Electrical characterization of organic (amorphous) materials Peter Stallinga Universidade do Algarve / Center for Electronics Optoelectronics and Telecommunications

ERRODADE DO

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Outline

- Introduction to organic electronics
- Today's Special (polemic): 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





Nano-tech, schmanotech. Centi-tech!



"There's a lot of room at the bottom"

- Good, make room at the top!

Fetish for nano-tech (*), while there is still a lot is to be understood and gained at the centi-tech scale.

The devices from the 20th century are better understood than those of the 19th century! I will cite today a paper of 1847, STILL NOT SOLVED.

Amorphous (or poly-crystalline) materials are not 'sexy'.

(*) Guaranteed winning project title 2011: "Self-assembled nano-particle bio-materials for medicine and renewable energies applications"



Organic Electronic Materials

Conjugated organics have paths with alternating single and double bonds





Conjugation: Delocalization and opening of energy gap makes them semiconductors





Organic Electronic Materials





Conduction Mechanism Theories

Amorphous ('disordered') materials are mostly modeled by **Variable Range Hopping / Percolation Theory** (1957)

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

Why? Are these materials so different?





Variable Range Hopping

Energy diagram consists of only localized states

Probability to jump to other localized state:

$$P(R,W) = \exp(-\alpha R - \frac{W}{kT})$$

- *R* is distance in **space** (far away is less likely)
- *W* is **energy** difference (high energy is less likely)

Can explain experimentally observed phenomena → mobility depends on bias, temperature, transient effects, etc.



Percolation Theory



The device can be divided into squares (or alt. 'connections') "Size does not matter" ('scale-free' theory)

A square can be conductive or insulating. Randomly distributed. p chance of conductive.

Conductive squares form 'clusters'

For p = 59.2746....% (percolation threshold): Cluster size is **critically** infinite. Conductive path from one side to other







G ∯ IFPAN

[1] Newman, Contemp. Phys. 46, 323 (2005)

VRH = Percolation Theory

Percolation and (Variable range) Hopping Theory normally fused

$$P(R,W) = \exp(-\alpha R - \frac{W}{kT})$$

Can define a radius $R_0(T)$ that is conductive



Very similar to squares of Percolation Theory



[1] Shklovskii, Phys. Lett. 51A, 289 (1975)

Conduction Mechanisms



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



Lets go back in history (beginning of 20th century)













Forget about semiconductors. They suck! They're useless. (Behavior depends too much on tiny details)









The 'crystal tripartition' led to the development of Quantum Mechanics, the understanding of nature at its purest state

Initially 1/2-cons were ignored. "Shitty materials"

Later: Exactly this dependence on impurities makes them extremely powerful

"As a growing competitor to the tube amplifier comes now the Bell Laboratories' transistor, a three-electrode germanium crystal of amazing amplification power, of wheat-grain size and low cost. Yet its frequency limitations, a few hundred kilocycles, and its strict power limitations will never permit its general replacement of the Audion amplifier." 1952, Lee de Forest (inventor of vacuum valve)



Semiconductor (device) theory

(For electronic device physics)

The entire band structure can 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

μn

EC

ED

EV

μρ



William of Occam / Saint-Exupéry



"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



Crystal schmystal

Dutch: "Physics" = "Natuurkunde" (nature knowledge)

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 (The Global Warming threat)



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!



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De Mythe van Klimaatsveranderingen



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The Great Global Warming Swindle "De Mythe van Klimaatsveranderingen", Peter Stallinga (376 pages, Lulu, 2009)



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"

- loffe, Regel and Gubanov [1]



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





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)



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)



Amorphous TFT



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

1)
$$\rho = \rho_T + n$$

2) $\rho = -V_g C_{ox}$
3) $I = -n \mu dV(x)/dx$
I $Si: \gamma = 1$
Organics: can be 7
(not a small perturbation!)

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



Ad

We will be right back after this commercial break



Worked out the idea of amorphous band theory

- Simple
- Powerful
- For all measurement techniques and devices
- For all materials (not only 1/2-cons)
- Controversial (esp. TFT)

[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 $-\frac{1}{2}$ -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.

[1] Stallinga, Org. Electr. 8, 300 (2007)



Metal transistor



Side effect: should be one order of magnitude **faster than** state-of-the art **silicon** transistor [2]

[1] Stallinga, Adv. Mat. **20**, 2120 (2008) [2] Bastos (UAlg), work in progress



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Nature Asia Materials

npg asia materials in association with TOKYO INSTITUTE OF TECHNOLOGY

research highlight

Electronics: Golden Transistors

Published online 06 August 2008

Transistors are the essential components in modern electronic devices and conventional wisdom dictates that they function because their main component is made of a semiconductor, typically silicon. However, researchers from The University of Hong Kong and University of Algarve, Faro, Portugal have now demonstrated that practical transistors can be practically produced with any material, including metals¹.



Fig.1: The scanning electron microscope image shows a monolayer of gold deposited between



Metal TFT / Percolation



Substantial current way below percolation threshold Current while visibly without continuous path

No sign of any 'criticality'







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





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!





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**)





"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]



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



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Summary

Organic (amorphous) electronic have future

Percolation / Variable Range Hopping compared with Band Theory

 \rightarrow Band Theory wins

Organic Electronic Devices Characterization

- Thin Film Transistor
- Transients



