Electrical Characterization of Organic Semiconductors

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Amsterdam
August 2000
Measurements in Faro

Devices:
- bulk
- Schottky barrier
- pn-junction
- FETs

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

Information:
- conduction model
- carrier type
- shallow levels
  - position
  - density
- deep levels
  - position
  - density
- dielectric constant
- carrier mobility
- barrier height
Why 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:
- Unstable in air (so far!)
- Slow! Forget application of fast electronics

Applications:
- LEDs,
- Displays (background illumination), solar cells, tagging
“Plastics are conductors ?!”

• Every semiconducting polymer has a “backbone” of under-coordinated carbon atoms
  
  example: \(- \text{CH} – \text{CH} – \text{CH} – \text{CH} -\)

• 4th electron is in weak \( p_z - p_z \) bonds. Loosely bound \( \rightarrow \) metal

• deformation of backbone: creation of alternating single and double bonds
  \(- \text{CH} = \text{CH} – \text{CH} = \text{CH} -\)

• This causes opening of a bandgap
  \( \rightarrow \) semiconductor

• bandgap \( \pm 2.5 \text{ eV} \)

• wide bandgap \( \frac{1}{2} \text{con} \)

<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>
Examples

Conjugated polymers have paths with alternating single and double bonds.
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!
A standard conjugated polymer is not soluble. It can be made soluble by adding sidechains. Then they can easily be spin-coated onto the substrate (glass, ITO, etc). Otherwise, they can be vacuum sublimated. (more difficult)
Schottky Barrier

- metal and ½con have different Fermi level
- electrons will flow from metal to ½con
- 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)

$$V_{bi} = \chi + V_n - \phi_m$$
\[ C = A \sqrt{\frac{q \varepsilon N_A}{2(V_{bi} - V)}} \]

\[ C^{-2} = 2(V_{bi} - V)/A^2 q \varepsilon N_A \]

- slope reveals \( N_A \)
- extrapolation reveals \( V_{bi} \)
DC conduction

Thermionic emission theory:

\[ J = A^* T^2 \exp(-q\phi_{Bp}/kT) [\exp(qV/nkT) - 1] \]
\[ = J_0 [\exp(qV/nkT) - 1] \]

From a single scan we can find
- the rectification ratio \( J_0 \)
- the ideality factor, \( n \)
- the conduction model

Repeating with different \( T \):
- barrier height, \( \phi_{Bp} \)

In practice this doesn’t work so well, due to hopping conduction process.
Bulk-limited Current (Schottky barrier)

- Large bias: bulk resistance dominates
- This causes a bending of IV
- Theory for bulk currents can be applied again.
Displacement Current (Schottky barrier)

- Every time the bias is changed the capacitance has to reach the new amount of charge stored
- This flow of charges is the displacement current, $I_{\text{disp}}$

$$I_{\text{disp}} = C \frac{dV}{dt} + V \frac{dC}{dt}$$

$$= C \frac{dV}{dt} + V \frac{dC}{dV}(\frac{dV}{dt})$$

So, scan slower!
Deep levels

- Increasing bias
- less band-bending
- (EF moves down)
- at $V>V_x$ deep level completely above $E_F$. Stops contributing
- reduced capacitance and increased slope in $C^{-2}-V$ plot

![Diagram showing energy levels and charge density with deep level positions and corresponding capacitance plots.]
Frequency response

Only shallow levels:

$$C, \frac{G}{\omega}$$

Plus deep levels:

$$\tan\delta = \frac{G}{\omega C}$$
Interface states

Special type of deep states: only present at interface

- **a) forward**: not visible in C, G
- **b) no bias**: increased C and G
- **c) reverse**: not visible in C, G

Graphs:
- $1/C^2 - V$
- $\log(G) - V$
- $G/\omega, C - \omega$
Summary of C-V and G-V

\[ C^{-2} - V \quad \text{Log}(G) - V \quad \text{Spectra} \]

\[ C, G/\omega - \omega \quad \tan \delta - \omega \]

shallow homogeneous

+ deep homogeneous

+ interface
Admittance Spectroscopy
Loss tangent

Maximum at

\[
1/\omega_{\text{max}} = R_b \sqrt{C_b (C_b + C_d)}
\]

\[
R_b \sim \exp(-E_a/kT)
\]

(remember from bulk samples?)

We can determine the bulk activation energy from the tan\(\delta\) data
Admittance Spectroscopy
Cole-Cole Plots

\[ C_b = C_{\text{geo}} = \varepsilon A/d \] ("metal plates")

Cole-Cole plot is
\[ G/\omega \text{ vs. } V \]

yields \( \varepsilon \)

(if we know electrode area and film thickness)
Field Effect Transistor

\[ I_{SD}^{\text{SAT}} = \left( \frac{Z}{L} \right) \mu_p C \left[ (V_G - V_T)^2 \right] \]

<table>
<thead>
<tr>
<th>symbol</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>(L)</td>
<td>Channel length</td>
</tr>
<tr>
<td>(Z)</td>
<td>Channel width</td>
</tr>
<tr>
<td>(d)</td>
<td>Oxide thickness</td>
</tr>
<tr>
<td>(V_G)</td>
<td>Gate voltage</td>
</tr>
<tr>
<td>(V_D)</td>
<td>Drain voltage</td>
</tr>
<tr>
<td>(I_{SD})</td>
<td>Drain current</td>
</tr>
<tr>
<td>(\mu)</td>
<td>(hole) mobility</td>
</tr>
<tr>
<td>(C)</td>
<td>Oxide capacitance</td>
</tr>
<tr>
<td></td>
<td>(= A \varepsilon / d)</td>
</tr>
</tbody>
</table>
Optical Effects: Photo detector/solar cell

In photo-detectors / solar cells
- Energy of photon is absorbed by creation of e-h pair
- Electric field in active region breaks the e-h pair
- Individual carriers are swept out of region and contribute to external current
Optical effects: LED

- electrons and holes are injected into the active region
- here they recombine -> photon
- “color” of photon is $E_g$. With polymers blue is possible
- Limiting mechanisms:
  - unbalanced carrier injection (choice of electrodes)
  - presence of non-radiating-recombination centers
Electrical Characterization of Semiconductors

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Basic Kinetics

A “trap” is a deep level, localized in space. Difficult to get the charge out of there — long relaxation time

Trap “thermalization time” is increasing with
- $E_T$ (level depth, $E_a$)
- $T$ (temperature)

Mid-gap levels in silicon are already slow, so in polymers …… forget fast electronics!

$$\frac{1}{\tau} = e_p = \gamma T^2 \sigma \exp\left(-\frac{E_a}{kT}\right)$$
Capacitance Transients

“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.
1. Free holes move out of interface region. Immediate increase of $W (C_l)$
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

\[ \frac{1}{\tau} = e_p = \gamma T^2 \sigma \exp(-E_a/kT) \]

Monitoring \( \tau \) over temperature will give us \( E_a \)

Very sensitive and very accurate!
A "minority trap" communicates with the minority band.

Under bias, the minority Fermi level moves in opposite direction.

This time electrons are emitted and the space charge decreases.

Slowly increasing $W$ and decreasing $C$ over time.
Example of C-transients:

MEH-PPV on Silicon
• 2 minority traps: a, c
• 1 majority trap: b

\[ \frac{1}{\tau} = e_p = \gamma T^2 \sigma \exp(-E_a/kT) \]

Note the timescale (seconds!)
**DLTS (deep-level transient-spectroscopy)**

- 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: $\tau_0T^{-2}\exp(E_a/kT) = (t_2-t_1)/[\ln(t_1/t_2)]$

Two scans, with different time window $(t_1, t_2)$ will yield $E_a$
DLTS summary

DLTS is
- Very easy to perform. “Walk-away” measurements
- Sensitive
- Reliable data with accurate energy determination
- “Fingerprint” spectra of defects
- Can determine density of defects. \[ \Delta C/C = \frac{N_T}{2(N_A - N_D)} \]

Modern improvement Laplace DLTS:
- Use entire transient in analysis
  - Higher sensitivity
  - Higher resolution
- Made possible by abundance of cheap computing power
  (can be done even on-line)
**TSC** (thermally stimulated current)

“Cool down the sample under (forward) bias and warm up without”

- a) 0V, RT, thermal equilibrium
- b) Forward bias, RT, thermal equilibrium
  
  cool down, remove bias

- c) Zero bias, 77 K, no-equilibrium

- d) Warm up, charges are emitted; external current
  
  until all levels are empty. \( I \) back to 0. We see a peak in \( I \)

\[
\frac{1}{\tau} = e_p = \gamma T^2 \sigma \exp\left(-\frac{E_a}{kT}\right)
\]
Position of the peak $T_m$ depends on the scanning speed $\beta = dT/dt$: fast scan: the levels have no time to empty. high $T_m$
slow scan: low $T_m$

$$\ln \left( \frac{T_m^4}{\beta} \right) = \frac{E_a}{kT_m} + C$$

$I$ is negative:
holes move towards p-side of junction which is equivalent to reverse current

Integral $\int I \, dt$ is constant
is independent of scanning speed and reveals the deep level density
# Summary of Electrical Measurements

<table>
<thead>
<tr>
<th>Device Structure</th>
<th>Shallow Level position</th>
<th>Shallow Level density</th>
<th>Deep Level position</th>
<th>Deep Level density</th>
<th>Free carrier mobility</th>
<th>Conduction Model</th>
<th>Interface states</th>
<th>Difficulty</th>
<th>cost</th>
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<tbody>
<tr>
<td>IV Schottky Bulk</td>
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<td>+</td>
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<td></td>
<td>+ +</td>
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<td>CV Schottky p-n</td>
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<td>+ +</td>
<td></td>
<td></td>
<td>8</td>
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</tbody>
</table>
Future work

- **PRAXIS project: Bio-FETs** (deposit living cells on bio-compatible organic FET structures and measure their activity)

- **EPR** work on organic semiconductors. This seems to become a hot topic. 
  very narrow lines possible (2 \( \mu \)T)

- search for **improved materials** with our European partners (Bologna, Paris, Lisboa, Mons) 
  improved mobility, conductivity, no traps, etc.
Thank you
For your attention

Faro sunset, 1999
Calculation of Depletion Width

Poisson’s equation:
\[ V = \iint \frac{\rho(x)}{\varepsilon} \, dx^2 \]

\[ \rho(x) = \begin{cases} N_A & (x < W) \\ 0 & (x > W) \end{cases} \]

\[ E(x) = \int \rho(x) \, dx = \left( \frac{qN_A}{\varepsilon} \right) (x - W) \]

\[ V(x) = \left( \frac{qN_A}{2\varepsilon} \right) (x - W)^2 \quad V_{bi} = V(0) \]

\[ W = \sqrt{2\varepsilon \left( V_{bi} - V_{ext} \right)/qN_A} \]

\[ Q = N_A W \]
Capacitance (Schottky Barrier)

• Every time the bias is changed a new depletion width is formed
• More (or less) space charge \( Q \)

\[
C = \frac{dQ}{dV} = A \sqrt{\frac{q\varepsilon N_A}{2(V_{bi} - V)}}
\]

\[
C = \frac{A\varepsilon}{W}
\]

A Schottky barrier is equivalent to metal plates (area \( A \)) at mutual distance \( W \), filled with dielectric \( \varepsilon \)
Numerical calculation of $C$

Riemann integration until

$$V = (V_{bi} - V_{ext})$$

then:

$$C = \frac{dQ}{dV}$$

$$C = \left. \frac{(dQ/dx)}{(dV/dx)} \right|_{x=W}$$

or: two-pass calculation:

$$C = \frac{\Delta Q}{\Delta V}$$
AC: Conductance

\[ V(t) = V + \nu \sin(\omega t) \rightarrow I(t) = I + i \sin(\omega t) \]

DC: \[ 1/R = I/V, \quad AC: G = i/\nu \]

Small \( \nu \): conductance \( G \) is the derivative of the IV-curve

\[ J = J_0 \left[ \exp(qV/nkT) - 1 \right] \]

\[ G = G_0 \exp(qV/nkT) \]

Frequency independent

Loss: \[ L = G/\omega \]

Loss-tangent: \[ \tan\delta = G/\omega C \]
Admittance Spectroscopy
Equivalent circuits

Admittance spectroscopy: $C$, $G$, tan$\delta$ as function of $\omega$

\[
C = \frac{R_d^2 C_d + R_b^2 C_b + \omega^2 R_d^2 R_b^2 C_d C_b (C_d + C_b)}{(R_d + R_b)^2 + \omega^2 R_d^2 R_b^2 (C_d + C_b)}
\]

\[
G = \frac{R_d + R_b + \omega^2 R_d R_b (R_d C_d^2 + R_b C_b^2)}{(R_d + R_b)^2 + \omega^2 R_d^2 R_b^2 (C_d + C_b)}
\]

Resembles deep states picture:
"Hey, that is nice, we can simulate deep states with equivalent circuits!"
(even if it has no physical meaning)
or: $\tau = RC$
**Hall measurements**

(remember) conductivity:

\[
\sigma = qp \mu_p \\
\sigma = (I/V_x)(l_x/W_y d_z)
\]

\[
F^B_y = q B_z \nu_x \\
F^E_y = -q E_y
\]

\[
\nu_x = J_x/qp = I_x/(W_y d_z qp) \\
E_y = V_y/W_y
\]

\[
qp = B_z I_x/V_y d_z \\
\mu_p = l_x V_y / B_z V_x W_y
\]

In the Hall measurements we can measure the hole mobility \(\mu_p\)
Parameters that characterize a solar cell:

- open-circuit voltage \((I=0)\) \(V_{oc}\)
- short-circuit current \((V=0)\) \(J_{sc}\)
- maximum power output \(P_{max}\)
Bulk Samples

- bar of material with only **ohmic** contacts

\[ \text{Conductivity: } \sigma = e \mu_p p \]

\[ p \sim T^{3/4} \exp(-E_A/kT) \]

- acoustic phonons: \( \mu_p \sim T^{-3/2} \)
- ionized impurities: \( \mu_p \sim T^{3/2} \)
- optical phonons: \( \mu_p \sim T^{3/2} \)