Ciência na Universidade do Algarve

Science at the University of The Algarve

P. Stallinga,
Universidade do Algarve (FCT, OptoEI, CEOT)
Amesterdão, 17 de Junho de 2005
Overview

Introduction to UAlg
OptoEl
CEOT
Cooperations
Research examples
  • Organic Electronics
    • LEDs: admittance spectroscopy, DLTS
    • FETs
    • LEFETs
  • DNA sensor
  • TNT sensor
  • Bio electronics
Universidade do Algarve (UApg)

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

P. Stallinga, Amsterdam juni 2005
OptoElectrónica
Universidade do Algarve
Founded: 1997
2 members (PhD)

Prof. Henrique Leonel Gomes

Specialized in electronic characterization of organic electronic devices.
Sensitive equipment with custom made control software.
  DLTS (the only “organic” DLTS)
  Organics-specific FET measurement system
  Admittance spectroscopy
  Environment ideal for studying solar cells

P. Stallinga, Amsterdam juni 2005
Centro de Electrónica, Opto-Electrónica e Telecomunicações

Founded in 2001
9 members (PhD)

Electronics (design of RF electronic circuits)

Opto-Electronics (characterization of electronic materials, sensors)

Telecommunications. (Comm. protocols, network design, etc)

P. Stallinga, Amsterdam juni 2005
In 2003, CEOT was evaluated by an external committee of FCT (Portuguese equivalent of FOM) as “very good” and received a 640 k€ equipment investment bonus in 2004 apart from the normal individual project grants.
OptoEl Projects

Electrical characterization of novel electronic materials
Sensors and actuators
Scientific instrumentation
Organic materials, a.k.a. “plastics”

The world is better with plastics ….

In many areas plastics have replaced traditional materials

Clothes
http://www.mischabarton.net/mbimages/misc/misc-nylon.jpg

Transportation

A plastic car, because of its light weight can get more miles per gallon than a steel car
http://www.cnn.com/TECH/ptech/9902/25/plastic.cars/

Construction
http://www.solvayindupa.com.br/aplic/prod.htm

… why not electronics?

P. Stallinga, Amsterdam juni 2005
Electronics of the past
Electronics of the Future
“ Ambient intelligence”
Cheap electronics:
Electronic barcodes
Low performance electronics (medicine)
Disposable electronics

Example: a computer of Si technology @ 3 GHz, a ring oscillator of organics @ 3 kHz.

but there are things you can do only with organics

Flexible electronics
Printed electronics
Printable electronics: electronics on paper

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

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

… only organic electronics!

Reinhard Baumann,
MAN Roland Druckmaschinen AG, Germany
Semiconductor means “with electronic bandgap”

Organic semiconductors means “with conjugated backbone”

\[ \cdots 
\text{C} = \text{C} - \text{C} = \text{C} - \text{C} = \cdots \]

<table>
<thead>
<tr>
<th>Material</th>
<th>Band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>&gt;10 eV</td>
</tr>
<tr>
<td>C (diamond)</td>
<td>5.47 eV</td>
</tr>
<tr>
<td>GaN</td>
<td>3.36 eV</td>
</tr>
<tr>
<td>Polymers</td>
<td>2.5 eV</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42 eV</td>
</tr>
<tr>
<td>Si</td>
<td>1.12 eV</td>
</tr>
<tr>
<td>Ge</td>
<td>0.66 eV</td>
</tr>
</tbody>
</table>
Conjugated organics have paths with alternating single and double bonds.

Examples:

- Very good for FETs
- Very good for LEDs
The metallic properties of organic materials were discovered by **accident** in a laboratory in Japan. New wave of organic electronics research.

Groups like Cambridge (Richard Friend) and Santa Barbara (Alan Heeger) focus(sed) on the LEDs. **Nobel prize** in chemistry in 2000, Alan Heeger, Alan McDiarmid, Hideki Shirakawa.

**Companies** like Philips, Samsung and EPSON soon joined the wagon.

First **commercial** products are already on the market.
Next slides:

Some projects of OptoEl in Organic Electronics.

In 1997 the research group was formed and started with acquiring knowledge and building equipment for measuring organic electronics. A continuation of the PhD work of Henrique Gomes in Bangor (Wales).
OptoEl LEDs

Admittance spectroscopy. Interface states in MIS diode

(a) forward  (b) no bias  (c) reverse

Filling and emptying of states with time constant
\[ \tau = \exp\left(\frac{E_T}{kT}\right) \]
.. can be modeled by electronic circuit
\[ \tau = RC \]

P. Stallinga, Amsterdam juni 2005
The so-called Loss Tangent ($\tan\delta = 1/\omega RC$) has a peak at
$\omega_m = 1/\tau = \omega_0 \exp(-E_T/kT)$
Measuring $\omega_m$ as a function of $T$ yields $E_T$
Interface states

For interface states, $\tau$ depends on bias:
- Reverse bias: deeper states, $\tau$ longer.
- Forward bias: shallower states, $\tau$ shorter.
For bulk states, $\tau$ doesn’t depend on bias.

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

The problem of DLTS

In a transient, $C_i$ changes and contains the information. However, the bulk part filters everything off. Do not use commercial DLTS equipment (working at 1 MHz).
P. Stallinga, Amsterdam juni 2005

DLTS

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

<table>
<thead>
<tr>
<th>label</th>
<th>type</th>
<th>activation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF0</td>
<td>acceptor</td>
<td>0.12 eV</td>
</tr>
<tr>
<td>AF1</td>
<td>majority</td>
<td>0.30 eV</td>
</tr>
<tr>
<td>DF1</td>
<td>minority</td>
<td>0.48 eV</td>
</tr>
<tr>
<td>AF2</td>
<td>majority</td>
<td>1.0 eV</td>
</tr>
<tr>
<td>DF2</td>
<td>minority</td>
<td>1.3 eV</td>
</tr>
</tbody>
</table>

T(°C) =

T(K) =

\[
\ln(cT^2) = k \lambda T + E_A
\]

1.3 eV
1.0 eV
0.48 eV
1.3 eV
0.30 eV

\[
\tau = 100 \text{ s}
\]
\[
\tau = 10 \text{ s}
\]
\[
\tau = 2 \text{ s}
\]
Three-terminal devices: thin-film FETs

Three-terminal devices are transistors (bipolar junction transistors or thin-film field-effect transistors)

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, because (FET)

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

SAT: \[ I_{ds} = (W/L) \ C_{ox} \ \mu \ (V_g - V_t)^2 \]
Standard inversion channel FETs

\[ I_{DS} = \mu \left( \frac{Z}{L} \right) C_{ox} (V_G - V_T) V_{DS} \]

LIN:

\[ I_{DS} = \frac{1}{2} \mu \left( \frac{Z}{L} \right) C_{ox} (V_G - V_T)^2 \]

SAT:

http://www.ualg.pt/fct/adeec/optoel/theory/fet/
Three-terminal devices: thin-film FETs

Organic layer: sexithiophene (T6) or PMeT or DH4T

D

“bottom gate”

S

Au

Organic

SiO₂

Si (n+)

C₆H₁₃

P. Stallinga, Amsterdam juni 2005
Organic FETs

In the so-called linear region:

\[ I_{ds} = \frac{W}{L} C_{ox} \mu (V_g - V_t)^{1+\gamma} V_{ds} \]

\( \gamma = 5 \) is not a small perturbation!
Organic FETs

This can be explained by assuming high density of trap states, as in the model of Shur and Hack for $\alpha$-Si.

Other effects explained by trap states:

Non-exponential current transients: $I_{ds} = I_0 \exp(-t/\tau)^\alpha$

Stressing: $V_t$ increases with time

Thermally activated current: $I_{ds} = I_0 \exp(-E_T/kT)$

Meyer-Neldel Rule

What is the Meyer-Neldel Rule?

Observation without explanation*

The thermal activation energy of a process ($P$) depends on a certain parameter ($z$).

There exists a temperature ($T_{MN}$) where the dependence of $P$ on $z$ disappears.

\[ P = P_0 \exp\left(-\frac{E_A}{kT}\right) \]

\[ P_0 = P_{MN} \exp\left(\frac{E_A}{kT_{MN}}\right) \]

* Original article: W. Meyer and H. Neldel, Z. Techn. 18, 588 (1937).
### Examples of the Meyer-Neldel Rule

<table>
<thead>
<tr>
<th>Processes</th>
<th>Parameters</th>
<th>Devices/materials</th>
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<tbody>
<tr>
<td>current diffusion*</td>
<td>gas concentration</td>
<td>α-Si</td>
</tr>
<tr>
<td>ionic currents</td>
<td>pressure</td>
<td>organic ½cons</td>
</tr>
<tr>
<td></td>
<td>electrical bias</td>
<td>gas detectors</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High-Tc supercons</td>
</tr>
<tr>
<td></td>
<td></td>
<td>glasses</td>
</tr>
<tr>
<td></td>
<td></td>
<td>liquid ½cons</td>
</tr>
<tr>
<td></td>
<td></td>
<td>polycryst. Si</td>
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<tr>
<td></td>
<td></td>
<td>CCDs</td>
</tr>
</tbody>
</table>

* Here the MNR is called the Compensation Effect.

Cross disciplinary!
### Examples of the Meyer-Neldel Rule

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<tr>
<td>current diffusion*</td>
<td>gas concentration</td>
<td>$\alpha$-Si</td>
</tr>
<tr>
<td>ionic currents</td>
<td>pressure</td>
<td>organic $\frac{1}{2}$cons</td>
</tr>
<tr>
<td></td>
<td>electrical bias</td>
<td>gas detectors</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High-Tc supercons</td>
</tr>
<tr>
<td></td>
<td></td>
<td>glasses</td>
</tr>
<tr>
<td></td>
<td></td>
<td>liquid $\frac{1}{2}$cons</td>
</tr>
<tr>
<td></td>
<td></td>
<td>polycryst. Si</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CCDs</td>
</tr>
</tbody>
</table>

All less-than-perfect-crystalline materials

* Here the MNR is called the Compensation Effect.
Meyer-Neldel Rule in T6 TFT

Phase transition (?) at 200 K
Amorphous silicon: Shur & Hack

\[ I_{ds} = \frac{q\mu_0 W}{L} f(T, T_2) \left[C_{ox} \left(|V_g - V_t|\right)\right]^{\left(\frac{2T_2}{T}\right) - 1} V_{ds} \quad (53) \]

\[ f(T, T_2) = N_V \exp \left(\frac{-E_{F0}}{kT}\right) \frac{kT\epsilon}{q} \left(\frac{\sin(\pi T/T_2)}{2\pi\epsilon T_2 kT g_{F0}}\right)^{T_2/T} \quad (51) \]
**Simulation FET+traps**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>value</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_V$</td>
<td>$10^{19}$</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$C_{ox}$</td>
<td>$1.92 \times 10^{-4}$</td>
<td>F/m$^2$</td>
</tr>
<tr>
<td>$E_{F0}$</td>
<td>484</td>
<td>meV</td>
</tr>
<tr>
<td>$V_{ds}$</td>
<td>-0.1</td>
<td>V</td>
</tr>
<tr>
<td>$g_{F0}$</td>
<td>$10^{16}$</td>
<td>cm$^{-3}$eV$^{-1}$</td>
</tr>
<tr>
<td>$T_2$</td>
<td>450</td>
<td>K</td>
</tr>
<tr>
<td>$W$</td>
<td>1</td>
<td>cm</td>
</tr>
<tr>
<td>$L$</td>
<td>30</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>3</td>
<td>cm$^2$V$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>$5\epsilon_0$</td>
<td></td>
</tr>
</tbody>
</table>

**Note:** No measurements possible at/close to $T_2$ (currents drop and diverge).

P. Stallinga, H.L. Gomes, accepted Org. Electr. (2005)
A light-emitting field-effect transistor would be useful. It would eliminate the need for a separate LED and thus reduce the number of processing steps in the fabrication of an active-matrix display.
You are looking at the first picture ever taken showing light coming out of an FET ... (Bologna, 2003)

OptoEl Projects

Electrical characterization of novel electronic materials
Sensors and actuators
Scientific instrumentation
TNT Sensor

Need for a reliable and cheap sensor.

… so many mines to be deleted from this planet.
Why use an organic FET for a TNT sensor?

FETs are **multi-parametric**
Organics can be **functionalized** easily
Organics are **cheap** to produce
Organic Electronics are our **expertise**
4 basic types of inversion channel FETs

- **p-channel**
  - normally on: Increasing $I_d$ with $V_g$
  - normally off: Constant $I_d$ with $V_g$

- **n-channel**
  - depletion: $I_d$ constant with $V_g$
  - enhancement: Increasing $I_d$ with $V_g$

S.M. Sze, Physics of semiconductor devices, p.455
The detection principle

A TNT molecule is very reactive and can interact with the organic layer.

for example:
(1) stealing electrons (acceptor) or
(2) introducing deep traps or
(3) changing the charge mobility.
The detection principle using transfer curves

Thus, the detection is multi-parametric:

- changes in $V_t$
- changes in leakage current
- changes in mobility
- changes in conduction model (band conduction to hopping conduction)
Response to TNT

Organic active layer: DH4T

$V_g = 0 \, \text{V}, \, V_{ds} = -0.5 \, \text{V}$
O QCM é um detector de massa. A frequência de ressonância de oscilação é uma função da massa depositada em cima do cristal. Sauerbrey:

\[ \Delta f = -K \Delta m \]

\[ K = \frac{2f_0^2}{A(\rho \mu)^{1/2}} \]

Por isso, é muito usado em medições de espessura de filmes, etc.

Muito sensível (exemplo standard 5 MHz cristal, 1 Hz ruído):

17.6 ng ou 1.77 \times 10^{-7} \text{ kg/m}^2 \text{ ou } 0.35 \text{ Å} \text{ ou } 0.1 \text{ ML}
O princípio de detecção

**Meio líquido**

**X-tal**

**Reagente I**

**Reagente II**

**tempo**

**Injeção do reagente II**

**frequency**

**tempo**
Aplicações

II: Detector HIV

Funcionalização

Detecção

Anticorpos ou antigénio

Virus HIV
Electrónica

Modelo electrónico do cristal

Capacitância dos electrodes paralelos e cabos

Modelo das oscilações mecânicas

Acoplamento: Piëzo-eléctrico

$C_0$ tem nada a ver com os processos de interesse (oscilações mecânicas) e tem de ser compensado.
Barkhausen critério: ressonância quando a fase $\beta = 180^o$ (parte imaginária 0)

$$Z(\omega) = \left( i\omega C_0 + \frac{1}{R_m + i(\omega L_m - \frac{1}{\omega C_m})} \right)^{-1}$$

C_0 tem de ser compensado! Neste caso:
$$\omega_r = \frac{1}{(L_m C_m)^{1/2}}$$
$$Z_r = R_m$$

Usar apenas um oscilador e um frequencímetro perda informação
Implementação CBME / OptoEl

Spectro do cristal obtido pelo *network analyzer*:

O uso do *network analyzer* pode dar informação suplementar.
Newtonian fluids:
\[ \omega L_2 = R_2 \]

Rigid films
\[ R_3 = 0 \]

\[ L_m = L_1 + L_2 + L_3 \]
\[ C_m = C_1 \]
\[ C_0 = C_x + C_y \]
\[ R_m = R_1 + R_2 + R_3 \]
Detection of interaction of living cells

Oysters

Parasites
Microelectrode array structures used

$L = 2 \text{ mm}$

$W = 10-20 \mu\text{m}$

Gap = 10-20 $\mu\text{m}$
Detecting cells by measuring the impedance

Large top electrode

Microelectrodes

cells
Measurements between two adjacent electrodes
The equivalent circuit

Medium

Electrical double layer

0.35 nF

18 nF

5 MΩ

150 Ω

90 Ω
Summary

Electrical measurements:
- characterizing novel materials
- characterizing novel devices
- sensors
- instrumentation
- signal processing, modelling, etc.

Thanks to all people in the various cooperations over Europe and in Portugal.
Special thanks to Prof. Henrique Gomes, eng. Eduardo Bentes and eng. João Encarnaçao