Electrical characterization of organic semiconductor devices

P. Stallinga, Universidade do Algarve, Portugal

Hong Kong, January 2007

Universidade do Algarve (UAlg)

10,000 students, 5 Faculties, 4 campi, 700 profs., 60 courses.

Faculdade de Ciências e Tecnologia (FCT), 90 profs.

Departamento de Engenharia Electrónica e Informatica (DEEI), 20 profs.

3 Courses (ESI, EI and I)

Areas of ESI: Electrónica, Control, Signal Processing, Telecommunications

The university is the heart of The Algarve


Faro, 6 Oct. 2004; 26 ^{o}C

OptoEl

Centro de Electrónica, Opto-Electrónica e Telecomunicações

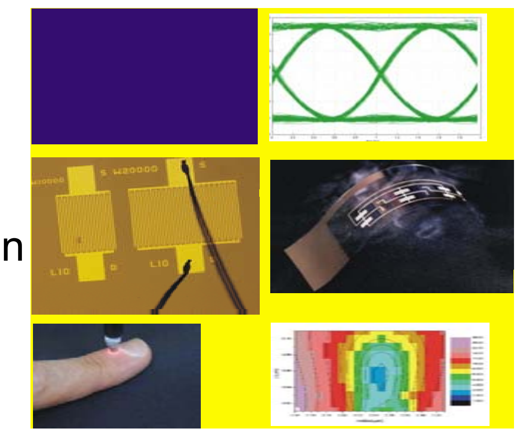
Founded in 2001

9 members (PhD)

Electronics (design of RF electronic circuits)

Opto-Electronics (characterization electronic materials, sensors)

Telecommunications. (communication protocols, network design, etc)



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OptoEl

OPTO-ELECTRONICS
UNIVERSIDADE DO ALGARVE

* Characterization of organic materials and devices
* Sensors (ex. TNT)
* Instrumentation (ex. HIV detection)

Founded: 1997, 2 members (PhD)

Specialized in electronic characterization of organic electronic devices.

Sensitive equipment with custom made control software.

- DLTS (the only “organic” DLTS in the world)
- Organics-specific FET measurement system
- Admittance spectroscopy
- Environment ideal for studying solar cells ☺

OptoEl Cooperations in last 6 years

Organic Materials

"Organic electronic materials" is a hot topic.

Tremendous advances in chemistry

Electrical description: standard textbook!

Electronics of the past

Electronics of the Future
“Ambient intelligence”

Organic Materials

If organic materials are going to be a success in the real world they need to focus on strong points:

- cheap and flexible

Devices based on expensive techniques (MBE, lithography, vacuum deposition, etc.) are doomed to fail

The successful devices are “shitty devices”

Don’t compete with silicon (“if it *can* be done in silicon, it *will* be done in silicon”)

We need to focus our studies on bad devices
(Remember what they initially said about ½cons: “semiconductors are not worth to study. They are dirty science”)

Printable electronics: electronics on paper

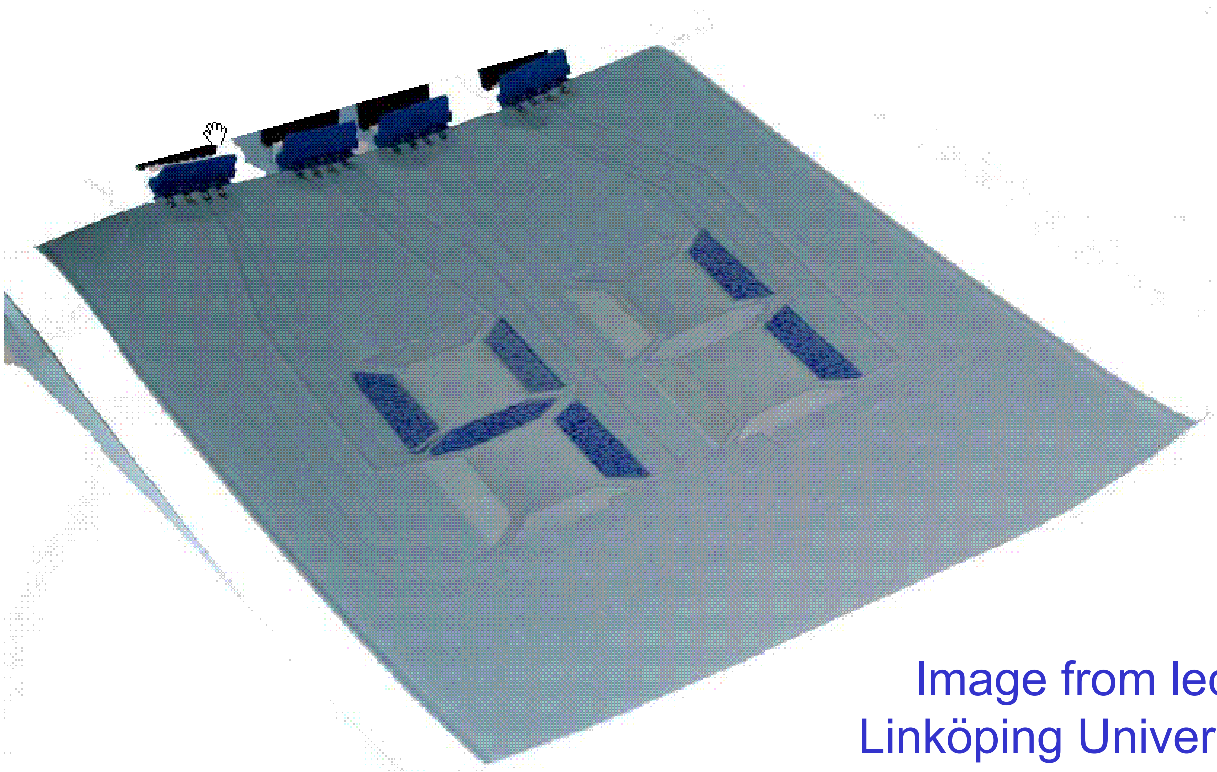
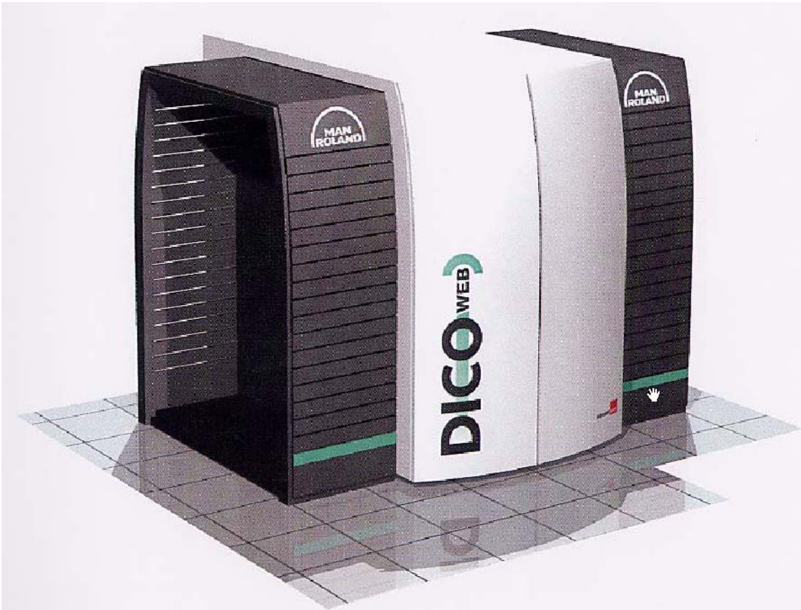


Image from lecture of Magnus Berggren, Linköping University at TPE04 (Rudolstadt)

Printed electronics



MAN ROLAND

WE ARE PRINT.™

Using existing technologies (offset, gravure and flexo printing) to produce electronic circuits

… only organic electronics!

Reinhard Baumann,
MAN Roland Druckmaschinen AG, Germany

Our work: modeling. Inspiration: simplicity is the key!

"One should not increase, beyond what is necessary, the number of entities required to explain anything"

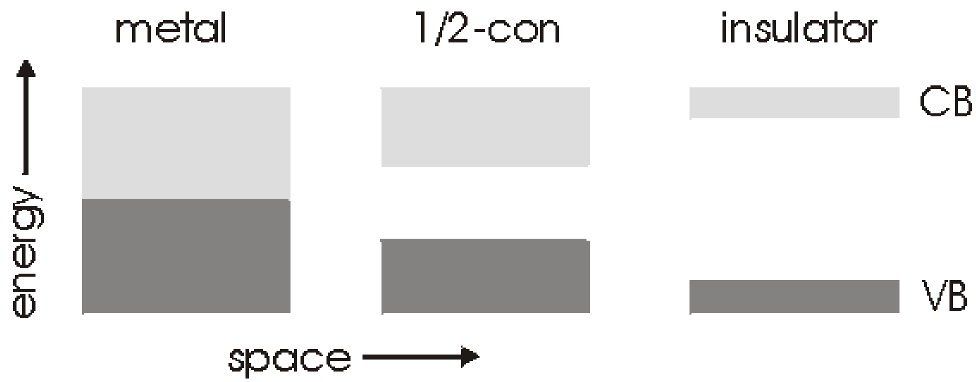
William of Occam, 1288-1348

"Perfection is reached not when there is nothing left to add, but when there is nothing left to take away"

Saint-Exupéry 1900-1944

Semiconductors

Semiconductor means "with electronic bandgap"



Material	Band gap
SiO_2	>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

IR

Organic semiconductors means
"with conjugated backbone"

···· -C=C–C=C–C=····

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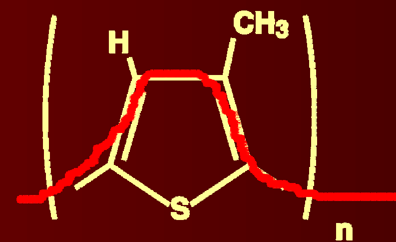
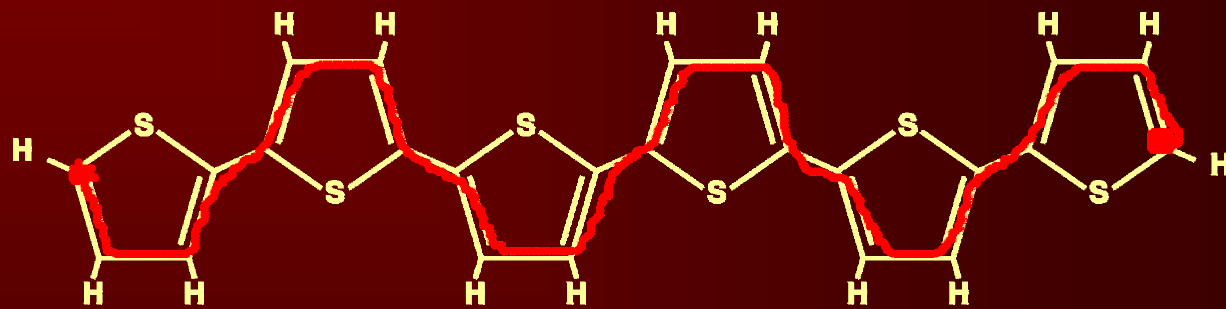
Examples

Conjugated organics have paths with alternating single and double bonds



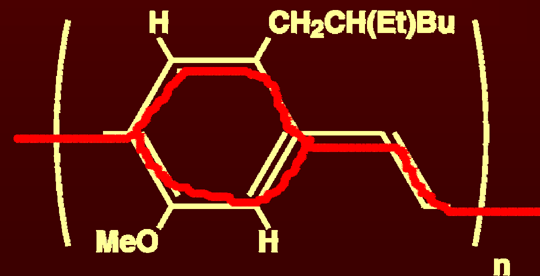
PMeT



αT6

Very good for FETs

Very good for LEDs



MEH-PPV

A semiconductor does not conduct!
4 ways to make it conduct:

1 Chemically ("doping")

$$A \rightarrow A^{-} + h$$
$$D \rightarrow D^{+} + e$$

2 Optically

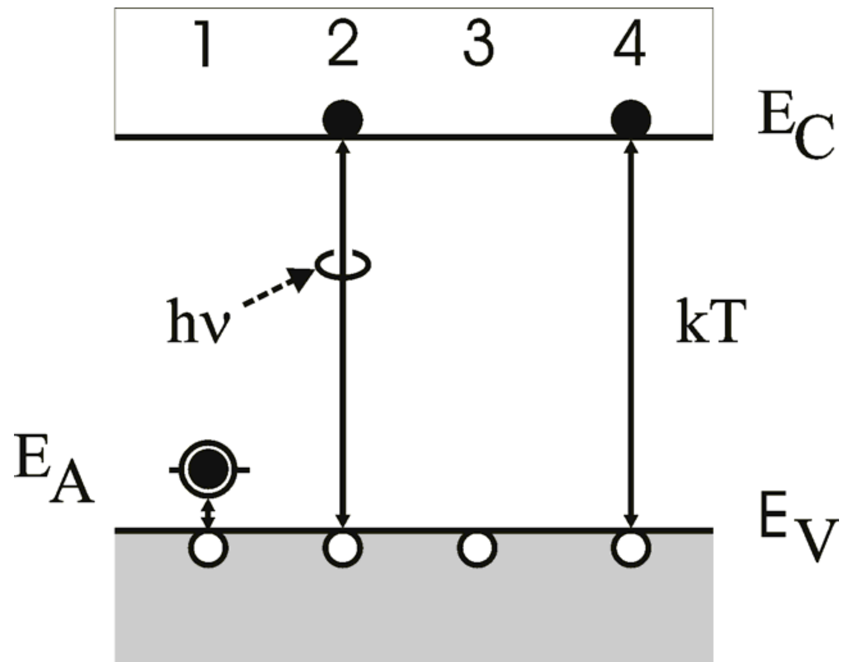
$$h\nu \rightarrow e + h$$

3 Electrically ("field effect")

$$p \sim V_g$$

4 Thermally

$$kT \rightarrow e + h$$



T=300 K: kT = 26 meV: n=p ~ Exp(-500/26) ~ 0

Diodes

example: admittance spectroscopy to determine interface states

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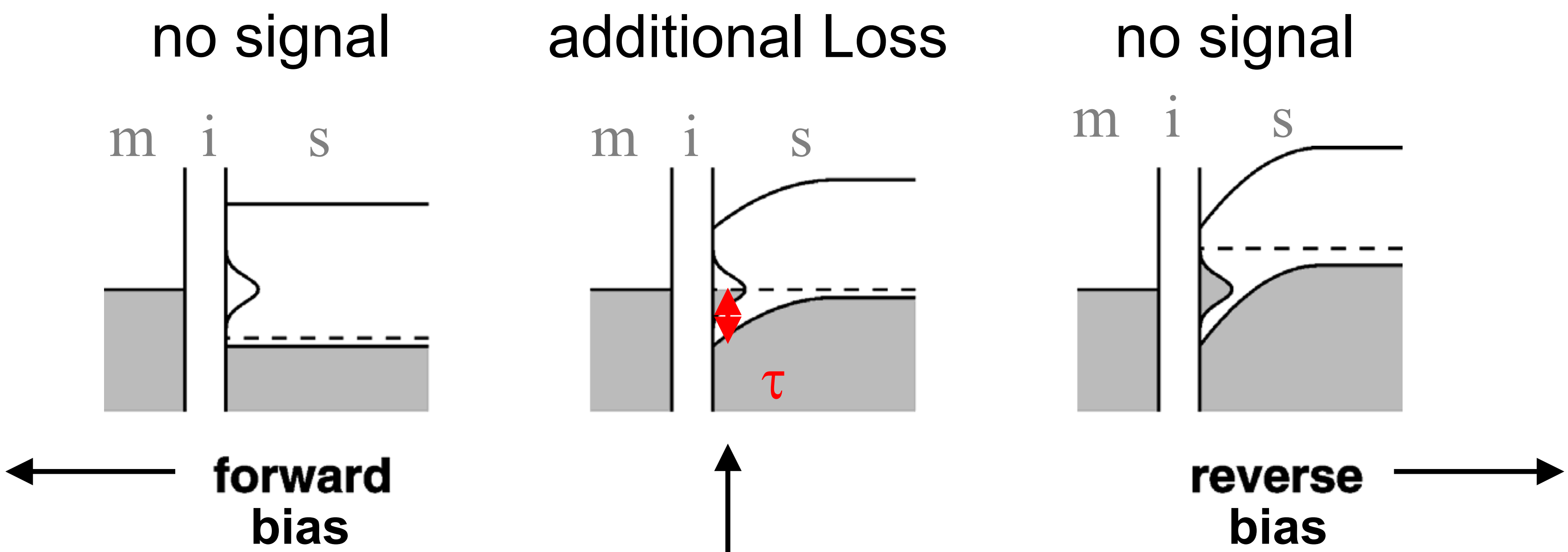
Admittance spectroscopy. Interface states in MIS diode



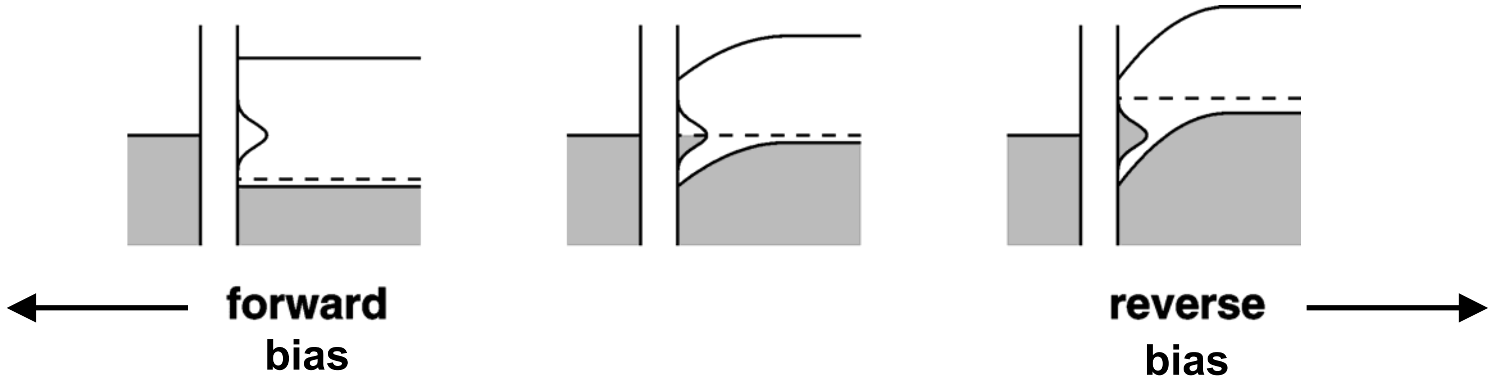
When bias is correct: Filling and emptying of states with time constant

$\tau = \exp(E_T/kT)$

Admittance spectroscopy: Loss: $L = 1/\omega R$

maximum at $\omega_m = 1/\tau$

Interface states



For interface states, τ depends on bias:
Reverse bias: deeper states, τ longer.
Forward bias: shallower states, τ shorter.
For bulk states, τ doesn't depend on bias.

Intensity of peak in Loss ($L = 1/\omega R$) directly proportional to density of states.

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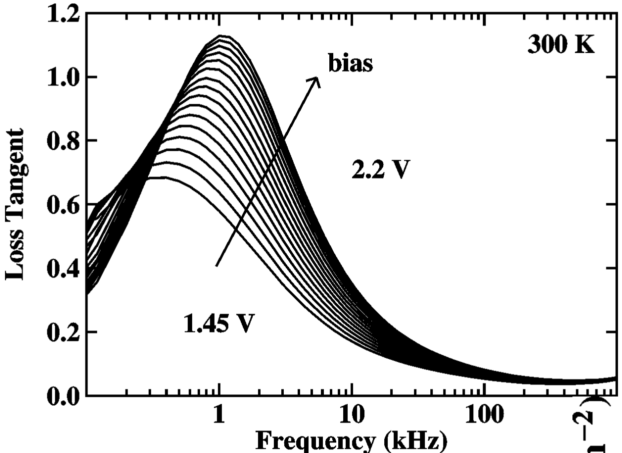
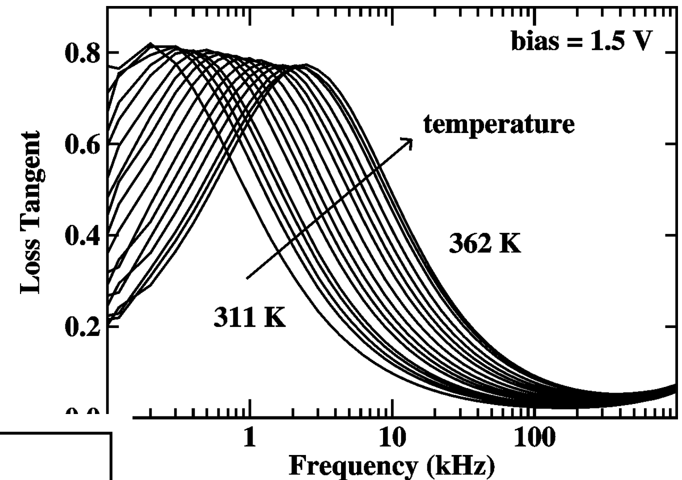
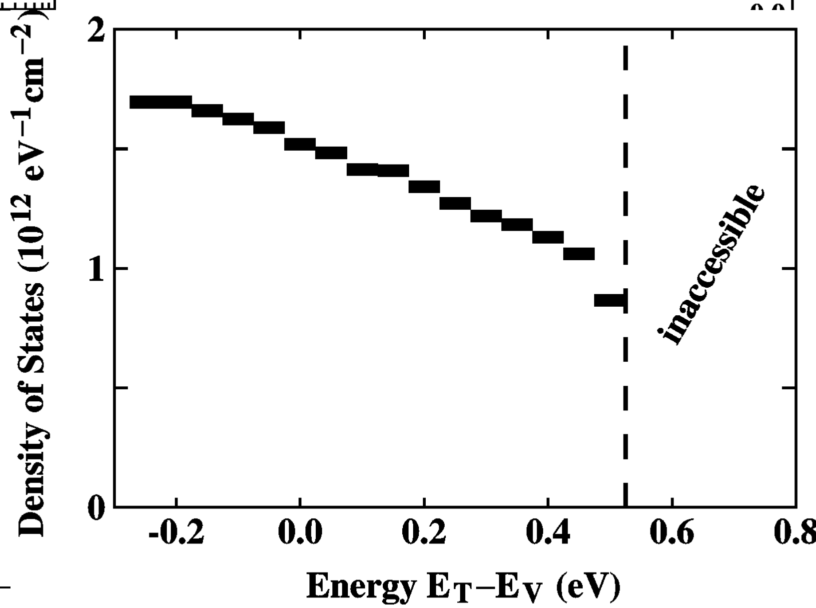
Interface states







P.Stallinga et al.,
Org. Electr. **3**, 43 (2002)

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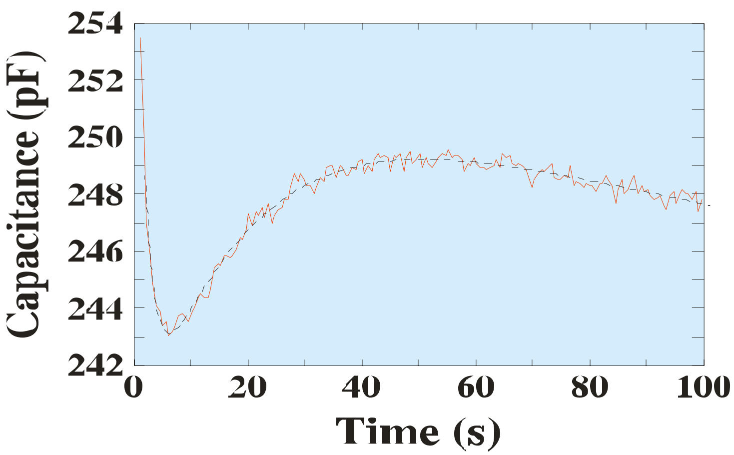
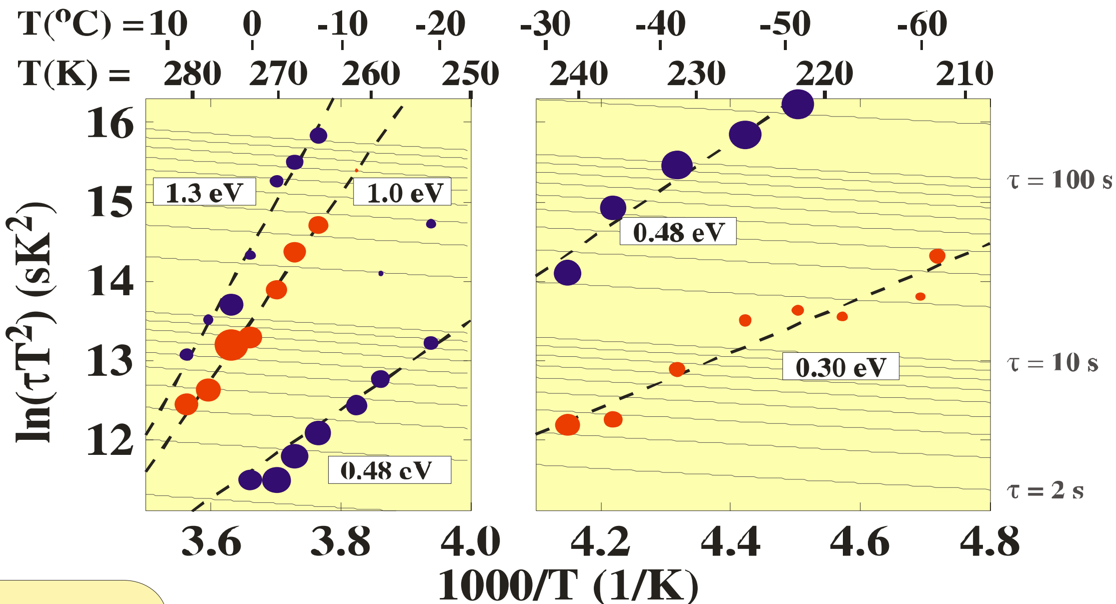
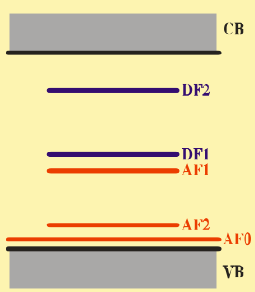
DLTS: measuring τ via capacitance transients





label	type	activation energy
AF0	acceptor	0.12 eV
AF1	majority	0.30 eV
DF1	minority	0.48 eV
AF2	majority	1.0 eV
DF2	minority	1.3 eV



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

TFTs

The Algarve model

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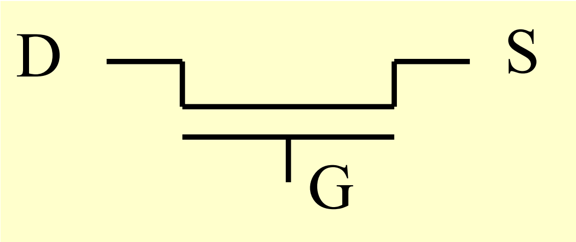
Three-terminal devices: thin-film FETs

Thin-film field-effect transistors are three-terminal devices (Source, Drain, Gate)

As an application, three-terminal devices are used to control the current in, for instance, active matrix displays.

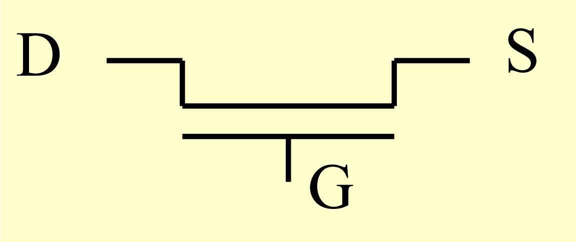
As a research tool, they serve to measure the mobility



Three-terminal devices: thin-film FETs

The MOS-FET model is the de facto standard for analyzing the thin-film transistors.

It seems to describe it well and "**why do you need another model if you already have a working one?**"



LIN: $I_{ds} = (W/L)\, C_{ox}\, \mu\, (V_g - V_t)\, V_{ds}$

SAT: $I_{ds} = (W/L)\, C_{ox}\, \mu\, (V_g - V_t)^2$

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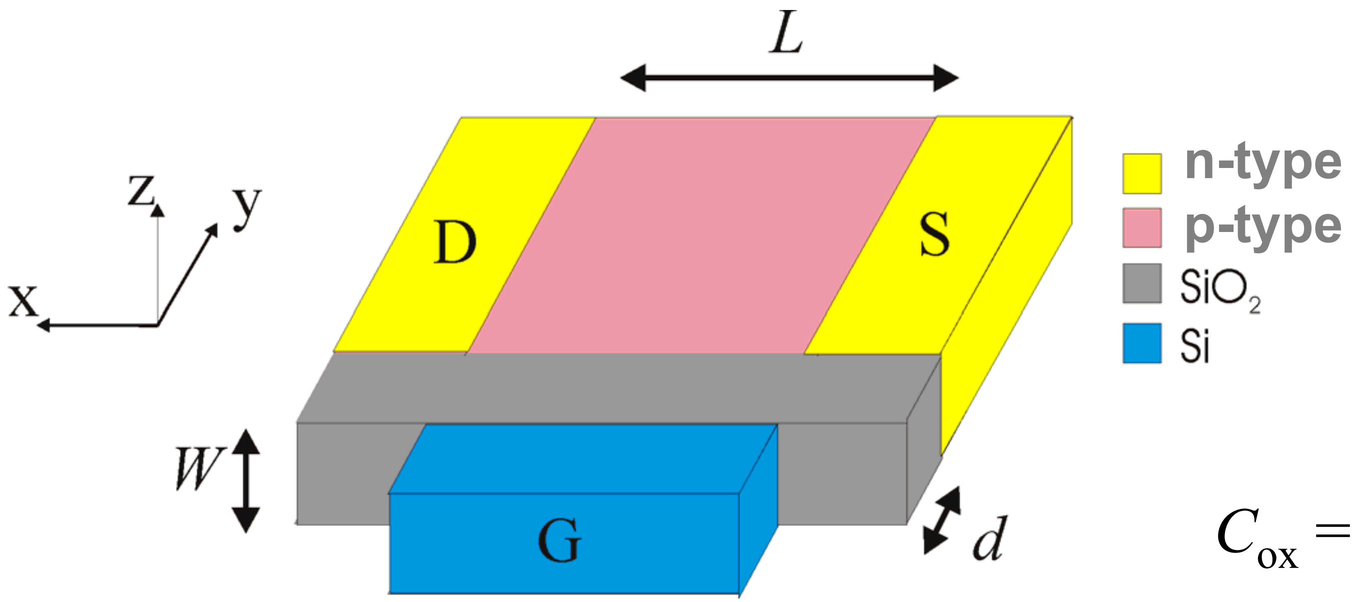
Inversion-channel MOS-FET



$$C_{ox} = \varepsilon_{ox}/d$$

taken from our OptoEl theory pages, http://www.ualg.pt/fct/adeec/optoel/theory

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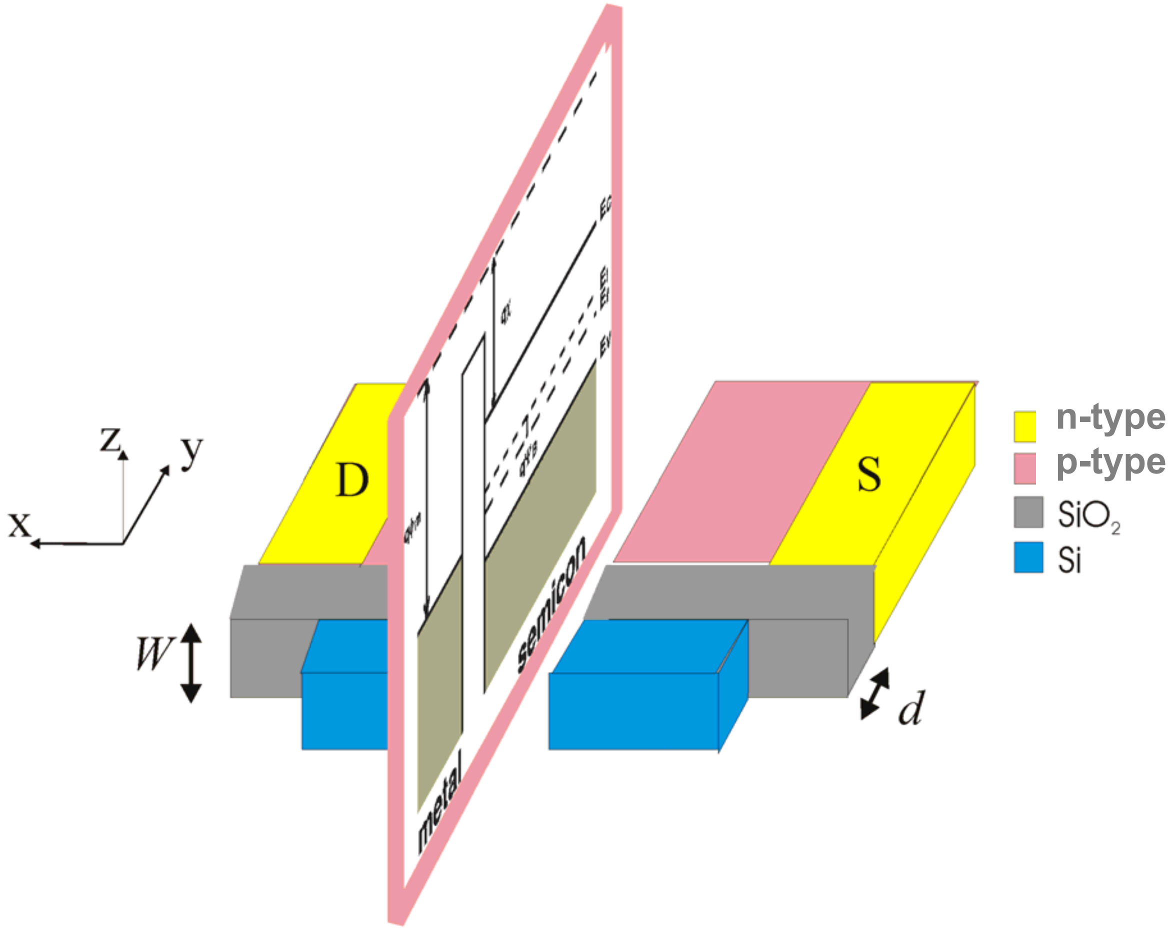
Inversion-channel MOS-FET

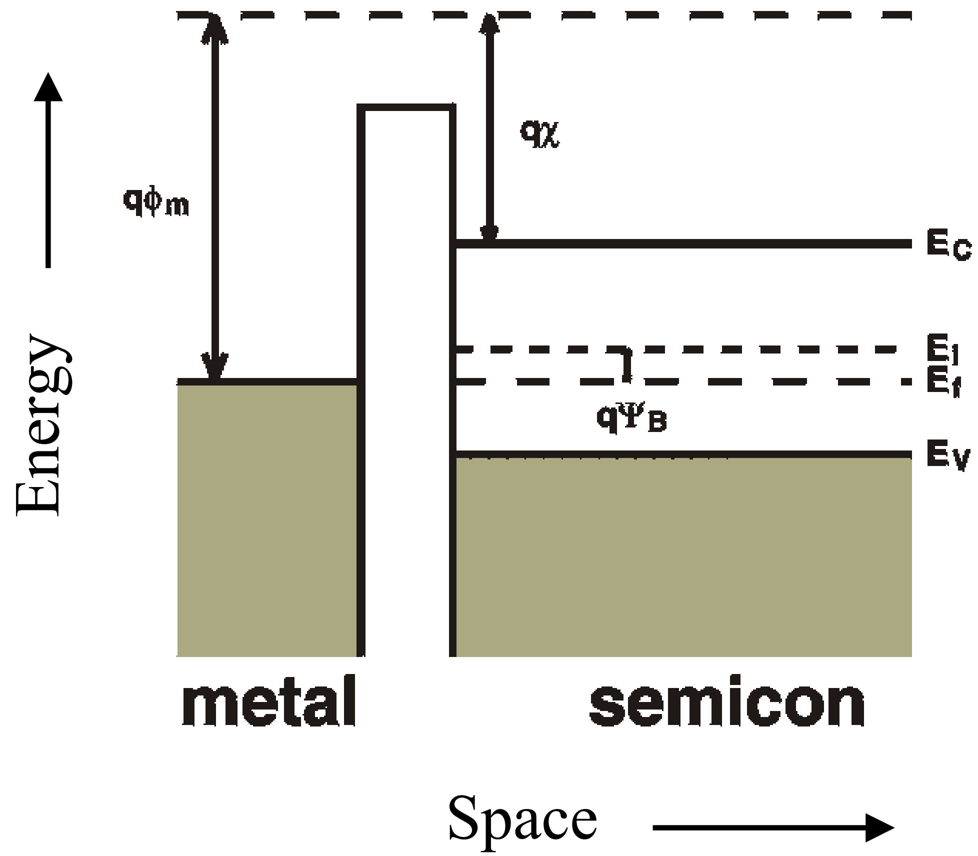


Next slide: look at cross-section of device

Inversion-channel MOS-FET

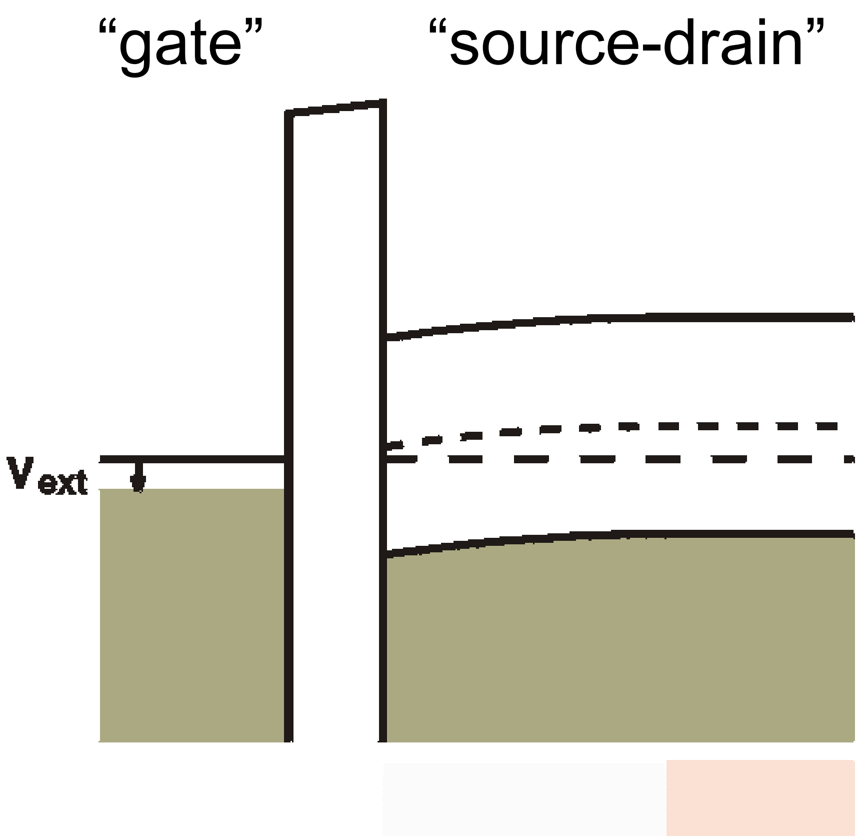
"Flat-band" situation
bulk is p-type

Starting structure: MIS diode
(= FET without electrodes)

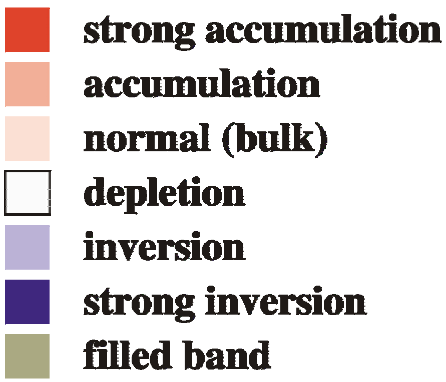


Inversion-channel MOS-FET

"Depletion" Applying bias



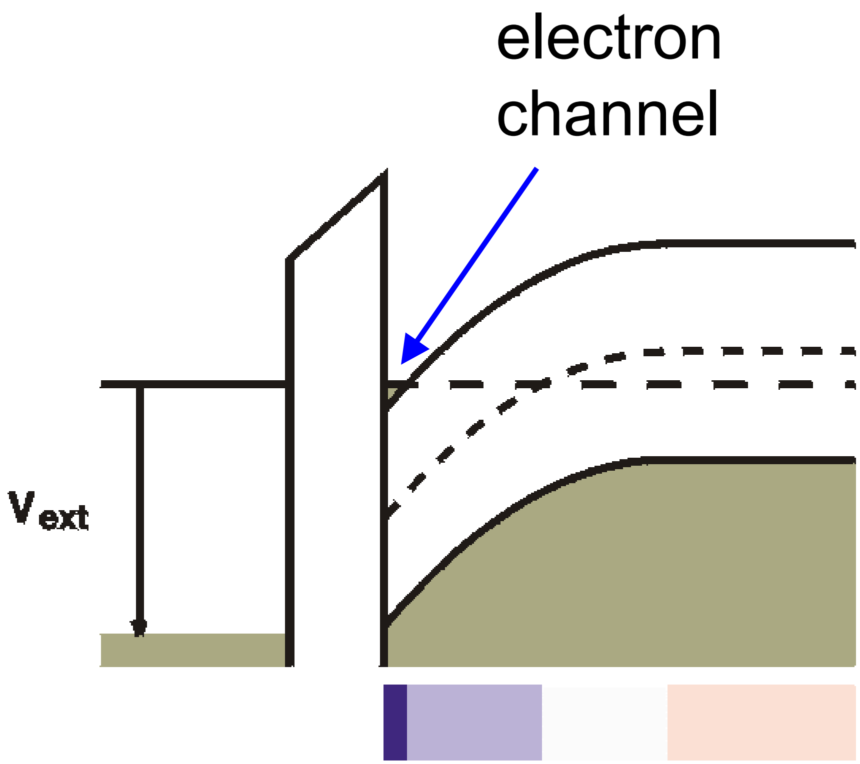
$$V(x) = \iint \rho(x)dx^2$$
$$= \iint N_A^- dx^2$$



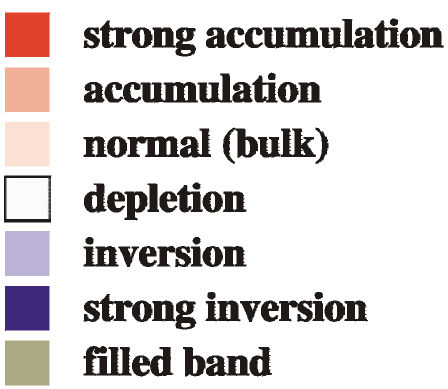
Inversion-channel MOS-FET

"Strong inversion"

Free charge density n grows linearly with bias



Defines "threshold voltage" Vt as voltage needed to start a channel



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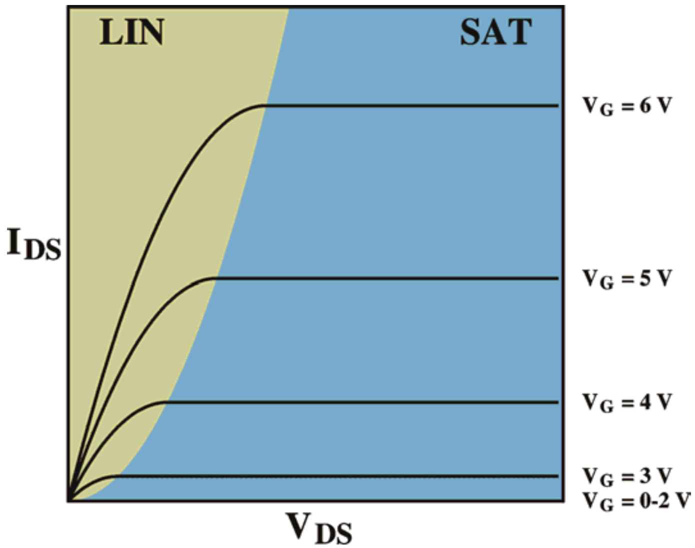
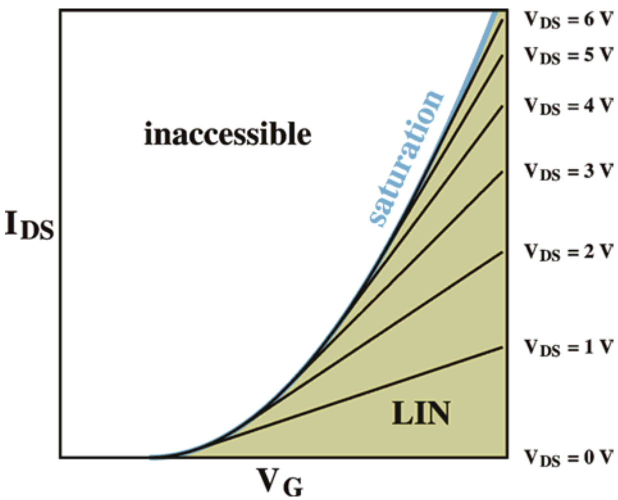
Standard inversion channel FETs

IV curves



transfer curves



LIN: $I_{DS} = \mu(Z/L)\, C_{ox}\, (V_G - V_T) V_{DS}$

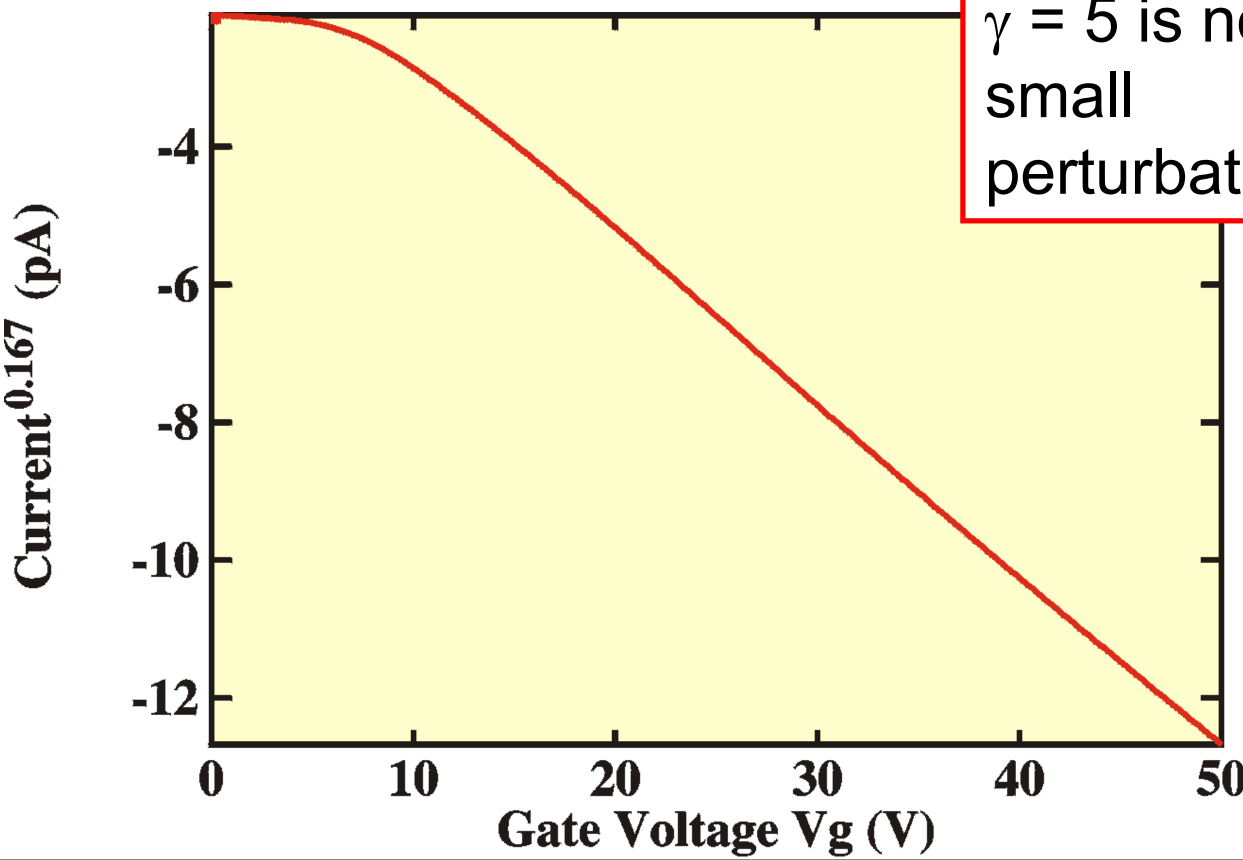
SAT: $I_{DS} = (1/2)\mu(Z/L)\, C_{ox}\, (V_G - V_T)^2$

http://www.ualg.pt/fct/adeec/optoel/theory/fet/

Organic FETs

In the so-called linear region:

$$\text{LIN:}\quad I_{ds} = (W/L)\, C_{ox}\, \mu\, (V_g - V_t)^{1+\gamma}\, V_{ds}$$



γ = 5 is not a small perturbation!

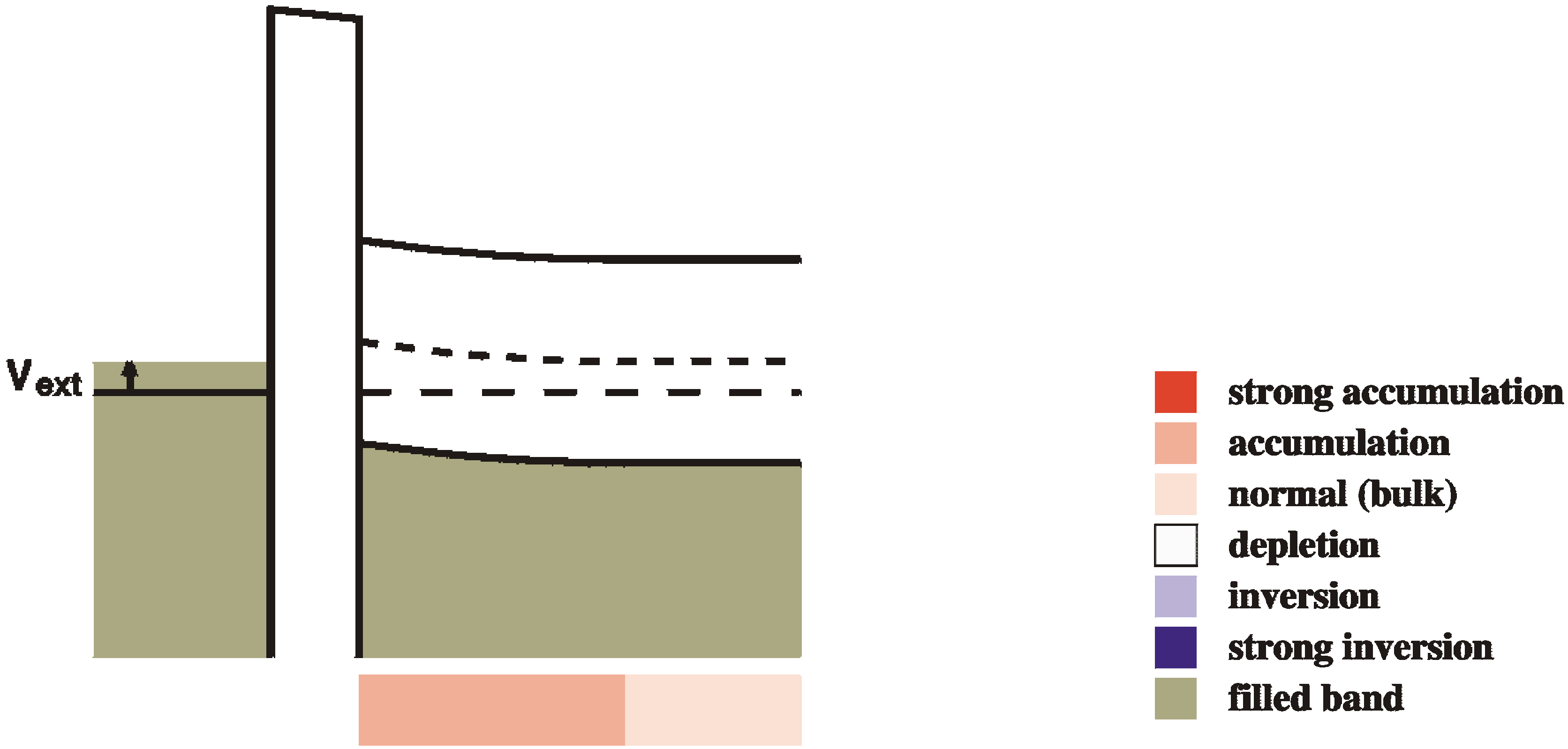
Accumulation-channel MOS-FET?

“Accumulation”

Convention in literature

p ?

Just reverse band bending!



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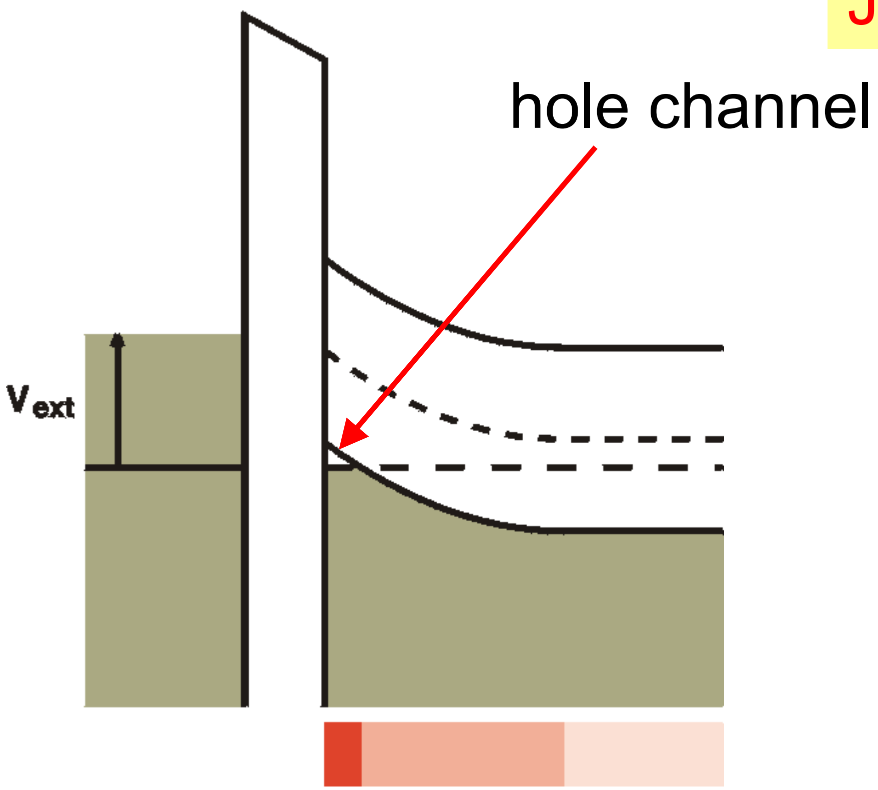
Accumulation-channel MOS-FET?

"Strong Accumulation"

Convention in literature
p ?
Just reverse band bending!



- strong accumulation
- accumulation
- normal (bulk)
- depletion
- inversion
- strong inversion
- filled band

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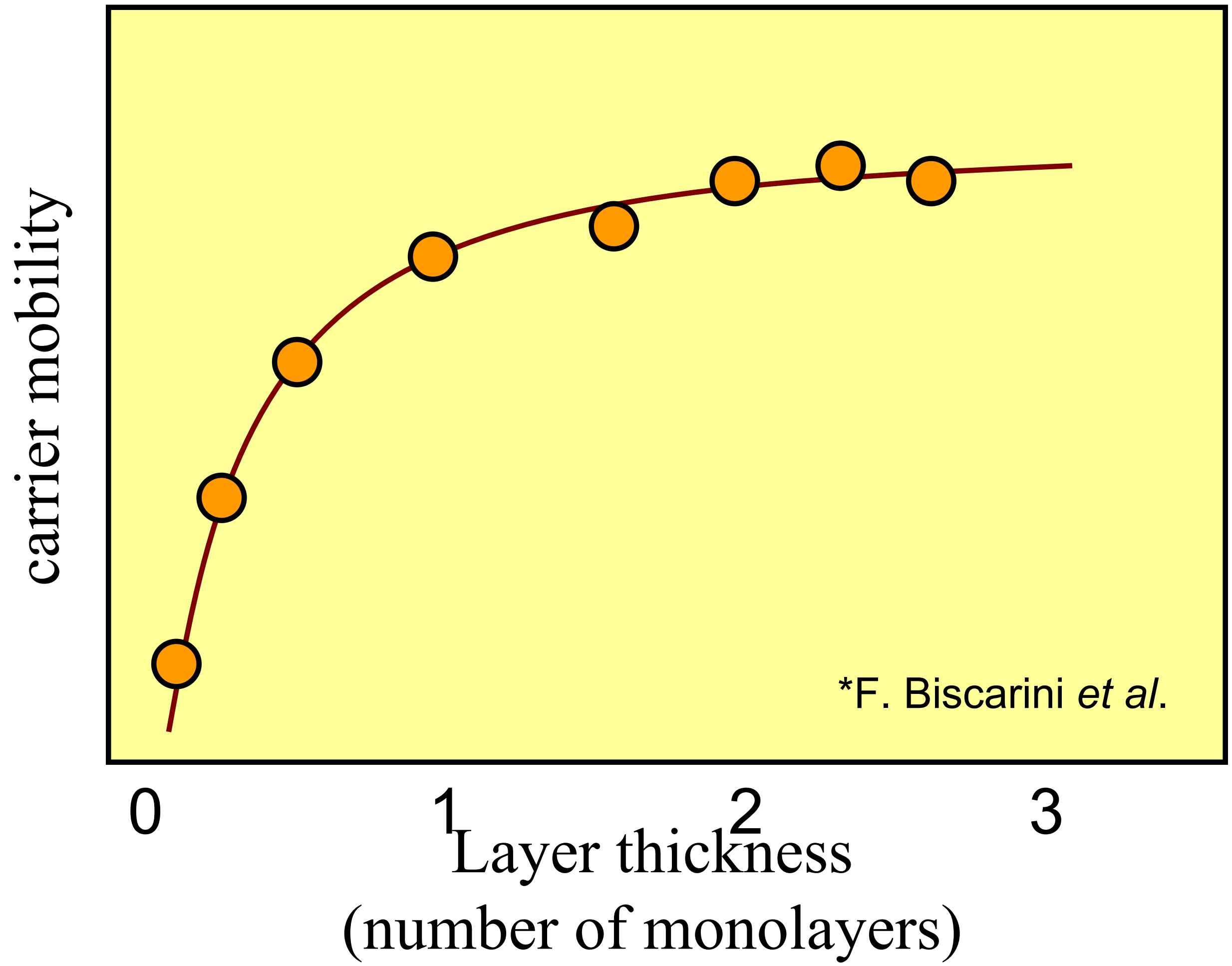
Thin-film transistors (TFTs)

Why a TFT is not a MOS-FET?

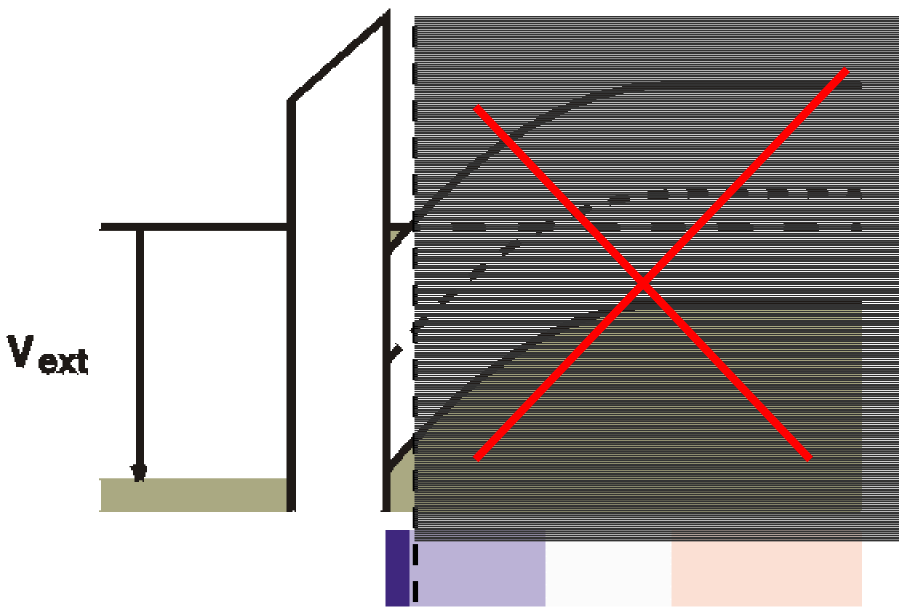


Only first monolayer is important*

The MOS-FET model

Why a TFT is not a MOS-FET?

1. A TFT is made of a **thin** film and cannot accommodate band bendings. No space!



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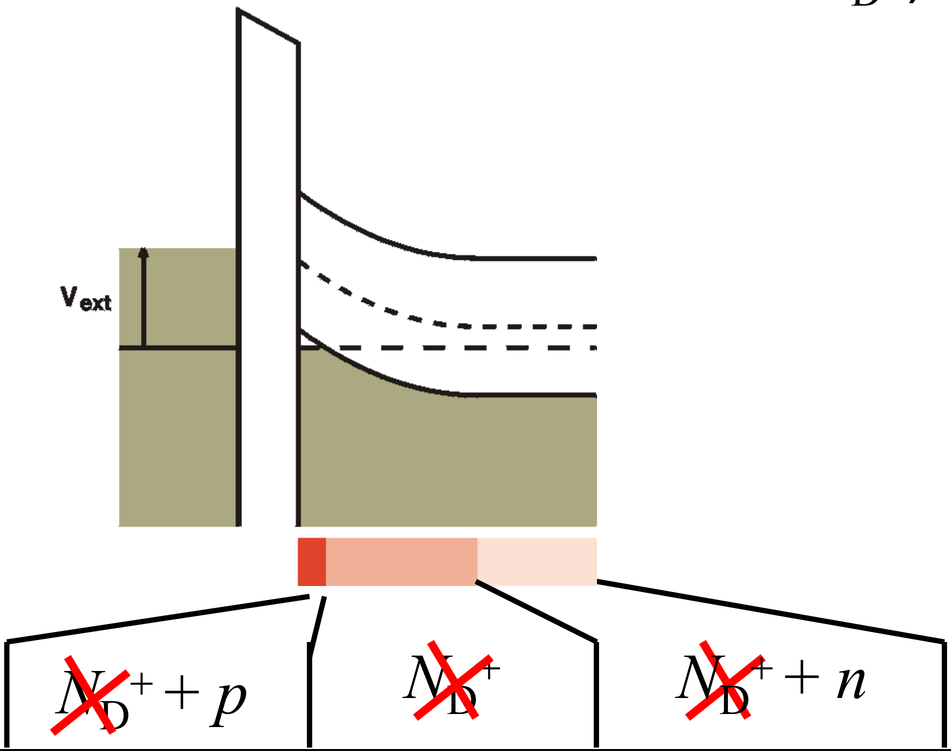
The MOS-FET model

Why a TFT is not a MOS-FET?

2. A TFT normally works in **accumulation** and thus cannot store the immobile charge needed for band bendings (there are no electronic states, N_D^+).



Poisson:

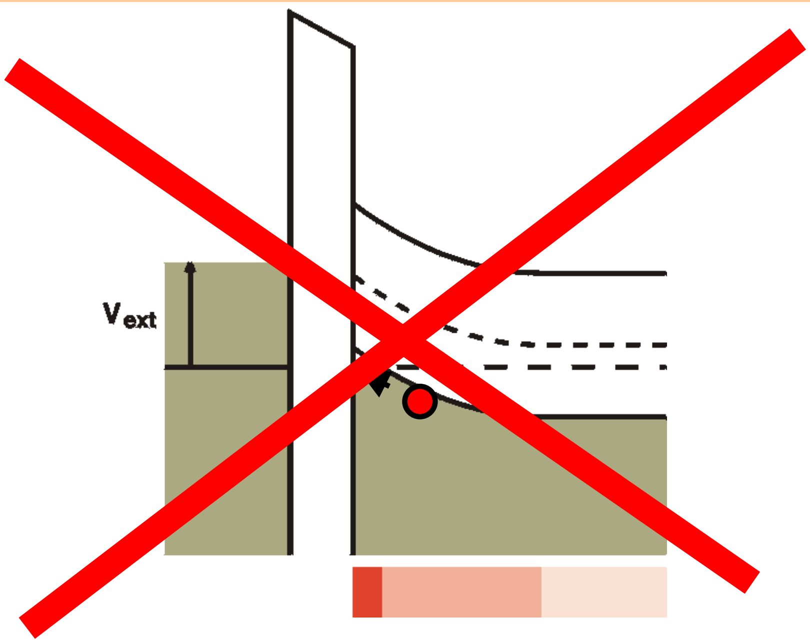
$$V(x) = \iint N_D^+ dx^2$$

Band bending in accumulation? Nonsense!

Poisson's Equation:

$$V(x) = \iint \rho(x) dx^2$$

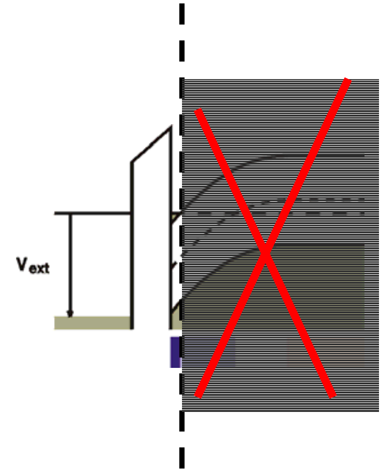
Accumulation:
Positive charge ρ can only appear in the material as free holes. They will therefore always move towards the interface. No space charge (band bending)



The MOS-FET model

Why a TFT is not a MOS-FET?

1. A TFT is made of a **thin** film and cannot accommodate band bendings.



2. A TFT normally works in **accumulation** and thus cannot store the immobile charge needed for band bendings (there are no electronic states, N_D^+).

There **are** no band bendings!

Not even in thick film transistors! Not even at contacts!

The Algarve TFT model

One single simple axiom:

Any charge induced by the gate is at the interface

The device is purely **two-dimensional**

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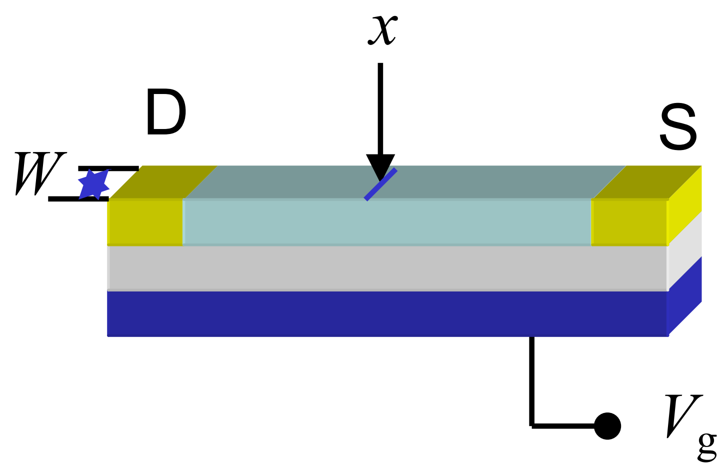
Postulate for TFT: Purely two-dimensional treatment

All charge is at the interface.

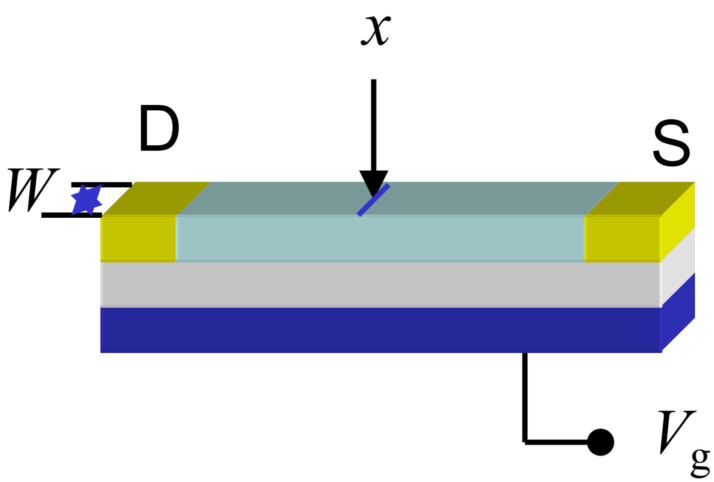


$$\rho(x) = C_{ox}[V(x) - V_g]$$

C/m² F/m² V

(note the two-dimensional units!)

Is this allowed? How thick is an accumulation layer?



$$\rho(x) = C_{ox}[V(x) - V_g]$$

Example: Silicon TFT, typical values:

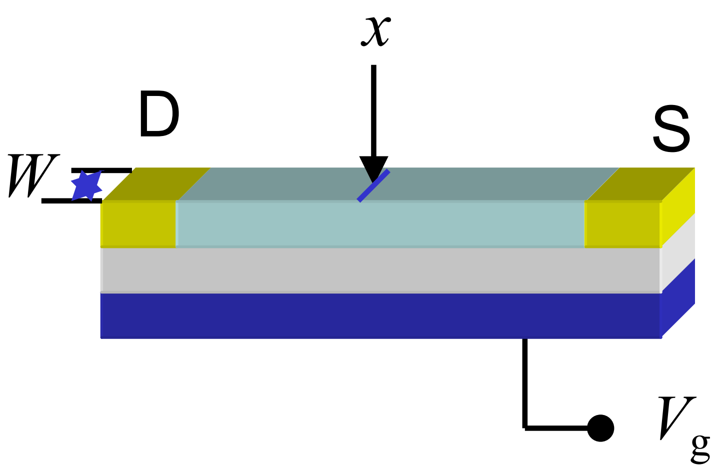
$V_g = -1$ V, $d_{ox} = 200$ nm ($C_{ox} = 170$ μF/m^2) :

$\rho = 0.17$ mC/m^2

with $N_V = 1.04 \times 10^{19}$ cm^{-3}:

$$\boldsymbol{d < 1\ \text{Å}}$$

Differential equations. Trap-free materials



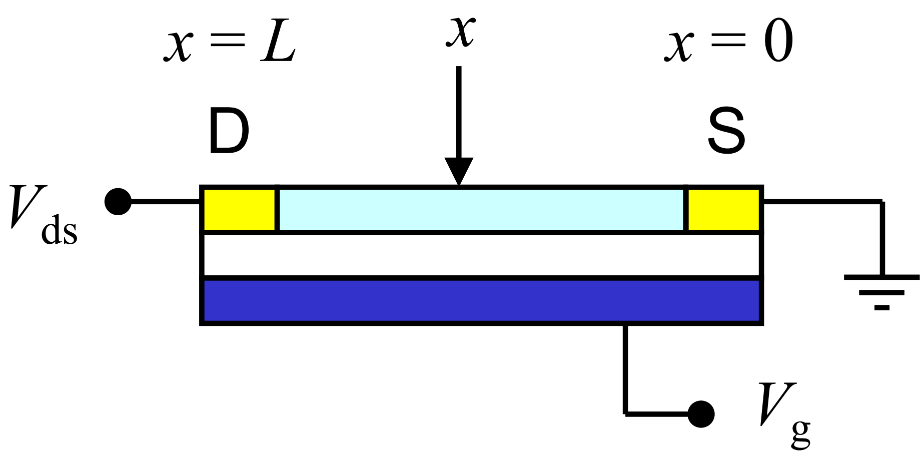
I: Assume ρ = p, free holes

II: Locally, current is proportional to charge density, mobility, electric field and channel width

$$p(x) = C_{ox}[V(x) - V_g]/q \qquad \text{(I)}$$

$$I_x(x) = p(x) q \mu W \frac{dV(x)}{dx} \qquad \text{(II)}$$

Solution



Boundary conditions:

$V(0) = 0$

$V(L) = V_{ds}$

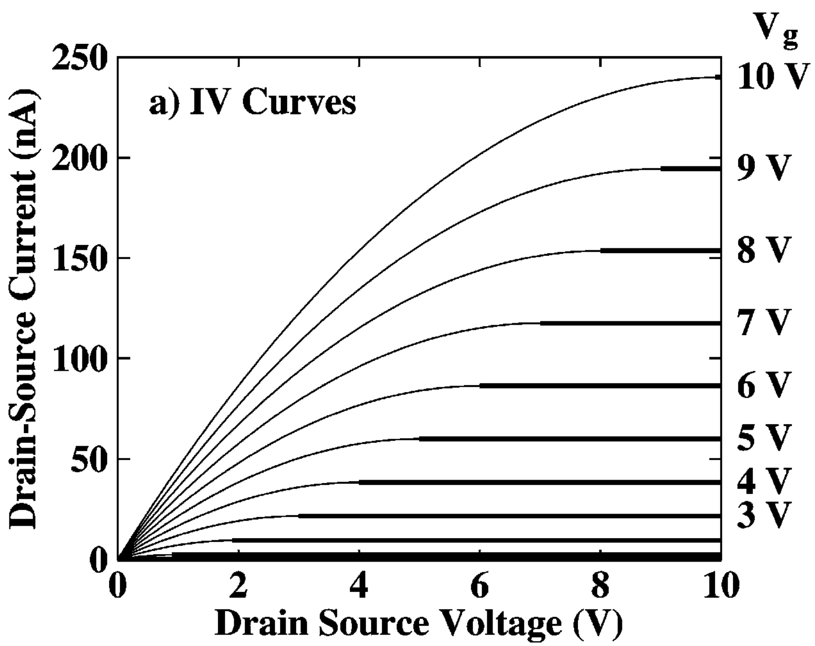
$I_x(x) = I_{ds}$

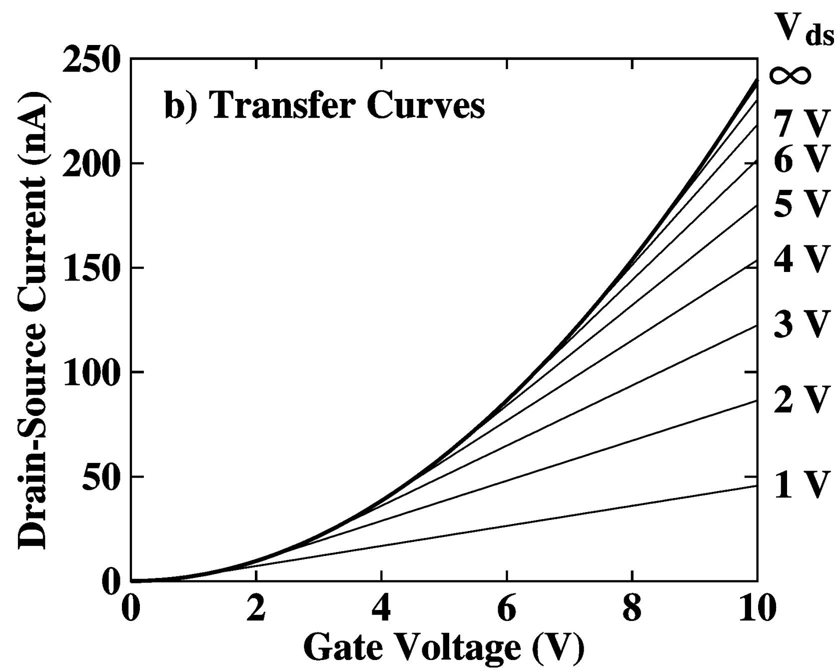
solution:

$$I_{ds} = \frac{W}{L} \mu C_{ox} (V_{ds} V_g - \tfrac{1}{2} V_{ds}{}^2)$$

Simulation

$$I_{ds} = \frac{W}{L} \mu C_{ox} (V_{ds} V_g - \tfrac{1}{2} V_{ds}{}^2)$$

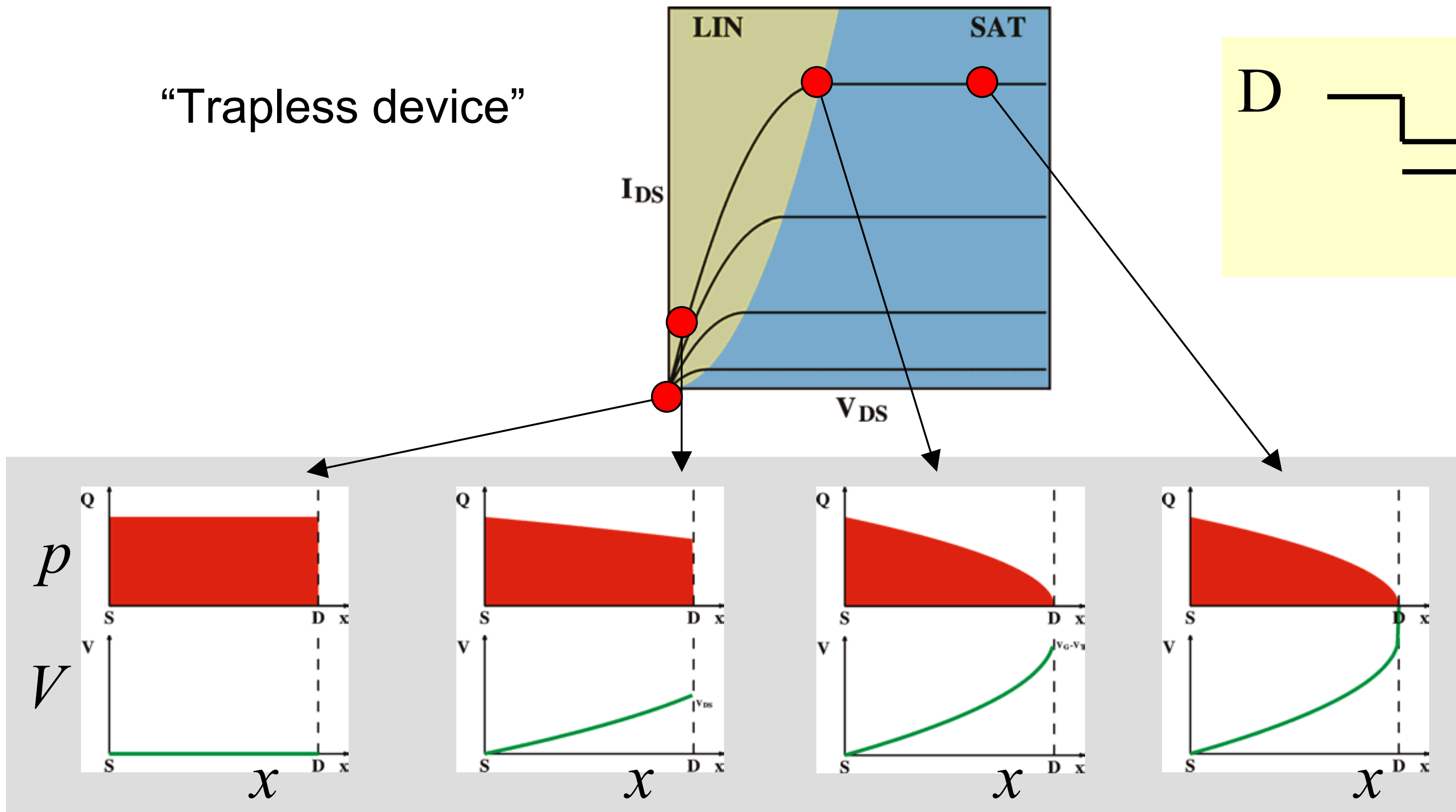


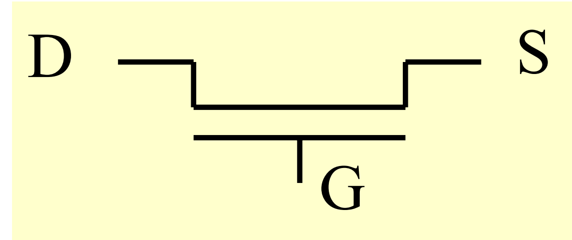


Exactly equal to MOS-FET model!

The Algarve TFT model

"Trapless device"





The Algarve TFT model

The simple model **doesn't** include (need)

- Donors or acceptors
- Flat-band voltage
- Diffusion currents

and still explain the data better (as will be shown)

William of Occam and Saint-Exupéry would be happy!

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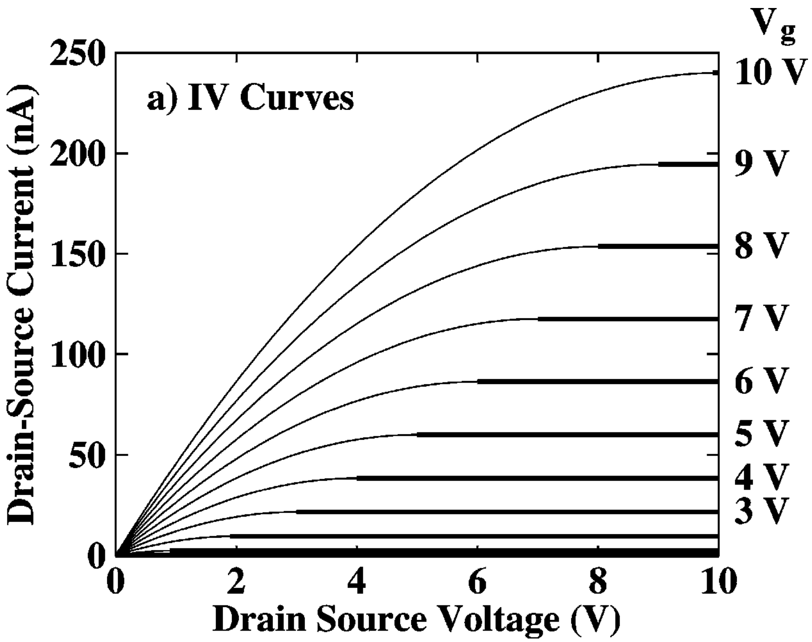
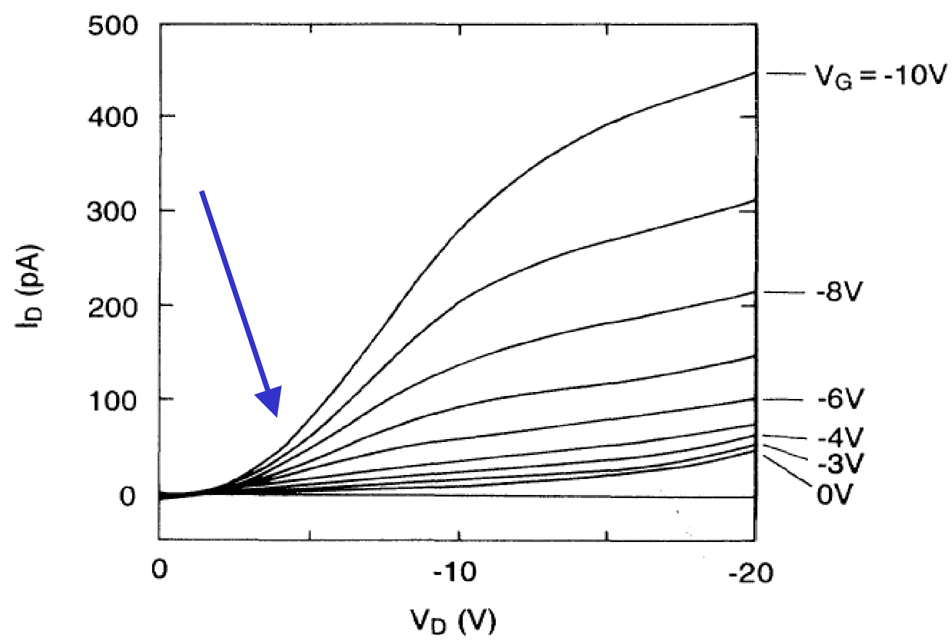
"Contact effects"

Theory:



Experiment:



Waragai, PRB **52**, 1786 (1995).

Literature: contact effects

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"Contact effects"

Literature: contact effects.

The idea is simple. Non-low-ohmic contacts hinder the injection of carriers and can cause non-linearities.

(Too) often used to explain the data.

"sweep-under-the-carpet" argumentation.

Next slides: simulations of high-resistive contacts and Schottky barriers.

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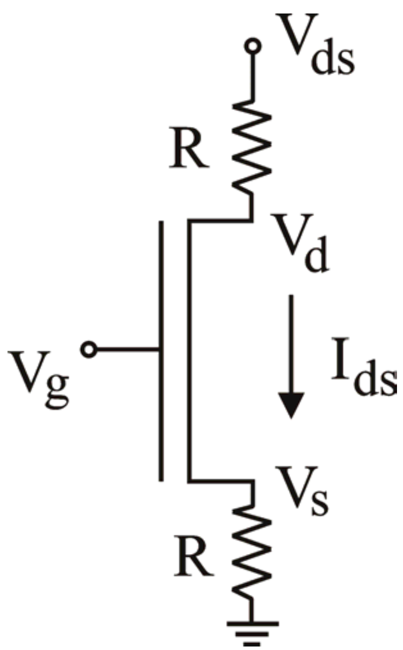
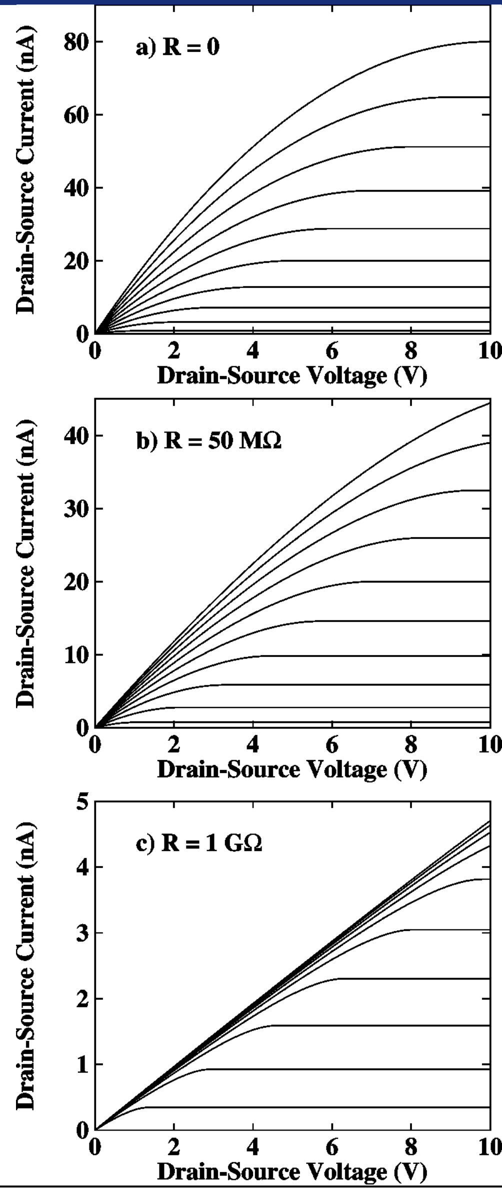
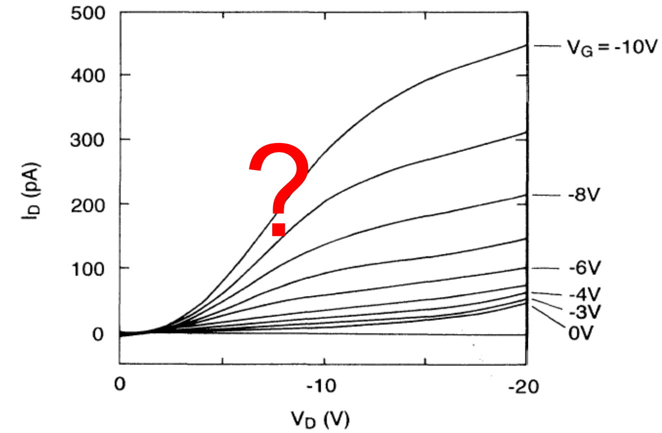
"Contact effects", simulation of contact resistance





experiment:



"current crowding" observed for high R (curves indep. of V_g)

No non-linearities

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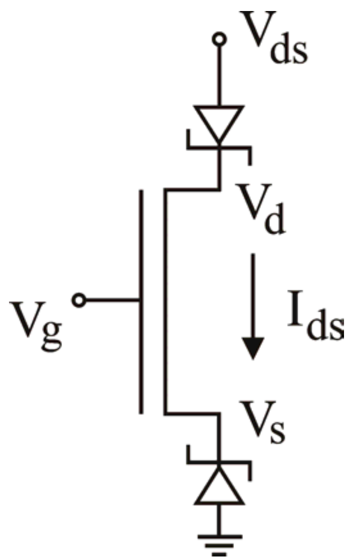
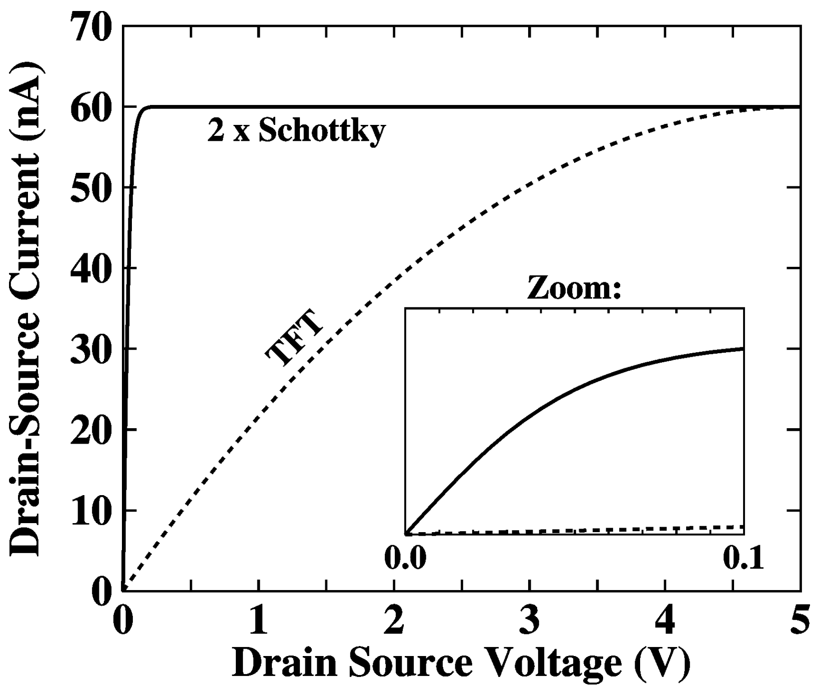
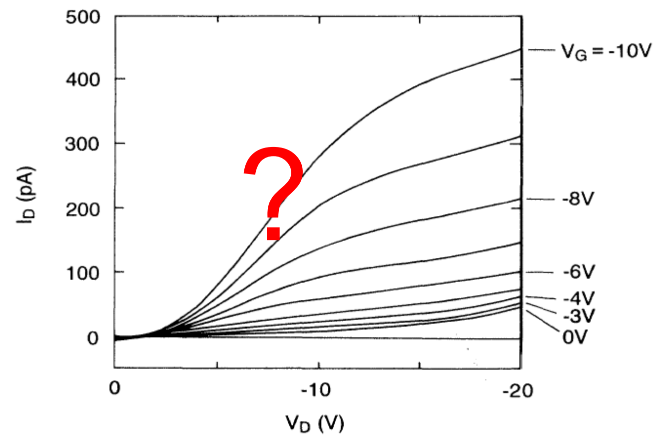
“Contact effects”, simulation with Schottky barriers

Schottky barriers come in pairs!





experiment:



Double Schottky barrier:

$$I_{ds} = \tanh(V_{ds})$$

No non-linearities!

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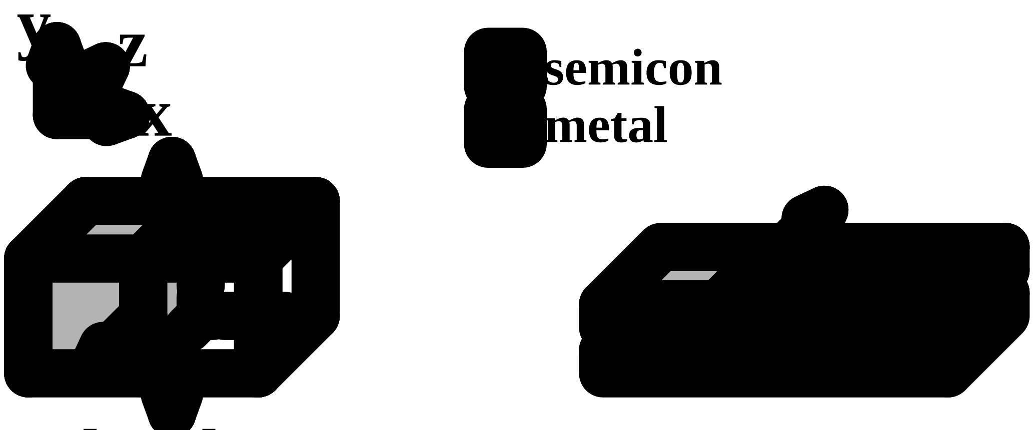
Modeling the contacts

Even the symmetry of a Schottky barrier is not correct:



Schottky **TFT**

Poisson's Equation can be used

$$V(x) = \iint N_D^+ dx^2$$

Poisson's Equation cannot be used

Modeling the contacts

“If you don’t give a solution, you are part of the problem!”

If non-linearities are not because of resistance or Schottky barrier, what is their cause?

Traps!

Simulation with Poole-Frenkel

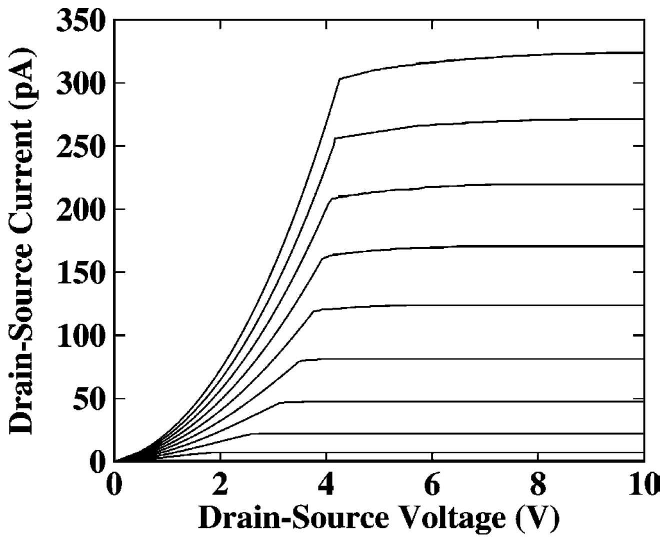
$$p(x) = C_{ox}[V(x) - V_g] \qquad \text{(I)}$$

$$I_x(x) = p(x) q \mu(x) W \frac{dV(x)}{dx} \qquad \text{(II)}$$

$$\mu(x) = \mu_0 \exp(dV(x)/dx) \qquad \text{(III)}$$

Poole-Frenkel:
"Field-assisted thermal activation from traps"

Simulation:
fits, with only 1 (one) fitting parameter (ε)



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Modeling the contacts

This is, of course, only half the story.

If contacts are not resistance nor Schottky barrier, what are they?

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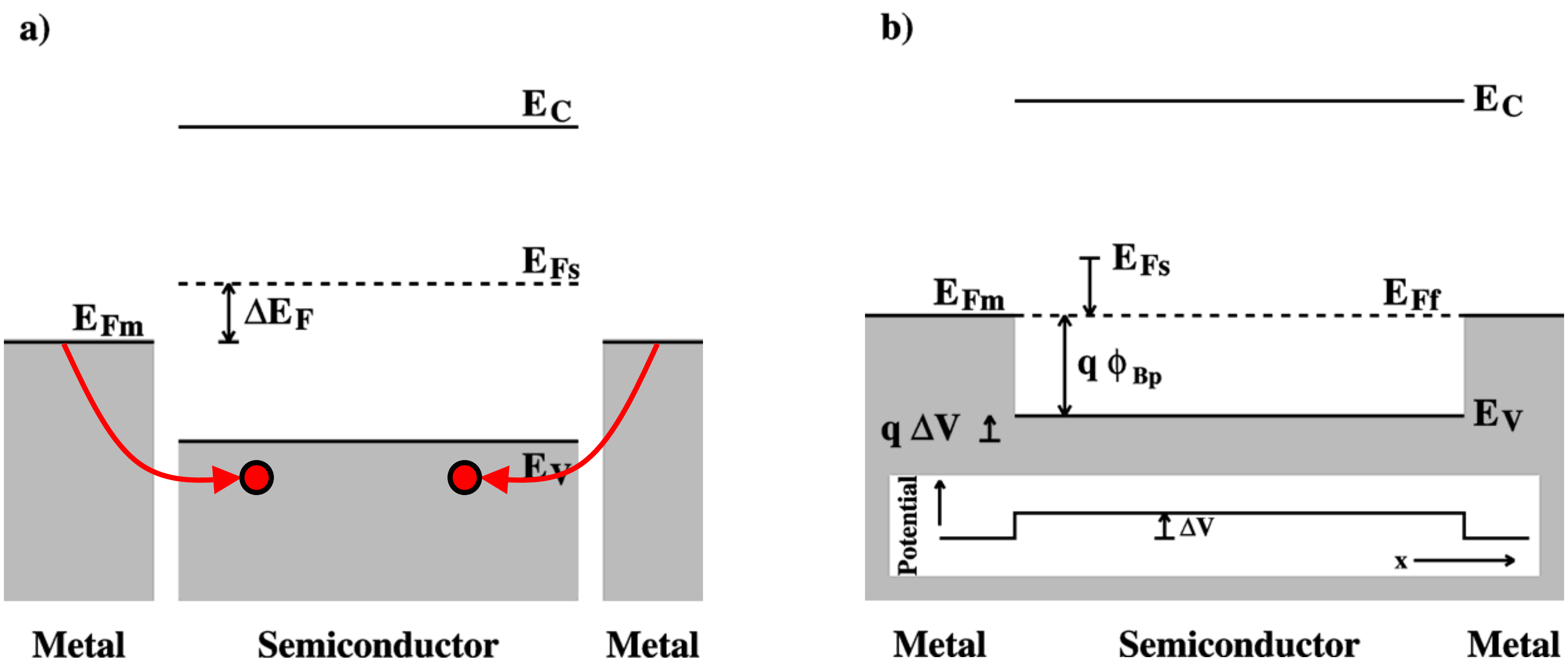
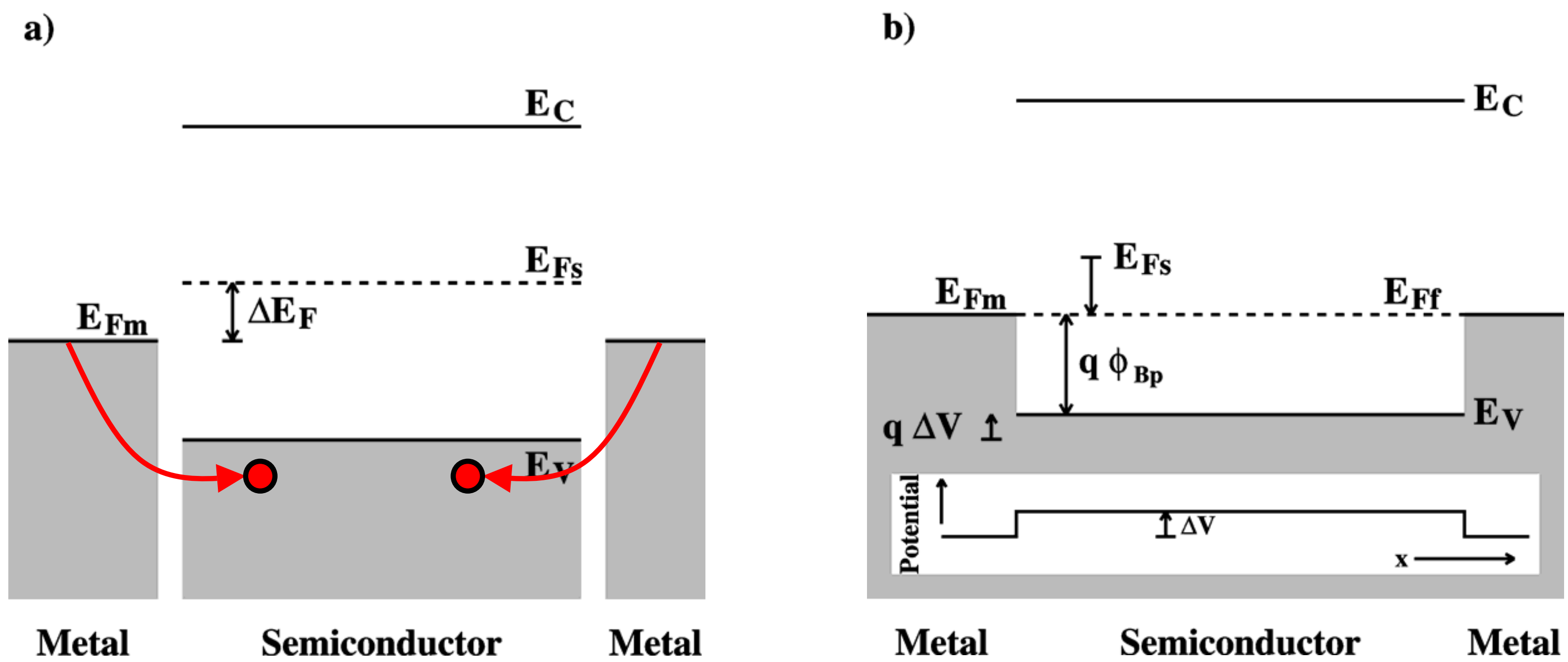
Metal-½con-metal contact



1: charge will raise potential V of channel ($p = C_{ox}V$)

2: charge will move Fermi level ($p = \mathrm{Exp}(-E_F/kT)$)

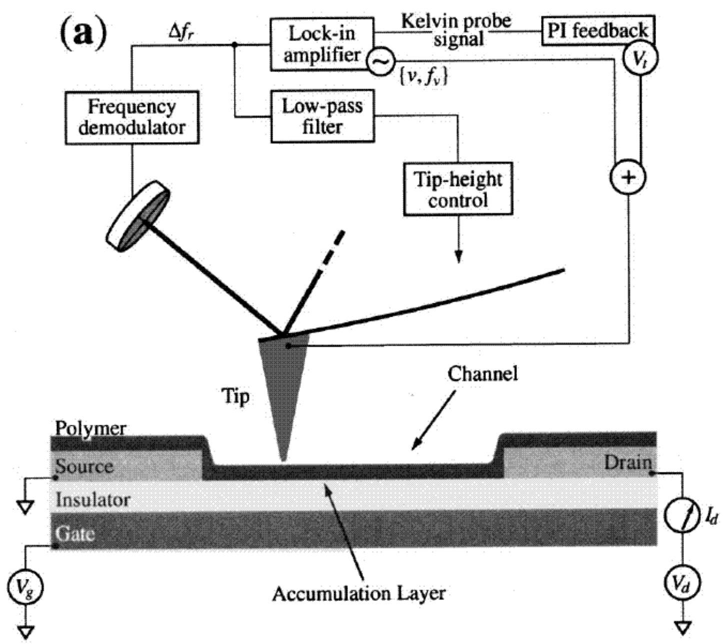
Metal-1/2con-metal contact

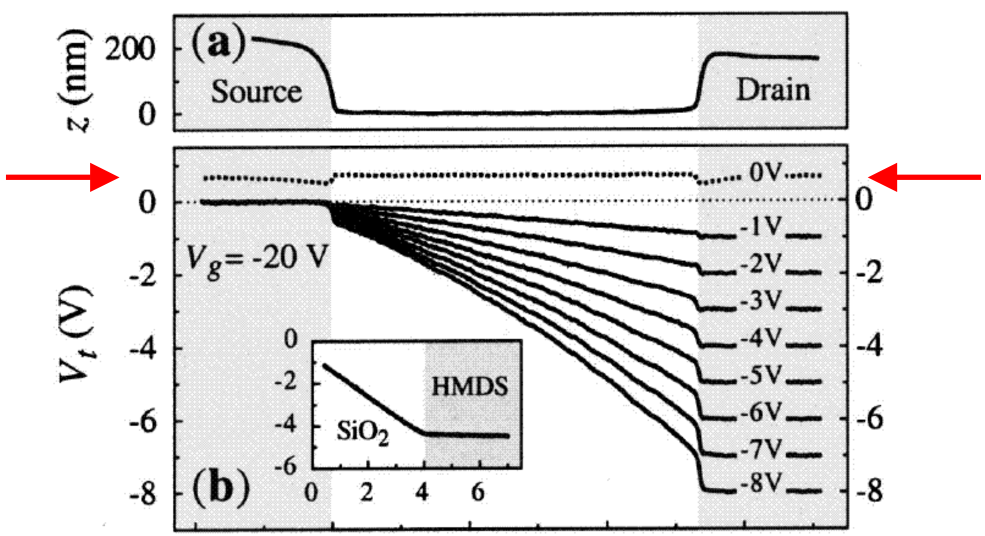


1: The channel has a potential ΔV, up to ~1 V even without bias

2: There exists a residual barrier $q\phi_B$ of order 50-100 meV (depends on bias!)

In-channel voltage profiling of Bürgi *et al.*





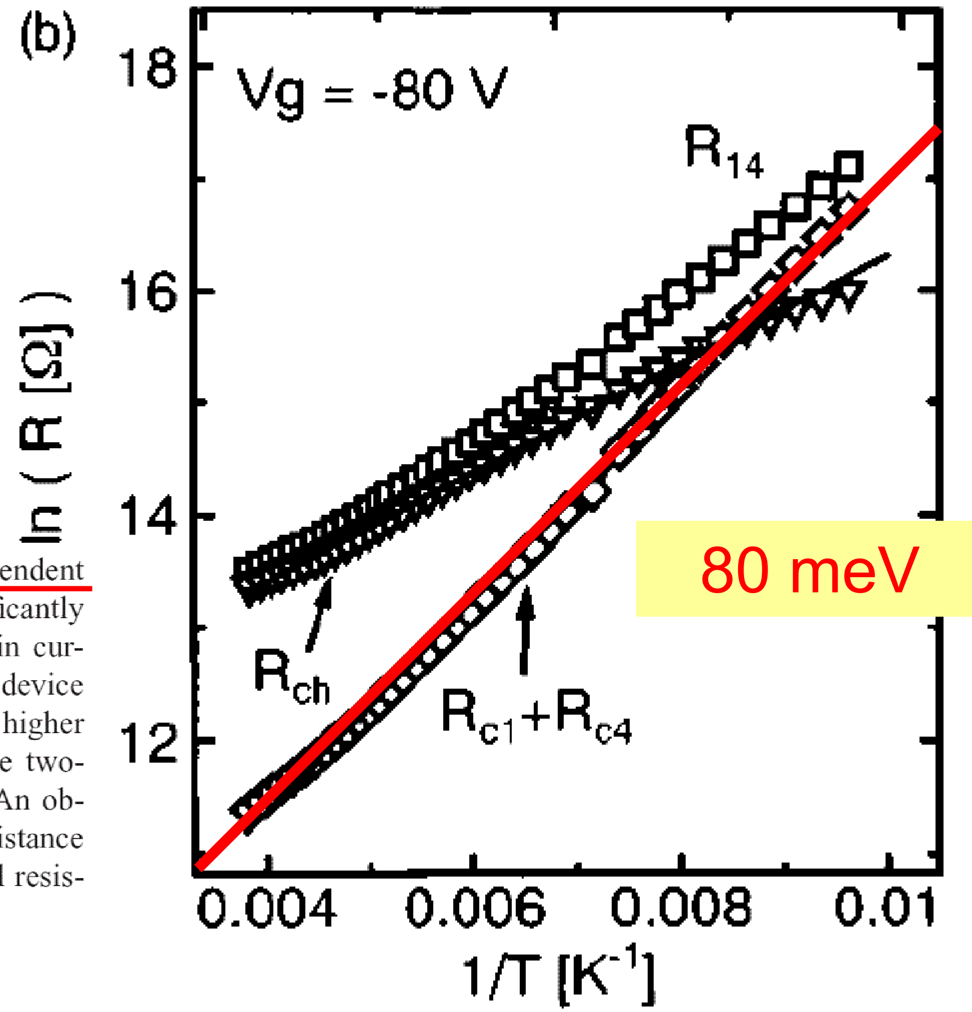
The channel has a potential ΔV, up to ~1 V even without bias

Bürgi Appl. Phys. Lett. 80, 2913 (2002)

Contact barrier height, Yagi *et al.*

There exists a residual barrier $q\phi_B$ of order 50-100 meV (depends on bias)

Pentacene TFT with gold electrodes



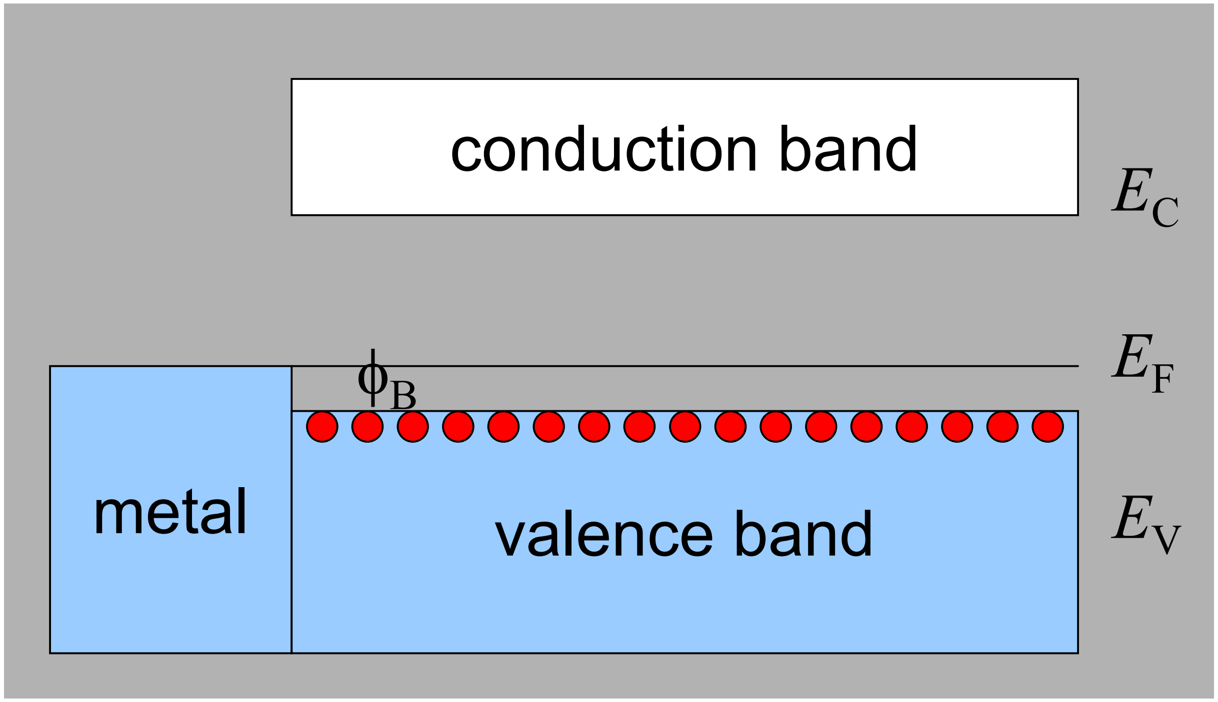
We obtained direct evidence of a gate-voltage-dependent contact resistance change: the induced charge significantly reduced contact resistance and increased source–drain current. Furthermore, the temperature dependence of the device clearly indicated that the contact resistance was much higher than the channel resistance and was dominated in the two-terminal total resistance of the device below 120 K. An observed activation energy of 80 meV for contact resistance was higher than that of 42 meV for pentacene channel resistance.

Yagi, Appl. Phys. Lett. **84**, 813(2004)

The Algarve TFT model

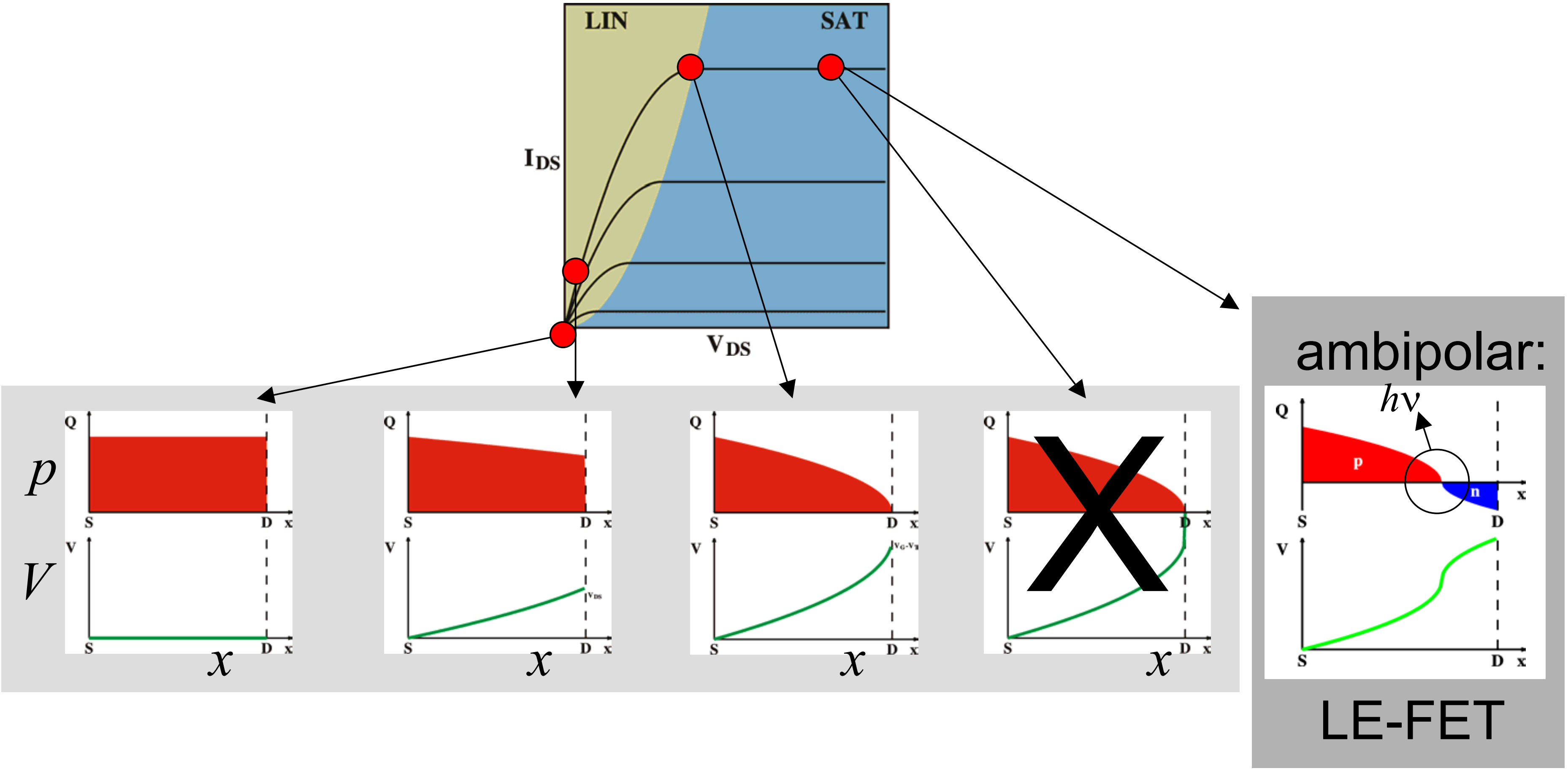
The **are** no "contact effects" !!

$$I \rightarrow p \rightarrow E_F - E_V \rightarrow \phi_B$$

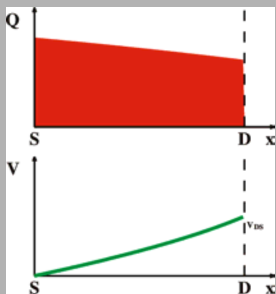


measurable current? ⟶ barrier is less than 100 meV!

The Algarve TFT model. Ambipolar



Ambipolar TFT (light emitting)

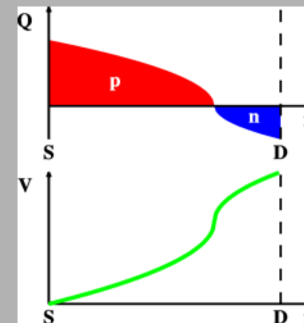


thin lines

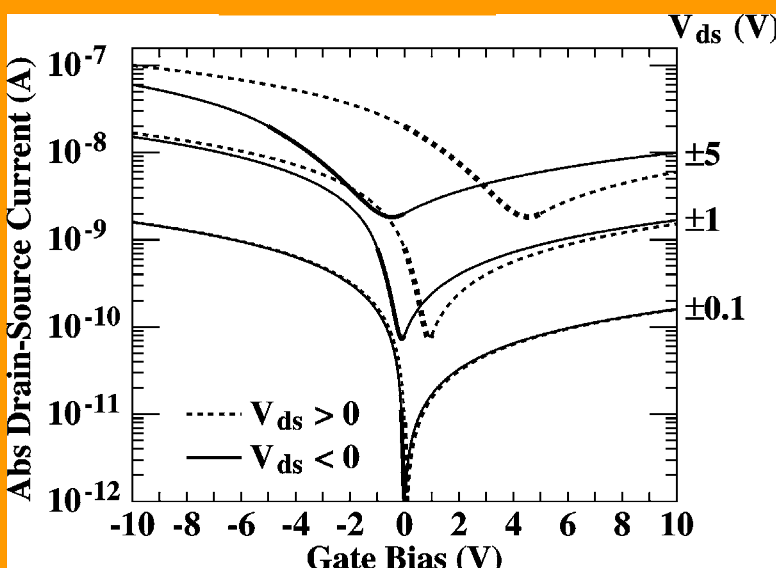
single injection
(large V_G)

thick lines

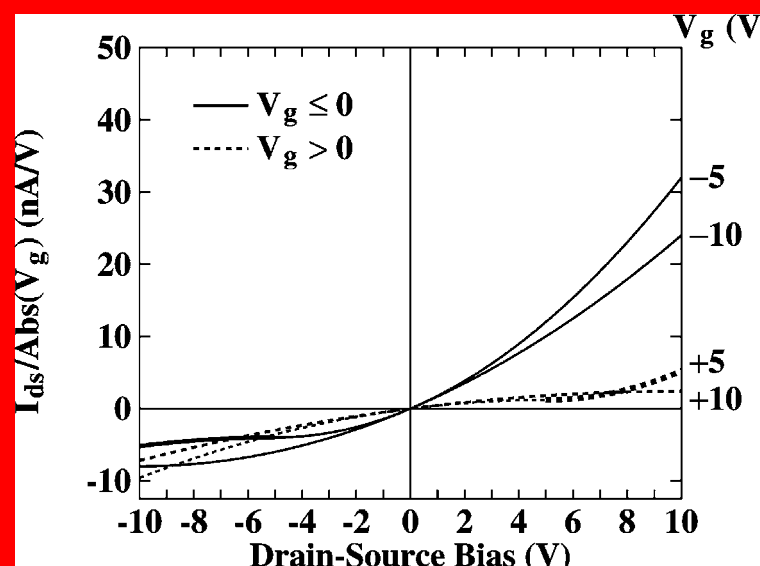
dual injection
(small V_G)

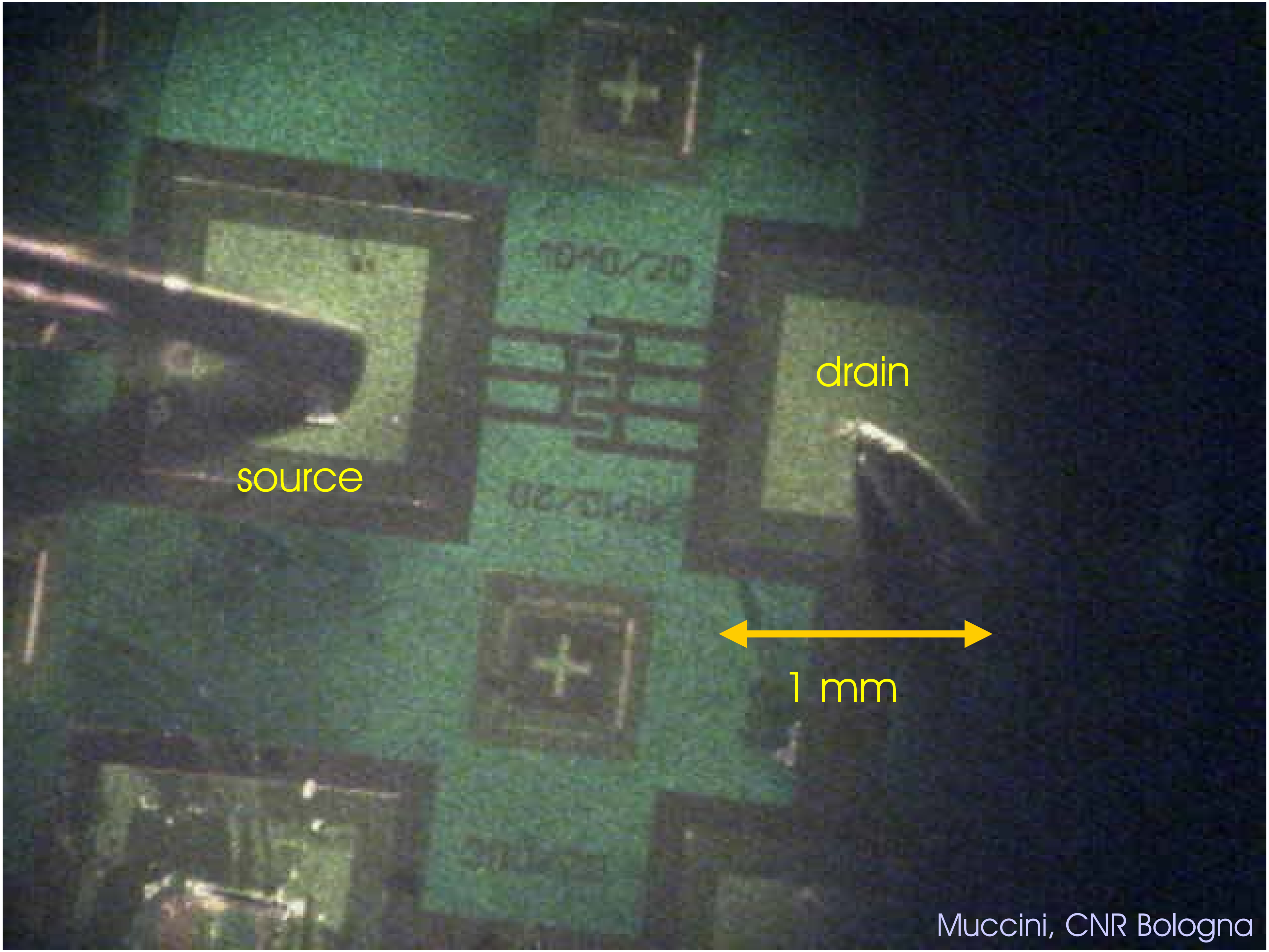


Transfer



IV




drain
source
1 mm
Muccini, CNR Bologna

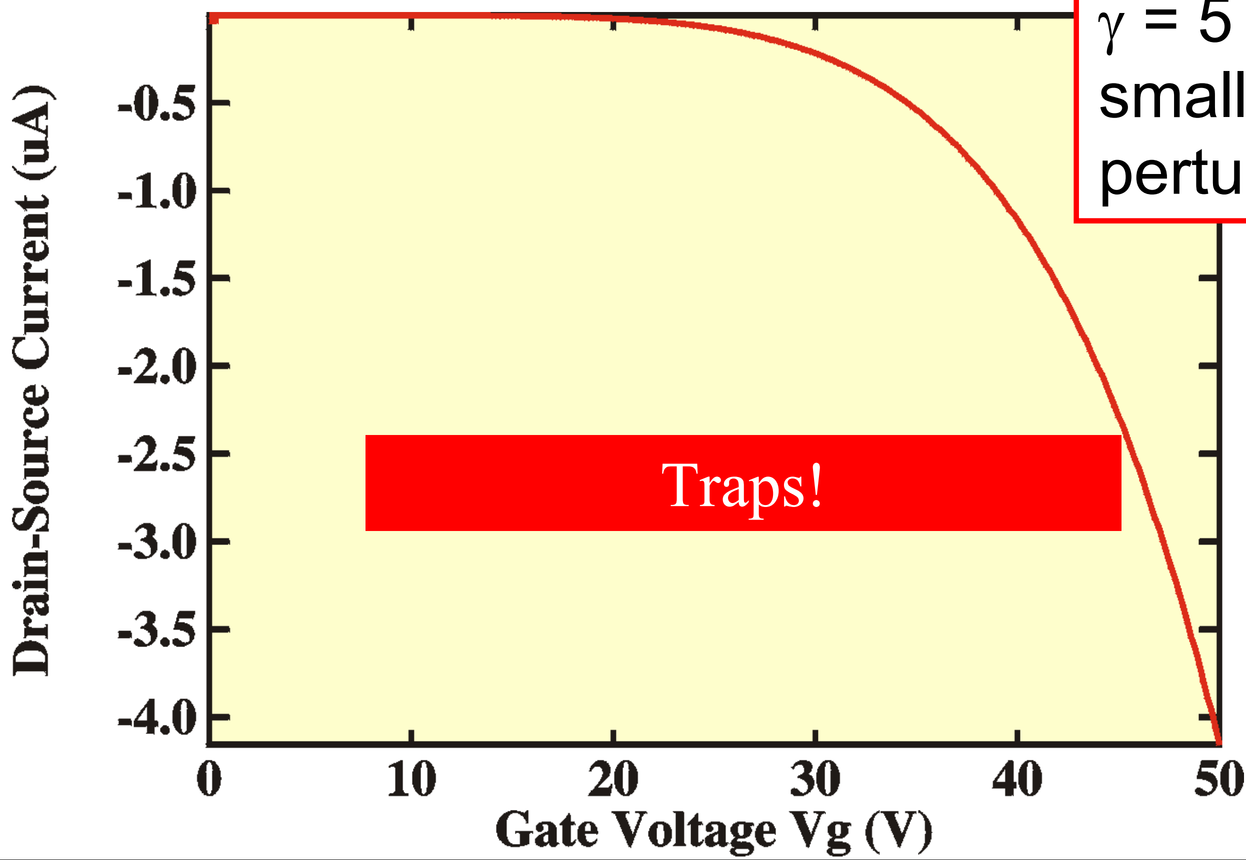
C. Santato *et al.*, Synth. Metals **146**, 329 (2004)

Non-linear transfer curves

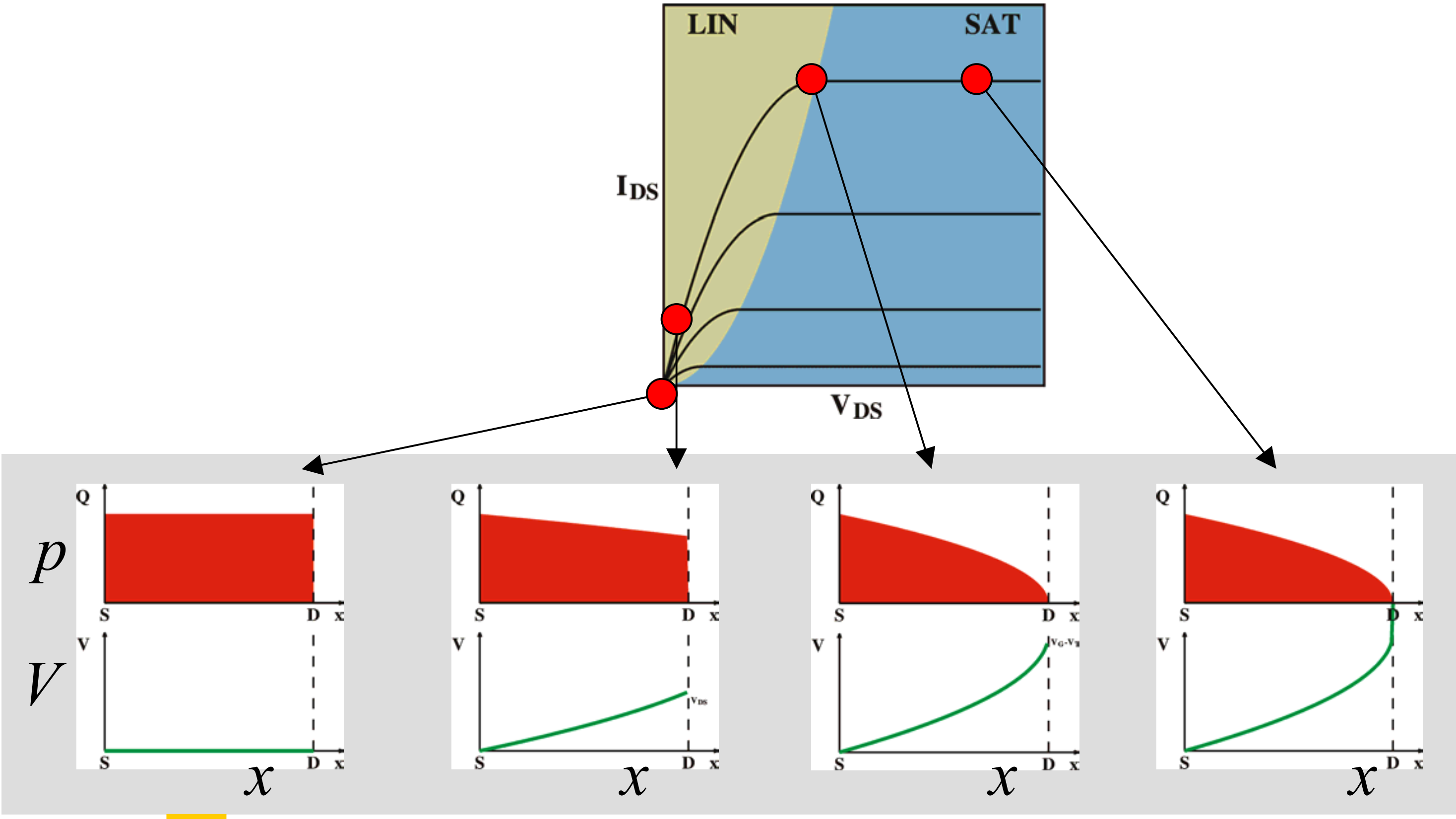
But, how to explain the non-linear transfer curves?

LIN: $I_{ds} = (W/L)\, C_{ox}\, \mu\, (V_g - V_t)^{1+\gamma}\, V_{ds}$

γ = 5 is not a small perturbation!



The Algarve TFT model. Traps



At small V_{ds},
homogeneous device

$$I_{ds}(V_g) \sim p(V_g)$$

Calculate p as a function of V_g will yield effective mobility μ_{FET}

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The Algarve TFT model. Traps

1: All charge is directly at interface

2: Charge can be free charge (h) or trapped charge (T^+)

3: Sum of them is depending on local bias ($p + N_T^+ \sim V_g - V(x)$)

4: Relative densities (can) depend on temperature and bias (Fermi-Dirac distribution $f(E)$)

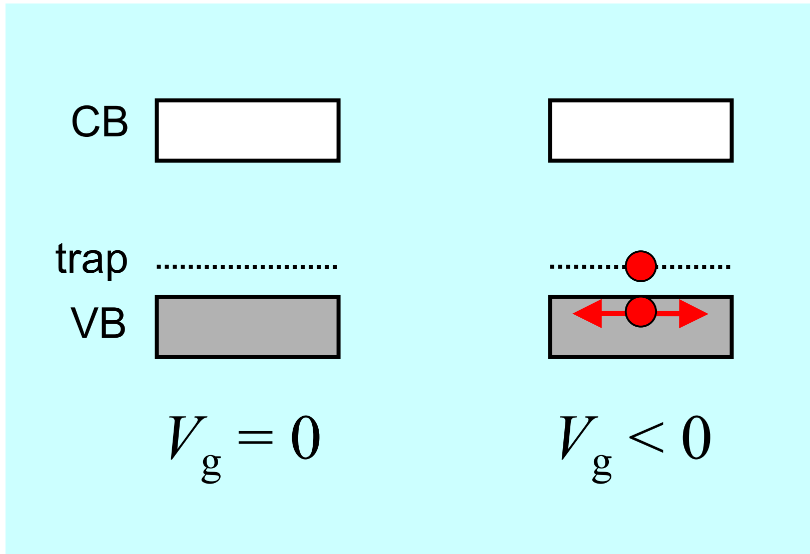
5: Thermal equilibrium reached instantaneously

6: Currents are proportional to free charge only ($I_{ds} \sim p$)

7: Mobility is defined via derivative of transfer curve in linear region ($\mu_{FET} \sim dI_{ds}/dV_g$)

No parameters. No N_A, V_T, V_{FB}, ε, E_g, etc.

Traps



$$p(V_g) + N_T^{+}(V_g) = -C_{ox}V_g/q$$

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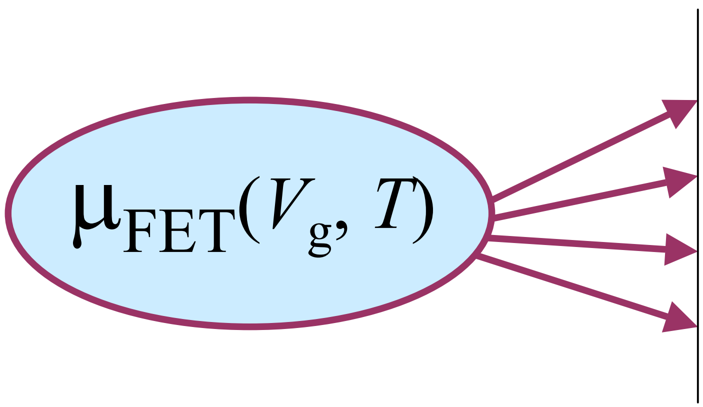
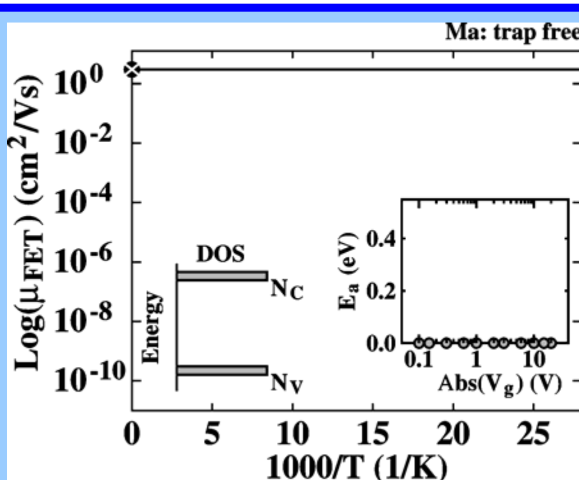
Traps

p and N_T^+ can depend on temperature and bias in a different way, thus the mobility can depend on temperature and bias

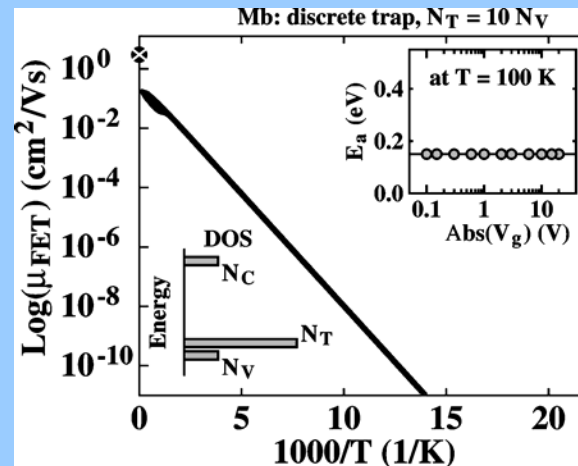


a: trap-free
b: abundant discrete trap
c: exponential trap
d: exponential trap and VB

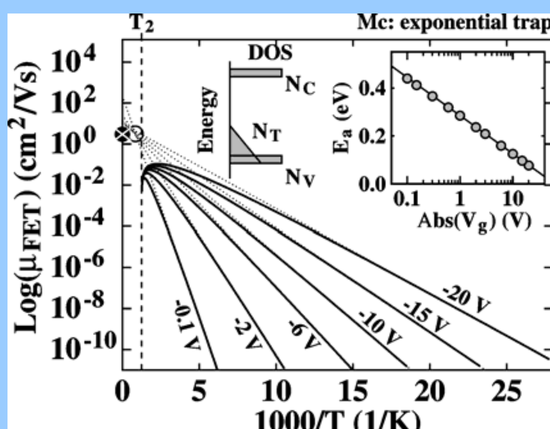
Traps, Arrhenius plots



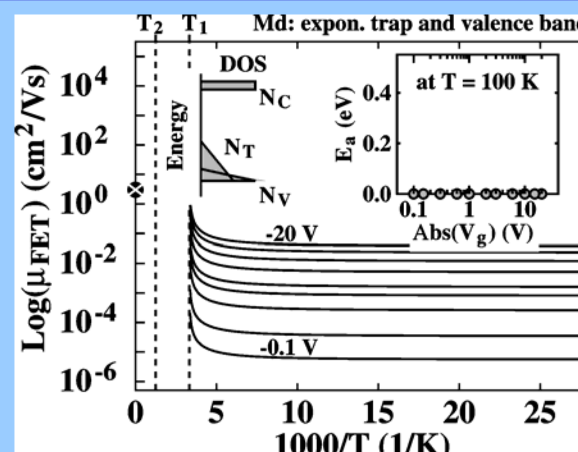
Trap free: "Standard MOS-FET"



Abundant trap: "Poole-Frenkel", $\mu = \mu(T)$



Expon. trap: Meyer-Neldel Rule

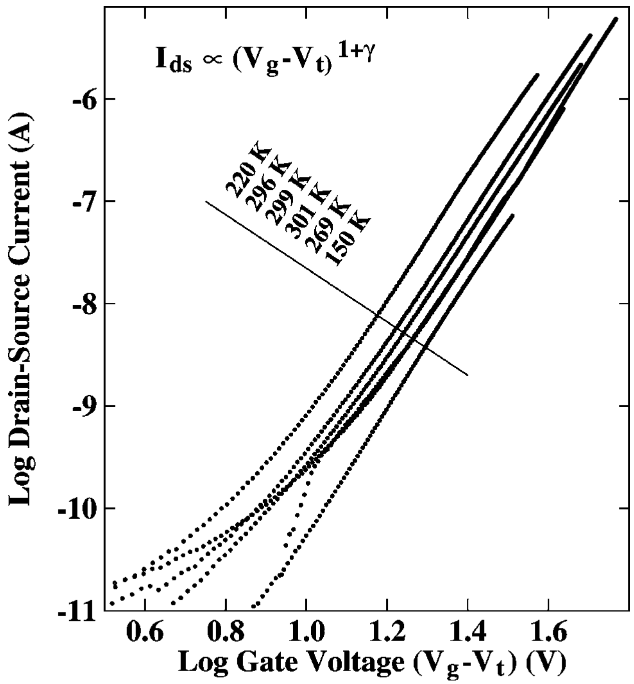


Expon. trap & VB: $\mu = \mu(V_g)$

Summary, Arrhenius plots

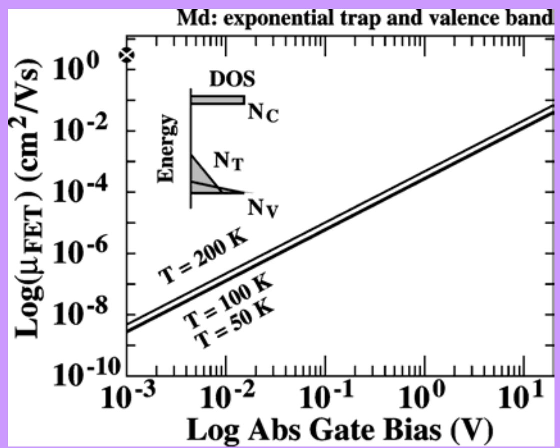
The only model that explains our experimental data

experiment:



Stallinga et al., JAP **96**, 5277 (2004)

theory:



Expon. trap & VB: $\mu = \mu(V_g)$

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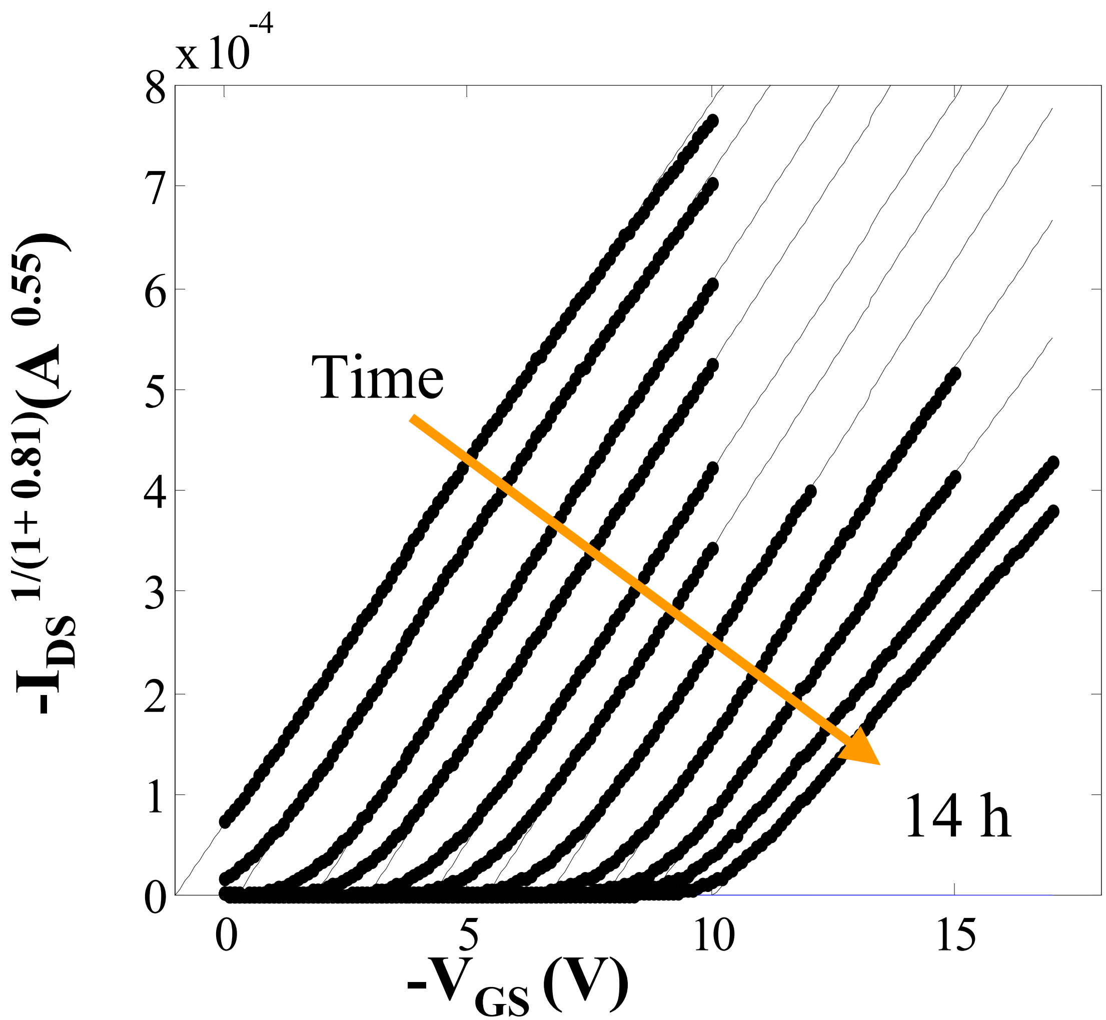
Stressing

If thermal equilibrium takes a long time to establish:



Conclusions 1

Algarve TFT model with traps

Is very, very simple

Can explain mobilities in wide range (10^{-8} – 10^{2} cm^2/Vs) …
… without change in conduction mechanism.

Can explain Vg-bias-dependent mobility (!)

Can explain non-linearities in IV curves

Can explain temperature-dependent mobility

Can explain bias-and-temperature-dependent mobility (Meyer-Neldel Rule)

Can explain contact effects

Can explain ambipolar devices

Can explain stressing effects

Can explain admittance spectra

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Conclusions 2

Algarve TFT model with traps

Because of it’s simplicity, measurements cannot elucidate conduction mechanism

only requirement: conductive states and immobile states

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Conclusions

10Q4ur@+¥

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projecto POCTI/FAT/47952/2002

FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA E DO ENSINO SUPERIOR Portugal

Related publications: Organic Electronics, Synthetic Metals (2006/2007)