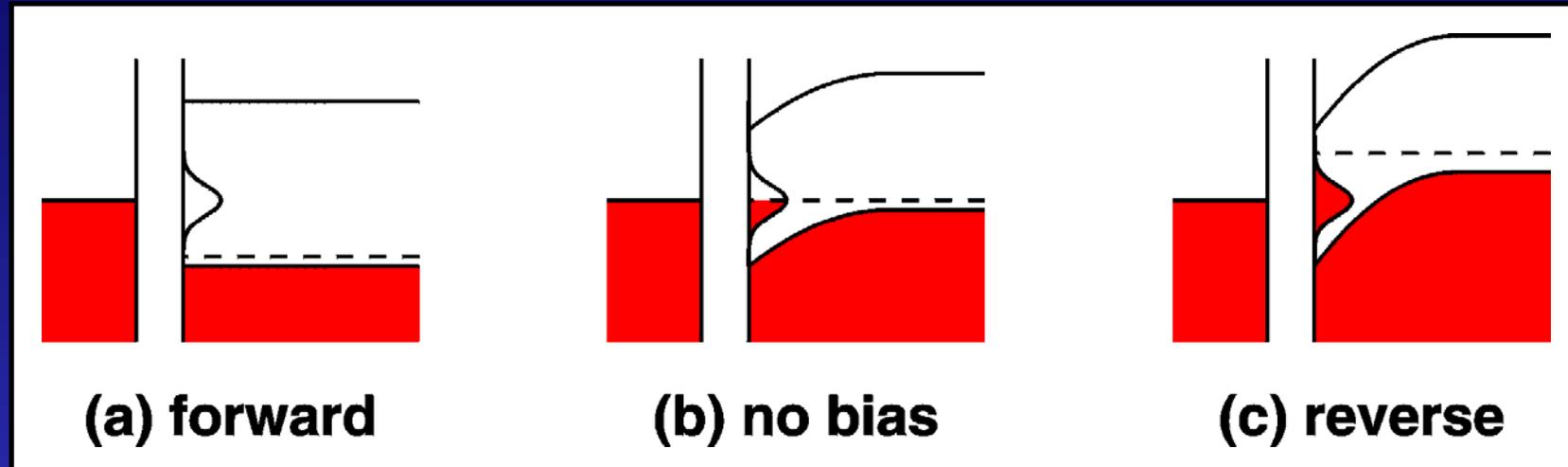
*Terrylene*



Interface states studied in Schottky barriers of  
Aluminum - Terrylene

Interface states are important because they can cause (un)wanted voltage drops at the interface and thus block/facilitate carrier injection .

# Interface states in Terrylene

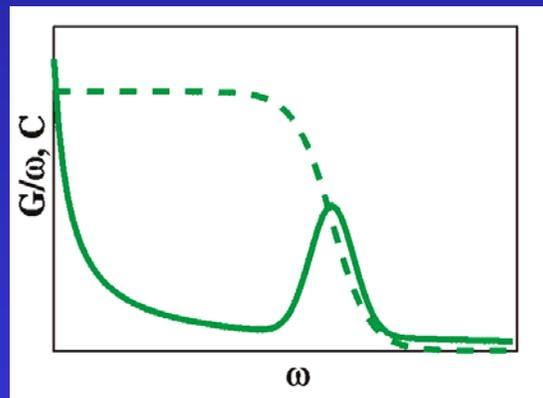
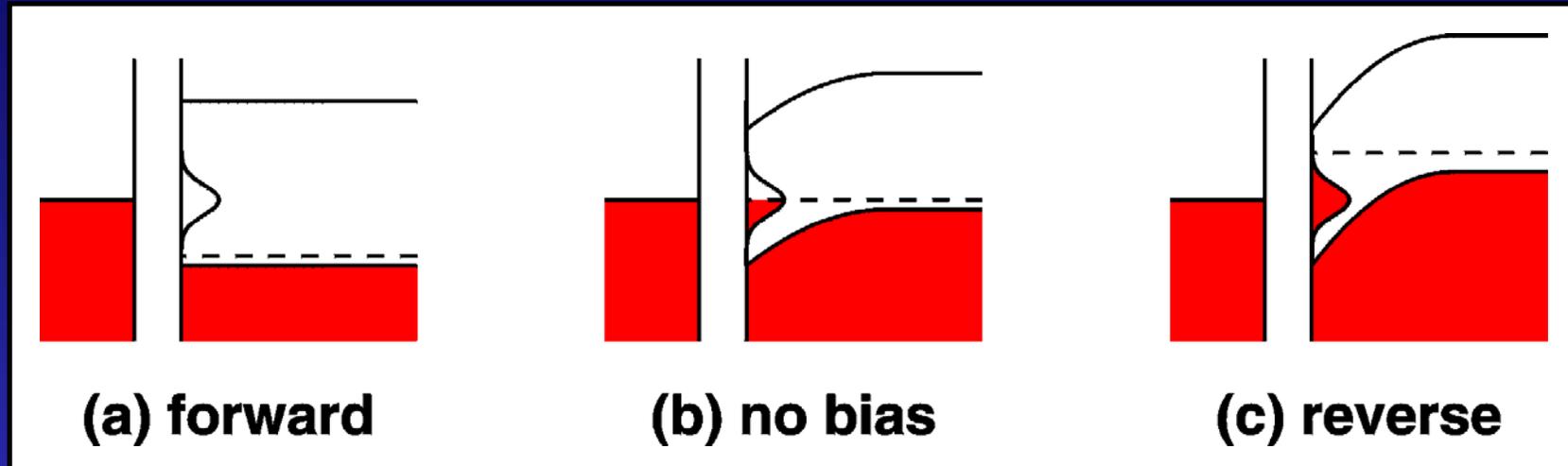


When the Fermi level is **resonant** with the interface states we see a contribution to the **capacitance** and **inductance**.

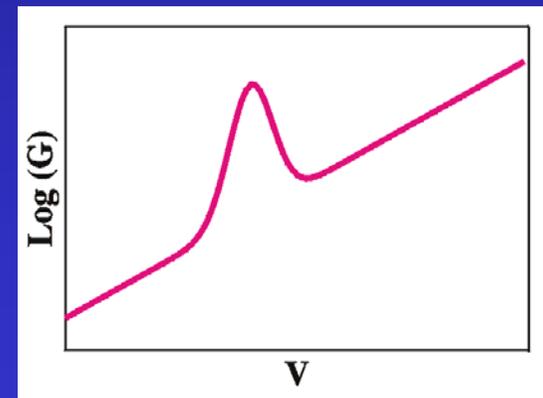
But only when the AC **frequency** is low enough

With the **bias** we select the bunch of interface states measured

# Interface states in Terrylene

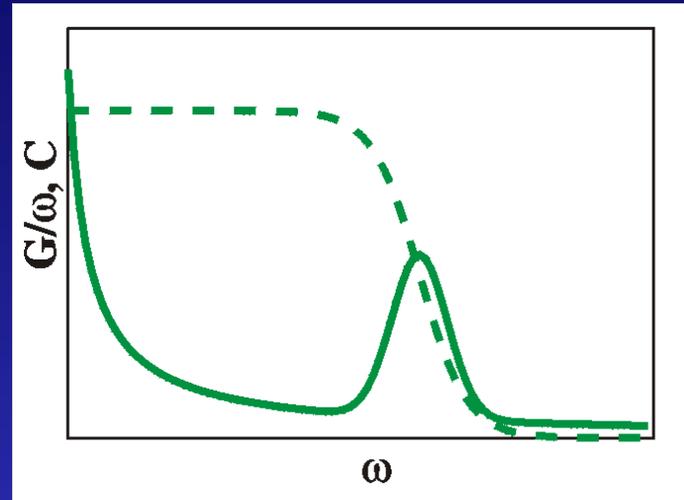


Fixed bias, scanning  $\omega$



Fixed  $\omega$ , scanning bias

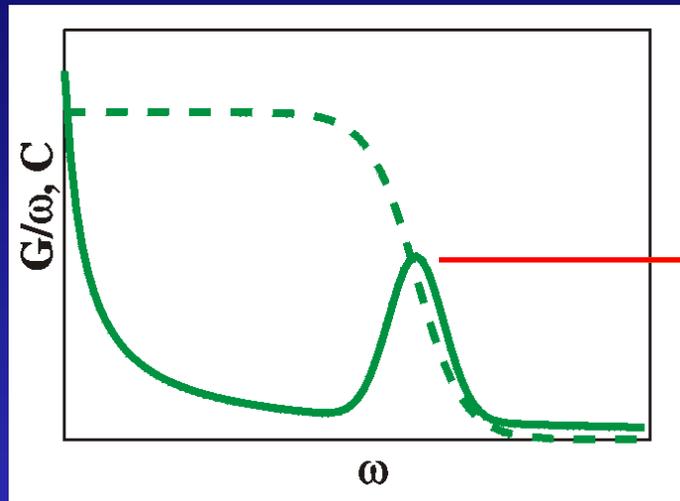
# Interface states in Terrylene



$$\omega_{\max} = 1/\tau = \exp(-E_d/kT)$$

The **depth** of the levels we can find from the **temperature** dependence.

# Interface states in Terrylene



$$G_{max} \sim V_{AC} N_{if}$$

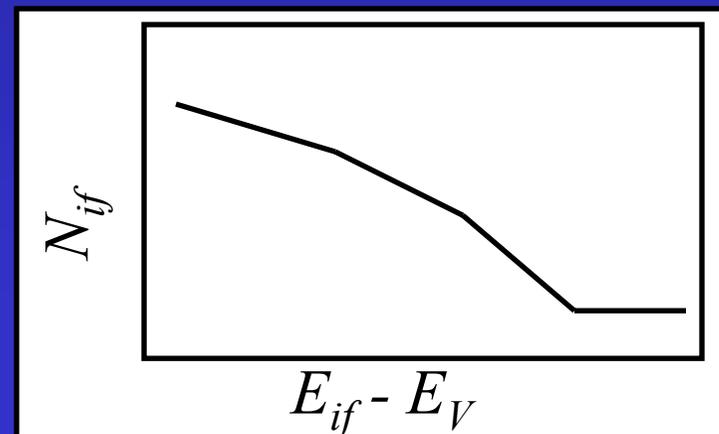
The **number of interface** states we can find from the height of the peak in conductance.

# Interface states in Terrylene

1: select the interface states with the bias

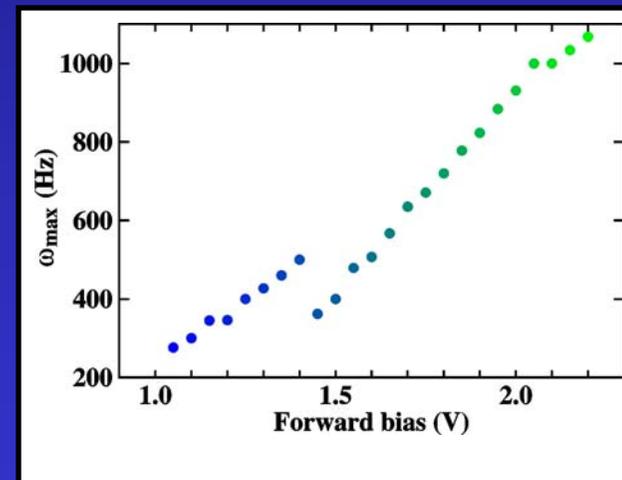
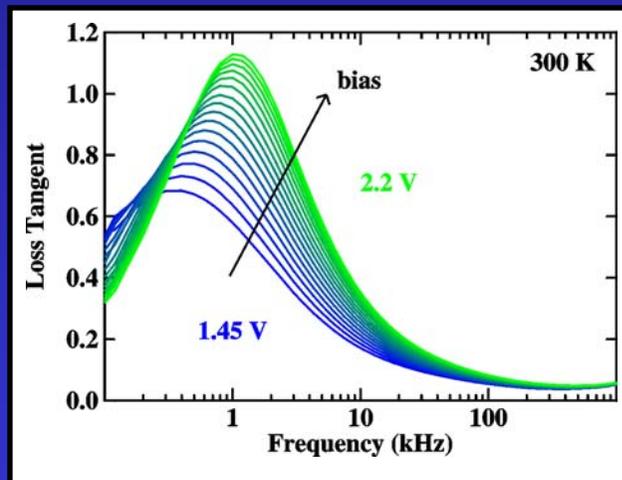
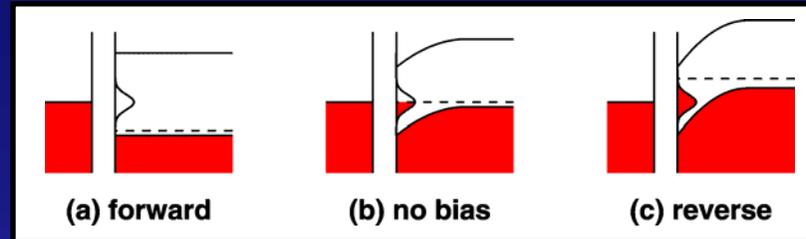
2: measure their activation energy via the temperature dependence

3: measure the density of states at  $E_A$  from the spectrum



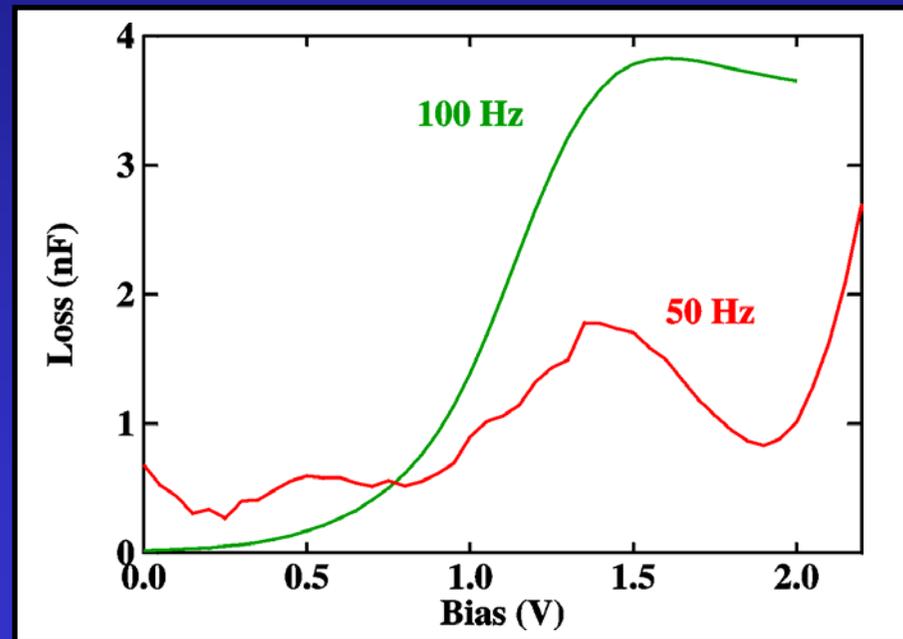
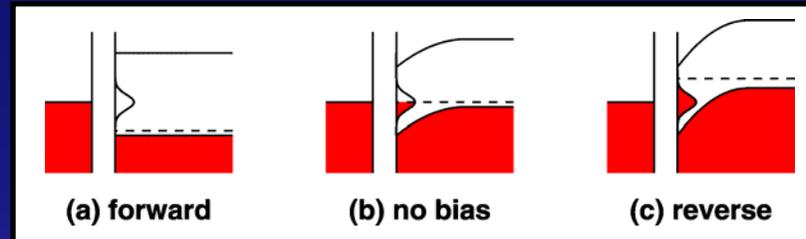
# Interface states in Terrylene

## Experiment



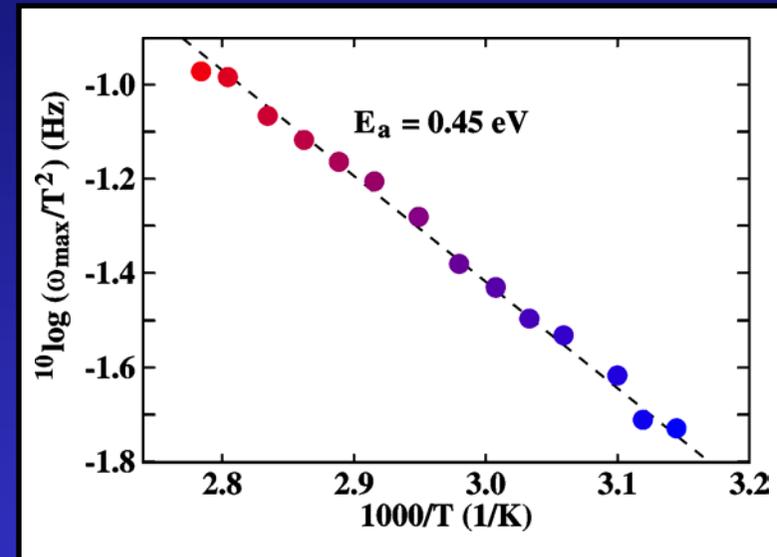
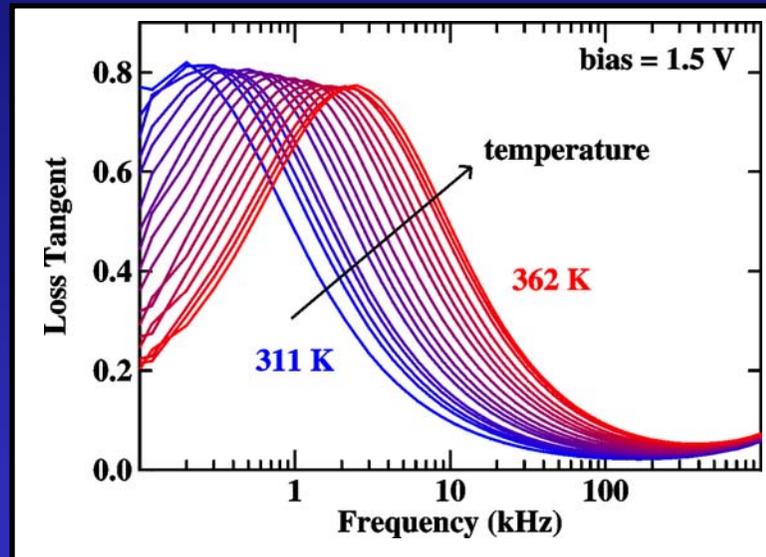
# Interface states in Terrylene

## Experiment



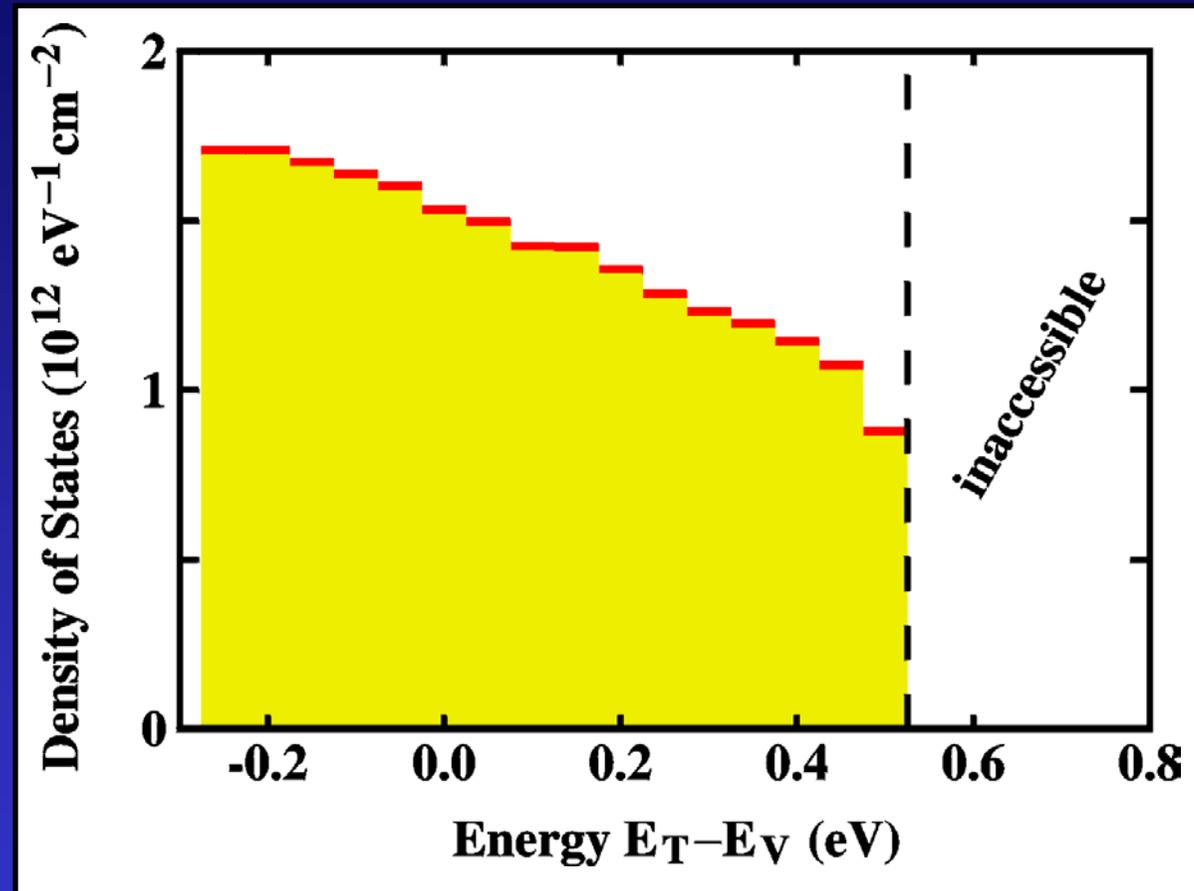
# Interface states in Terrylene

## Experiment



$$\omega_{\max} = 1/\tau = \exp(-E_a/kT)$$

# Interface states in Terrylene



First direct electrical observation of interface states in organic semiconductors, P. Stallinga *et al.* Organic Electronics, 2001.

Electrical Measurements in Faro:

DLTS in Si/MEH-PPV

Interface states in Terrylene/Al

Field Effect Transistors: transport model

10 Q for your attention