Electrical Characterization of Organic Semiconductors

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Measurments 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: $\cdot$CH – $\cdot$CH – $\cdot$CH – $\cdot$CH

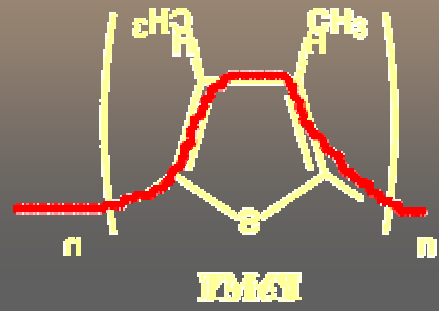
- 4th electron is in weak p_z-p_z bonds. Loosely bound -> metal
- deformation of backbone: creation of alternating single and double bonds

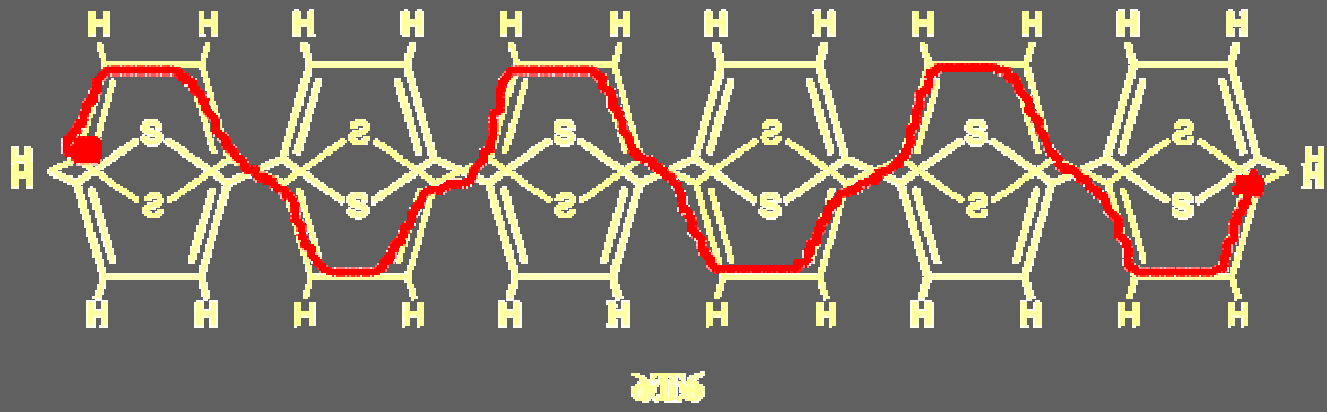
- CH = CH – CH = CH -

- This causes opening of a bandgap
  -> semiconductor
- bandgap ±2.5 eV
- wide bandgap ½con

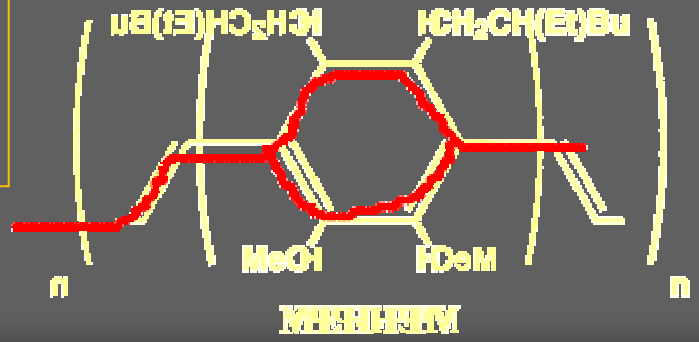
Material	Band gap
SiO_2	>10 eV
C (diamond)	5.47 eV
GaN	3.36 eV
Polymers	2.5 eV
GaAs	1.42 eV
Si	1.12 eV
Ge	0.66 eV

Examples





Conjugated polymers have paths with alternating single and double bonds

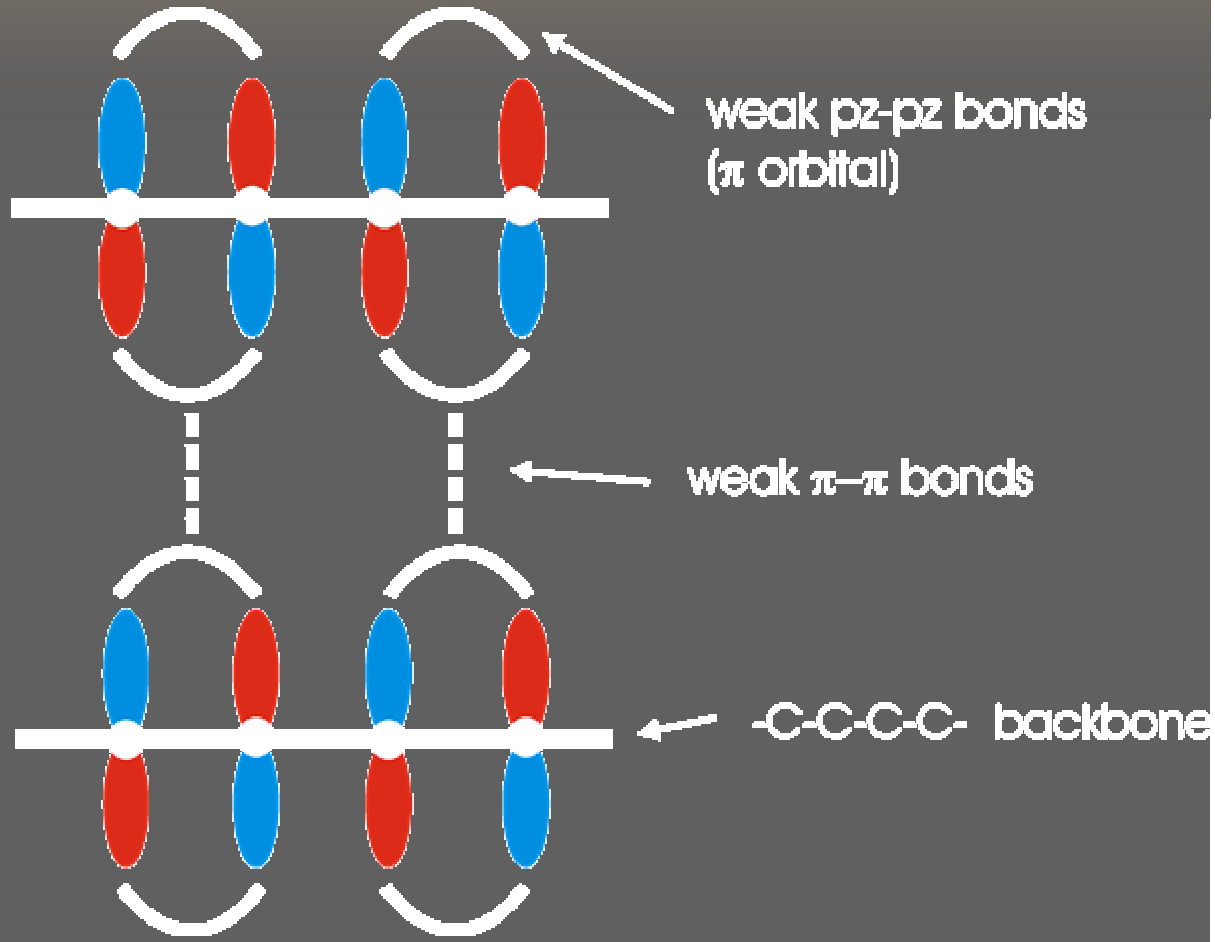


Conduction

Conduction along backbone is easy

Conduction from chain to chain is Difficult. Hopping Conduction

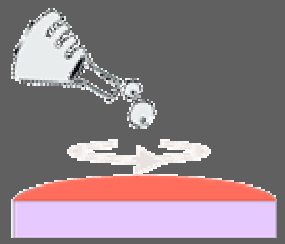
Two activation energies for conduction

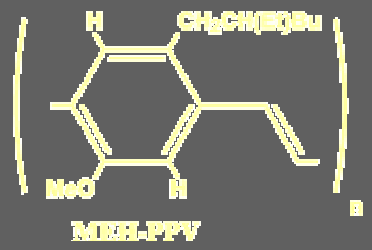


The **stacking of the molecules** is very important!

Sample preparation

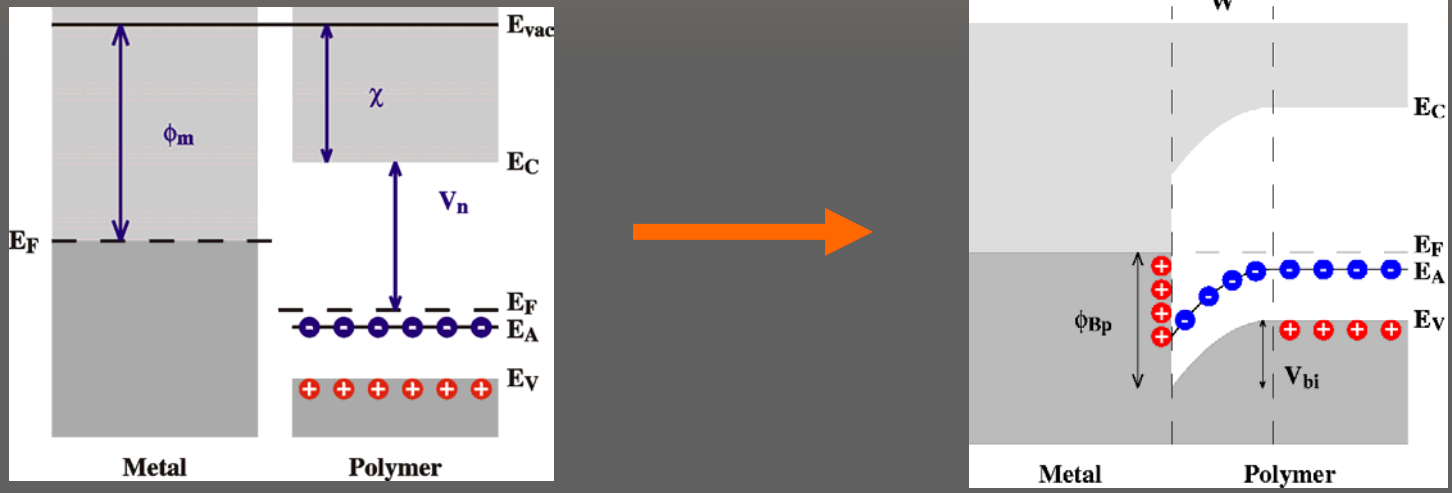
- A standard conjugated polymer is not soluble
- it can be made soluble by adding sidechains. Then they can easily be spin-coated onto the substrate (glas, ITO,etc)





- 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)

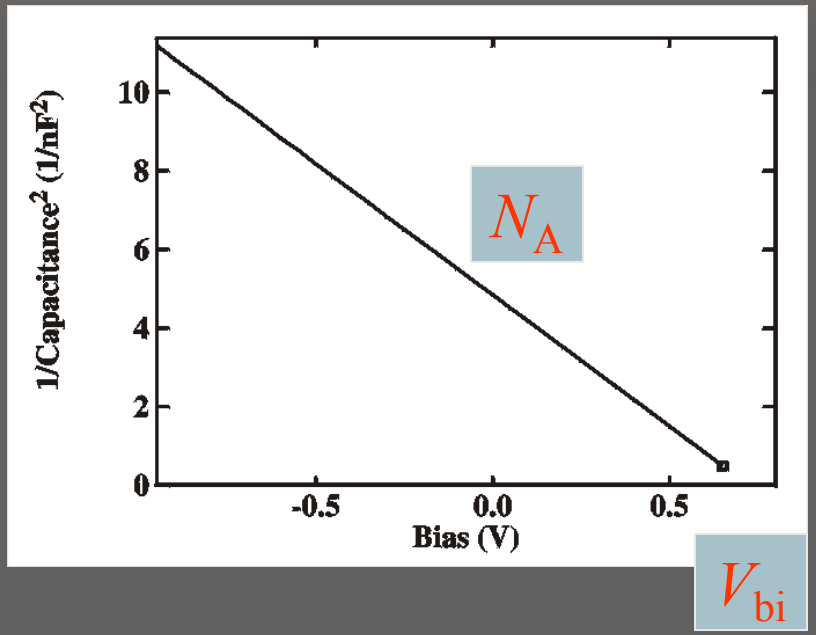
$$V_{bi} = \chi + V_n - \phi_m$$

Capacitance 2

doping density

$$C = A\sqrt{q\varepsilon N_A/2(V_{bi}-V)}$$

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



- slope reveals N_A
- extrapolation reveals V_{bi}

DC conduction (Schottky barrier)

Thermionic emission theory:

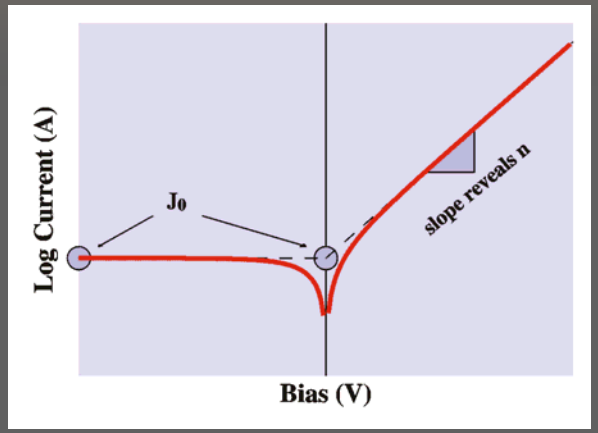
$$J = A^{*}T^{2}\exp(-q\phi_{Bp}/kT)\,[\exp(qV/nkT) - 1]$$
$$= J_0\,[\exp(qV/nkT) - 1]$$

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

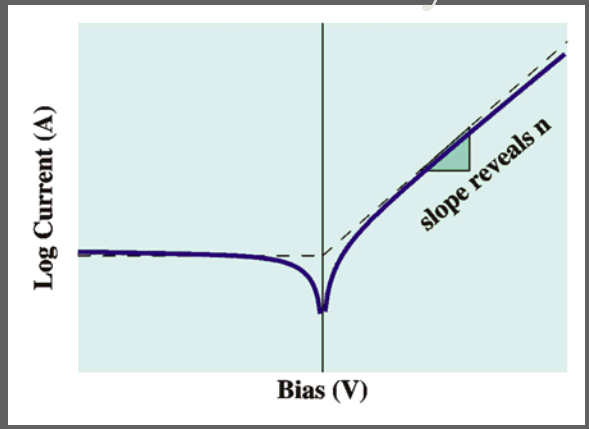
Repeating with different T:
- barrier height, ϕ_{Bp}

In practice this doesn't work so well, due to hopping conduction process.

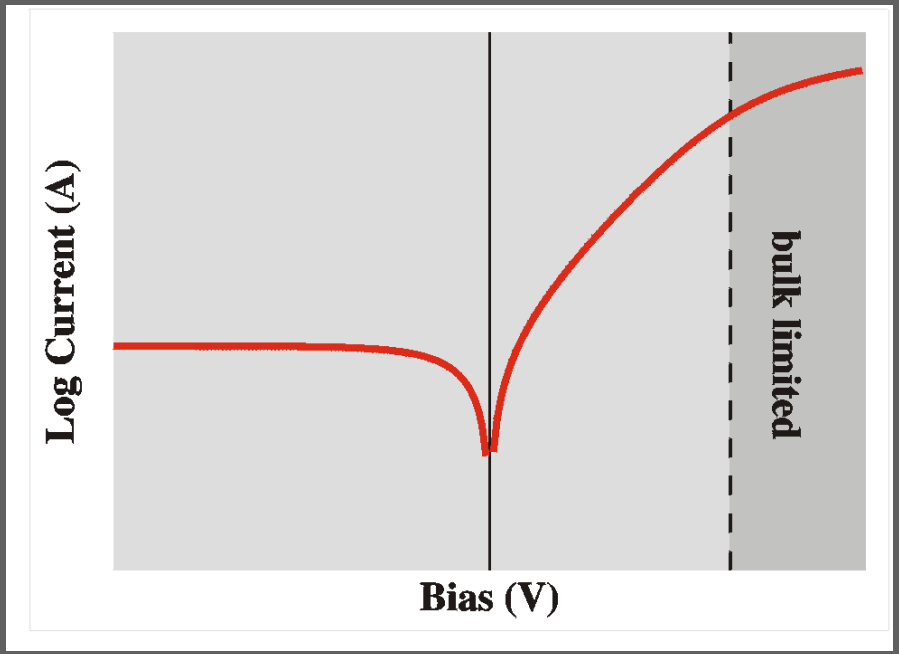
Thermionic-emission:



Diffusion theory:



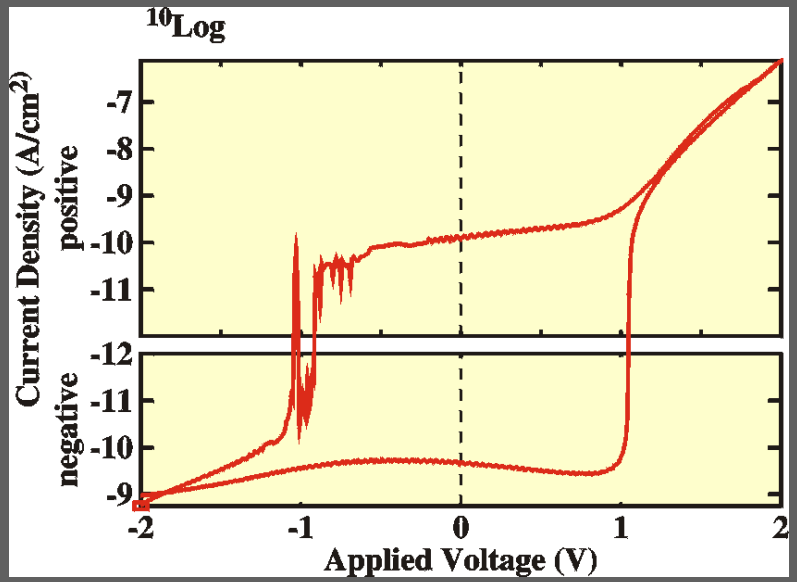
Bulk-limited Current (Schottky barrier)



- 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_{disp}

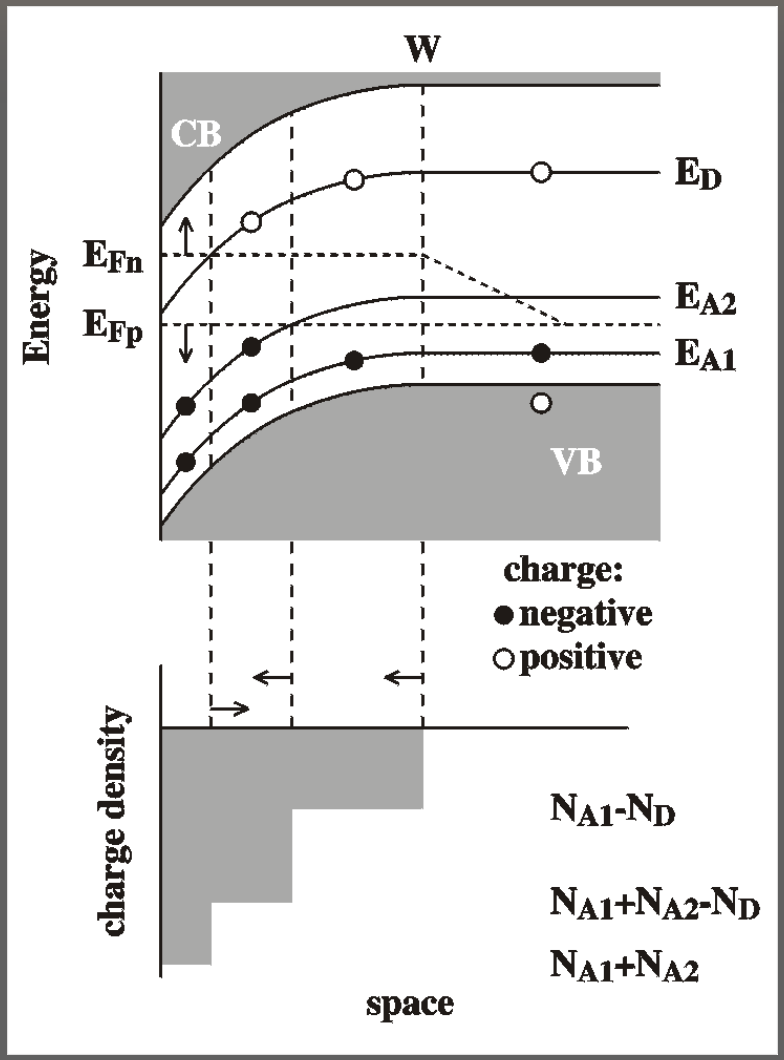


$$I_{disp} = C\,(\mathrm{d}V/\mathrm{d}t) + V\,(\mathrm{d}C/\mathrm{d}t)$$

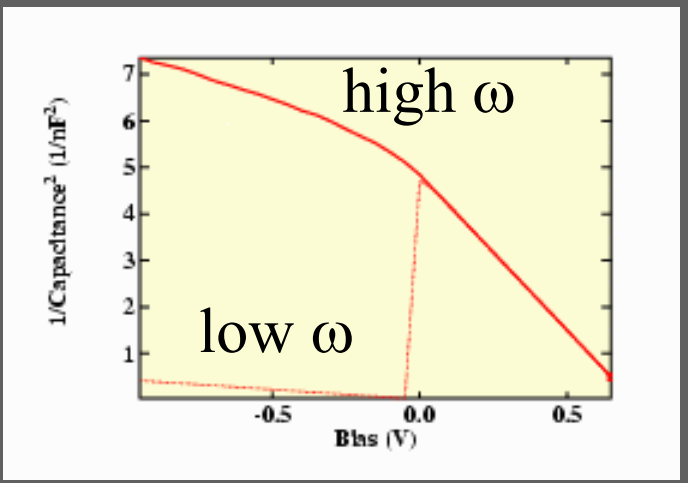
$$= C\,\mathrm{d}V/\mathrm{d}t + V\,(\mathrm{d}C/\mathrm{d}V)(\mathrm{d}V/\mathrm{d}t)$$

So, scan slower!

Deep levels



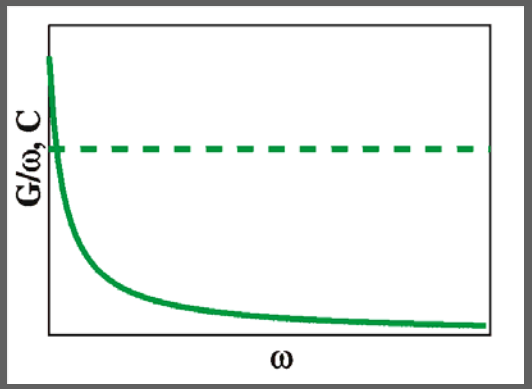
- Increasing bias
- less band-bending
- (EF moves down)
- at $V>V_x$ deep level completely above E_F. Stops contributing
- reduced capacitance and increased slope in C^{-2}-V plot

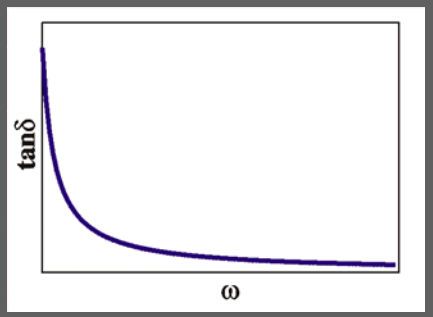


Frequency response

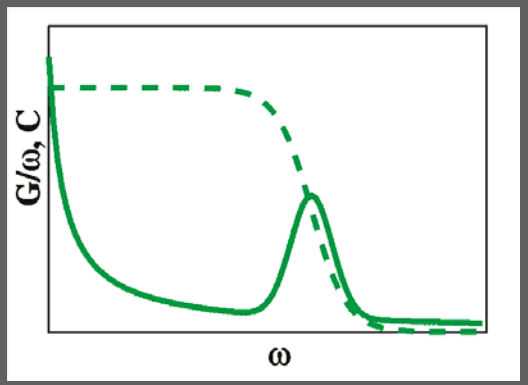
C, G/ω $\tan\delta = G/\omega C$

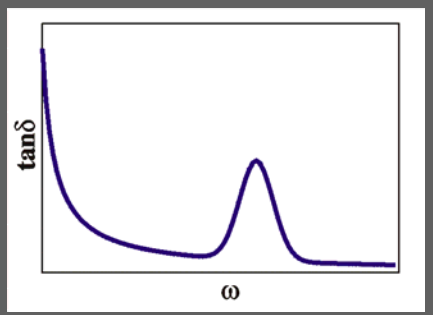
Only shallow levels:





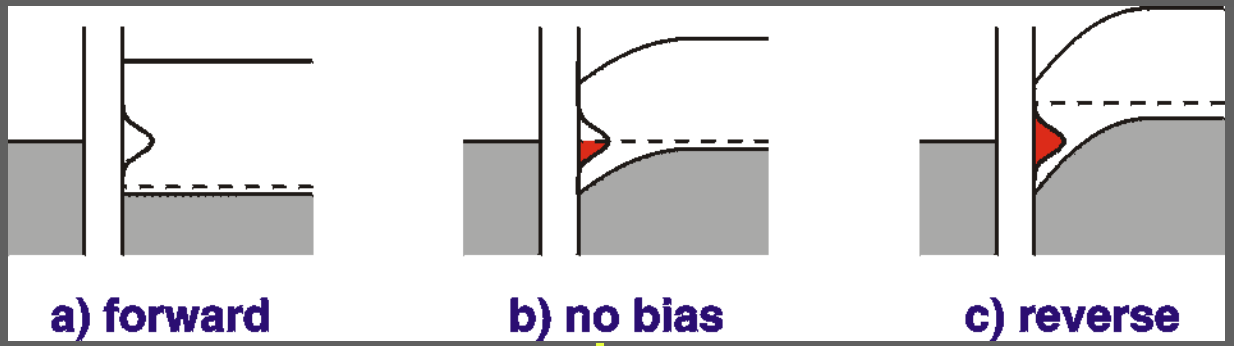
Plus deep levels:





Interface states

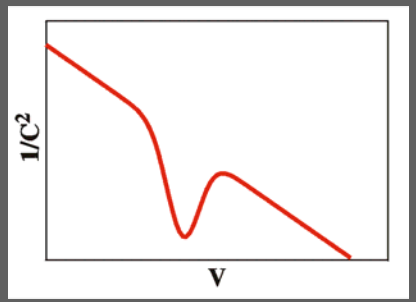
Special type of deep states: only present at interface



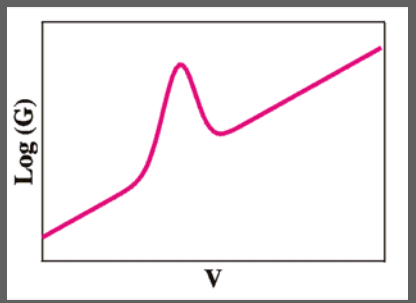
not visible in C, G

not visible in C,G

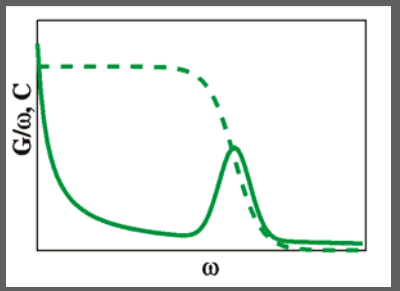
increased C and G



C^{-2}-V

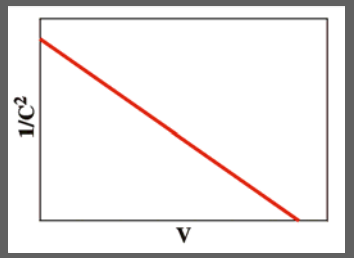
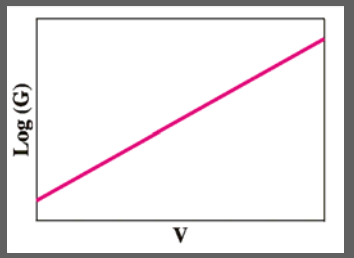
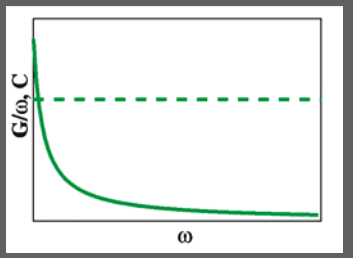
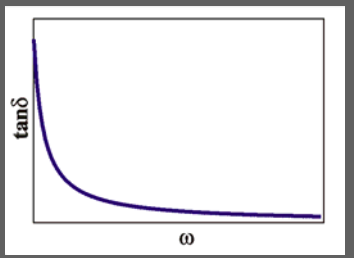
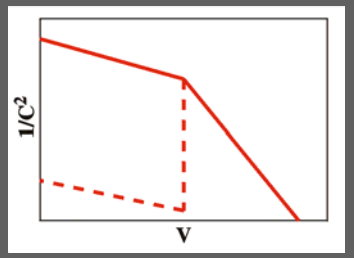
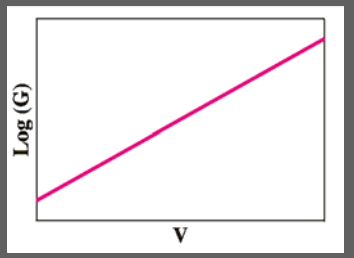
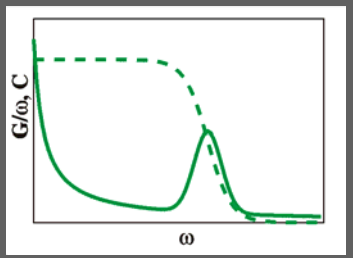
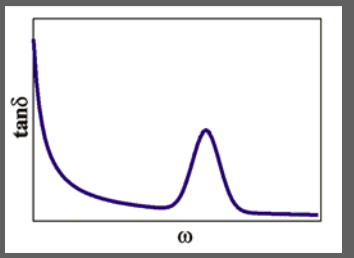
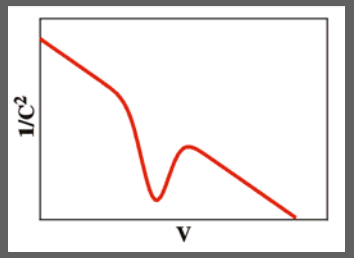
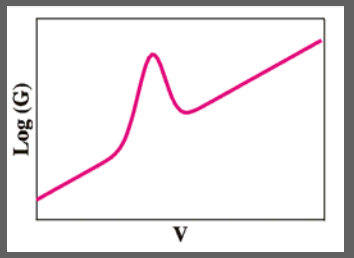
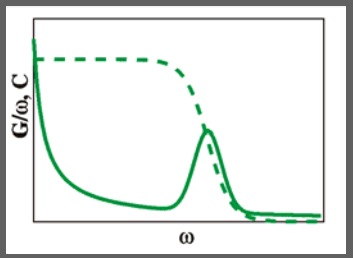
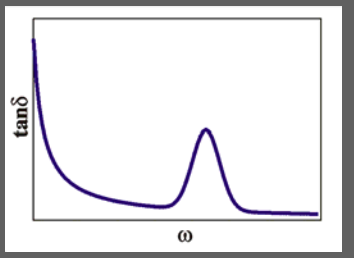


Log(G)-V

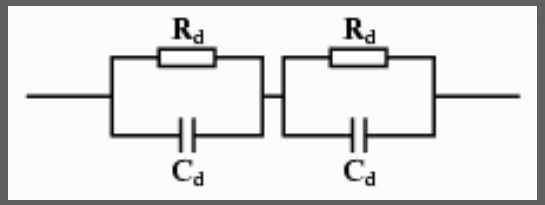


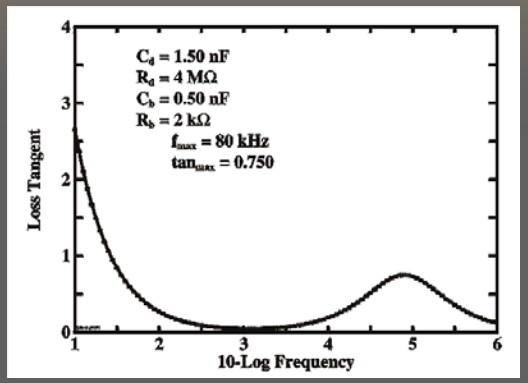
G/ω, C - ω

Summary of C-Vω and G-Vω

	C^{-2}-V	Log(G)-V	Spectra: C, G/ω-ω	Spectra: tanδ-ω
shallow homogeneous				
+ deep homogeneous				
+ interface				

Admittance Spectroscopy
Loss tangent



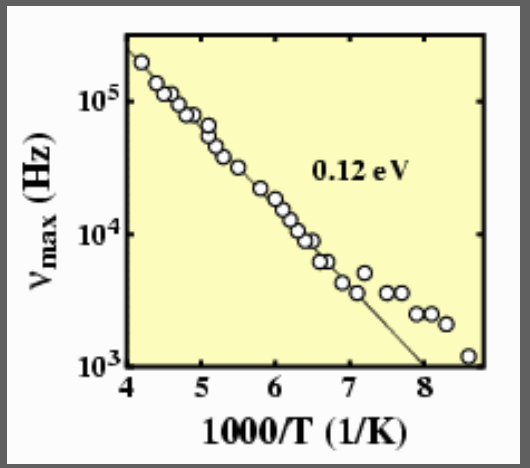


Maximum at

$$1/\omega_{max} = R_b\sqrt{C_b(C_b+C_d)}$$

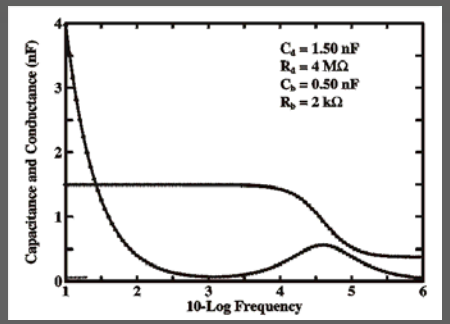
$R_b \sim \exp(-E_a/kT)$

(remember from bulk samples?)



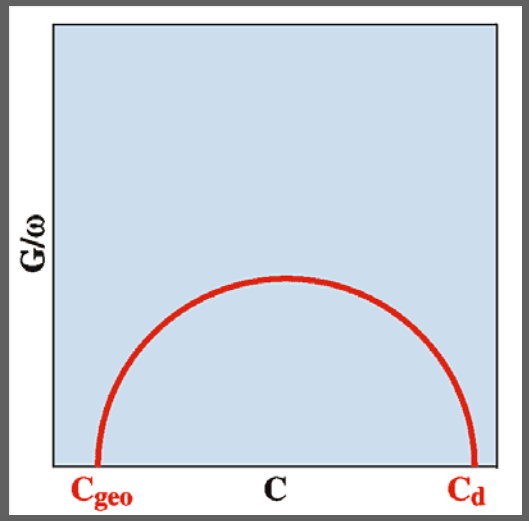
We can determine the bulk activation energy from the tanδ data

Admittance Spectroscopy
Cole-Cole Plots



	ω=0	ω=00
C	C_d	C_b
R	R_d	R_b

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

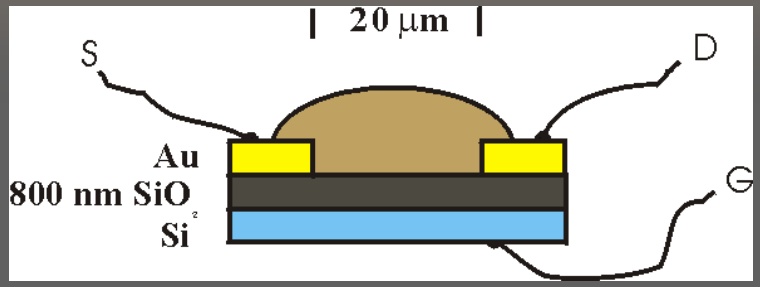


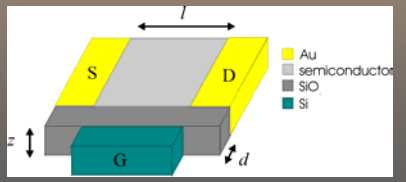
Cole-Cole plot is
G/ω vs. V

yields ε

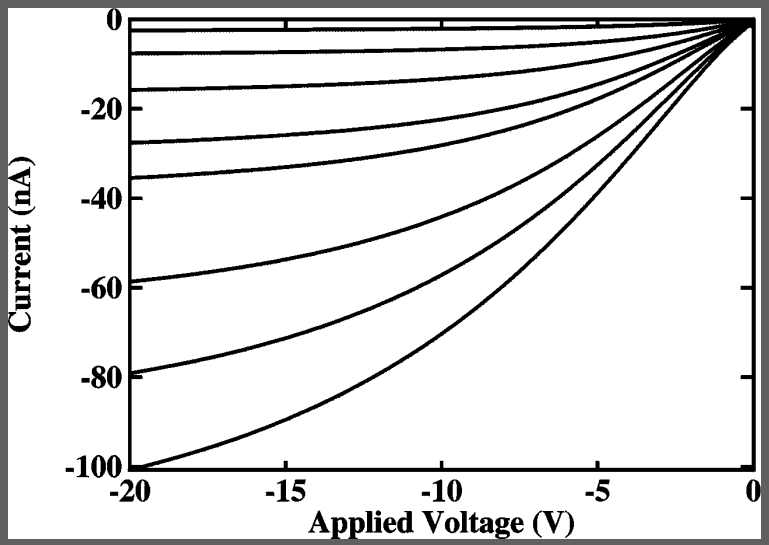
(if we know electrode area and film thickness)

Field Effect Transistor



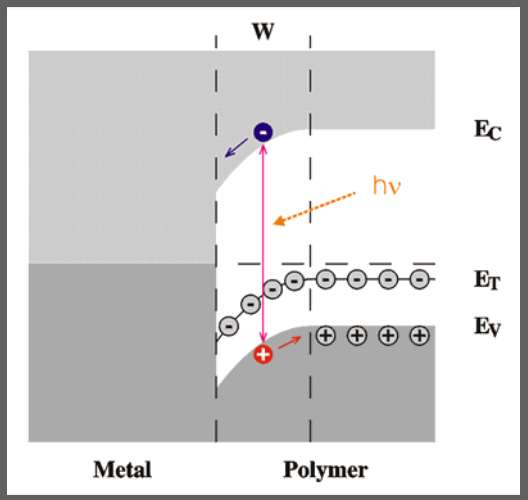


$$I_{SD}^{SAT} = (Z/L)\mu_p C\,[(V_G - V_T)^2]$$



symbol	Meaning
L	Channel length
Z	Channel width
d	Oxide thickness
V_G	Gate voltage
V_D	Drain voltage
I_{SD}	Drain current
μ	(hole) mobility
C	Oxide capacitance = $A\varepsilon/d$

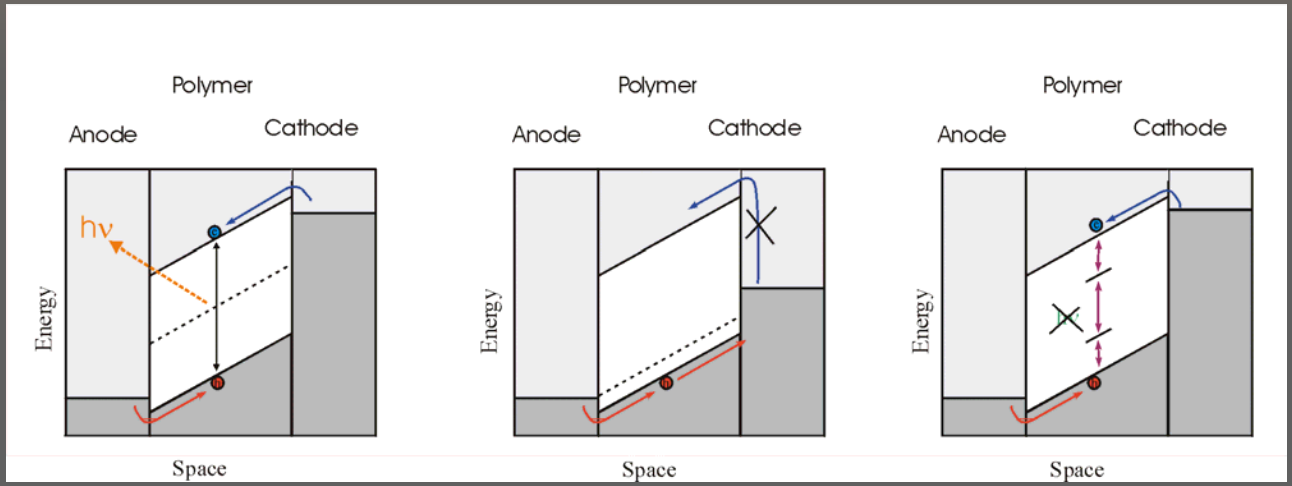
Optical Effects: Photo detector/solar cell



In photo-detectors / solar cells

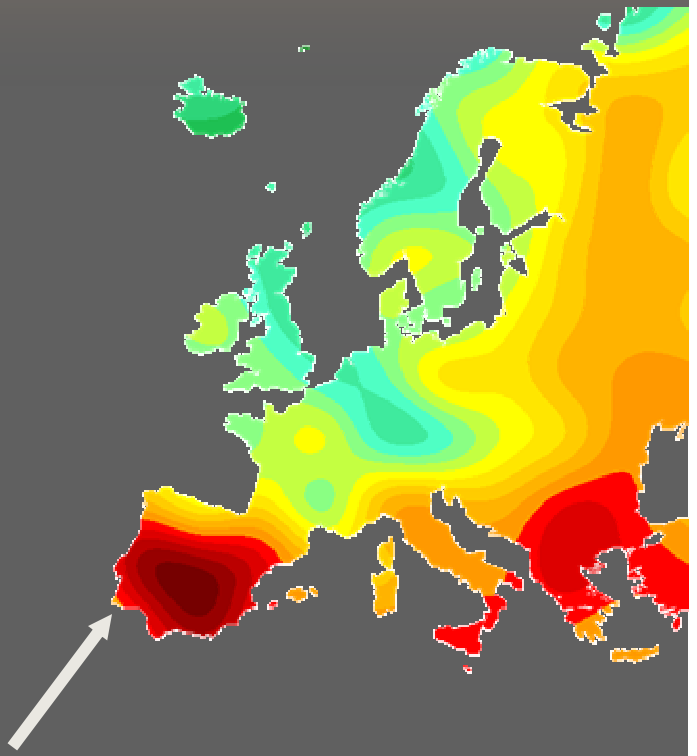
- Energy of photon is absorbed by creation of e-h pair
- Electric field in active region breaks the e-h pair
- Individual carriers are swept out of region and contribute to external current

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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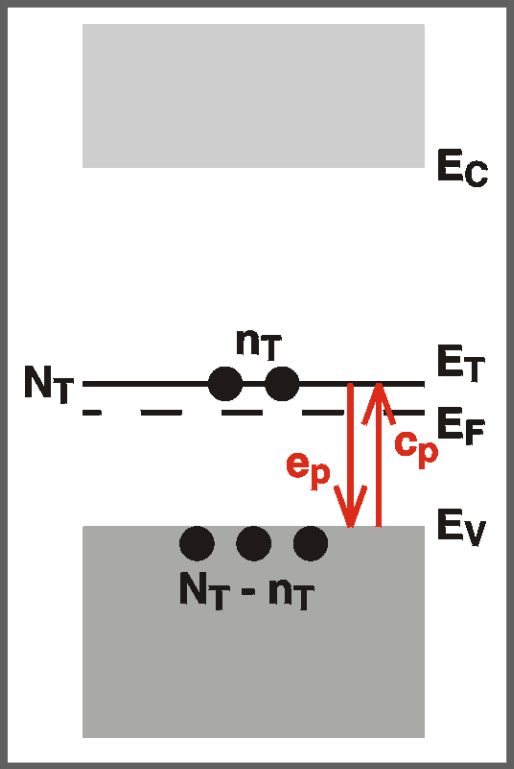
Basic Kinetics

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!

$$1/\tau = e_p = \gamma T^2 \sigma \exp(-E_a/kT)$$

Capacitance Transients

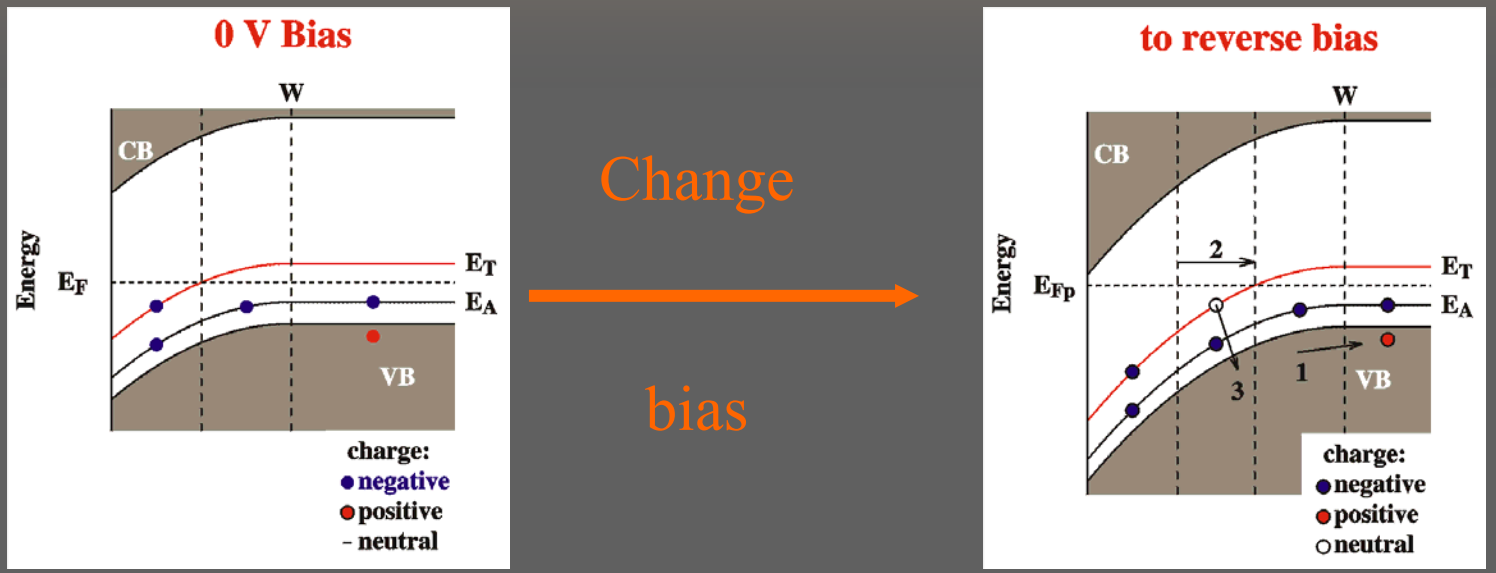
"Change the bias and let's look how the capacitance evolves over time"

- Capacitance depends on bias (remember, something like $C \sim 1/V^{1/2}$)
- A new depletion width has to be reached. At the end:

$$C = \varepsilon A / W$$

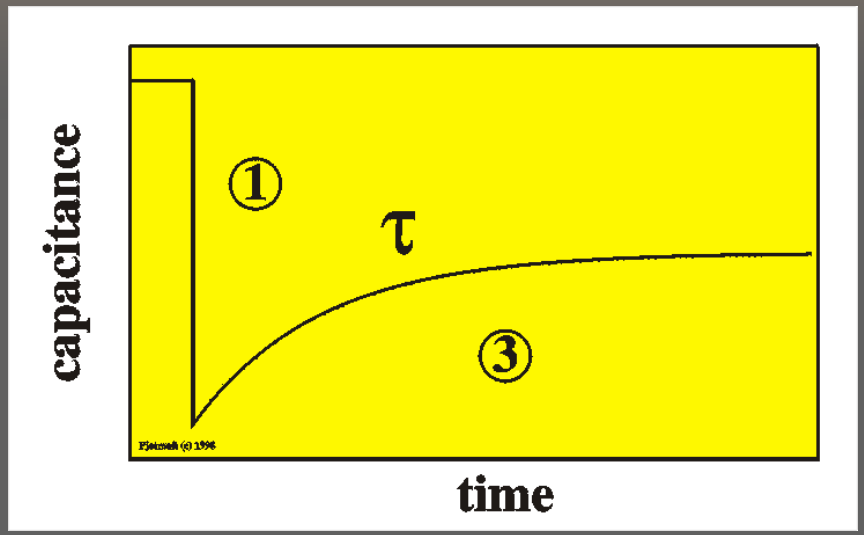
- For shallow levels: response is immediate. Limited only by speed at which free carriers can move out (μ_p).
- For deep levels: the charges have to come off there first.

Example: deep acceptor



1. Free holes move out of interface region. Immediate increase of W (C↓)
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 $f f_0^{W} \rho(x) d^2x = V_{bb}$
4. W slowly shrinks again a little. Increased capacitance

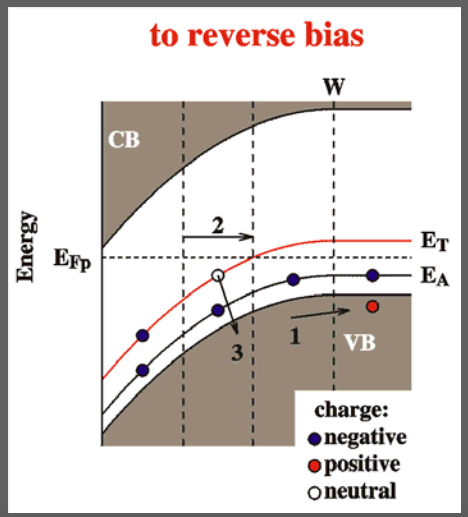
Transient



Summary:

1) Free carriers move out
2) Region off-equilibrium
3) Deep levels empty

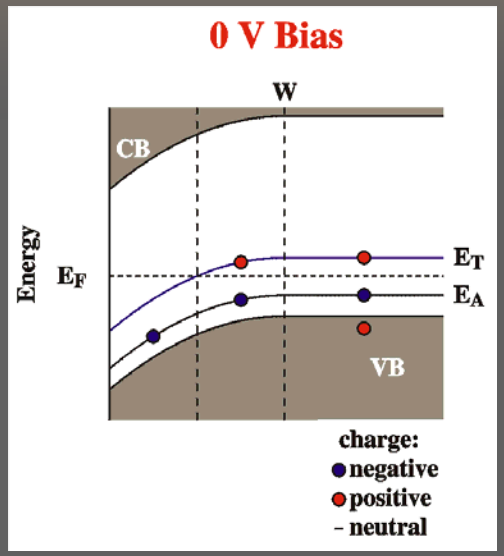
$$1/\tau = e_p = \gamma T^2 \sigma \exp(-E_a/kT)$$

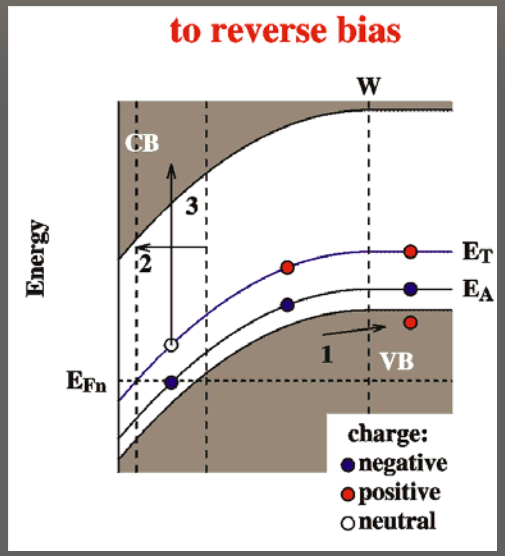


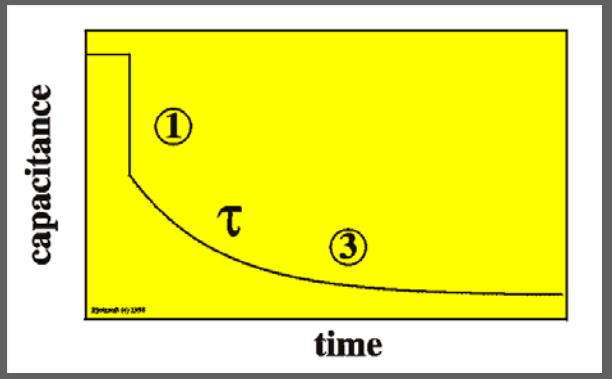
Monitoring τ over temperature will give us E_a

Very sensitive and very accurate!

Minority Traps

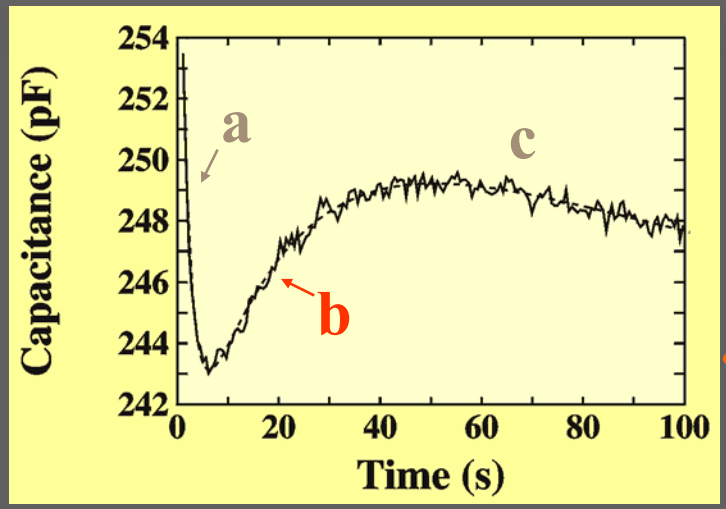






- A "minority trap" communicates with the minority band
- Under bias, the minority Fermi level moves in opposite direction
- This time electrons are emitted and the space charge decreases
- Slowly increasing W and decreasing C over time

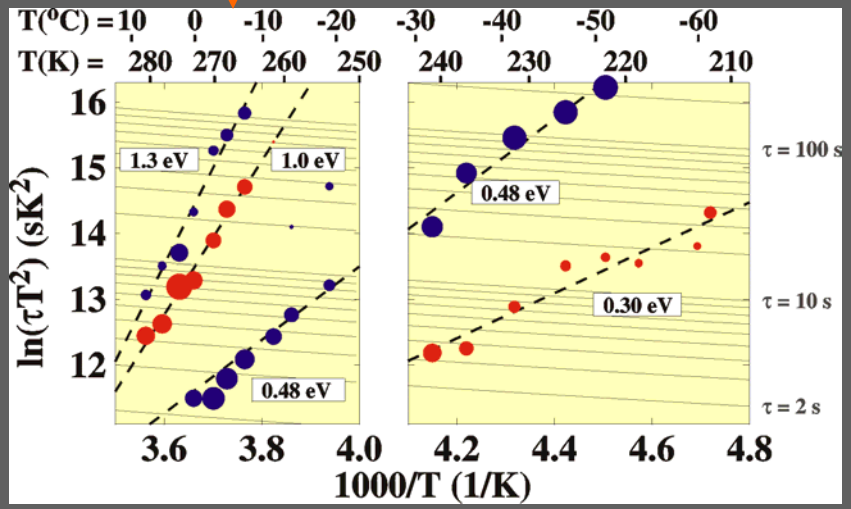
Example of C-transients:



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

$$1/\tau = e_p = \gamma T^2 \sigma \exp(-E_a/kT)$$

Note the timescale (seconds!)

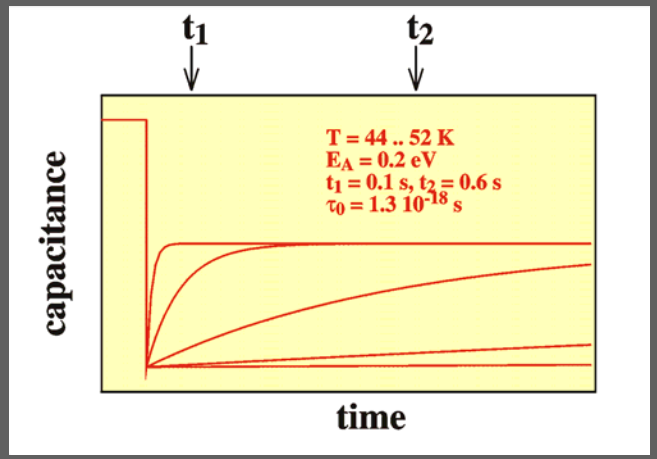


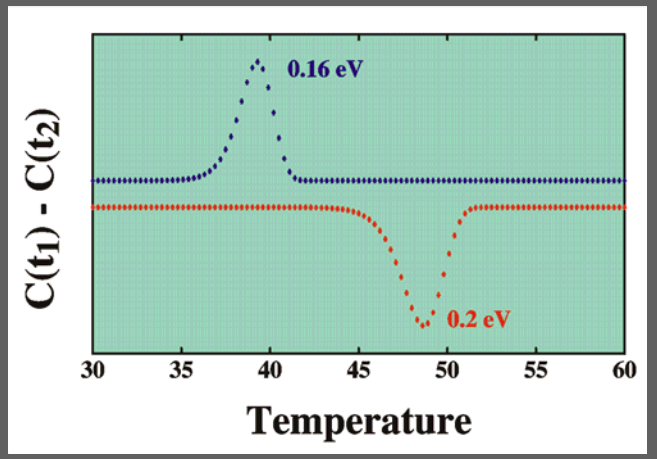
DLTS (deep-level transient-spectroscopy)

- 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: $\tau_0 T^{-2} \exp(E_a/kT) = (t_2 - t_1)/[\ln(t_1/t_2)]$





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

DLTS summary

DLTS is

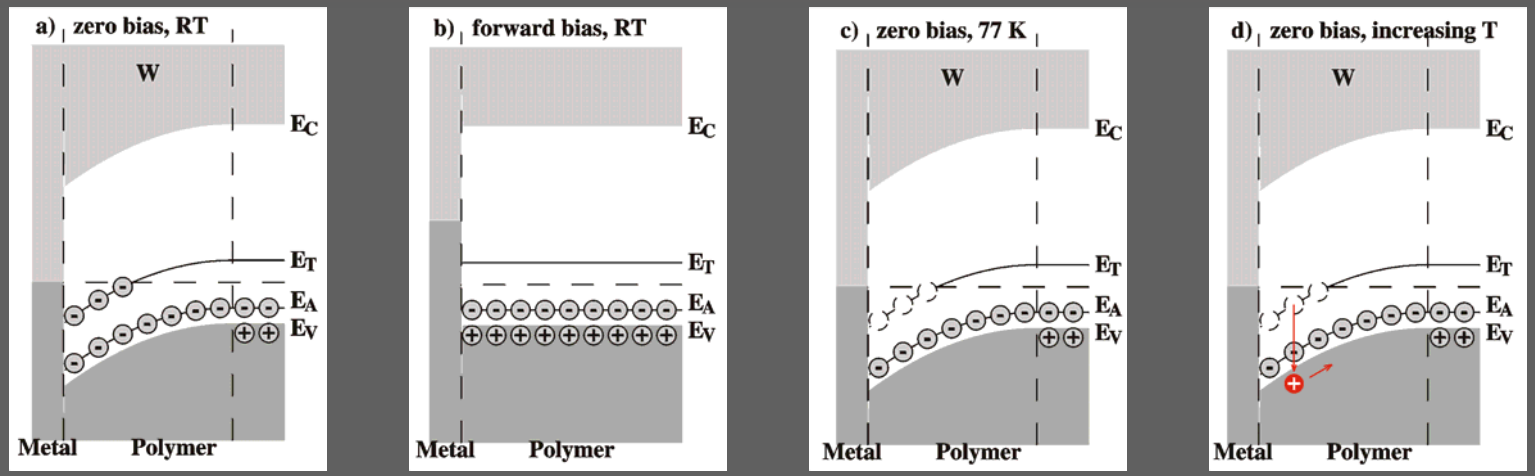
- Very easy to perform. "Walk-away" measurements
- Sensitive
- Reliable data with acurate energy determination
- "Fingerprint" spectra of defects
- Can determine density of defects. $\Delta C/C = N_T/2(N_A\text{-}N_D)$

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

$$1/\tau = e_p = \gamma T^2 \sigma \exp(-E_a/kT)$$

TSC (2)

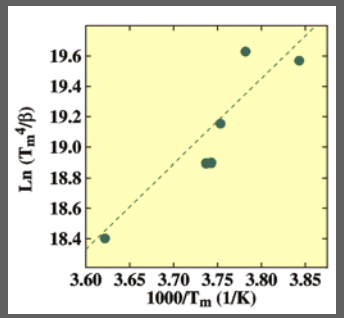
Position of the peak T_m depends on the scanning speed $\beta = dT/dt$:

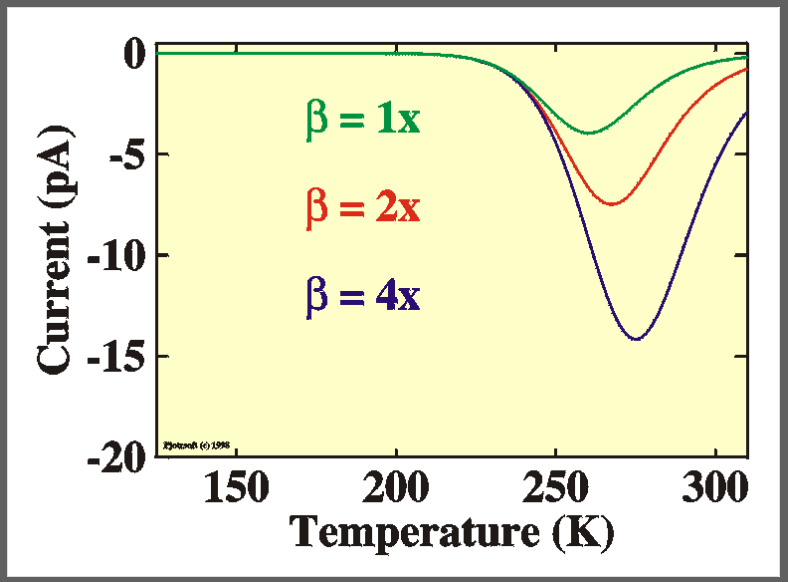
fast scan: the levels have no time to empty. high T_m

slow scan: low T_m

$$\ln (T_m^4/\beta) = E_a/kT_m + C$$

Example:





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

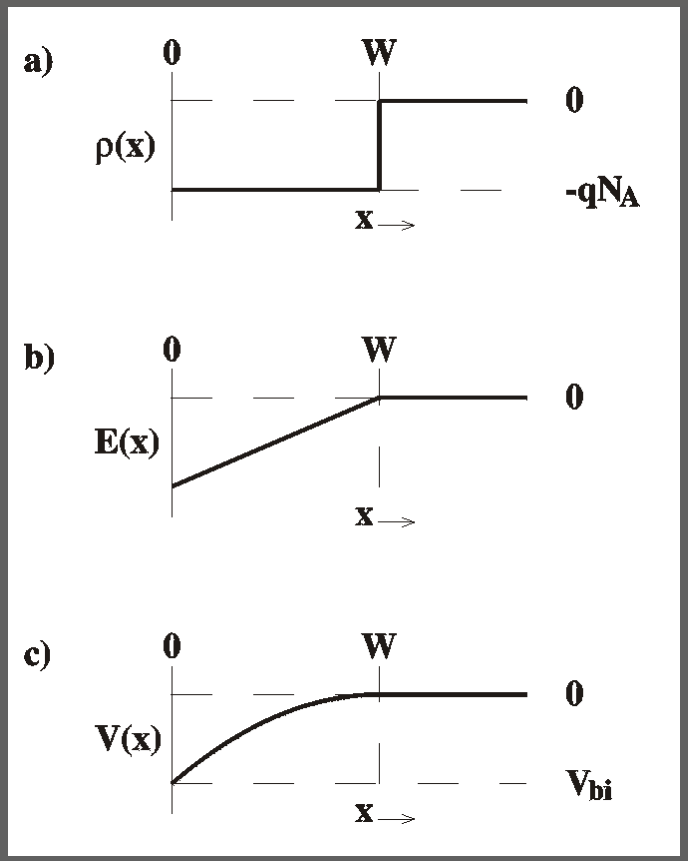
	Device Structure	Shallow Level position	Shallow Lelvel density	Deep level position	Deep level density	Free carrier mobility	Conduc-tion Model	Interface states	Difficulty cost
IV	Schoottky Bulk	+	+				+ +		1
CV	Schottky p-n		+ +					+	3
Admittance Spectroscopy	Schottky P-n	+ +							4
IV	FET					+ +			2
Hall	Bulk					+ +			8
TSC	Schottky P-n			+	+ +			+	3
DLTS	Schottky P-n			+ +	+			+	5
ToF	bulk					+ +			8

Future work

- PRAXIS project: Bio-FETs (deposit living cells on bio-compatible organic FET structures and measure their activity)
- EPR work on organic semiconductos. This seems to become a hot topic.
  very narrow lines possible (2 μT)
- 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:

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

∫ is integral sign

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

$$E(x) = \int \rho(x)\, dx = (qN_A/\varepsilon)\,(x-W)$$

$$V(x) = (qN_A/2\varepsilon)\,(x-W)^2 \qquad V_{bi} = V(0)$$

$$W = \sqrt{2\varepsilon(V_{bi}-V_{ext})/qN_A} \qquad Q = N_A W$$

Capacitance (Schottky Barrier)

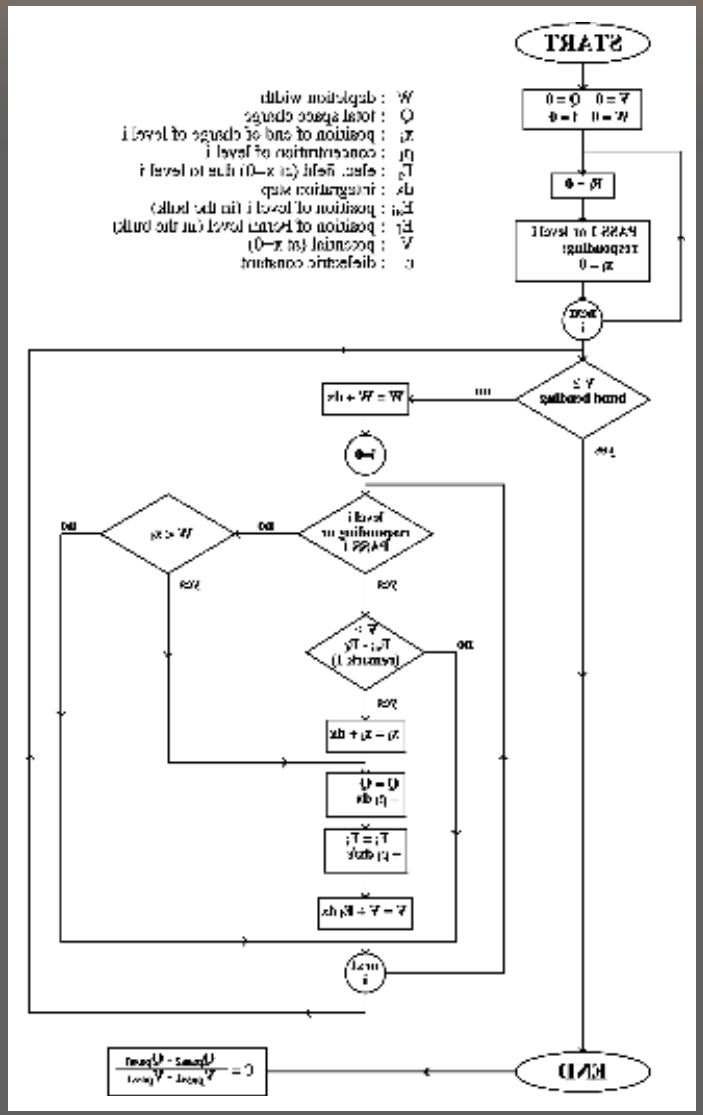
- Every time the bias is changed a new depletion width is formed
- More (or less) space charge Q

$$C = \mathrm{d}Q/\mathrm{d}V = A\sqrt{q\varepsilon N_A/2(V_{bi}-V)}$$

$$\boxed{C = A\varepsilon/W}$$

A Schottky barrier is equivalent to metal plates (area A) at mutual distance W, filled with dielectric ε

Numerical calculation of C



Riemann integration until

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

then:

$$C = dQ/dV$$

$$C = (dQ/dx) / (dV/dx)\,|_{x=W}$$

or: two-pass calculation:

$$C = \Delta Q/\Delta V$$

AC: Conductance (schottky barrier)

$V(t) = V + v \sin(\omega t) \longrightarrow I(t) = I + i \sin(\omega t)$

DC: $1/R = I/V$, AC: $G = i/v$

Small v: conductance G is the derivative of the IV-curve

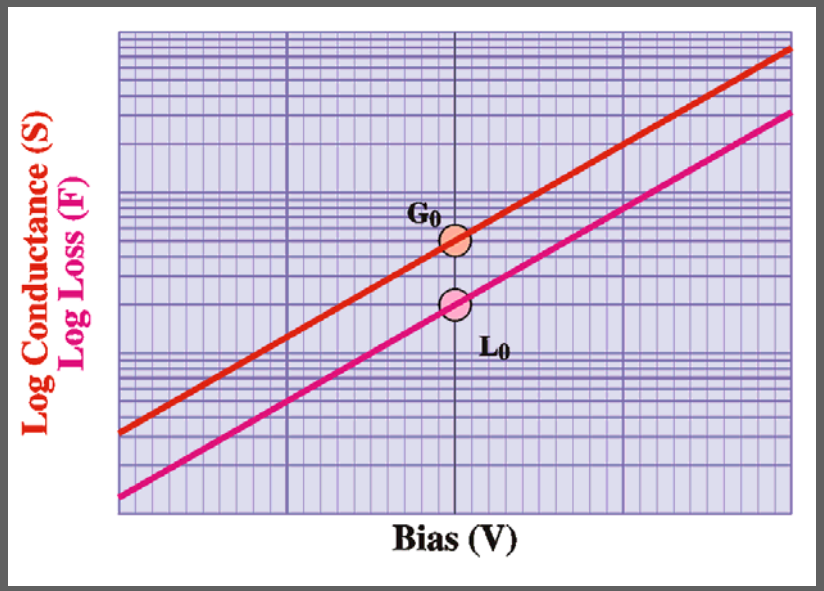
$J = J_0 [\exp(qV/nkT) - 1]$

$$G = G_0 \exp(qV/nkT)$$

Frequency independent

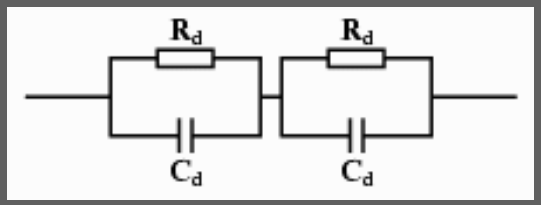
Loss: $L = G/\omega$

Loss-tangent: $\tan\delta = G/\omega C$



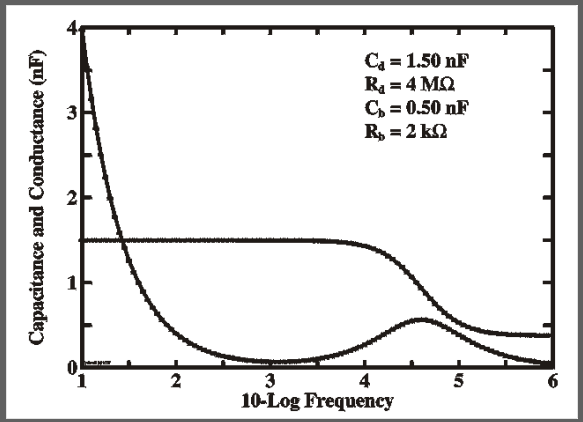
Admittance Spectroscopy Equivalent circuits

Admittance spectroscopy: C, G, tanδ as function of ω



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

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



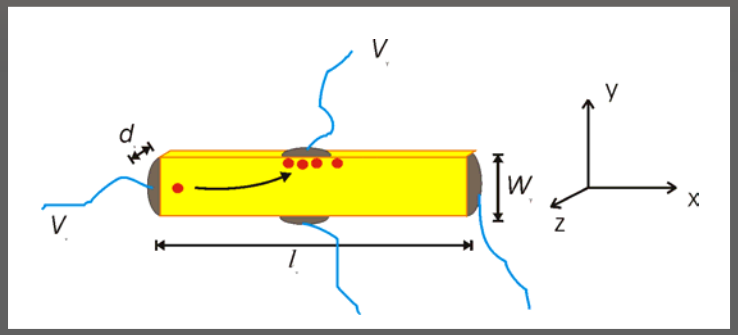
Resembles deep states picture:

”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:

$$\sigma = qp\,\mu_p$$

$$\sigma = (I/V_x)(l_x/W_y d_z)$$

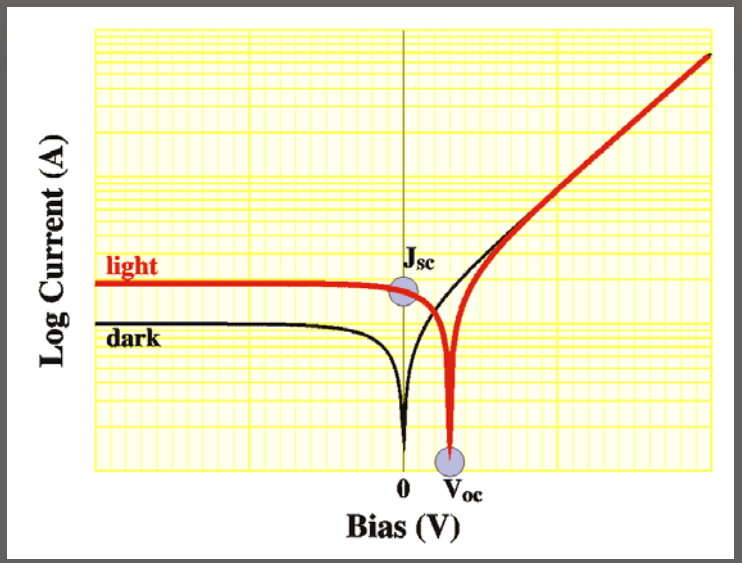
$$F_y^B = q\,B_z\,v_x \qquad F_y^E = -qE_y$$

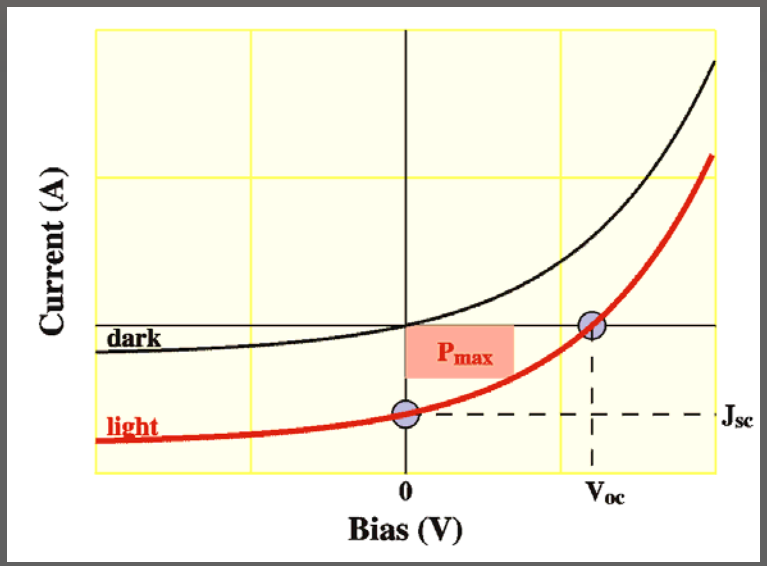
$$v_x = J_x/qp = I_x/(W_y d_z qp) \qquad E_y = V_y/W_y$$

$$qp = B_z I_x/V_y d_z \longrightarrow \boxed{\mu_p = l_x V_y / B_z V_x W_y}$$

In the Hall measurements we can measure the hole mobility μ_p

Solar Cell





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

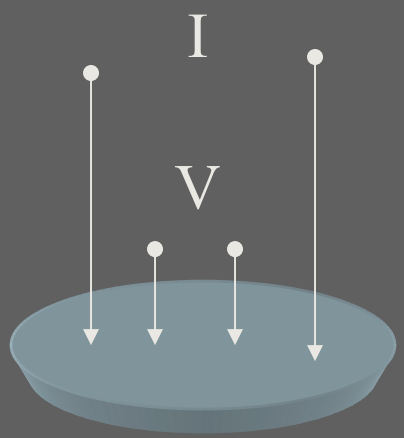
Conductivity: $\sigma = e\,\mu_p\,p$

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

acoustic phonons: $\mu_p \sim T^{-3/2}$

ionized impurities: $\mu_p \sim T^{3/2}$

optical phonons: $\mu_p \sim T^{3/2}$



4-point probe