Band tails and conductivity in disordered materials

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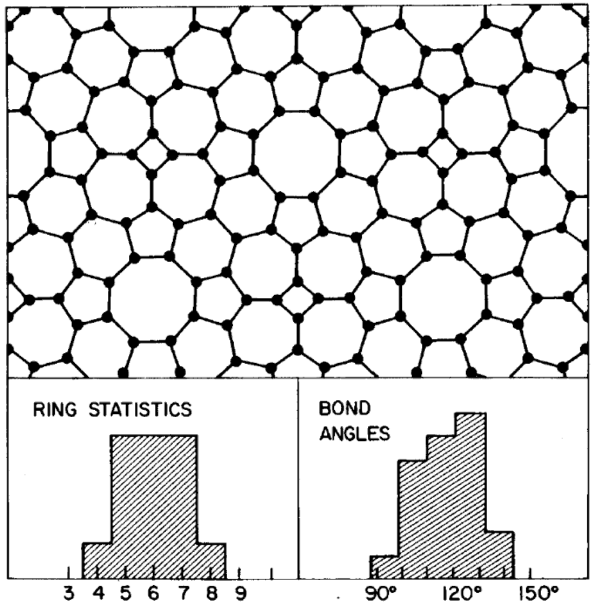
Disorder in amorphous silicon

- Waves with short wavelengths (high energy) feel short range order similar to the periodic crystal (four fold coordination of nearest neighbours)
- Waves with long wavelengths (low energy) are disturbed by lack of long range order (localization)

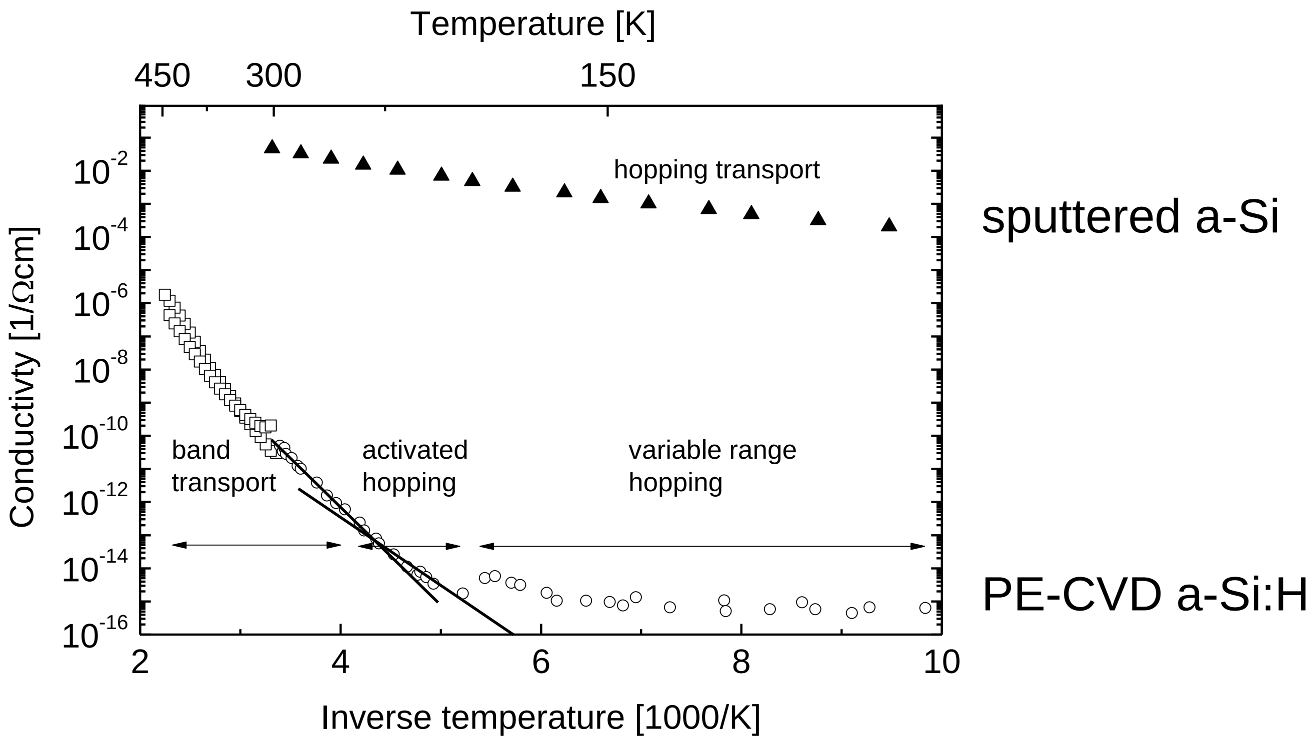


Consequence in Si:
- similar high energy interactions
- low energy interactions will be modified (properties close to **band edges**!)

DC-conductivity in a-Si and a-Si:H

F.-J. Haug

Temperature dependence of the conductivity



Arrhenius plot: slope => activation energy of transport process

LeComber, JNCS 11, p219 (1972)

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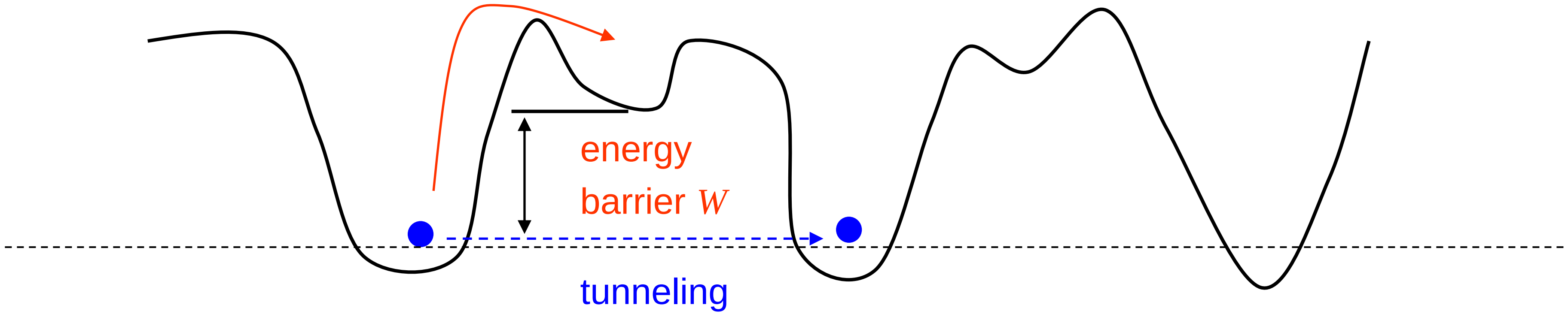
Hopping conductivity

If $g(E)$ is high within the gap (sputtered material):
hopping between localized states around E_F:



nearest neighbour hopping (below room temperature):

$$\sigma(T) = \sigma_0 e^{-W/kT}, \quad \sigma_0 = 2e^2 r^2 \nu_{ph} g(E_F) e^{-2\alpha_L r}$$

variable range hopping (very low temperature):

$$\sigma(T) = \sigma_0 e^{-B/T^{1/4}}, \quad \sigma_0 = e^2 r^2 \nu_{ph} g(E_F)$$

Mott, Phil. Mag. 19, p835 (1969)

Extended state conductivity

F.-J. Haug

For high T and low $g(E)$ within the gap (PECVD-material): extended state conduction (conduction by delocalized states around E_C or E_V):

$$\sigma(T) = en\mu = e\int_0^\infty g(E)\, f_{FD}(E,T)\,\mu(E)\,dE$$

$$\approx e\mu_0 \int_0^\infty g(E)\, f_{MB}(E,T)\,dE \approx \underbrace{e\mu_0 g(E_0)kT}_{\sigma_0}\, e^{-(E_0-E_F)/kT}$$

$(E_0\text{-}E_F) \approx 0.6$ - 0.8 eV, activated transport similar to crystalline semiconductors

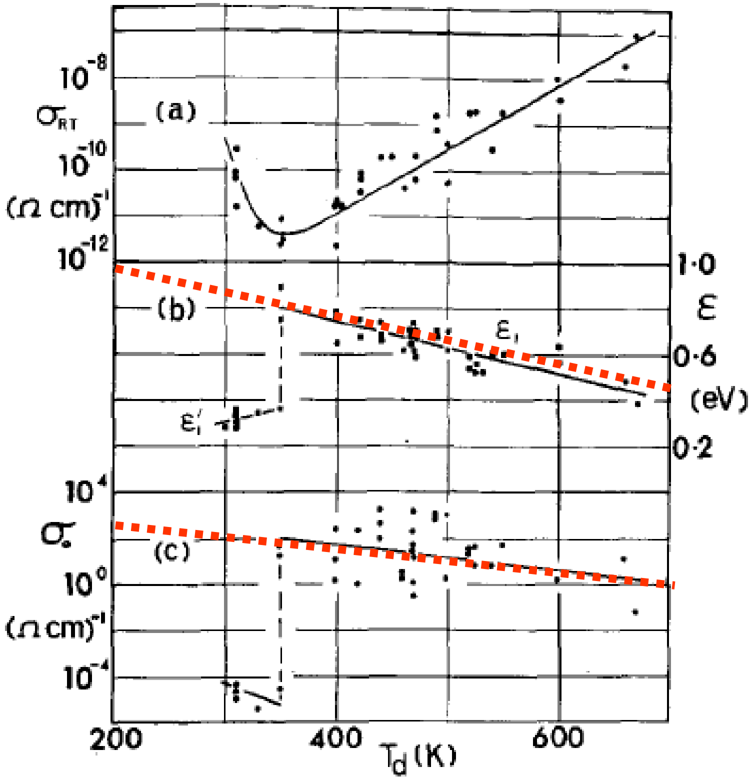
Activation energy

Attention: E_0 in the conductivity is close to, but not equal to, the band gap

Spear's data suggest a relation between the activation energy $E_a = (E_0 - E_F)$ and the pre-factor σ_0 (statistical shift)

$$\sigma_0 = \sigma_{00} e^{(E_0 - E_F)/E_{MN}}$$

Meyer-Neldel relation,
$E_{MN} \approx 50$ meV



Underlying reason :
presence of band tails!

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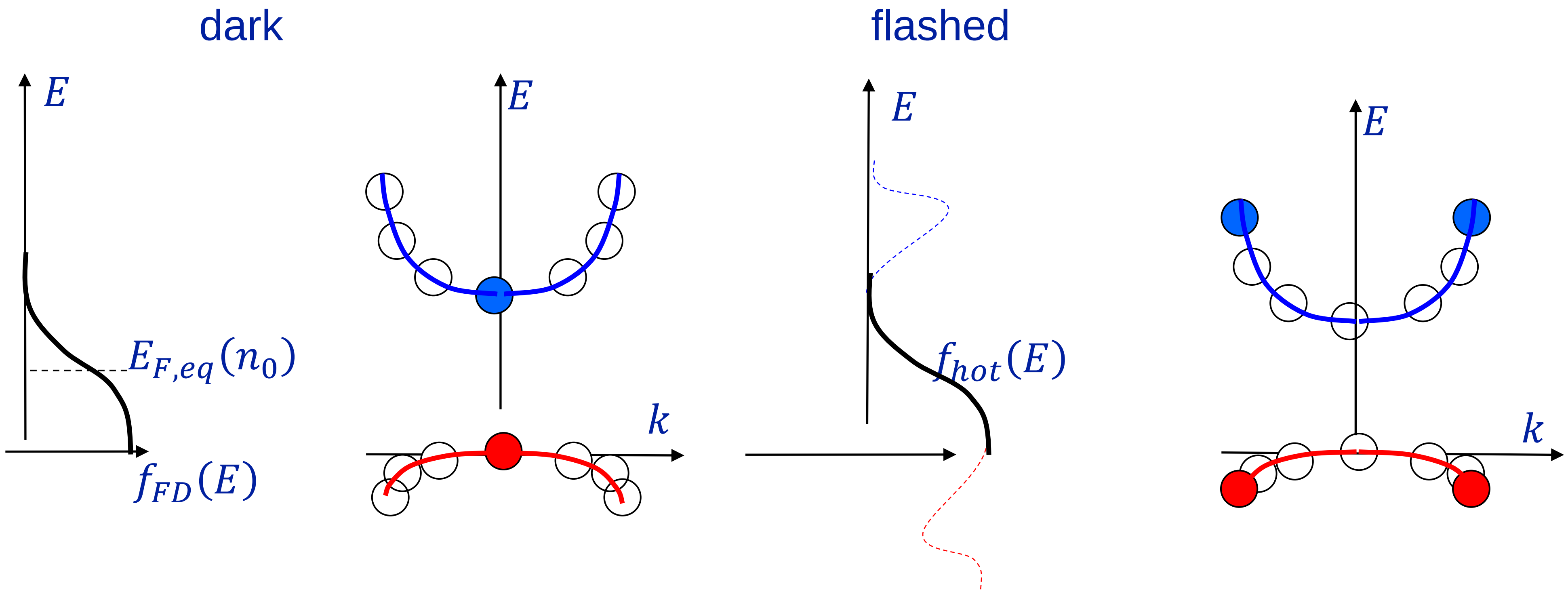
Spear, JNCS 8-10, p727, (1972)

Drift mobility

Equilibrium mobility too low for Hall effect => Use non-eq. drift mobility

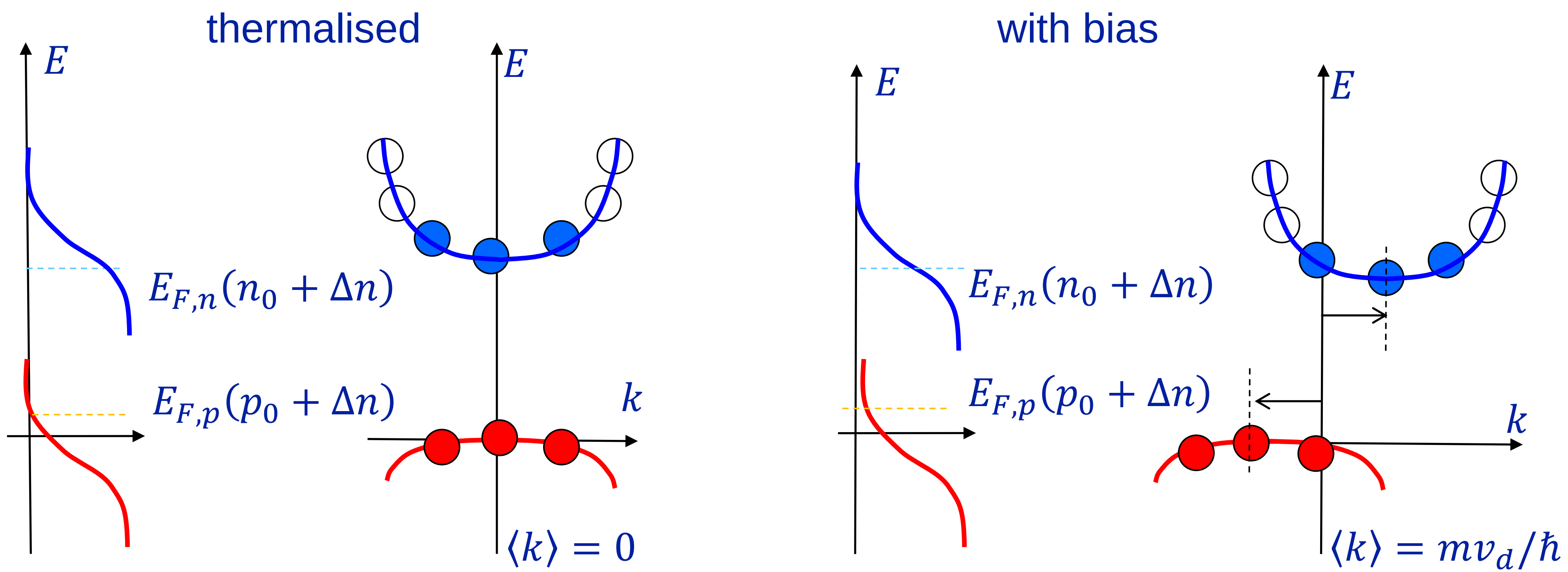
- excite with a short pulse of (blue) light
- injection of hot carrier distribution Δn (and Δp) close to surface



LeComber, JNCS 11, p219 (1972)

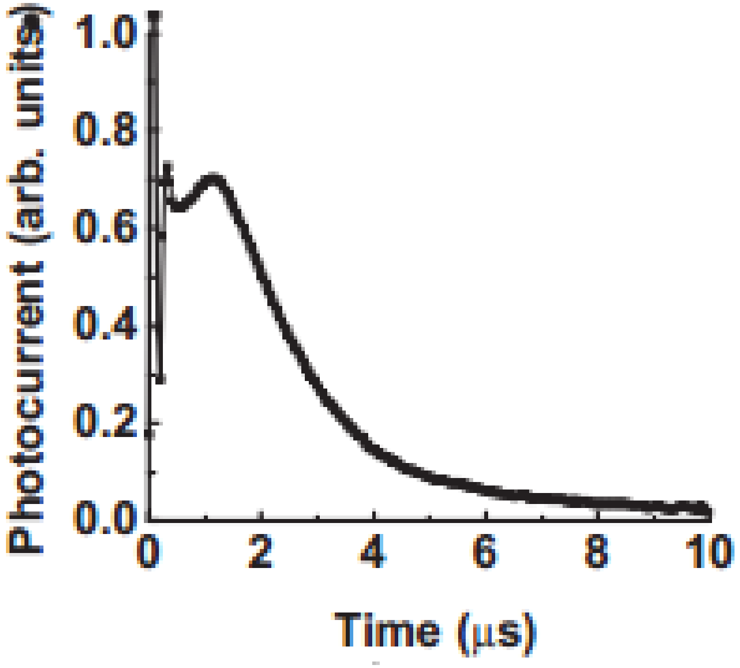
Drift mobility

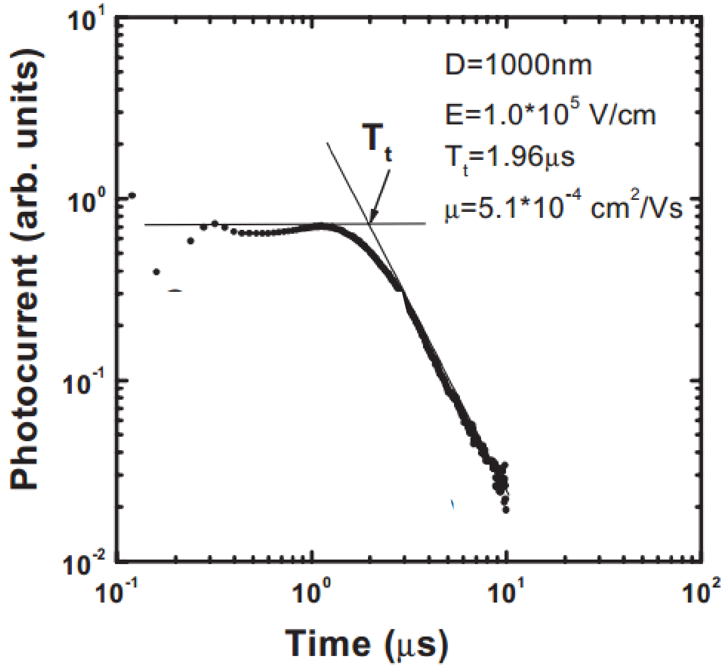
- after thermalisation (~ps) => two quasi eq. distributions with two QFLs
- apply bias voltage V across thickness d of the film
- Drift velocity $v_d = \mu E$, measure transit time t_T to other side; $v_d = d/t_T$



LeComber, JNCS 11, p219 (1972)

Example: drift in organic semiconductor



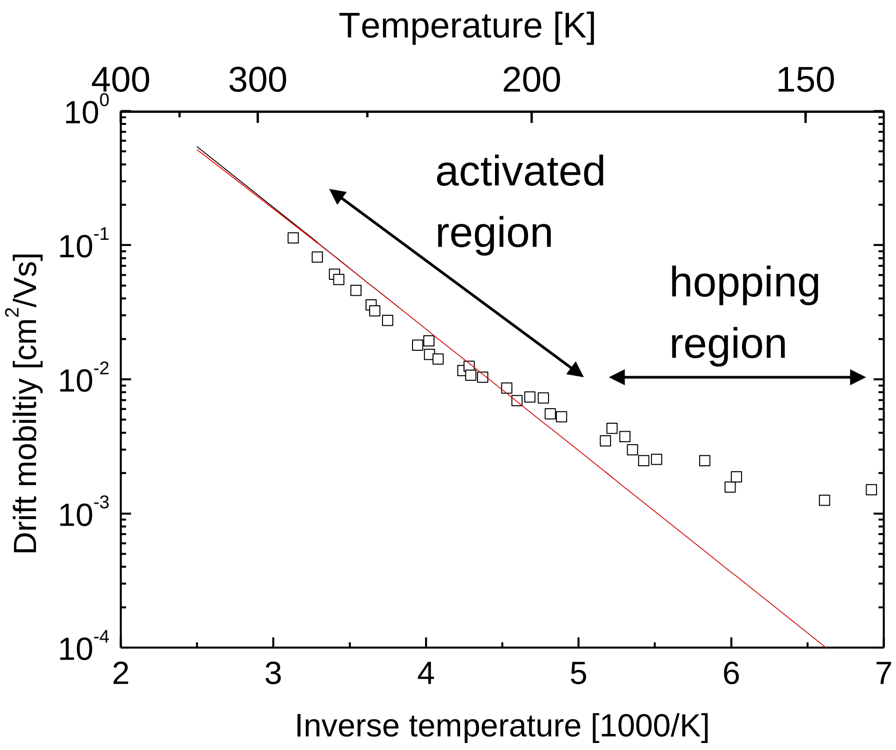


Drift mobility:

$$\mu_D = \frac{v}{E} = \frac{D}{t_T E}$$

Chen, JJAP (2000)

Temperature dependence of drift mobility



Arrhenius plot:

Linear region around RT: $E_{act} \approx 0.2$ eV

Note: non-equilibrium process, different from Hall mobility

LeComber, JNCS 11, p219 (1972)

Thermally activated drift mobility: trap level

F.-J. Haug

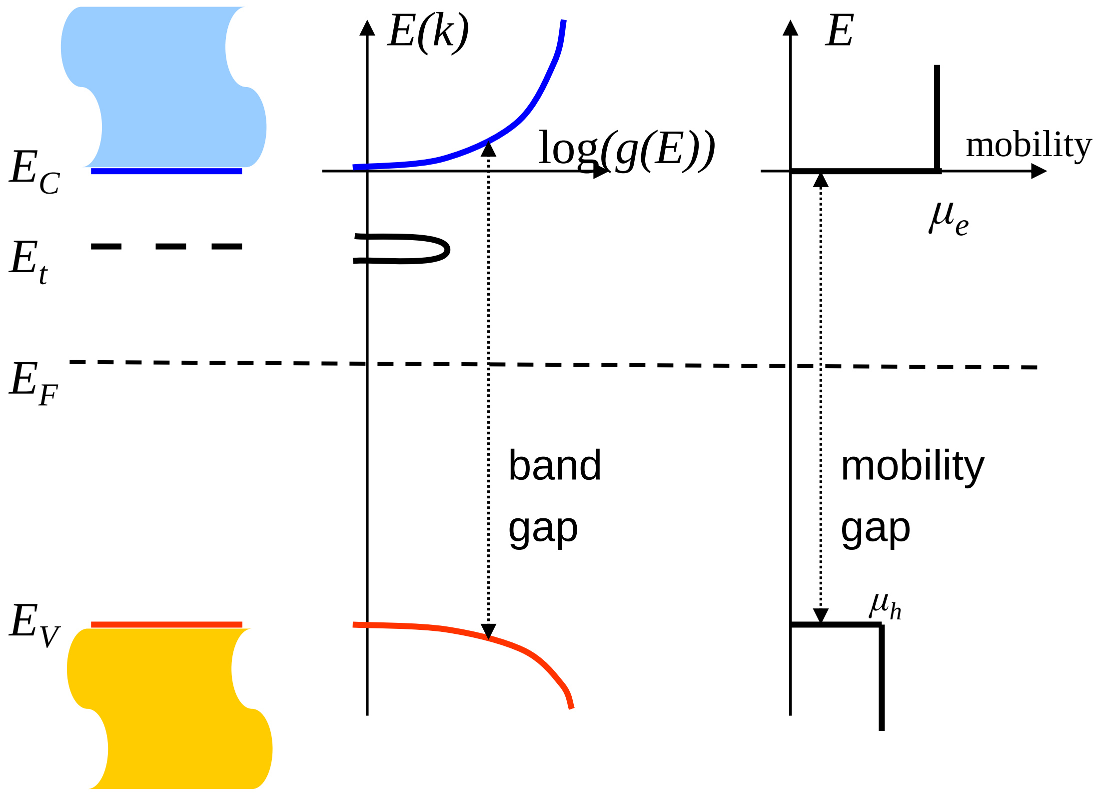
Assumption: only free carriers in bands can contribute to transport

$$\mu_d = \mu_0 \frac{n_{free}}{n_{total}} = \mu_0 \frac{n_{free}}{n_{trapped} + n_{free}}$$

Occupancy of CB (at $E = 0$), taking into account N_t trap levels:

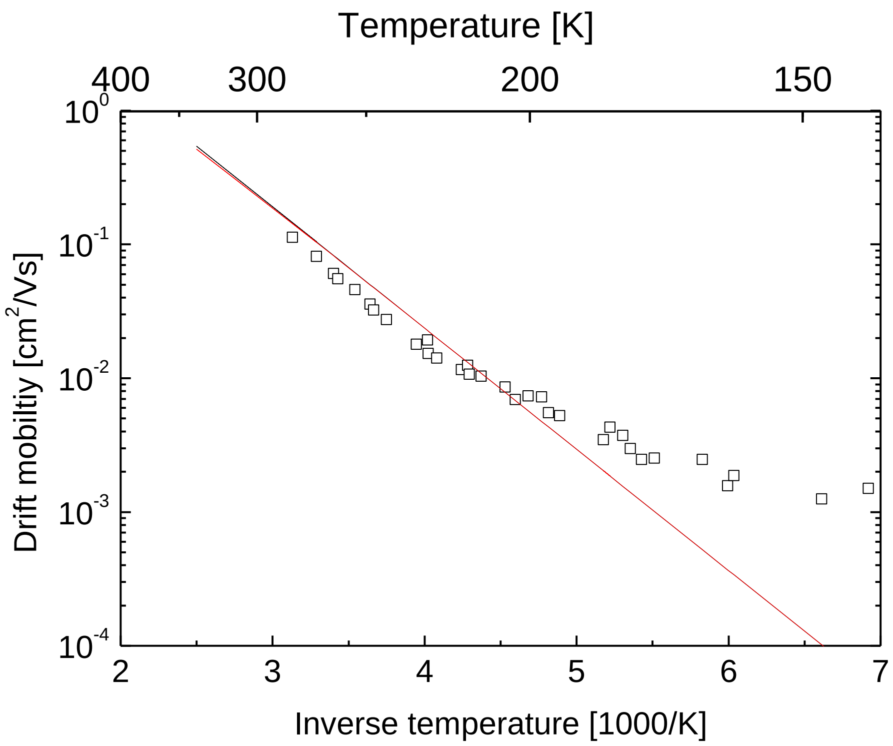
$$Q = \frac{N_c kT e^{-\frac{0}{kT}}}{N_c kT e^{-\frac{0}{kT}} + N_t e^{-\frac{-E_t}{kT}}}$$

$$\mu_d = \mu_0 \frac{N_c kT}{N_c kT + N_t e^{\frac{E_t}{kT}}}$$



Model assumes a mobility gap (sharp change close to band edge)

Drift mobility (non-equilibrium)



Model:

$$\mu_D = \mu_0 \frac{N_c kT}{N_c kT + n_t e^{E_t/kT}}$$

Boltzmann-like approximation

$$\mu_D \approx \mu_0 \frac{N_c kT}{n_t} \cdot e^{-E_t/kT}$$

E_t approximately 0.2 eV, approximation makes little difference in temperature range of interest

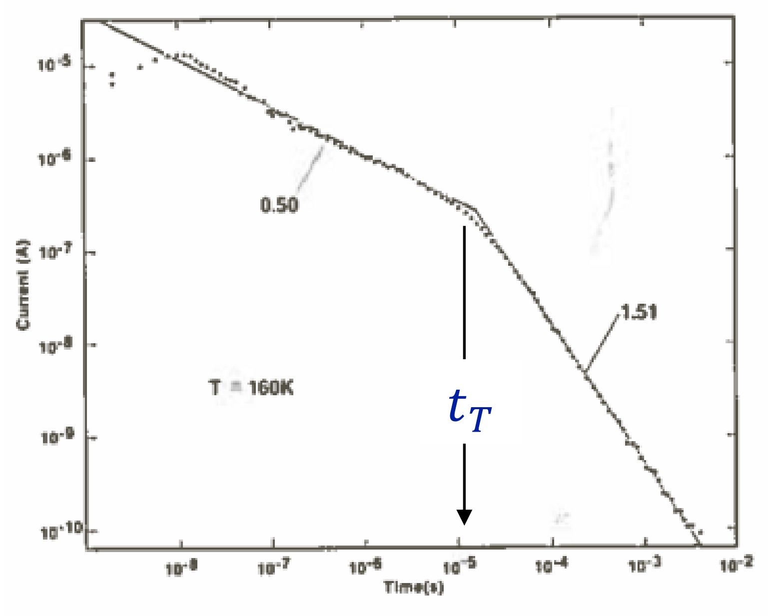
LeComber, JNCS 11, p219 (1972)

Second thoughts about drift experiments

Pulse shape not rectangular

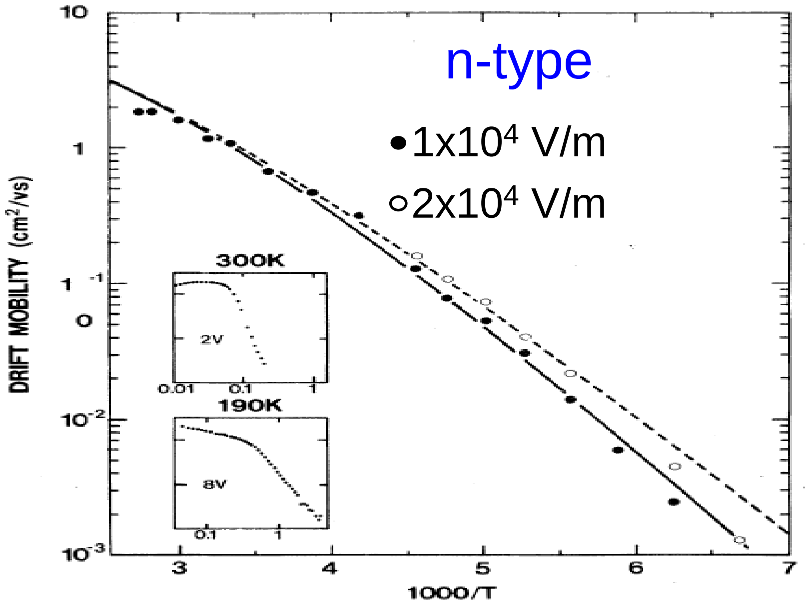
Two decay regimes

measured in a-Si(H)



Tiedje, in Physics of Hydrogenated a-Si (1984)

Mobility value depends on field
(higher mobility for faster sweep)



Tiedje, SSC 37 p49, (1980)

Tiedje, PRL 46(21) p1425, (1981)

Improved model: multiple trapping conduction

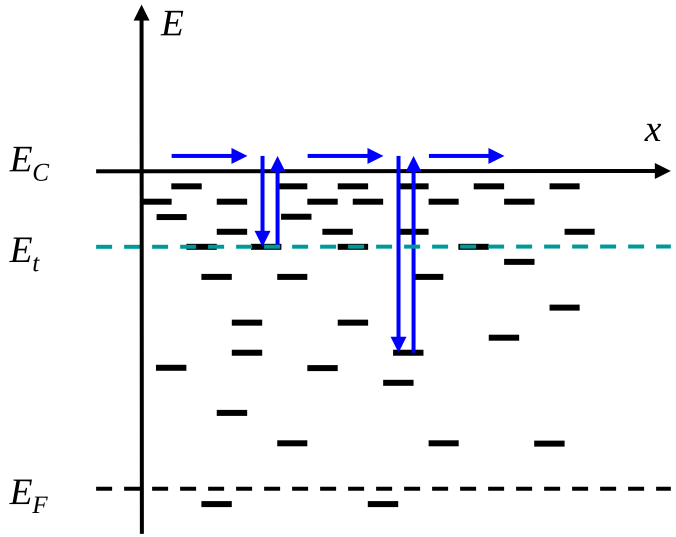
Assumptions:

Exponential distribution of states

$$N_t(E) = N_C e^{E/kT_0}$$

Residence time depends on trap depth because of thermal release

$$t = \nu^{-1} e^{E_t/kT}$$



Trap occupation: equilibrium between trapping and thermal release
=> maximum density of trapped carriers at an energy E_t below E_C

E_t depends on

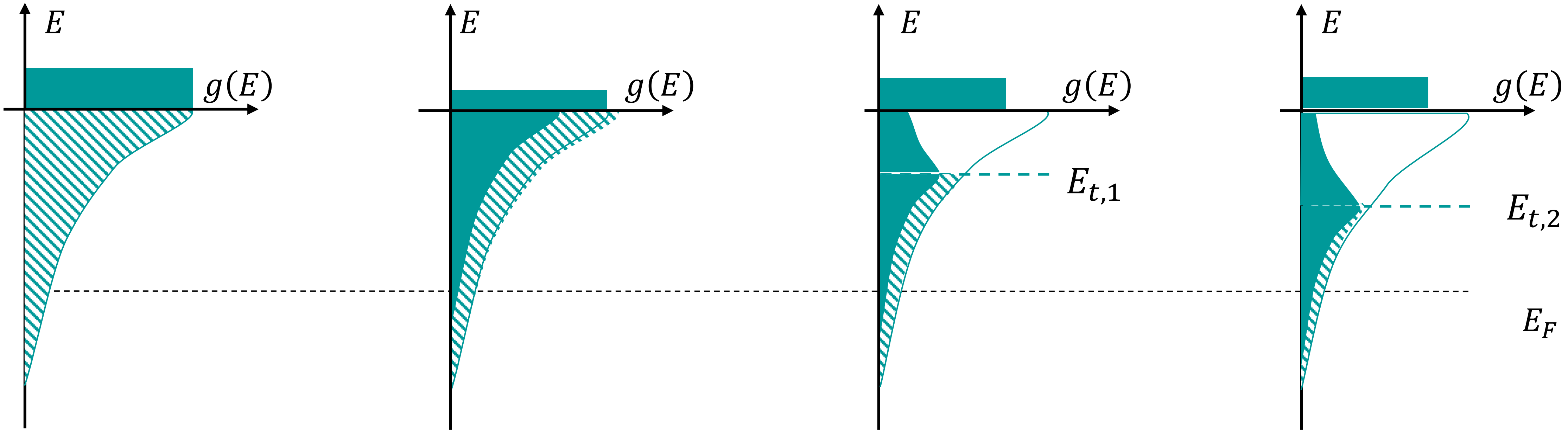
- temperature (thermal activation)
- time (release from deep states can happen, but takes longer)

Tiedje, SSC 37 p49, (1980)
Tiedje, PRL 46(21) p1425, (1981)

Time evolution of trapping statistics

F.-J. Haug

$$t = \nu^{-1} e^{E_t/kT} \quad \text{<=>} \quad E_t(t) = -kT \cdot \ln(\nu t)$$



Excitation into CB

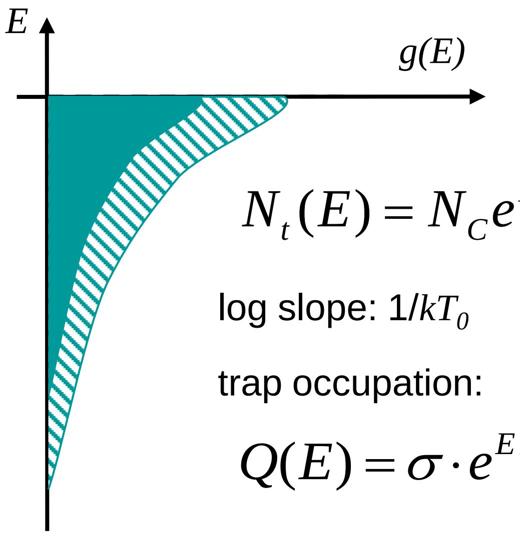
First trapping event: a share of σ (cross section) gets filled

Thermal excitation of upper part (and extraction)

The most probable trap energy E_t sinks deeper into the band tail

Effective value for trap density

first trapping event



$$N_t(E) = N_C e^{E/kT_0}$$

log slope: $1/kT_0$

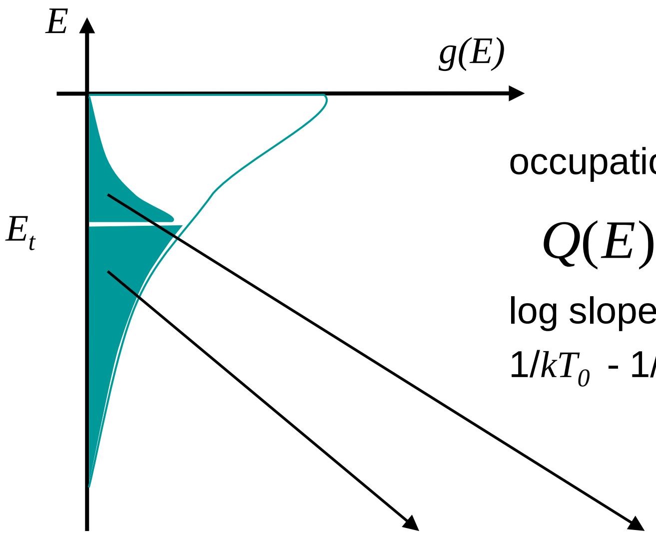
trap occupation:

$$Q(E) = \sigma \cdot e^{E/kT_0}$$

$$N_{trap} = N_t(0) \cdot \sigma \cdot kT_0$$

Quasi-equilibrium at later time:

- upper part: thermal excitation into conduction band
- lower part: complete trapping



occupation above E_t:

$$Q(E) \sim e^{E/kT_0} e^{-E/kT}$$

log slope above E_t:

$1/kT_0 - 1/kT = -(1-T/T_0)/kT$

$$N_{trap} = N_t(E_t) \cdot kT_0 + N_t(E_t) \cdot \frac{kT}{1 - T/T_0}$$

Tiedje, SSC 37 p49, (1980)

Drift mobility with trapping into band tail

Put most probable level N_t into occupation statistics of single trap level

$$\mu_D = \mu_0 \frac{N_c kT}{N_c kT + N_t(E_t) \cdot \left(kT + \frac{kT}{(1 - T/T_0)} \right) \cdot e^{\frac{E_t}{kT}}}$$

Use band tail density $N_t(E) = N_C e^{E/kT_0}$

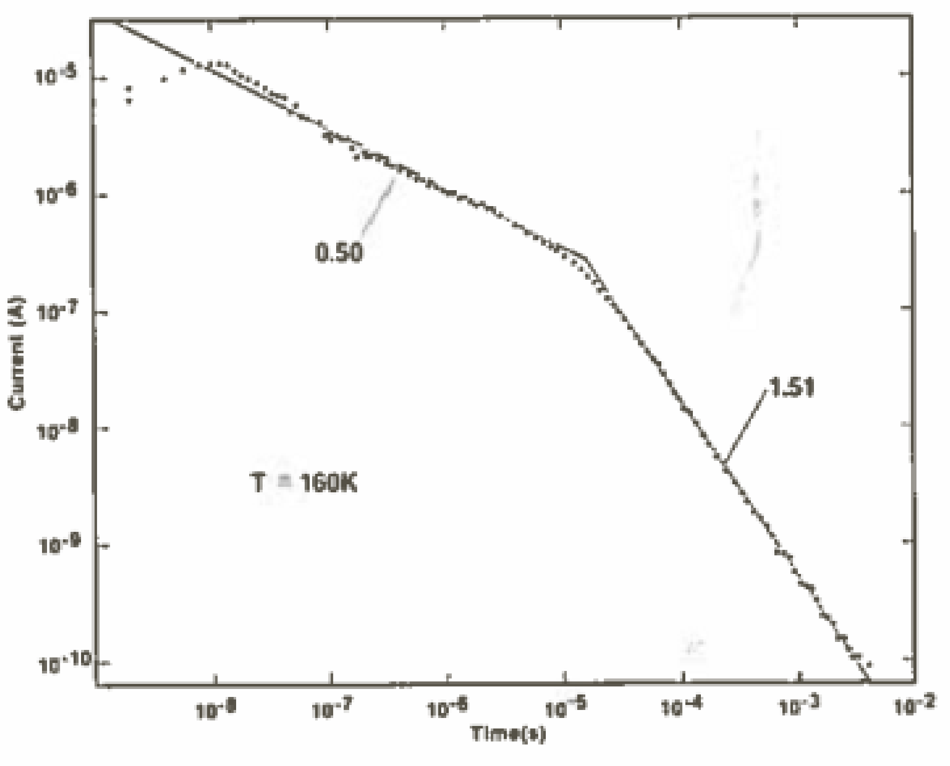
and “sinking” trap level $E_t(t) = -kT \ln \upsilon t$

$$\mu_D = \mu_0 \frac{1}{1 + (\upsilon t)^{(1-\alpha)} (T_0 / T + 1/(1 - T/T_0))}$$

$$\mu_D \approx \mu_0 \cdot \alpha (1 - \alpha) \cdot (\upsilon t)^{-(1-\alpha)}$$

Time dependent mobility ($\alpha = T/T_0$), result depends on measurement time!

Cross-check with measurement



Initial phase: transport with trapping from CB into sinking level (Tiedje)

$$\mu_D \approx \mu_0 \cdot \alpha(1-\alpha)\cdot(\upsilon t)^{-(1-\alpha)}$$

Later phase: hopping with trapping and delayed release (w/o derivation)

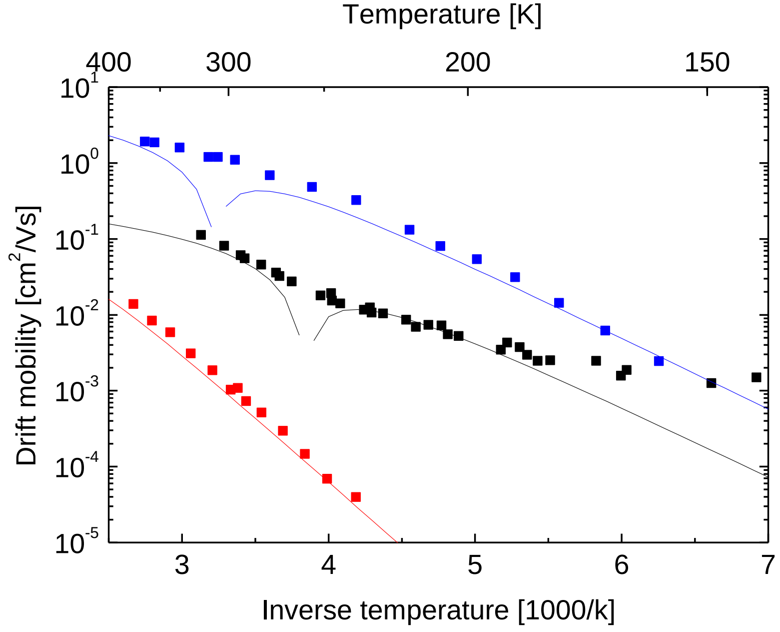
$$\mu_D \sim (\upsilon t)^{-(1+\alpha)}$$

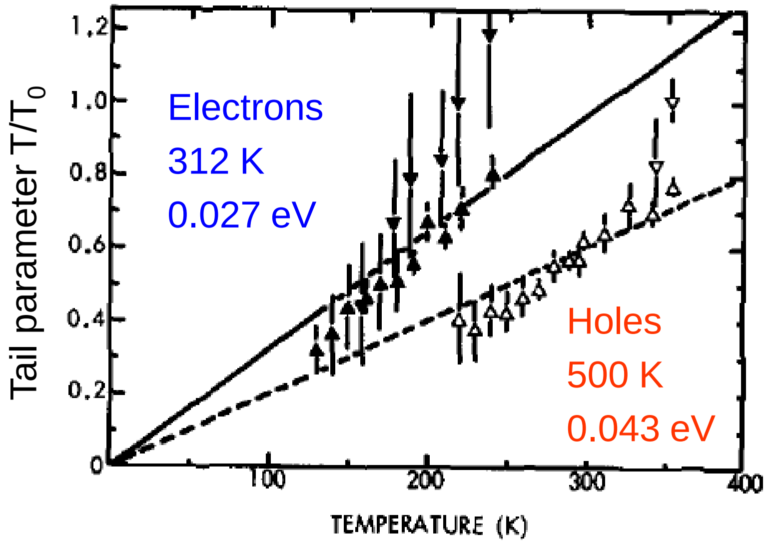
Here: α = 0.5, T_0 ≈ 320 K

Scher, PRB (1975)
Jakobs, PRB (1993)

Band tail slope from drift mobility

Drift mobility shows transition between dispersive (low T) and non-dispersive transport (high T); transition at T_0

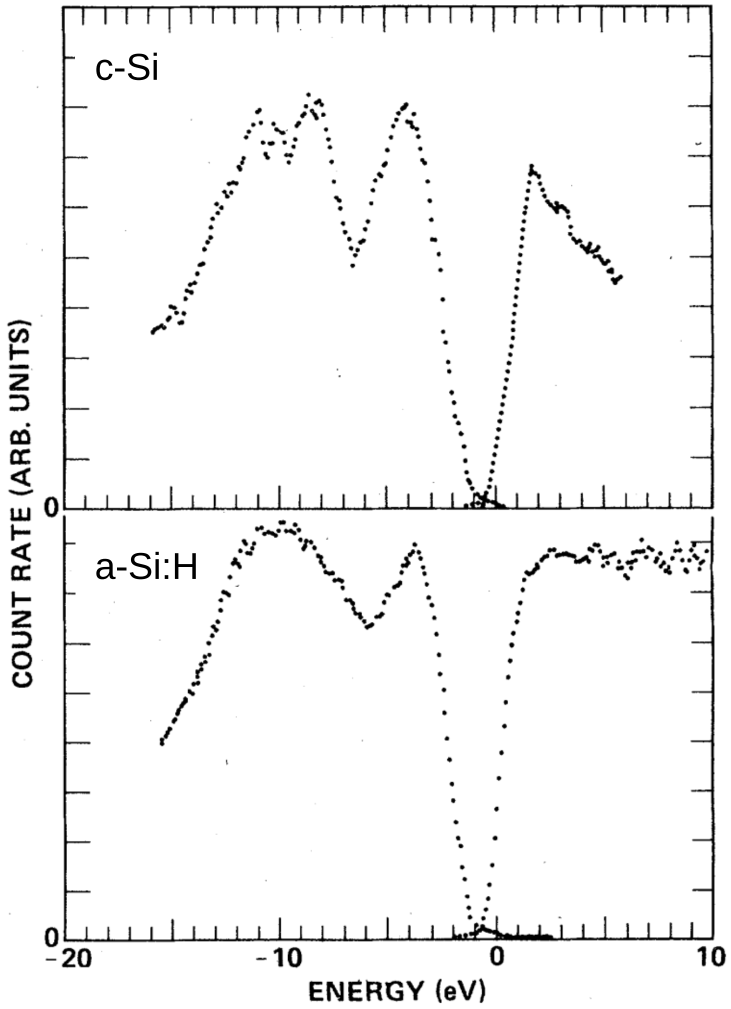




The detailed time- and temperature dependence of the signal dispersion yields the band tail slopes

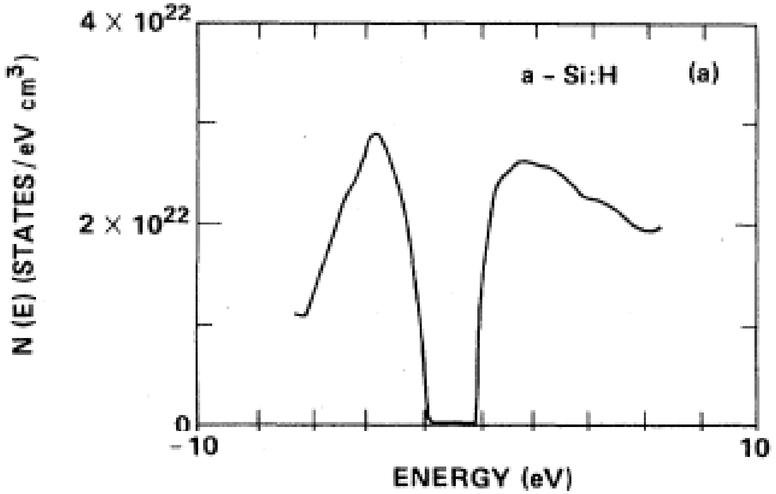
Tiedje, PRL 46(21) p1425, (1981)

XPS – direct measurement of bands tails



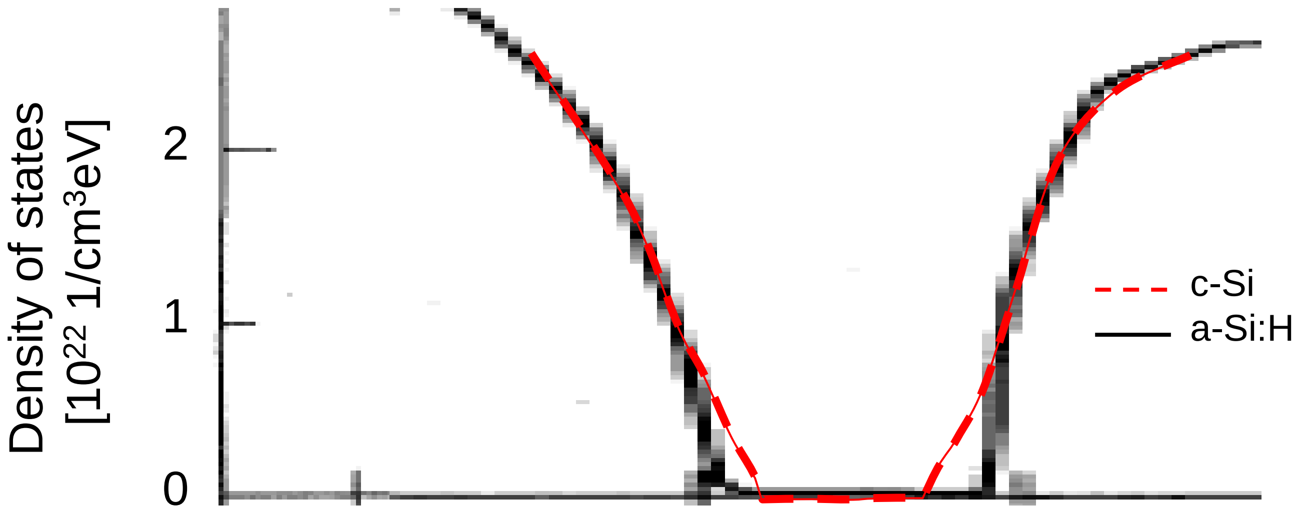
X-ray photoelectron spectroscopy (XPS)
excite e⁻ from filled states (VB)
inverse XPS: use light to pump electrons into empty states (CB), excite from there

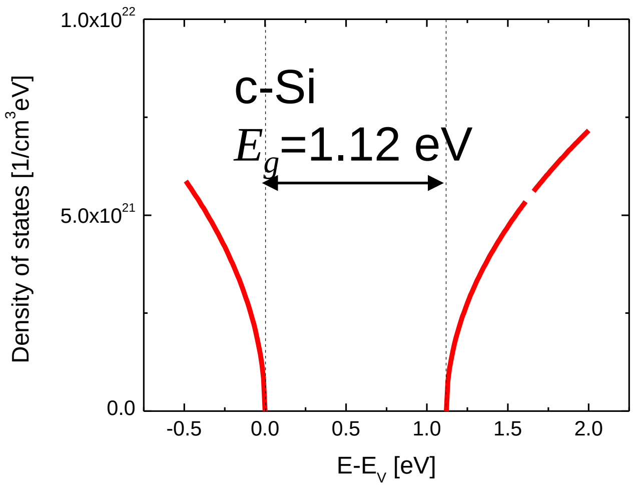
Determine density of states (DOS) for a-Si:H

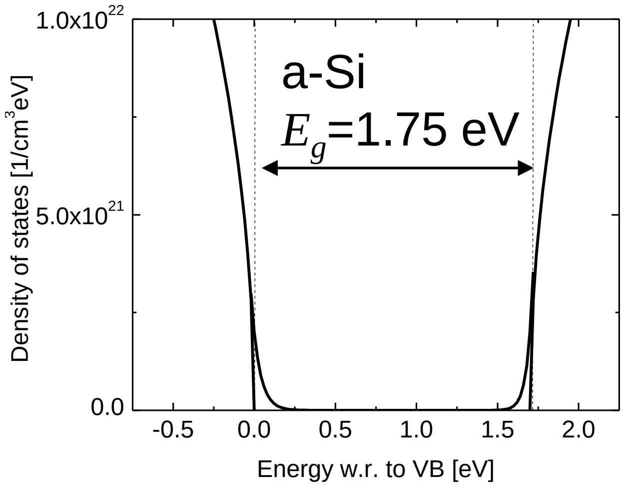


Jackson, PRB 31(8) p5187, (1985)

Detail: band edges of c-Si and a-Si

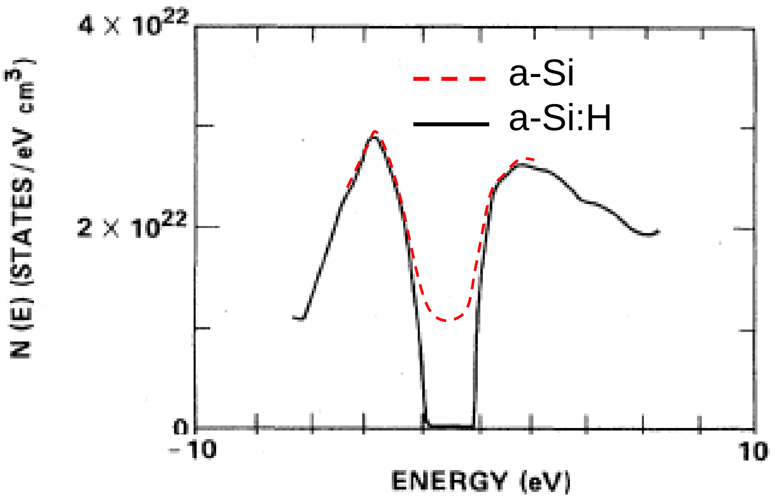




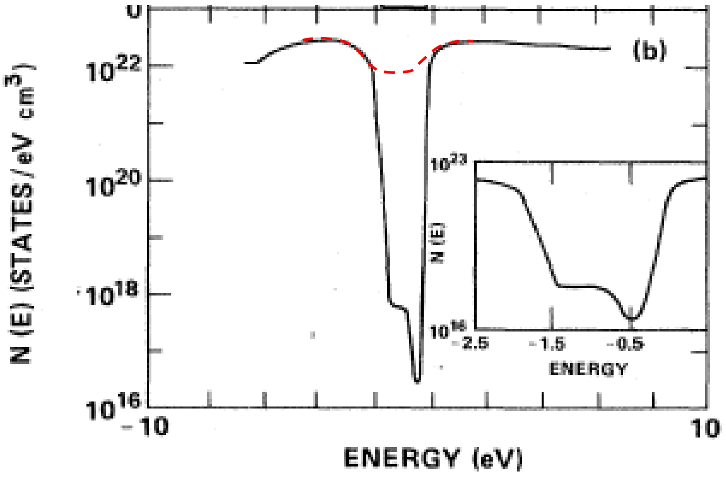


High resolution XPS

lin. scale



log. scale



Detailed band edge structure reveals band tails
(already suggested earlier on the basis of charge transport measurements)

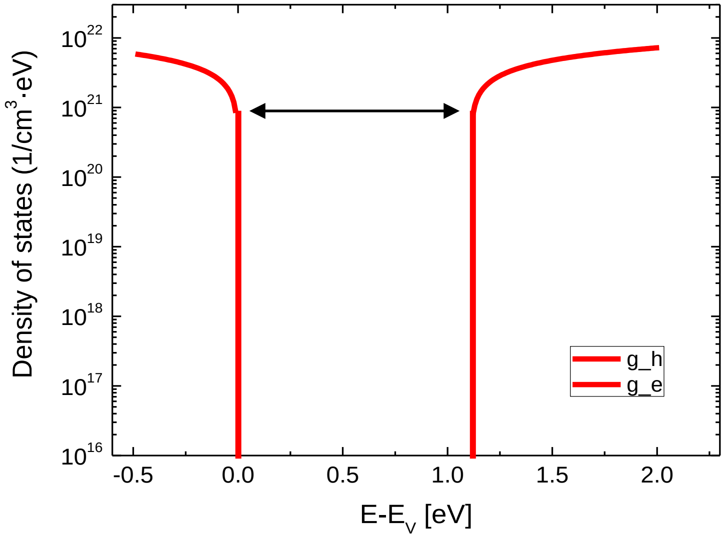
Jackson, PRB 31(8) p5187, (1985)

Detail of band edges

F.-J. Haug

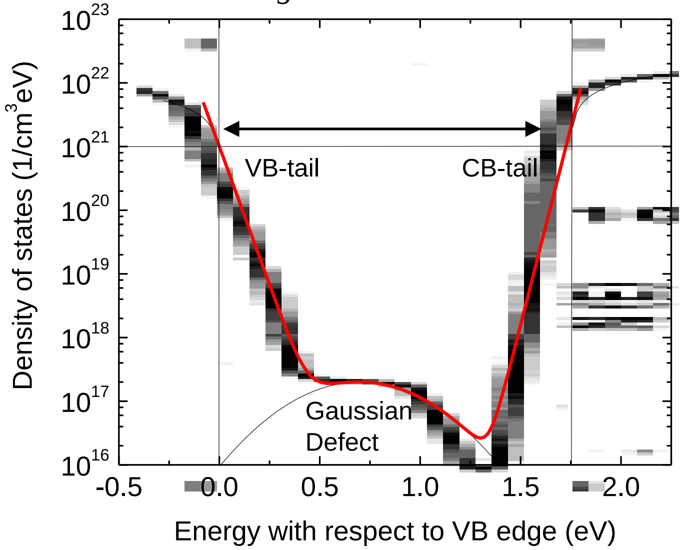
c-Si

E_g=1.12 eV



a-Si:H

E_g≈1.75 eV



Sharp band edges, no gap states

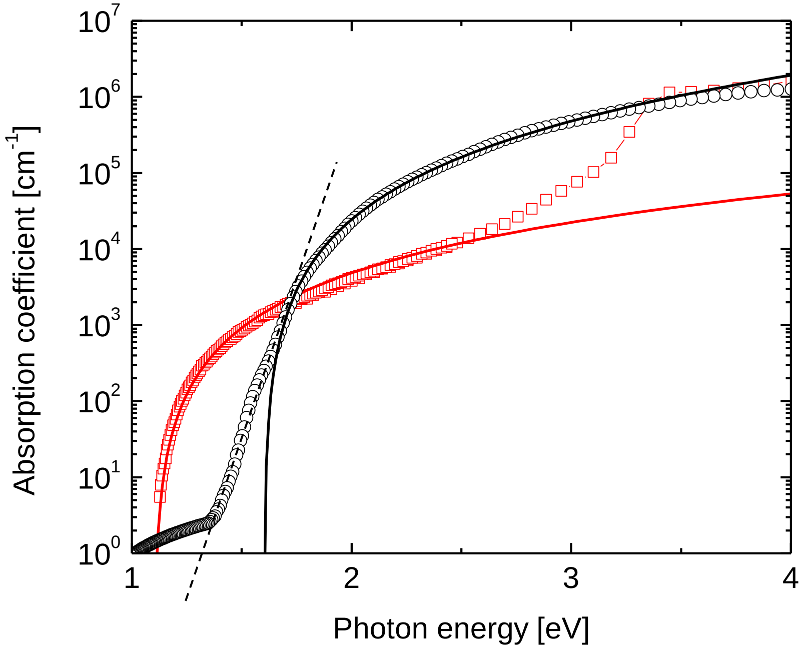
Band tails, mid-gap states

Optical signature of band tails

F.-J. Haug

High energy > 3.5 eV: similar to direct transition in c-Si

Band edge region 1.8 eV < E < 3.5 eV: non-direct gap, disorder



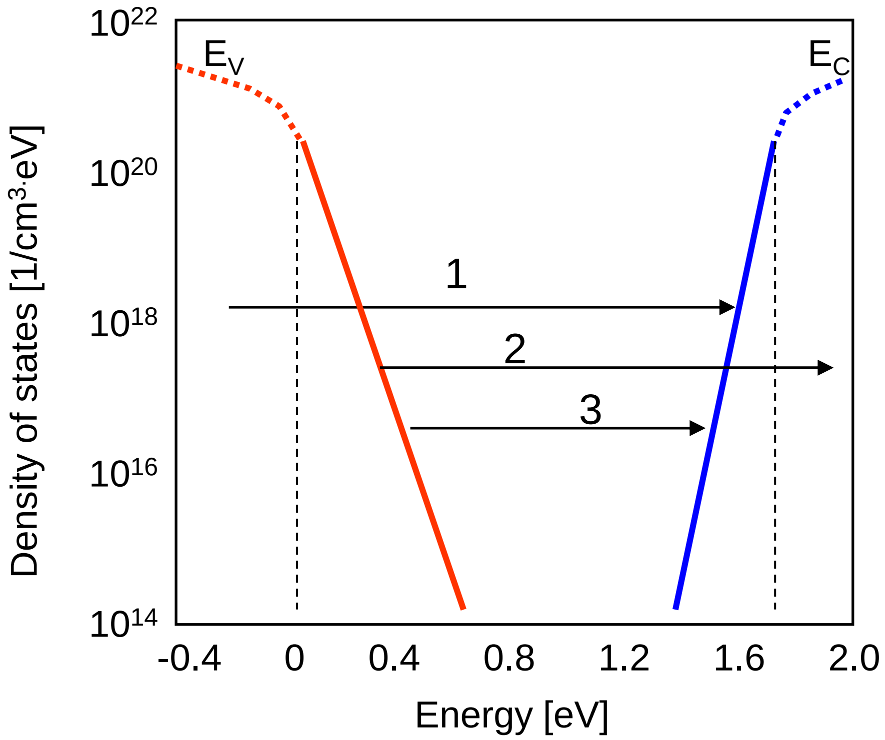
Band tail region 1.4 eV < E < 1.7 eV: absorption due to exponential tail

Low energy < 1.3 eV: defect absorption (see defect lecture)

Band tail absorption

Absorption processes:

1. VB to CB tail
2. VB tail to CB
3. VB tail to CB tail



E_C=0.027 eV

E_V=0.043 eV

E_U=0.045 eV

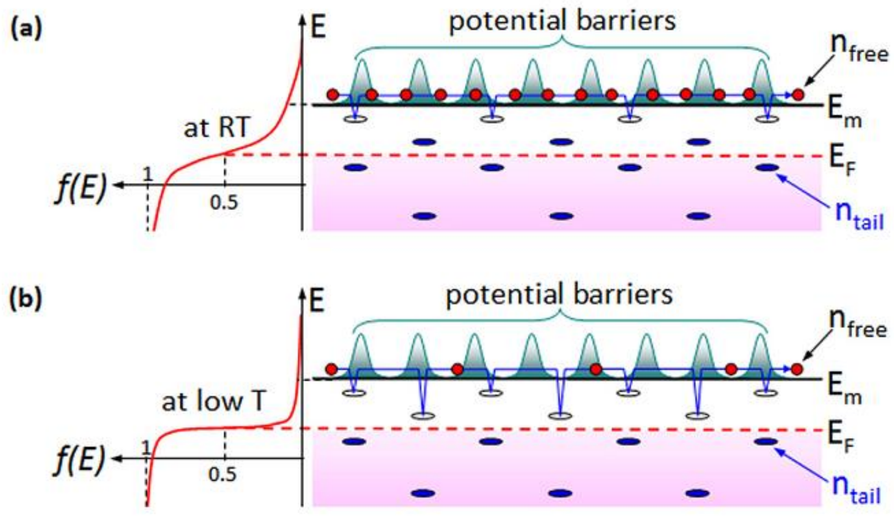
=> Slope of Urbach absorption is dominated by valence band

Redfield, SSC 44(9) p1347, (1982)

Band tails

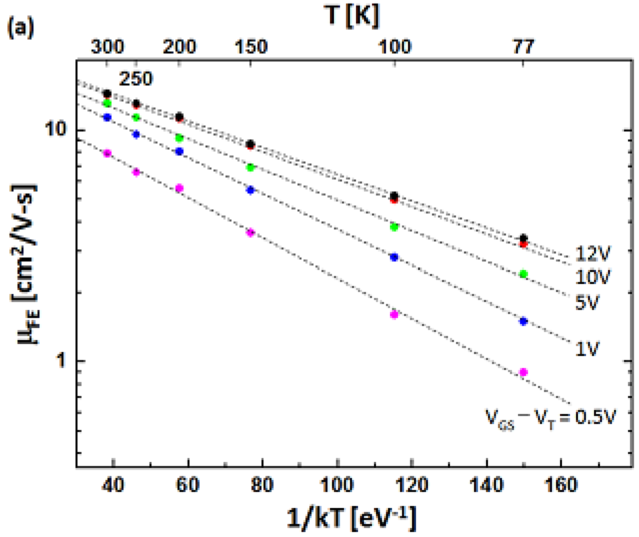
- band tails are a direct consequence of disorder
- several observations confirm their presence
  - dispersive transport
  - Urbach tail (band tail absorption)
  - Valence band structure in XPS
- the band tails are asymmetric
- in good material (PE-CVD grown):
  - VB tail slope 50 meV
  - CB tail slope 30 meV

Drift mobility in IGZO



RT:
CB transport w. trapping

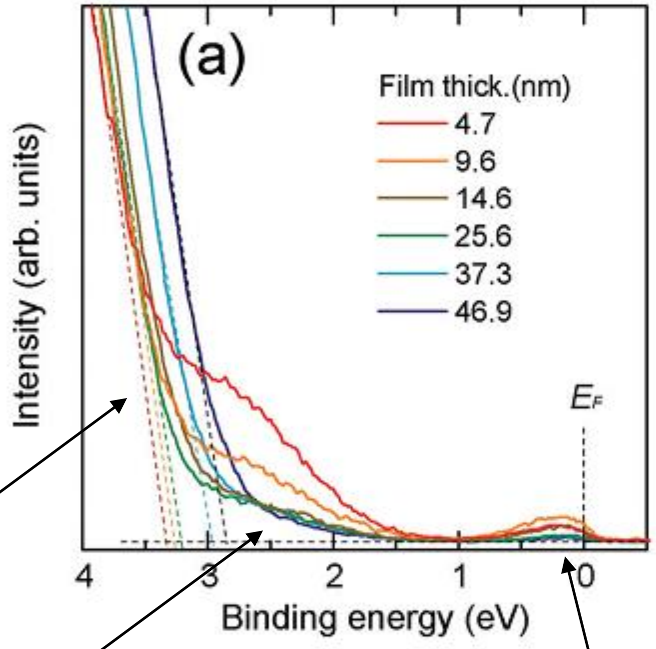
LT:
hopping transport
w. trap distribution



Dependence on bias voltage (related to faster sweep over trap sites, similar to a-Si:H)

Lee, APL (2012)

XPS analysis of VB structure in IGZO



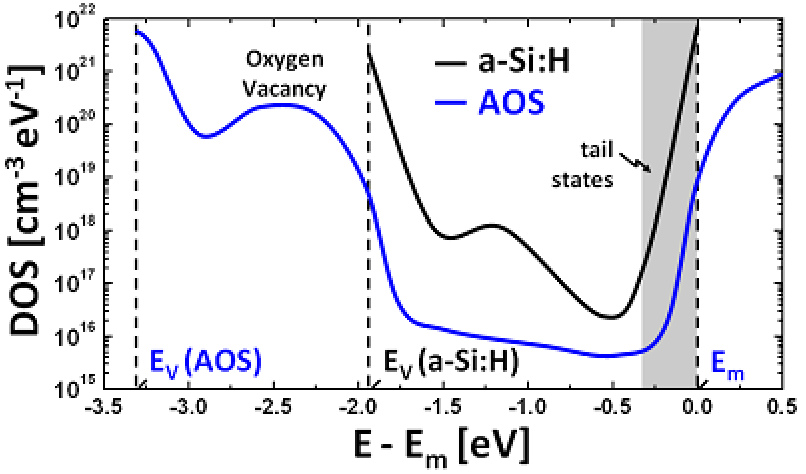
VB tail

deep state
(oxygen vacancy)

metastable shallow state?
(not trapping active in TFTs)

Nomura, JAP (2011)

Emerging picture



Similar transport processes (trapping into tail states)

IGZO: steeper CB tail, lower values for N_V and N_C

XPS suggests deep states

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Lee, IEEE IEDM (2011)