Electrical characterization of organic (amorphous) materials

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E-MRS Warszawa
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Symp. F 12.1

Abstract (for finding this doc on Google)

Electrical characterization of organic (amorphous) electronic materials

Organic electronic materials, or amorphous electronic materials in general, have relatively low conductivity and this limits their application to the low-frequency electronics market. To describe electronic conduction in these materials it is common to use Percolation or (Variable Range) Hopping Theory (the two being equivalent). This is an inheritance from the earlier organic materials that were invariably insulators, where conduction was a perturbation -- movement of charge was a rare event. It will be argued here that for electronic materials, instead, it is better to revert to classical semiconductor theories, like Band Theory[1]. If we include a large density of traps in the energy system, all observed phenomena are easily explained. This includes 1) Strong temperature dependent charge-carrier mobility, 2) Field-dependent mobility, 3) Anomalous transient behavior. Moreover, it is consistent with observations in many types of devices, ranging from two-terminal devices such as diodes to three-terminal devices such as thin-film transistors[2].

[1] P. Stallinga, 'Electronic Transport in Organic Materials: Comparison of Band Theory with Percolation/(Variable Range) Hopping Theory". Adv. Mat. 23, 3356 (2011).
[2] P. Stallinga, "Electrical Characterization of Organic Electronic Materials and Devices", Wiley (2009), ISBN: 978-0470750094.

Outline

Introduction to organic electronics

The conduction model

Amorphous materials

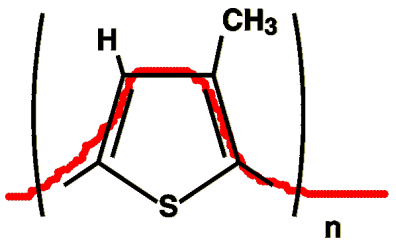
Theories:
- (Variable Range) Hopping
- Percolation Theory
- (Good old) Band Theory

Devices/measurements
- Thin Film Transistors
- (Anomalous) Transients (DLTS, etc.)
- Temperature and bias dependent mobility

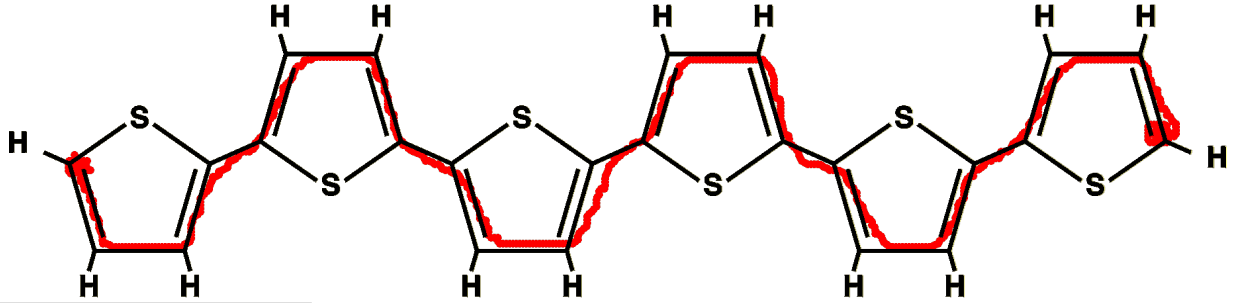
Organic Electronic Materials. 1/2-cons.

Conjugated organics have paths with alternating single and double bonds

Conjugation:
Delocalization and opening of **energy gap** makes them semiconductors



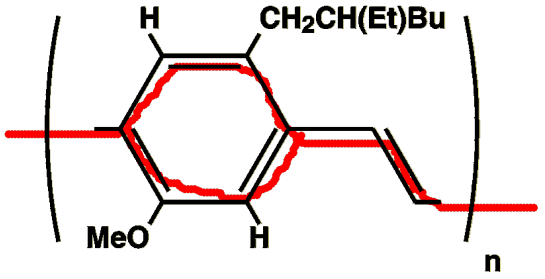
PMeT



αT6

Oligomers (small molecules)
Good for FETs
(High mob. because of better crystallinity)

Polymers
Good for LEDs
(Because of fewer impurities)

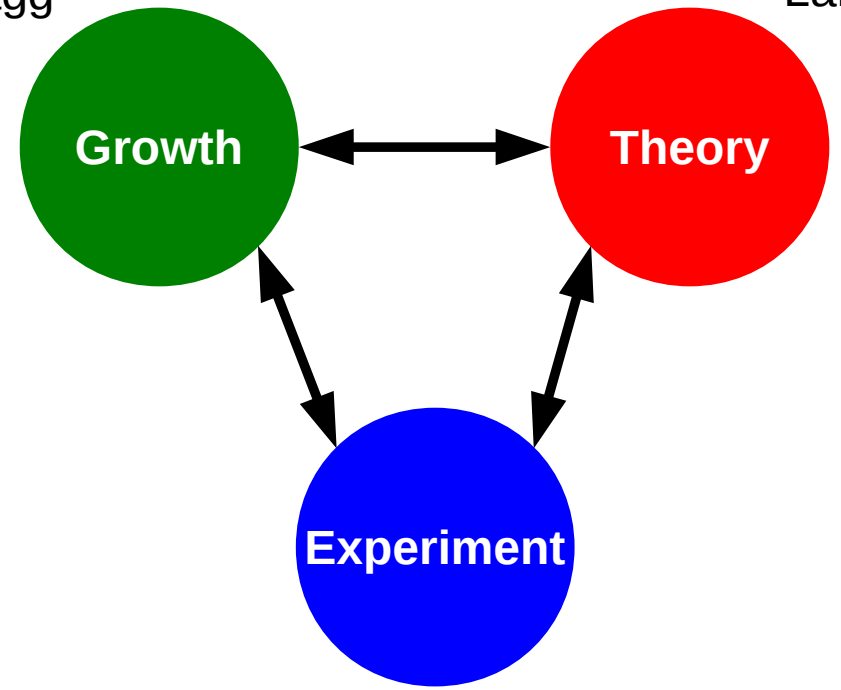


MEH-PPV

The solid-state **physics** tripartition

Making excellent samples
Float zone, Czochralski, etc.
Bragg

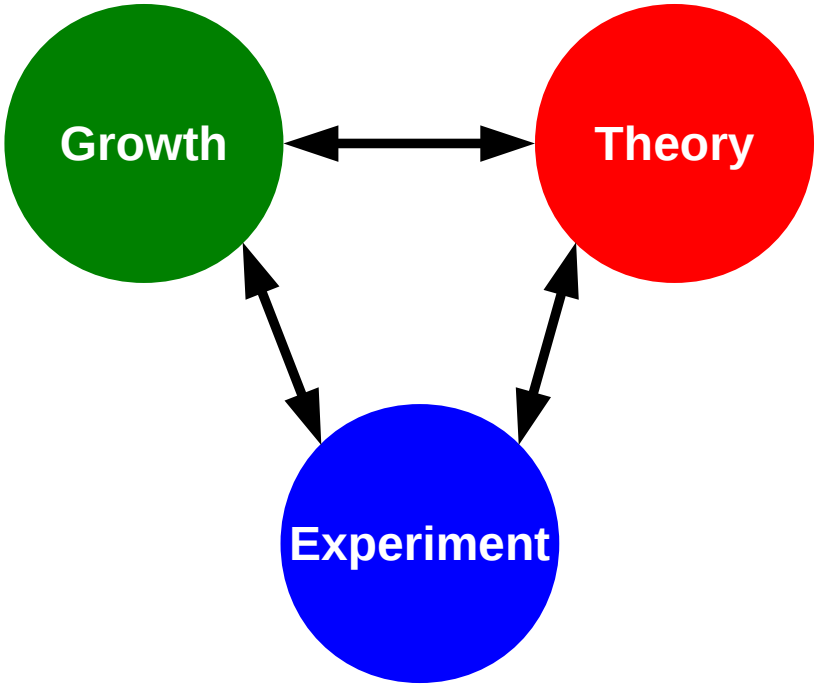
Developing excellent theories
Drude, Hartree-Fock, Bloch,
Landau



Doing excellent measurements
DLTS, Raman, FTIR, PL, AFM,
STM, ….

Keywords: predictability & reproducibility

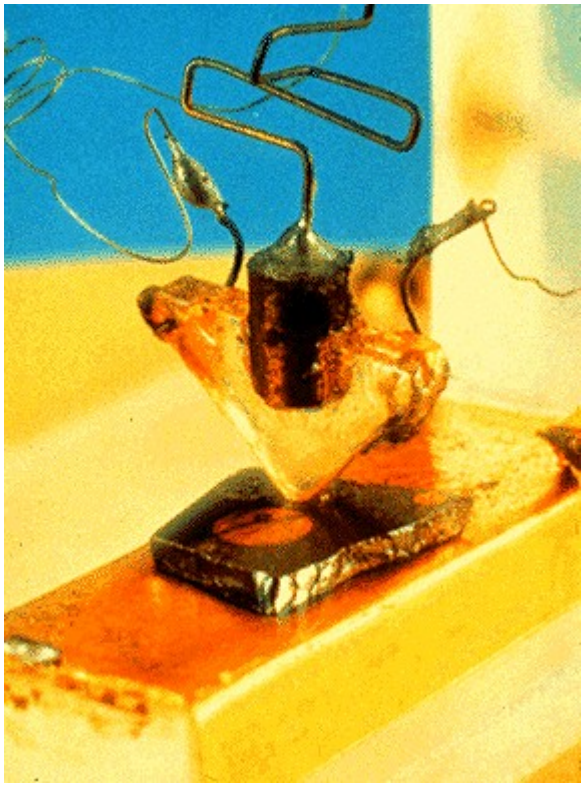
The solid-state physics tripartition



Initially 1/2-cons were ignored. “Shitty materials”

Later: Exactly this dependence on impurities makes them extremely powerful

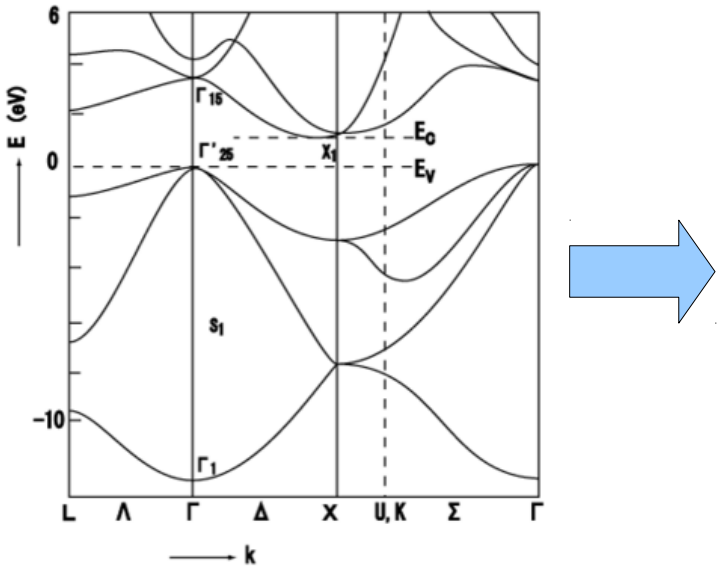
Semiconductor industry. Brought to you by physics!

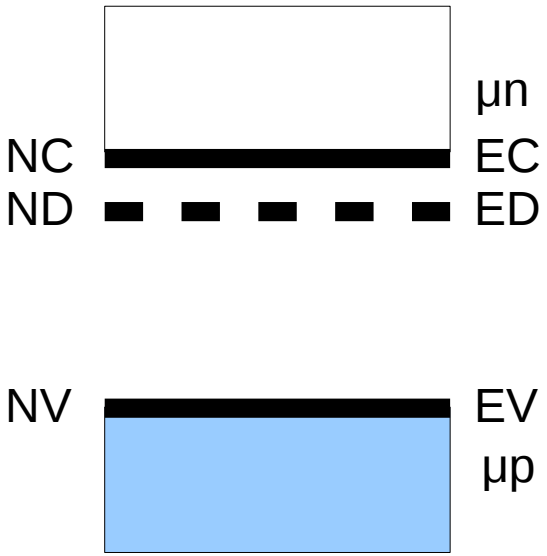


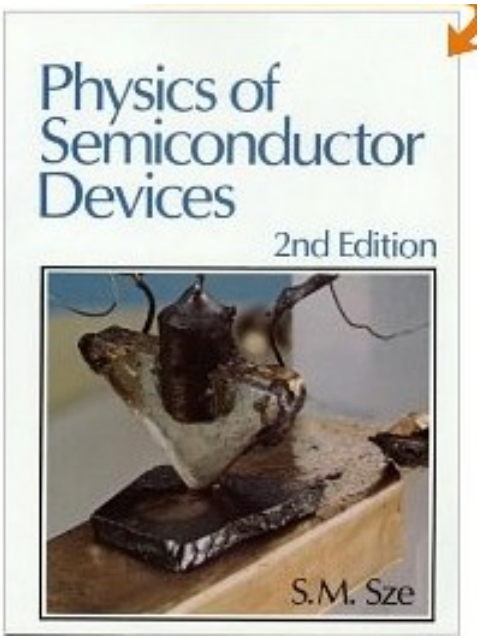
Semiconductor (device) theory

(For electronic **device physics**)
The entire band structure can **effectively** be summarized as

- NV full levels at EV
- NC levels at EC
- Effective mass (and μ)
- Donor and acceptor levels



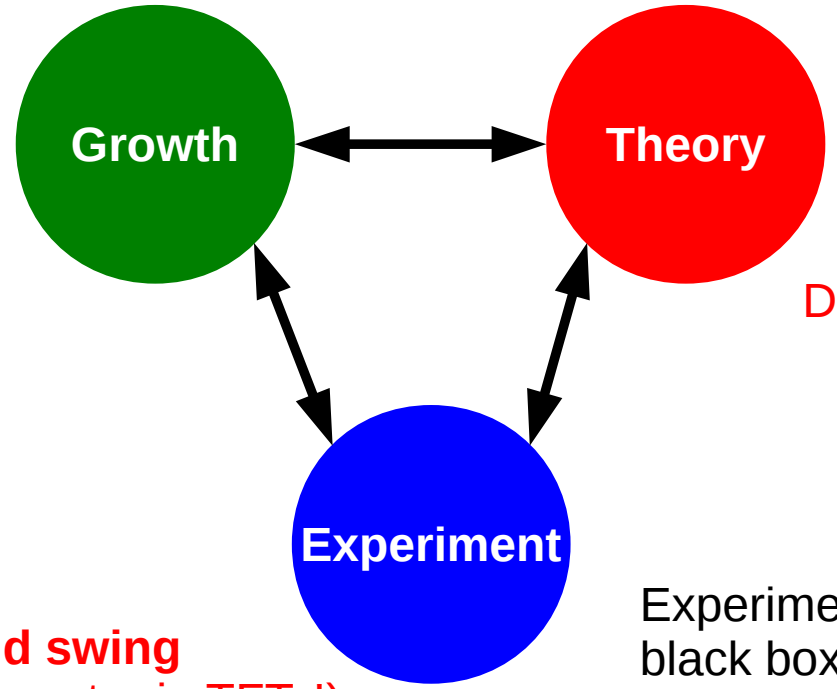




Sze: 800 pages of approximation
good enough to describe **all** electronic ½-con devices

The **chemistry** tripartition

Most effort spent here
Synthesis & Growth
(Very complicated!
Much worse than
non-organics)
Nano-structures!



Using theories of
non-conductive
materials (e.g. Hopping)

Doping is not relevant (yet)

Ex.: Sub-threshold swing
(which is not a parameter in TFTs!)

Experimental equipment is
black boxes with buttons

Chemistry dominates organic “plastic” material research
Plastics traditionally non-conductive

\+

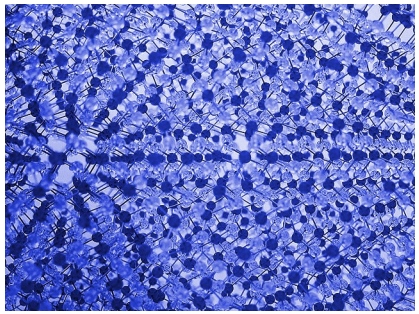
= Use of non-conduction models (also for conductive materials!)

Conduction Mechanism Theories

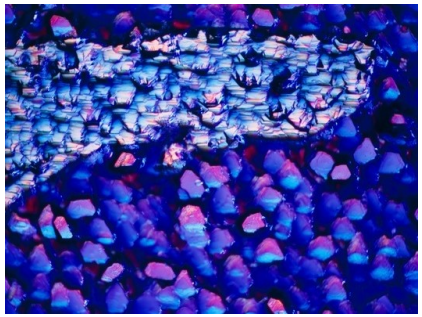
Amorphous ('disordered') materials are mostly modeled by **Variable Range Hopping / Percolation Theory** (Evros, Shklovskii, Mott, 1950's)

Crystalline materials are invariably modeled by **Band Theory**

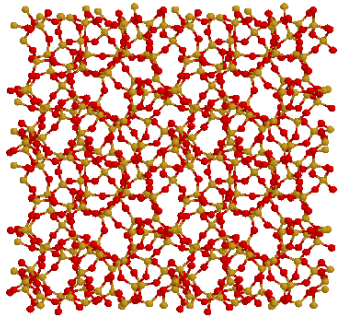
Why? Are these materials so different?



Crystalline



Poly-crystalline

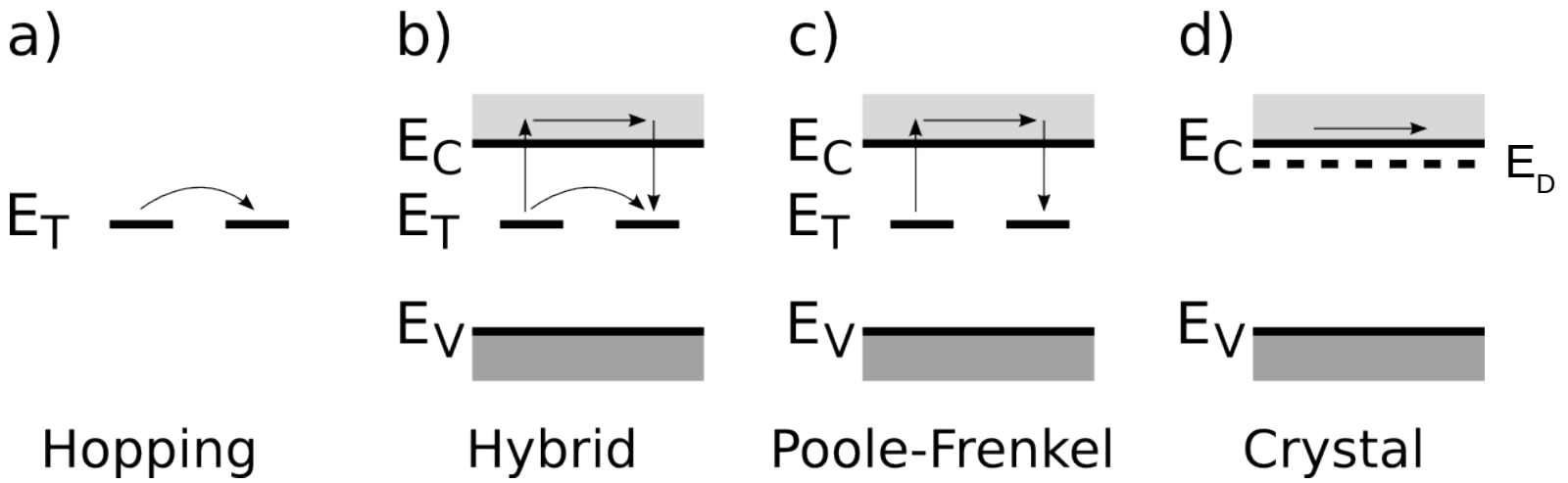


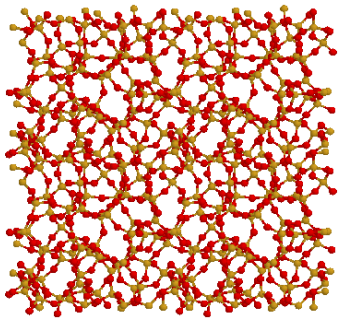
Amorphous

Band Theory

Percolation Theory / (Variable Range) Hopping

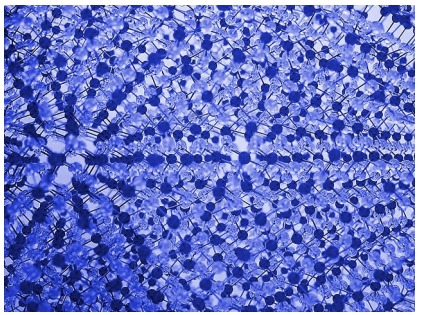
Conduction Mechanisms





Amorphous

<--- ? --->

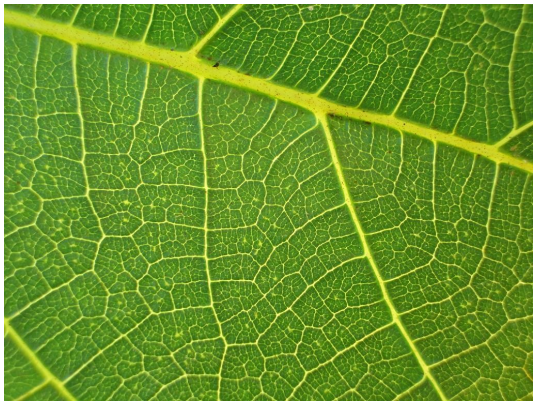


Crystalline

Both crystalline and amorphous materials have covalent bonds.
In crystals they give rise to band structure ....

Crystals were only used because they are easier to produce reproducibly.
Crystal theories apply to non-crystals too! (Ioffe, Regel, and Gubanov)

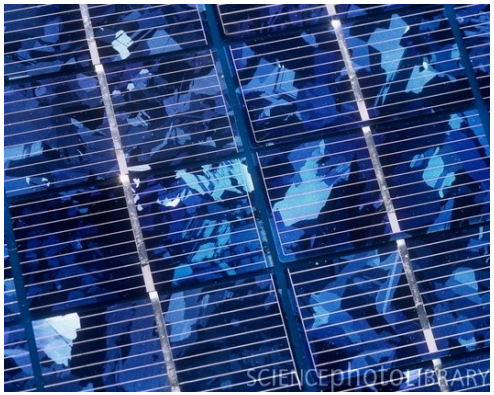
Crystal schmystal



By far the most materials in nature are amorphous

Crystalline materials: Scientists not describing nature,
but scientists creating a new universe to study
Get out of the sandbox and start studying nature!

Crystalline materials are not going to save the planet
(from the Global Warming threat [if it is not a scam*])



Poly-crystalline silicon solar panel:
30 years to return energy invested (no electronics can stand 30 years outside in the weather!)
There has not yet been renewable energies (except hydro) that saved oil!

*: Visit www.stallinga.org/Climate where the scam is exposed

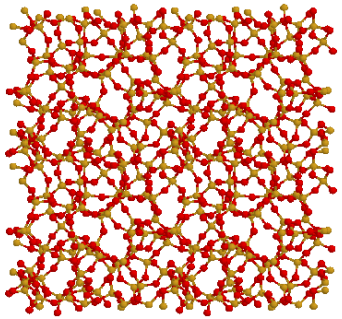
Non crystals

"The fact that devices were invented and theories developed for crystals, does not mean that the theories are valid **only** for crystals"

- (P.S. 2011)

"A periodic electric field of the lattice is not essential for the occurrence of typical semiconducting properties and the band model may be applied also in the case in which there is a loss of periodicity of the lattice"

- Ioffe, Regel and Gubanov [1]



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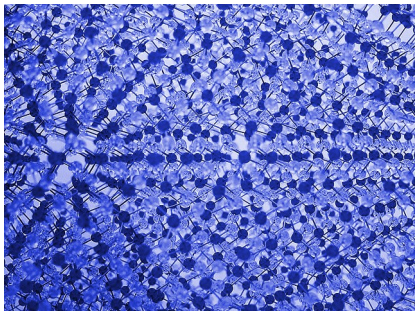


Amorphous

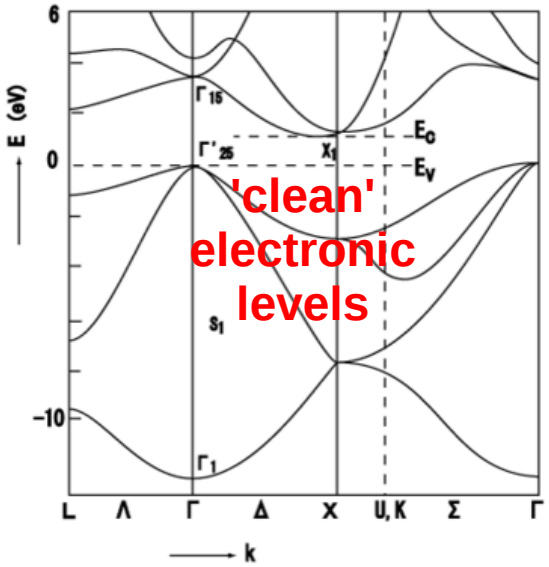
Crystalline

Both crystalline and amorphous materials have covalent bonds.
In crystals they give rise to **band structure** .... so … also **in amorphous materials**!

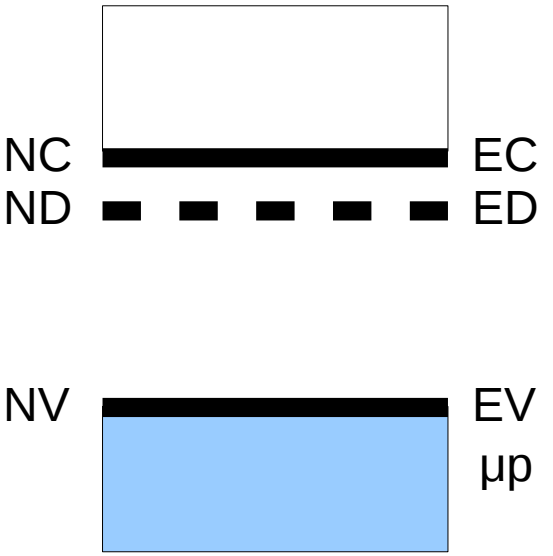
[1] Caserta, Phys. Stat. Sol. **35**, 237 (1969)

Band Theory for Amorphous materials

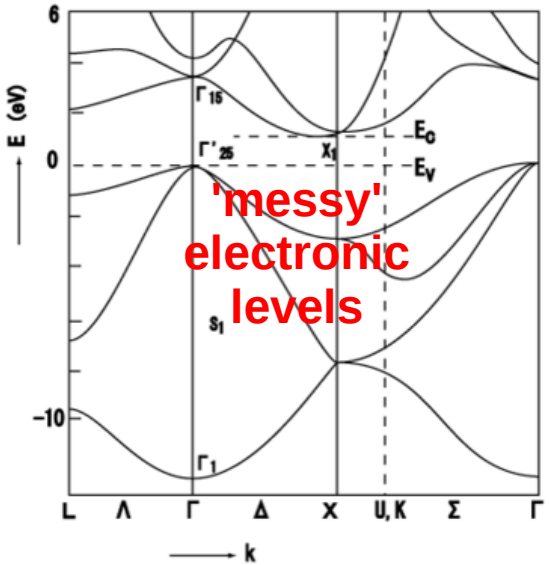
Crystal:



'clean' electronic levels



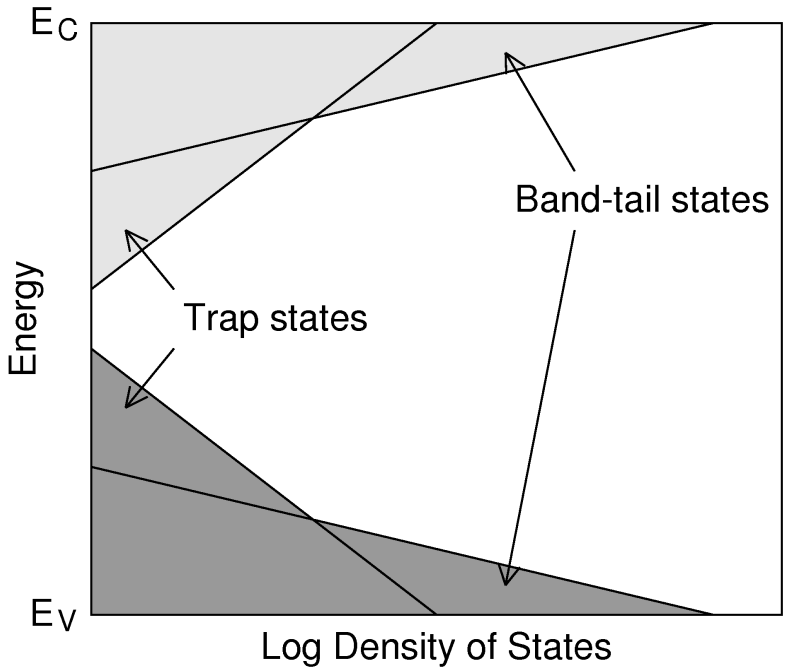
Amorphous:



'messy' electronic levels

?

Amorphous Band Diagram

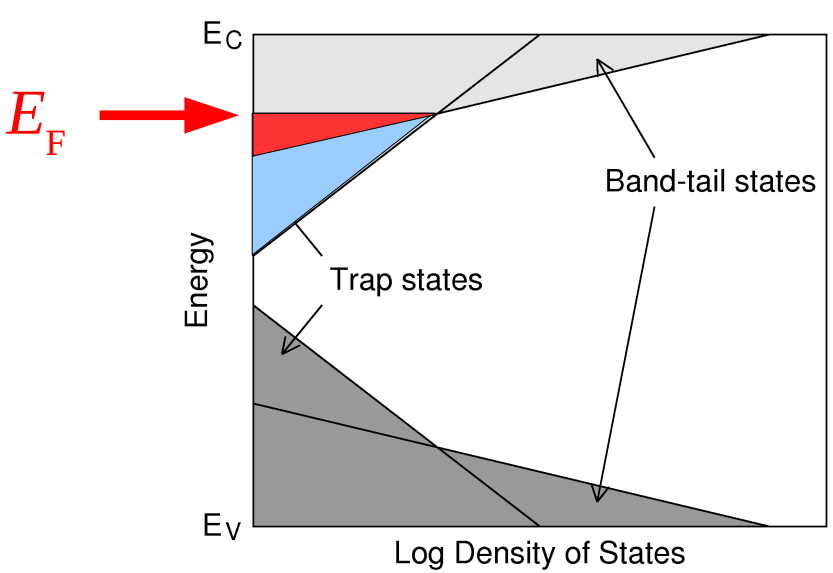


Energy diagram consists of
- conductive (delocalized) band states
- (localized) trap states

Successfully used to describe amorphous silicon thin-film transistors [1]

[1] Shur & Hack, J. Appl. Phys. **55**, 3831 (1984)

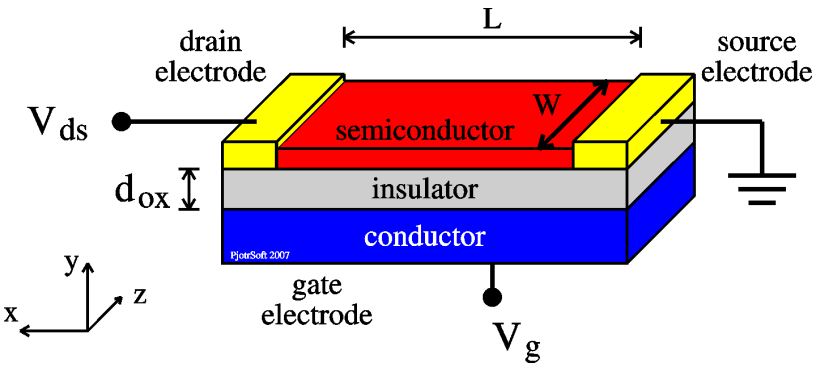
Amorphous TFT



free

trapped

} ρ: Total charge induced in channel by gate bias



Applied to organic thin-film transistors "The Algarve TFT Model" [1]

trapped + free

1) $\rho = \rho_T + n$

2) $\rho = - V_g C_{ox}$

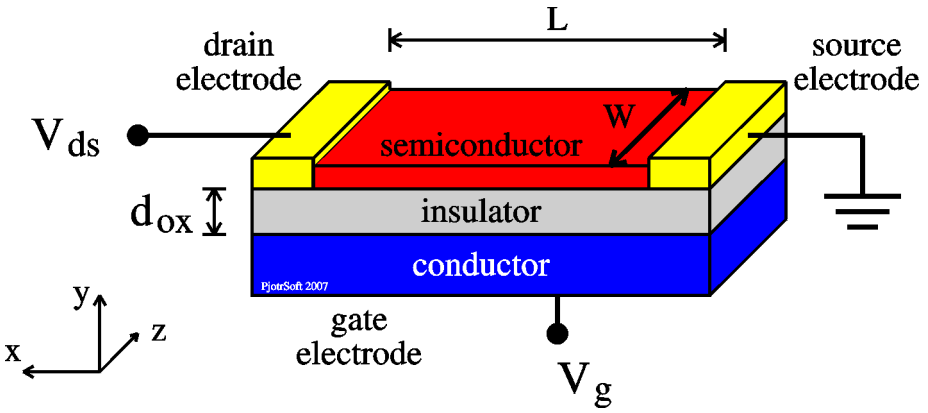
3) $I = - n \mu dV(x)/dx$

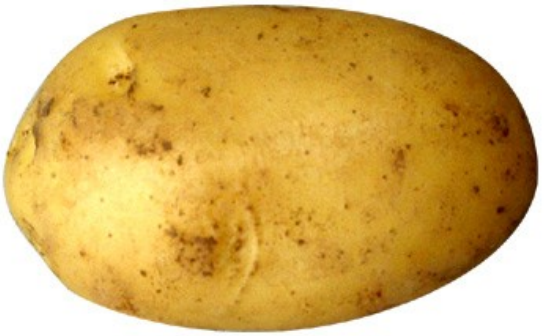
$\Rightarrow$ $I_{ds} \sim V_g^{\gamma}$

Si: $\gamma = 1$
Organics: can be **7**
(not a small perturbation!)

[1] Stallinga, "Electrical Characterization of Organic Electronic materials and Devices" (Wiley 2009)

TFT controversy





There are **no contact effects** [1]
People often imagine 'Schottky barriers' at the metal – ½-con interface
  This does not make sense
People often imagine resistors at the contacts
  This does not make sense
All observed 'anomalies' are caused by traps

Transistor (accumulation TFT) can be made of **any material**. Not limited to ½ conductors.
Can be a potato.
We made a **metal** transistor [2].

[1] Stallinga et al, Org. Electr. **8**, 300 (2007)
[2] Stallinga et al. Adv. Mat. **20** (2008)

Poole-Frenkel

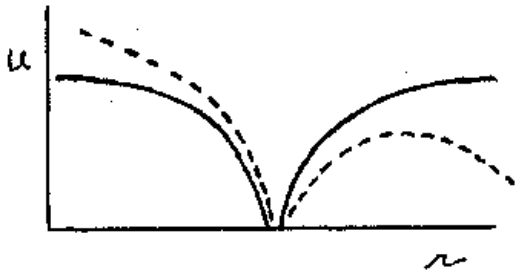


FIG. 1. Potential energy as a function of distance from the positive ion. Full line, without an external field, dotted line in the presence of the field.

full line represents the normal potential energy of the electron as a function of the distance from the positive ion while the dotted line represents the same quantity in the presence of the field. The height of the potential barrier is lowered in the field by the amount

$$\Delta U = eEr_0 + e^2/\epsilon r_0,$$

where r_0, the distance to the maximum from the ion, is given by $e^2/\epsilon r_0^2 = eE$. Thus $r_0 = (e/\epsilon E)^{\frac{1}{2}}$ and

$$\Delta U = 2eEr_0 = 2e(eE/\epsilon)^{\frac{1}{2}}.$$

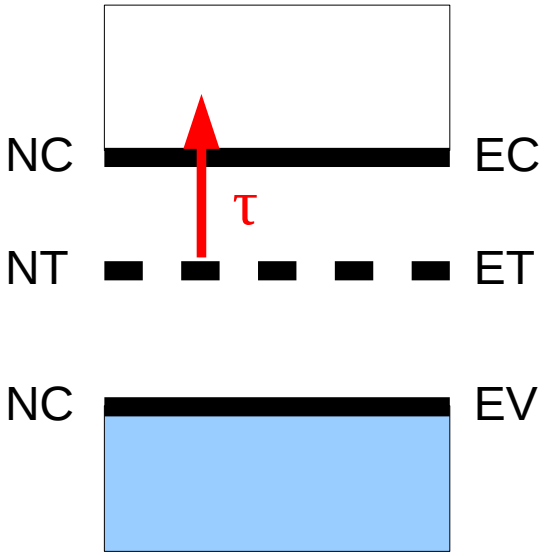
Trap 'depth' depends on electric field [1]:

$$\mu = \mu_0 \exp\left(-\frac{E_A}{kT}\right)$$

$$E_A = E_T - \sqrt{\frac{qE}{\pi\epsilon}}$$

[1] Frenkel, Phys. Rev. **54**, 647 (1938)

Transients



Crystalline Silicon:

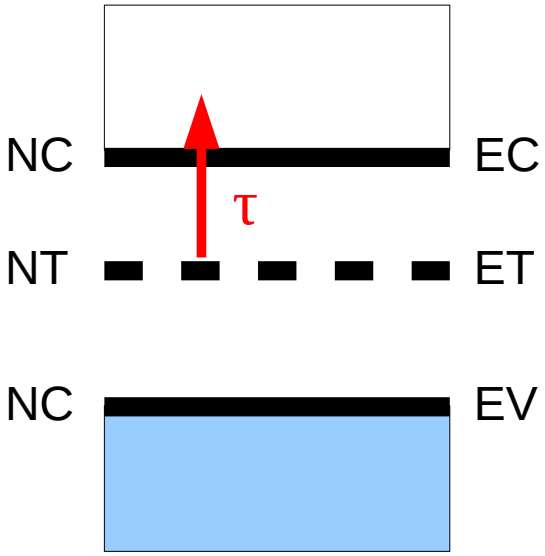
- Traps scarce
- Traps discrete
- Filling immediate
- Emptying thermally activated

$$\tau = \exp\left(-\frac{E_A}{kT}\right)$$

$$C(t) = \Delta C \exp\left(-\frac{t}{\tau}\right) + C_0$$

DLTS: measure τ as a function of T and you get E_A

Transients



Amorphous materials:

- Traps abundant
- Traps distributed in energy
- Filling thermally activated
- Emptying thermally activated

$$\tau = \exp\left(-\frac{E_A}{kT}\right)$$

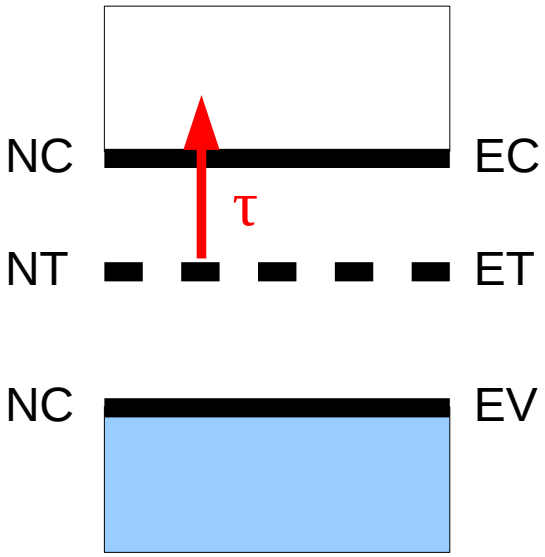
$$C(t) = \Delta C \exp\left(-\frac{t}{\tau}\right) + C_0$$

Abundant level: DLTS: ***C*(*t*) is not exponential**. C^2 is!

Distributed E_A and τ: **transient is not exponential**. DLTS will be a mess. LT-DLTS will be a mess

These scientists from the crystalline era had an easy life indeed!

Transients



Distributed E_A and τ: **transient is not exponential**.
DLTS will be a mess. LT-DLTS will be a mess.
Transient will be convolution of transients [1] …
… resulting **theoretically** in a **power law**, for example

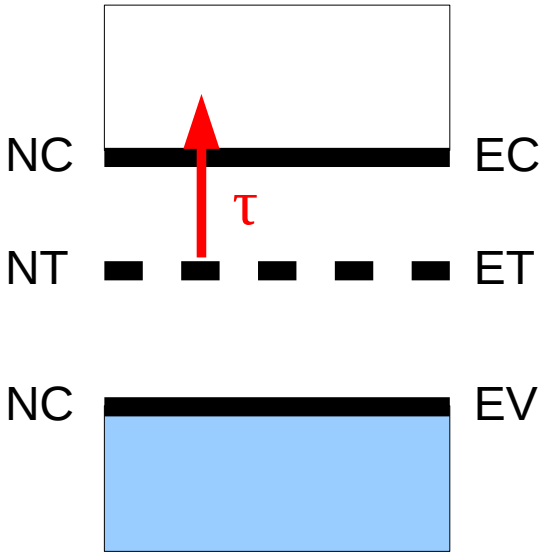
$$I_{ds}(t) = t^{-\alpha}$$

In practice, **empirically**, transients are more **stretched-exponential** [2]. Without, after nearly two centuries, no theoretical justification:

$$I_{ds}(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]$$

[1] Newman, Contemp. Phys. **46**, 323 (2005)
[2] R.Kohlrausch Ann. Phys. Chem. **72**, 353 (**1847**)

Transients



"In any finite critical system, it is well known that the power-law description must give way to another regime" [1]

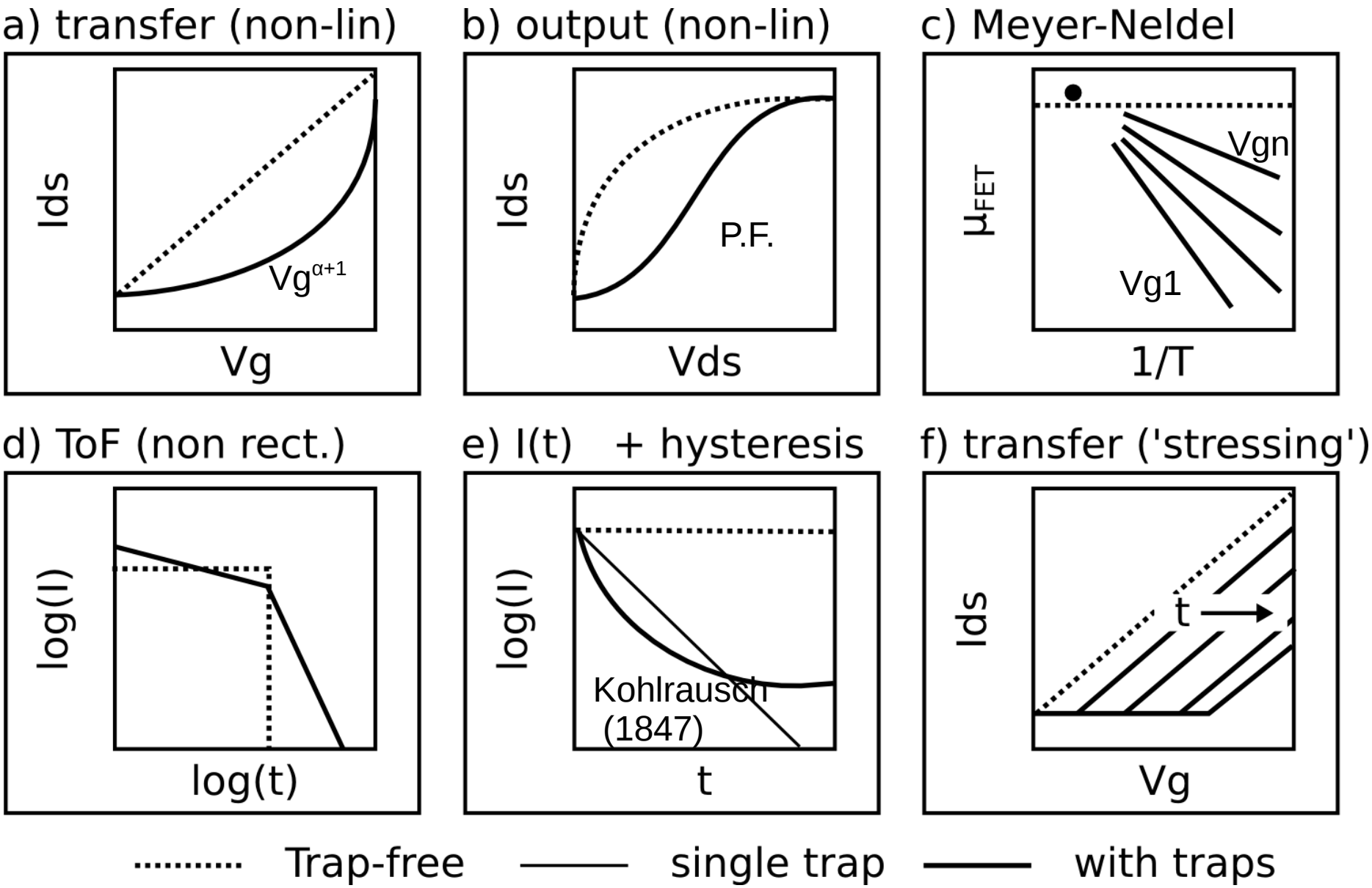
Any (finite, 'alpha-stable') distribution of relaxation times will result in a stretched exponential [2]

$$I_{ds}(t) = t^{-\alpha}$$ Theory

$$I_{ds}(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]$$ Experiment

[1] Laherrère and Sornette, Eur. Phys. J B **2**, 525 (1998)
[2] Trzmiel, J. Appl. Phys. **103**, 114902 (2008)

Effects of abundant traps (amorphous)



Summary

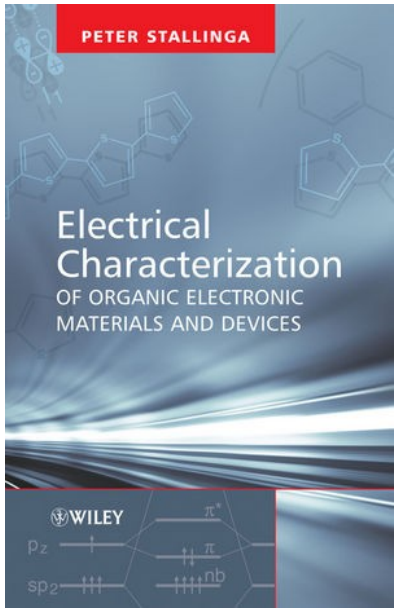
Organic (amorphous) electronic do have future outside sandbox

Percolation / Variable Range Hopping compared with Band Theory
→ Band Theory wins (with traps)

Organic Electronic Devices Characterization
- Thin Film Transistor
- Transients
Very complex! Not a black box plug-and-play measurement

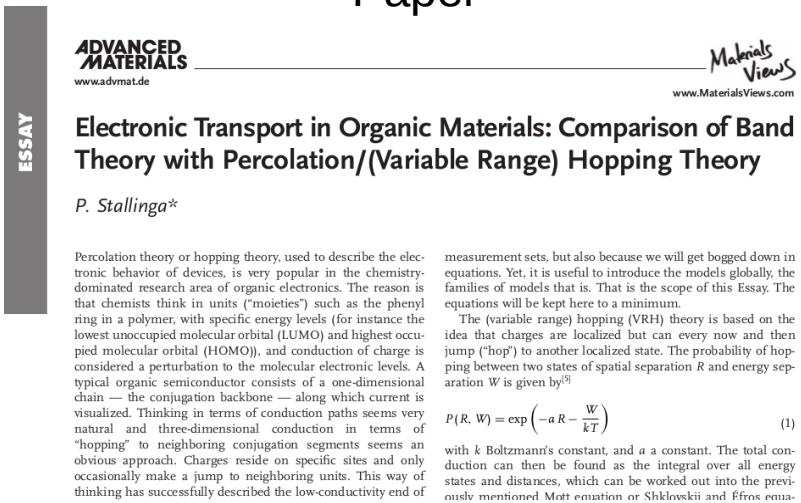
Advertisement

Book



Stallinga, “Electrical Characterization of Organic Electronic Materials and Devices” (Wiley 2009)

Paper



ESSAY

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www.advmat.de

Materials Views
www.MaterialsViews.com

Electronic Transport in Organic Materials: Comparison of Band Theory with Percolation/(Variable Range) Hopping Theory

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Percolation theory or hopping theory, used to describe the electronic behavior of devices, is very popular in the chemistry-dominated research area of organic electronics. The reason is that chemists think in units (“moieties”) such as the phenyl ring in a polymer, with specific energy levels (for instance the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO)), and conduction of charge is considered a perturbation to the molecular electronic levels. A typical organic semiconductor consists of a one-dimensional chain — the conjugation backbone — along which current is visualized. Thinking in terms of conduction paths seems very natural and three-dimensional conduction in terms of “hopping” to neighboring conjugation segments seems an obvious approach. Charges reside on specific sites and only occasionally make a jump to neighboring units. This way of thinking has successfully described the low-conductivity end of measurement sets, but also because we will get bogged down in equations. Yet, it is useful to introduce the models globally, the families of models that is. That is the scope of this Essay. The equations will be kept here to a minimum.

The (variable range) hopping (VRH) theory is based on the idea that charges are localized but can every now and then jump (“hop”) to another localized state. The probability of hopping between two states of spatial separation R and energy separation W is given by[5]

$$P(R, W) = \exp\left(-a\,R - \frac{W}{kT}\right) \quad (1)$$

with k Boltzmann’s constant, and a a constant. The total conduction can then be found as the integral over all energy states and distances, which can be worked out into the previously mentioned Mott equation or Shklovskii and Éfros equa-

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