F.-J. Haug

The weak bond model

PV-lab
IEM NEUCHATEL

Molecular orbitals: hydrogen

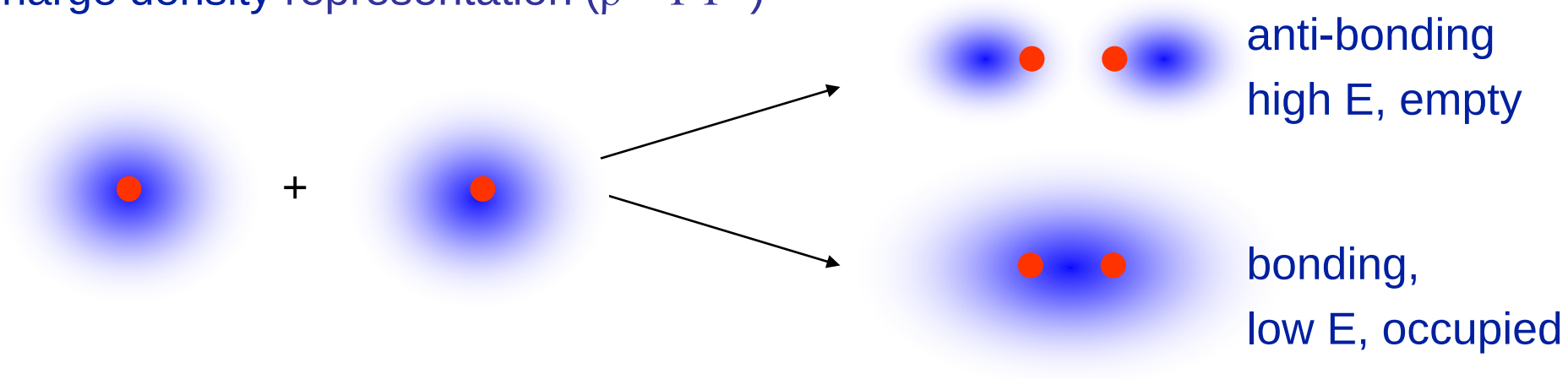
Chemical reaction

$$H + H \longrightarrow H_2$$

Wave function formation (no exchange integral)

$$\Psi_1(1s) + \Psi_2(1s) \longrightarrow (\Psi_1 + \Psi_2)$$
$$\Psi_1(1s) + \Psi_2(1s) \longrightarrow (\Psi_1 - \Psi_2)$$

Charge density representation ($\rho = \Psi\Psi^*$)



total number of states is preserved

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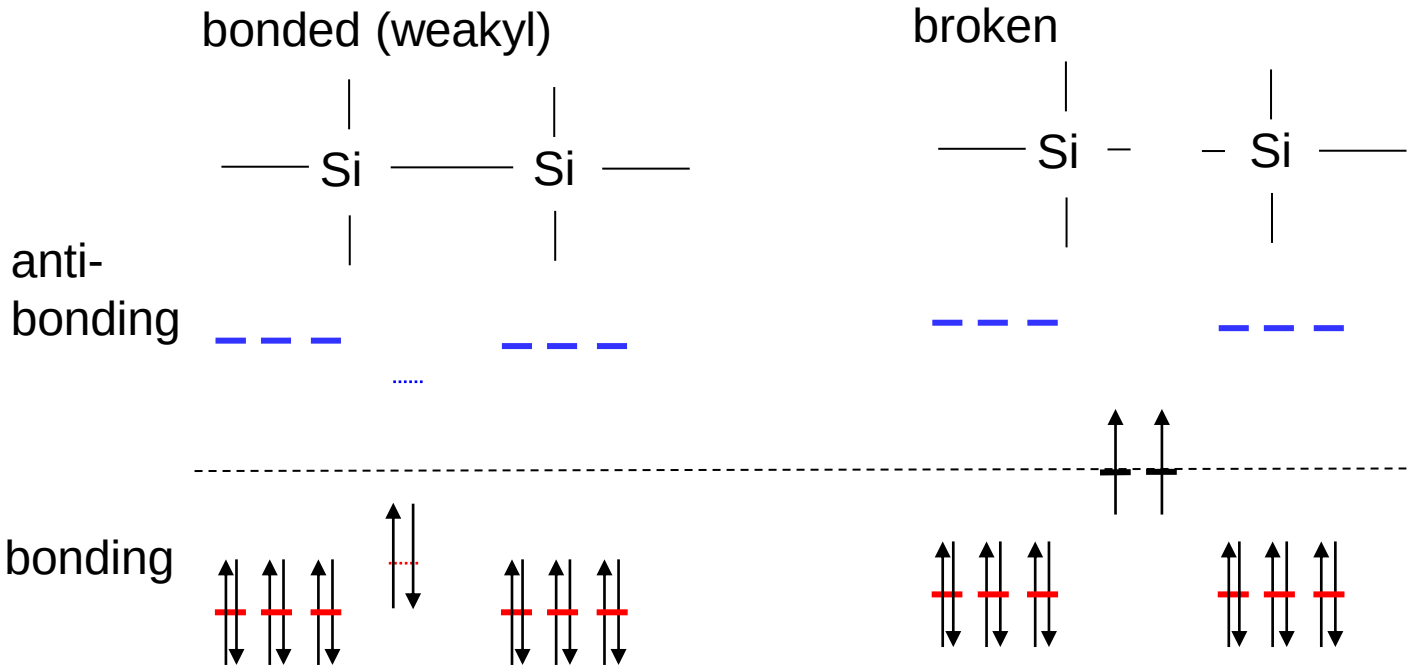
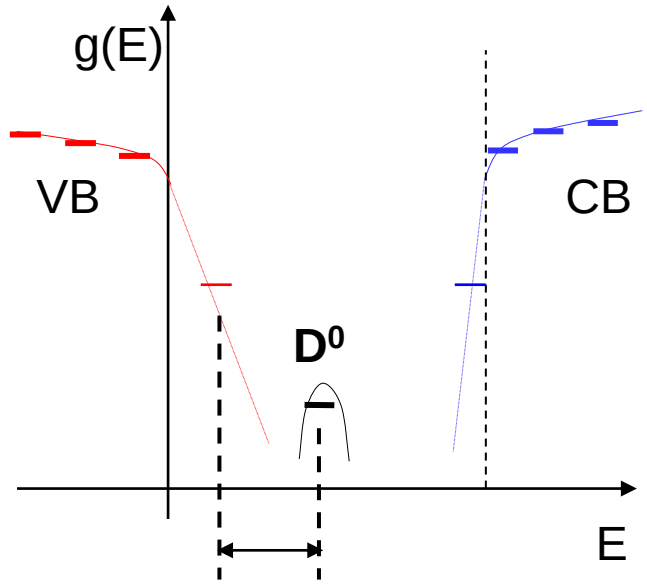
Weak bond model for silicon

Identify valence band and its tails with bonded molecular orbitals





bonding states (filled states) => valence band

anti-bonding states (empty) => conduction band

defect formation => create D^0 state, occupied with single electron

Stutzmann, Phil. Mag. 56(1) p63, (1987)

Density of weak bonds

Assume thermal equilibrium reaction between weakly bonded silicon $\mathrm{Si_{WB}}$ and neutral defects $\mathrm{D^0}$ (sum remains constant)

$$\mathrm{Si_{WB}} \rightleftharpoons \mathrm{D^0}$$

Apply mass action law

$$[\mathrm{D^0}] = [\mathrm{Si_{WB}}]e^{-E_{BB}/kT}$$

E_{BB} is typically 0.2 - 0.3 eV, $[\mathrm{D^0}] \approx 10^{16}$ cm^{-3}.

Thus: $[\mathrm{Si_{WB}}] \approx 10^{18} \ldots 10^{19}$ cm^{-3}.

=> Only a part of the available silicon (~5x10^{22} cm^{-3}) or hydrogen (~2…5x10^{21} cm^{-3}) is actually involved in defect creation

Note: $[\mathrm{Si_{WB}}] + [\mathrm{D^0}] = [N_0]$, thus: $N_D(E_{BB}) = N_0 \frac{1}{1 + e^{E_{BB}/kT}}$ (c.f exercises)

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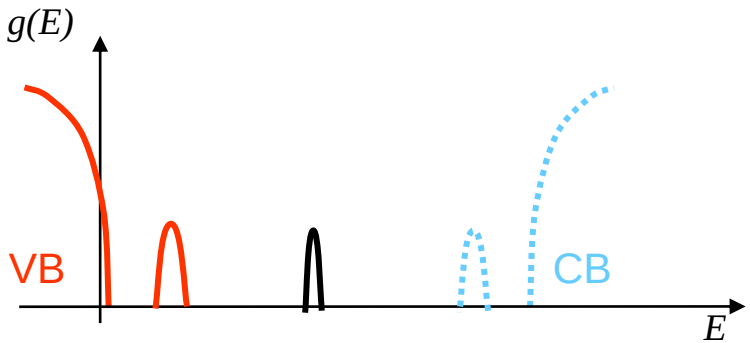
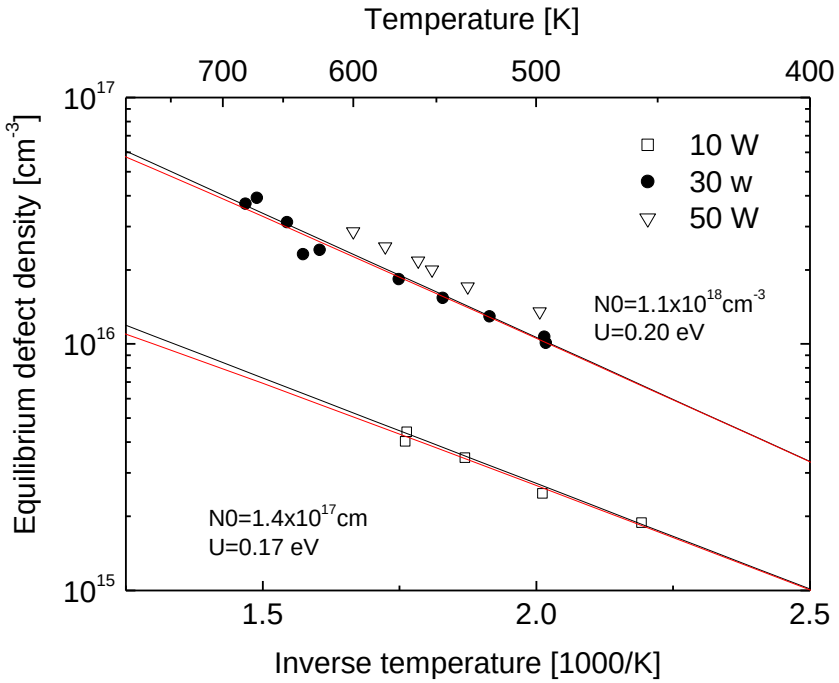
Simple density of states (DOS)



Bond breaking energy $E_{BB} = E_D - E_{WB}$

$$\Rightarrow DOS(E) = \underbrace{N_0 \cdot \delta(E - E_{WB})}_{\text{Weak bond state}} + \underbrace{N_0 \frac{1}{1+e^{E_{BB}/kT}} \cdot \delta(E - E_D)}_{\text{Defect density at } E_D} \text{ + anti-bonding state}$$

Equilibrium defect densities



On the measurement procedure:

- let sample reach equilibrium at high T
- quench (freeze) by rapid cooling
- measure defect density
- repeat

(recall: cooling of glass)

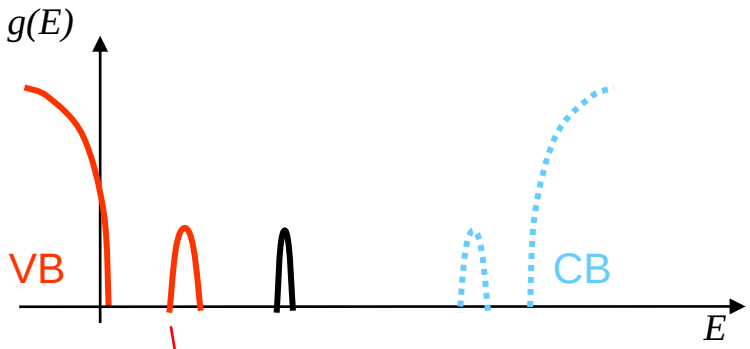
Fermi like: $N_D = N_0 \frac{1}{1 + e^{E_{BB}/kT}}$

Boltzmann like: $N_D \approx N_0 \cdot e^{-E_{BB}/kT}$

Question: What is the quantity N_0 ?

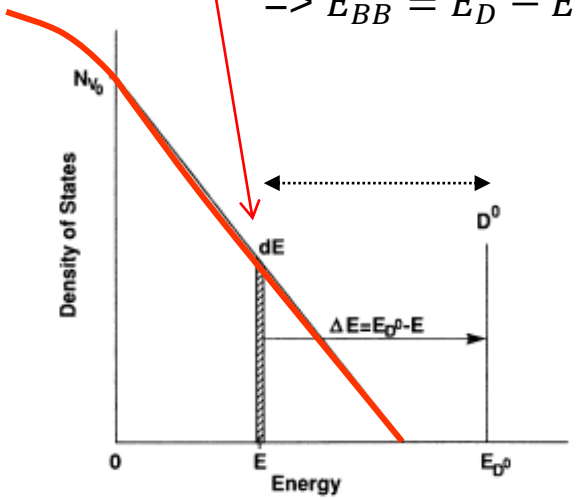
Data: Street, PRB 40(9), p6336 (1989)

Band tail model



E from VB, fixed E_D

=> $E_{BB} = E_D - E$



Take VB tail states as source of weak bonds!

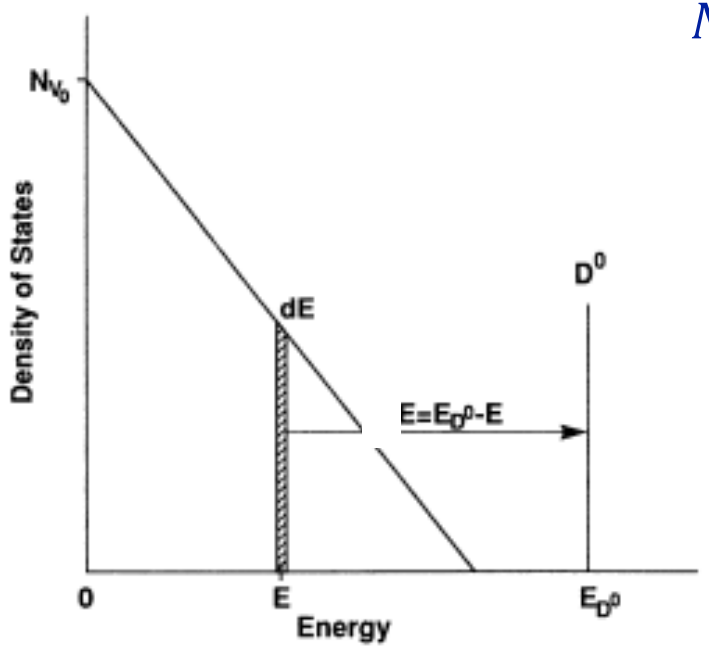
remember: $g(E) = N_V \cdot e^{-E/E_V}$

Contribution of VB slice $g(E)dE$

$$dN_D = g(E) \cdot \frac{1}{1+e^{E_{BB}/kT}} dE$$

Band tail model

How many defects are created in total?



$$N_D = \int_0^\infty g(E) \cdot \frac{1}{1 + e^{E_{BB}/kT}} dE$$

$$= \int_0^\infty N_V e^{-E/E_0} \cdot \frac{1}{1 + e^{E_{BB}/kT}} dE$$

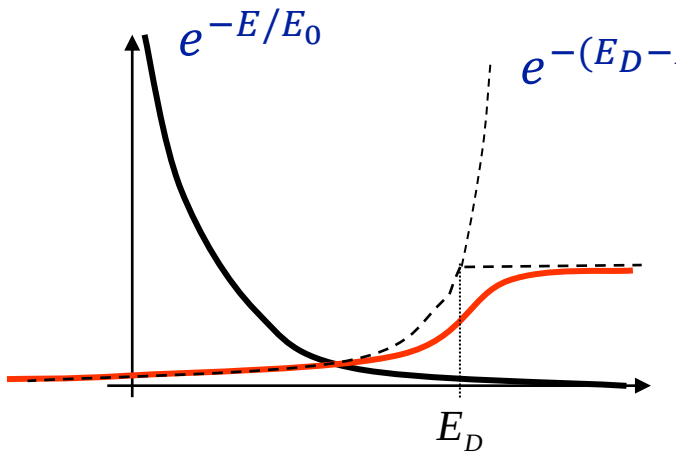
$$E_{BB} = E_D - E$$

Smith, PRL 59(6) p688, (1987)
Street, RPB 40(9), p6336 (1989)
Winer, PRB 41(17) p12150 (1990)

How to carry out the integration?

Fermi-Dirac type integrals: normally Sommerfeld approximation

(not allowed because of a) exponential, and b) high temperatures)



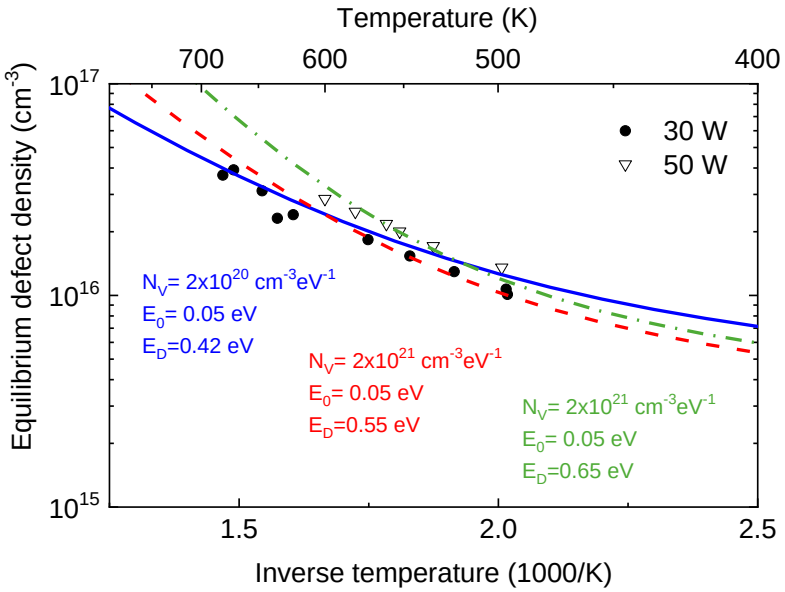
$$\frac{1}{1+e^{(E_D-E)/kT}}$$

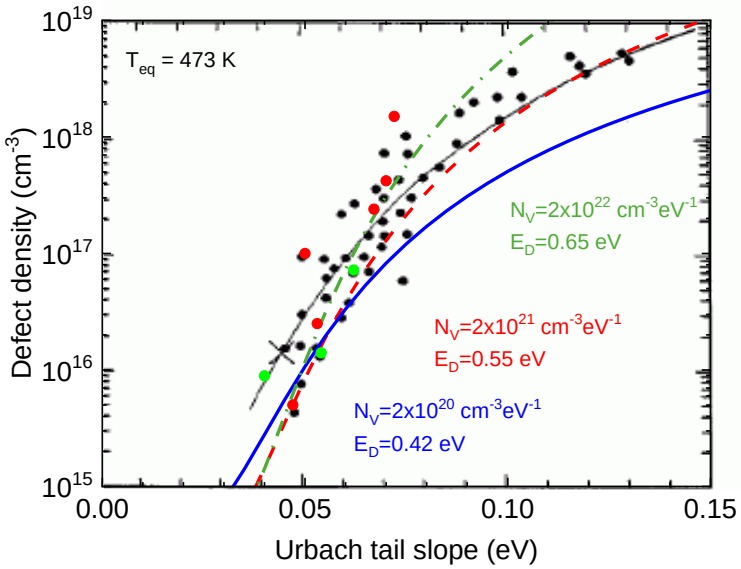
Here: use Boltzmann approximation below E_D, unity above E_D

$$N_D(E_D) \approx \int_0^{E_D} N_V e^{-\frac{E}{E_0}} e^{-\frac{E_D-E}{kT}} dE + \int_{E_D}^{\infty} N_V e^{-\frac{E}{E_0}} dE$$

$$= \frac{N_V E_0 kT}{E_0 - kT}\left(\frac{E_0}{kT} e^{-\frac{E_D}{E_0}} - e^{-\frac{E_D}{kT}}\right)$$

Equilibrium defect densities





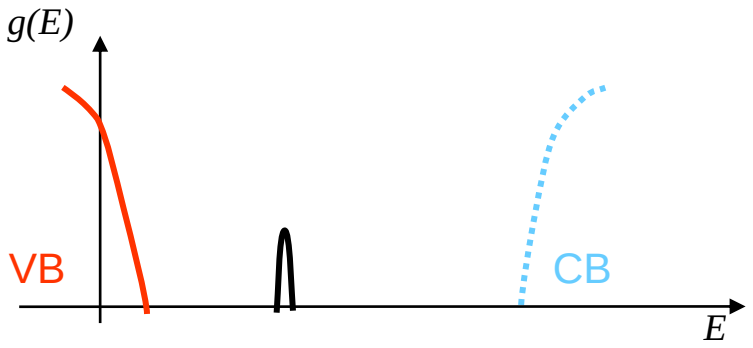
Band tail model: $$N_D = \frac{N_V E_0 kT}{E_0 - kT}\left(\frac{E_0}{kT} e^{-\frac{E_D}{E_0}} - e^{-\frac{E_D}{kT}}\right)$$

choice of E_0 and E_D is rather sensitive, N_V =2x10^{21} cm^{-3}eV^{-1} seems favourable

Street, PRB 40(9), p6336 (1989)

Data: Stutzmann, Phil. Mag. B 60, p531 (1989)

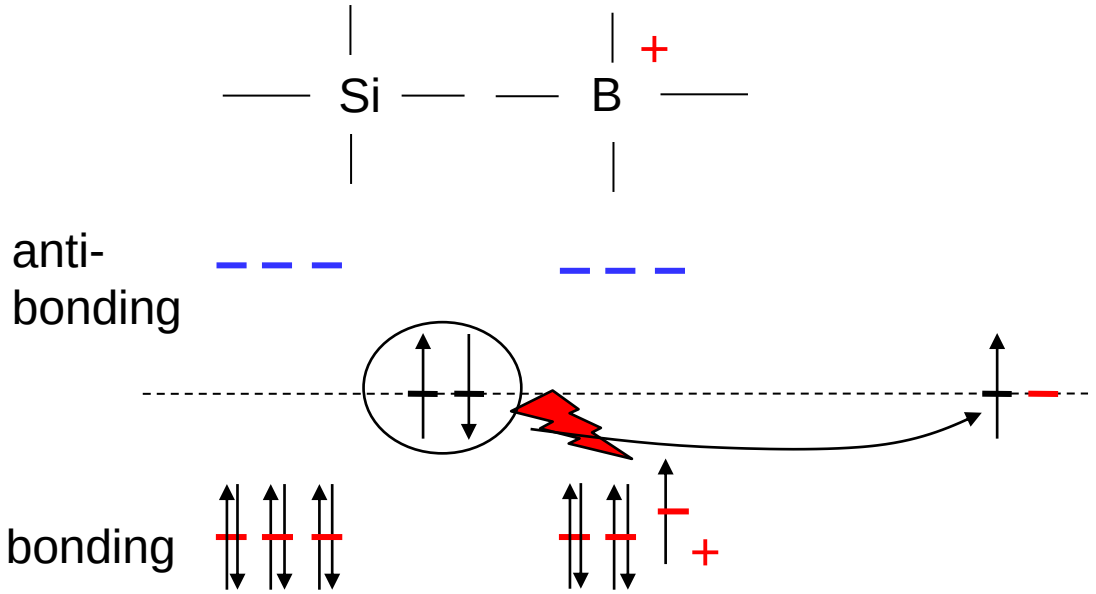
Density of states

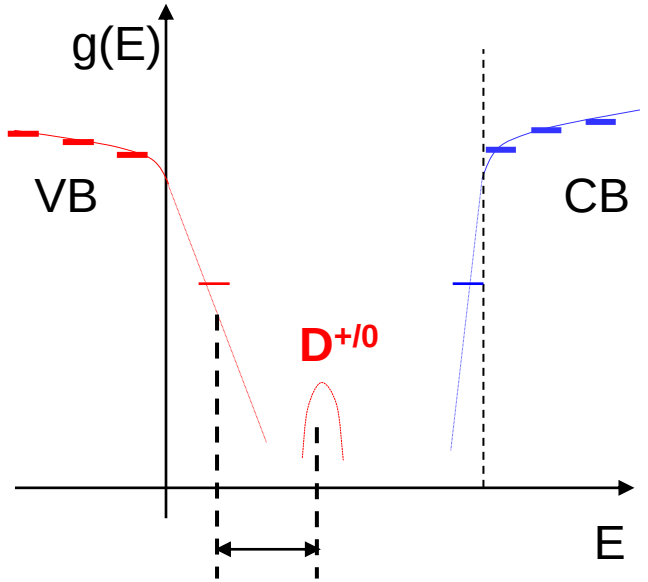


$$\Rightarrow DOS(E) = \underbrace{N_V e^{-\frac{E}{E_V}}}_{\text{Valence band tail}} + \underbrace{\frac{N_V E_V kT}{E_0 - kT}\left(\frac{E_0}{kT} e^{-\frac{E_D}{E_V}} - e^{-\frac{E_D}{kT}}\right) \cdot \delta(E - E_D)}_{\text{Neutral defect density at } E_D} + \text{CB}$$

Defect state with doping

Imagine a Boron atom close to a broken weak-bond state





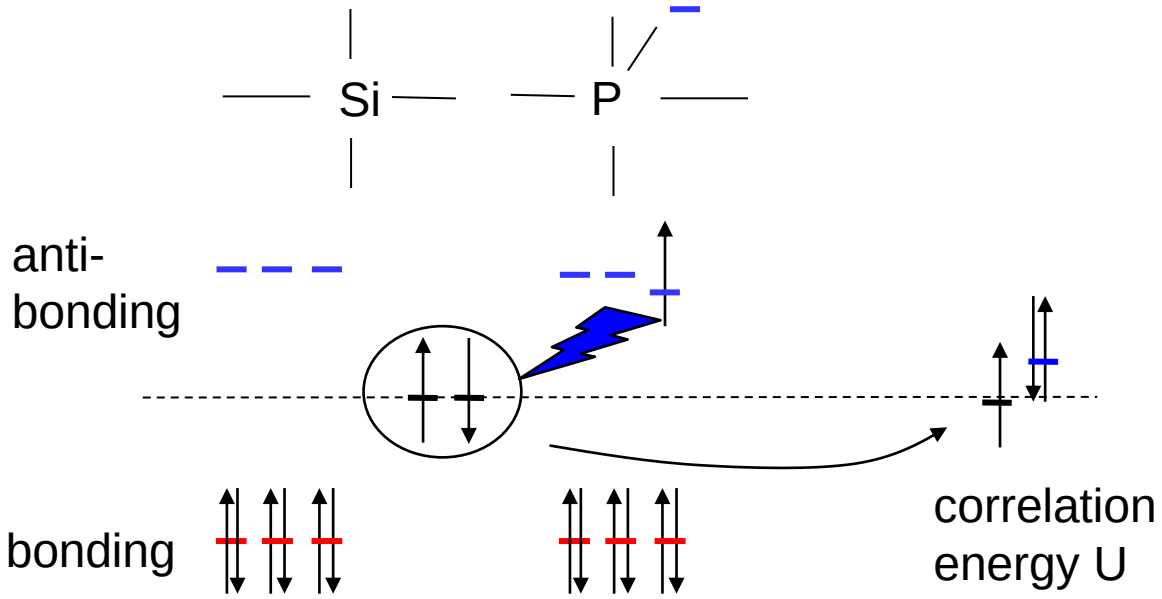
Filling of the (weak) bonding orbitas with two electrons results in a free hole

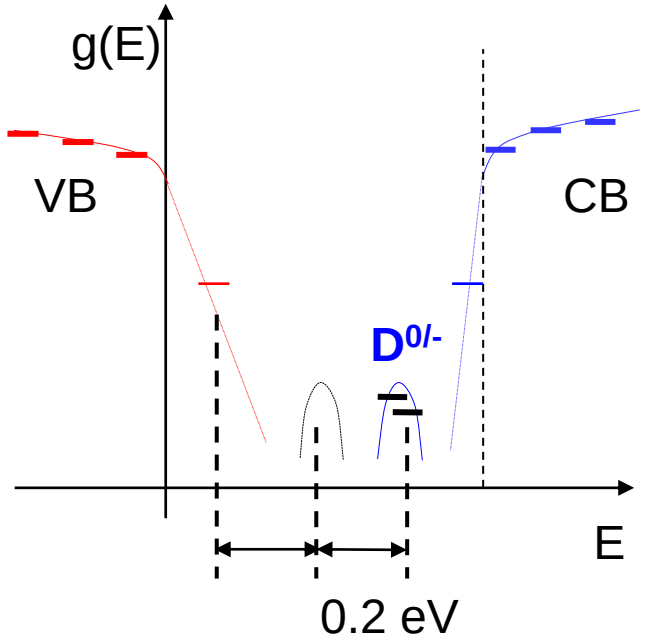
Close to a broken weak-weak bond: one of the electrons in the defect states

may drop to the VB and recombine with a hole, leaving behind one positive defect state

Defect state with doping

Imagine phosphorous close to a broken weak-bond state:





A free electron can drop into a broken weak-bond state, but it must overcome the repulsive correlation energy.

Recall: DOS diagrams of previous course showed that energetic of D^- was lower, not higher!

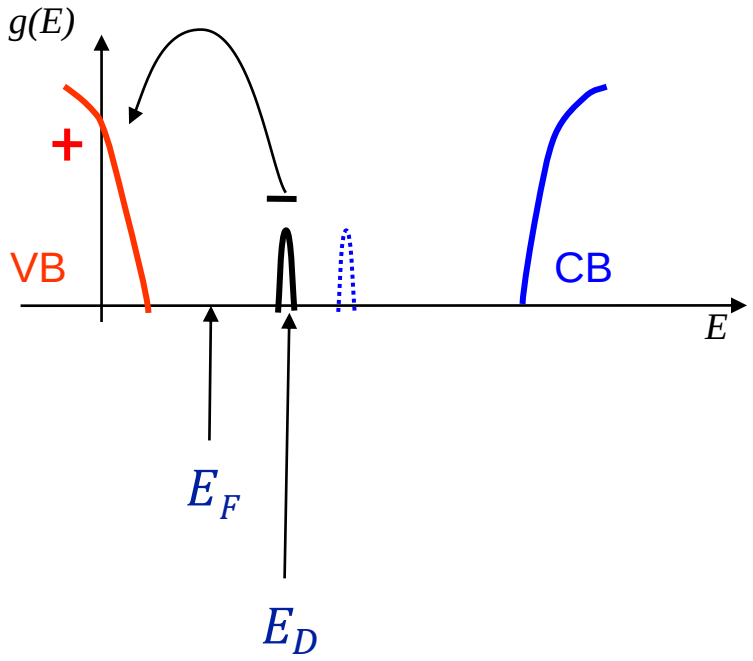
Occupation and defect charging

So far: we considered electrons w.r. to a defect state.

The Fermi-level would simply be at the defect energy (highest occupied electron state)

Now: let E_F vary, e.g. by doping or by external bias voltage in a TFT

Drop e- from defect to recombine with hole



Example I: p-doping (shift E_F close to VB)

=> a hole in VB and an occupied state above E_F

=> need to define energetics with a new quantity:

Formation enthalpy of charged defect: H

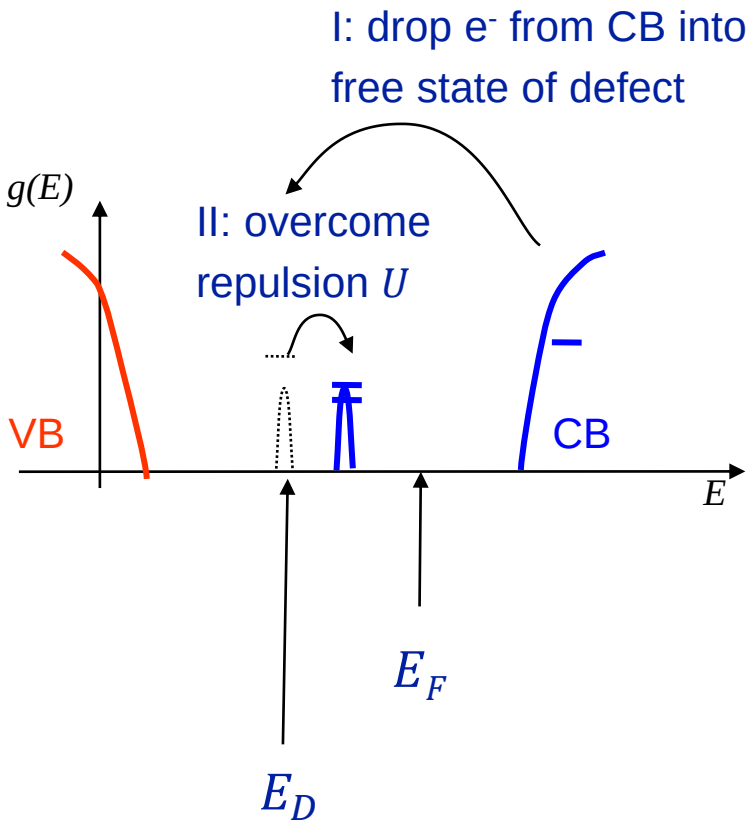
$$H(\mathrm{D}^+) = E_D - (E_D - E_F) = E_F$$

e- can drop to VB, liberating (minus) excess energy w.r. to E_F

put e- into E_D

Occupation and defect charging

Example II: n-doping (shift E_F close to CB)
=> free electrons in CB



Formation enthalpy of D^-

$$H(\mathrm{D}^-) = E_D - (E_F - E_D) + U$$

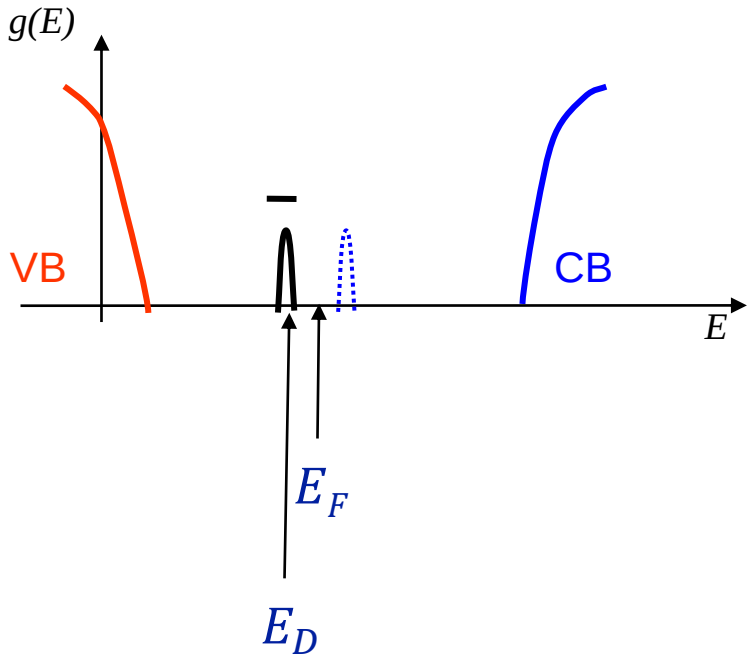
correlation energy (effort required for putting second e- into defect state)

excess energy w.r. to E_F

put e- into E_D

Occupation and defect charging

Original situation: E_F close to the defect state at E_D:

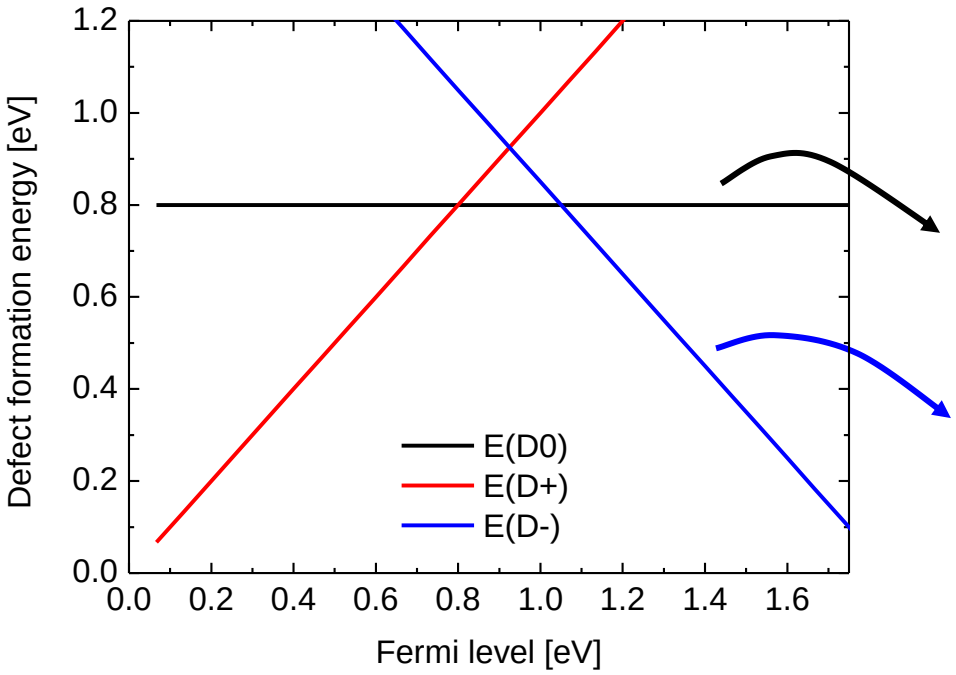


No transfer on electrons

=> The formation enthalpy of the neutral defect D^0 is equal to the energy of the electron in it:

$$H(\mathrm{D}^0) = E_D$$

Energetic cost of charging a defect at E_D

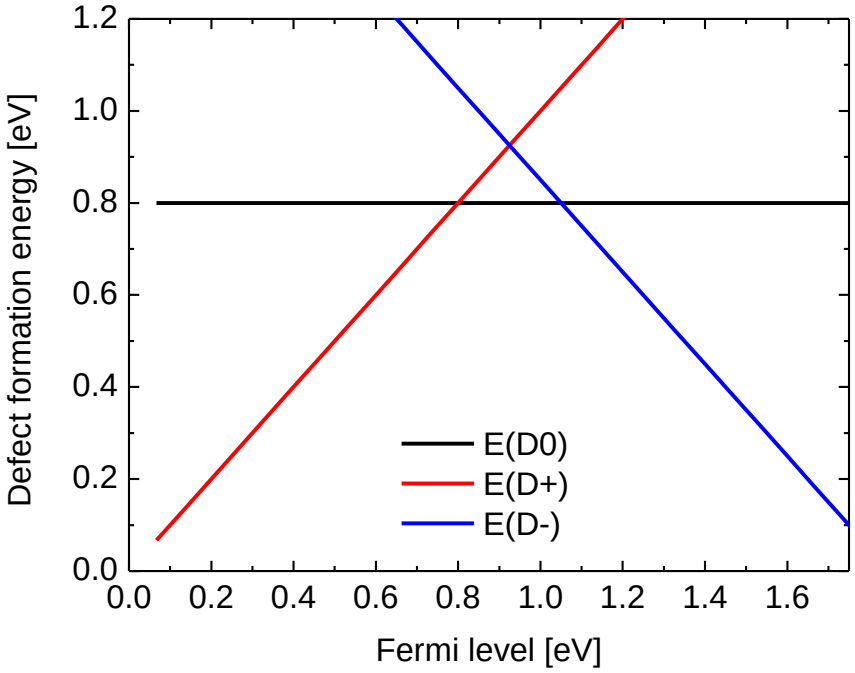


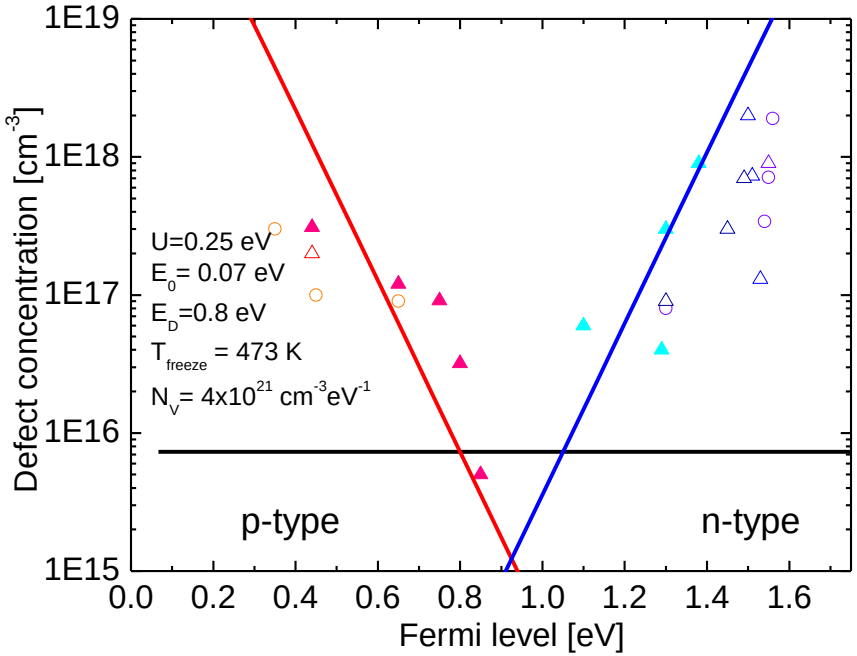
$H(D^+) = E_F$

$H(D^0) = E_D$

$H(D^-) = 2 \cdot E_D + U - E_F$

Defect density in doped a-Si:H

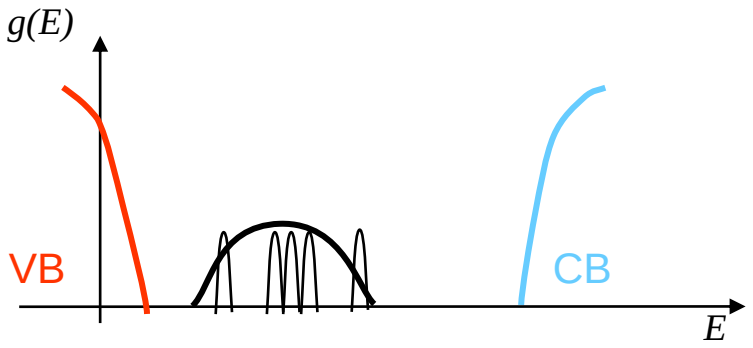




At given E_F, the most likely defect is the one with lowest energy

Data:
Street, PRB 24(2) p969 (1981)
Jackson, PRB 25(8), p5558 (1982)
Stutzmann, PRB 35(11), p 5666 (1987)

Generalization: defect pool

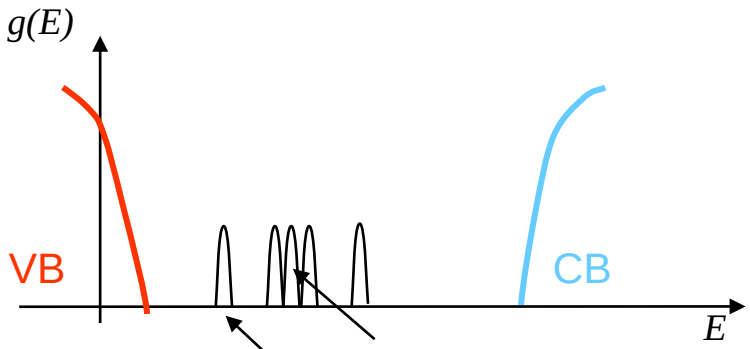


Replace fixed defect position E_D
by many defect energies with
Gaussian distribution centred at E_P

$$DOS(E) = N_V e^{-\frac{E}{E_0}} + \frac{N_V E_0 kT}{E_0 - kT}\left(\frac{E_0}{kT} e^{-\frac{H(D)}{E_0}} - e^{-\frac{H(D)}{kT}}\right) \cdot \delta(E - E_D) \quad + \text{CB}$$

$$DOS(E) = N_V e^{-\frac{E}{E_0}} + \frac{N_V E_0 kT}{E_0 - kT}\left(\frac{E_0}{kT} e^{-\frac{H(D)}{E_0}} - e^{-\frac{H(D)}{kT}}\right) \cdot \frac{e^{-\frac{(E-E_P)^2}{2\sigma^2}}}{\sqrt{2\pi\sigma^2}} \quad + \text{CB}$$

Defect distribution over bandgap



many defect states available (max of pool), but large energetic cost

few defect states available, but likely to create

Maximum of defect distribution ≠ maximum of pool; where is it?

Case I: neutral defect $H(\mathrm{D}^0) = E$ and $kT < E_0$:

$$DOS_D(E) = \frac{N_V E_0 kT}{E_0 - kT}\left(\frac{E_0}{kT}e^{-\frac{H(D)}{E_0}} - e^{-\frac{H(D)}{kT}}\right)\cdot\frac{e^{-\frac{(E-E_P)^2}{2\sigma^2}}}{\sqrt{2\pi\sigma^2}}$$

find max of $e^{-\frac{E}{E_0}}\cdot e^{-\frac{(E-E_P)^2}{2\sigma^2}}$ => $E_{max} = E_P - \sigma^2/E_0$

Position of the distribution in bandgap

p-doped material:

positive defect ($H(\mathrm{D}^{+}) = E_F$), same pool function:

find max of $e^{-\frac{(E-E_P)^2}{2\sigma^2}}$

$$\Rightarrow E_{max} = E_P$$

n-doped material:

negative defect ($H(\mathrm{D}^{-}) = 2E + U - E_F$), but pool of doubly charged defects:

find max of $e^{-\frac{2E+U-E_F}{E_0}} \cdot e^{-\frac{(E-(E_P+U))^2}{2\sigma^2}}$

$$\Rightarrow E_{max} = E_P + U - 2\sigma^2/E_0$$

Positions of the defect distributions

intrinsic material:

$D^0: E = E_P - \frac{\sigma^2}{E_0}$

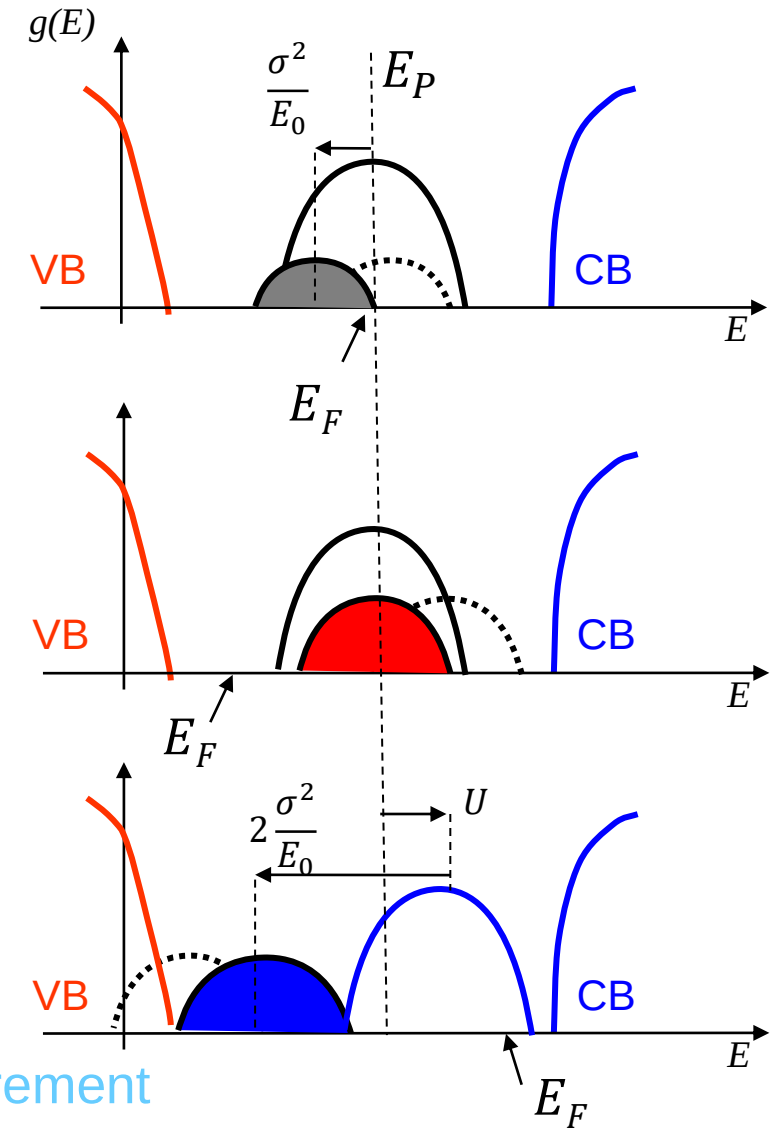
p-doped material:

$D^+: E = E_P$

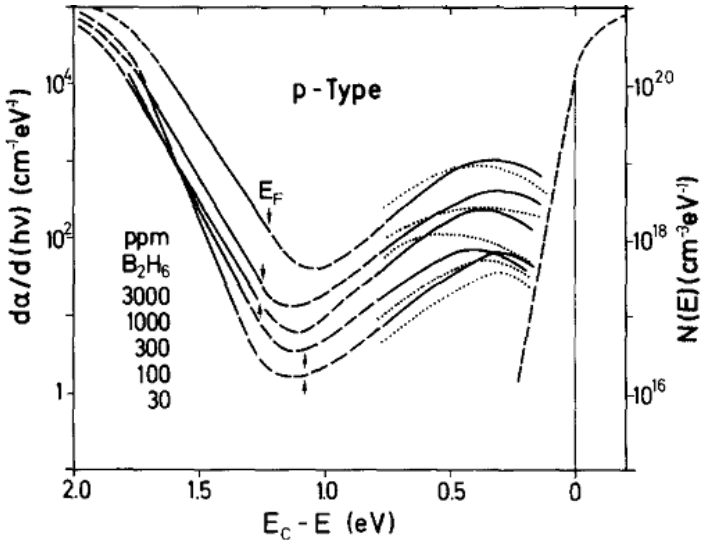
n-doped material:

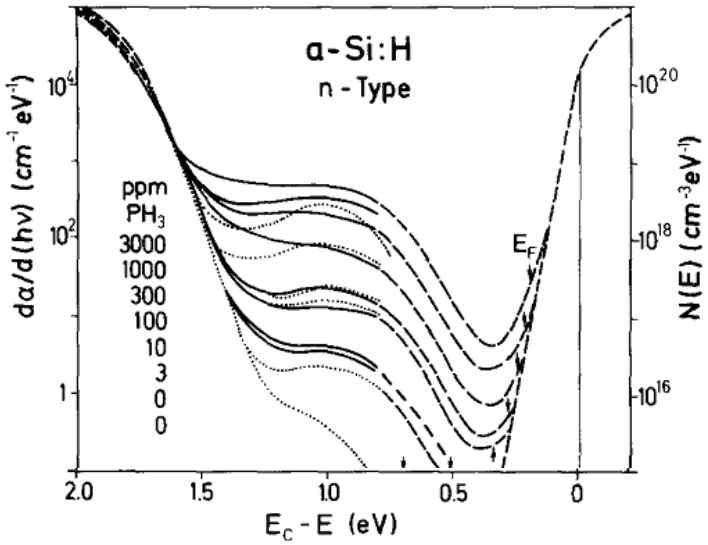
$D^-: E = E_P + U - \frac{2\sigma^2}{E_0}$

reconciles positive U with measurement



Energetic distribution of defects





p-type: low E_f => absorption from VB into free states

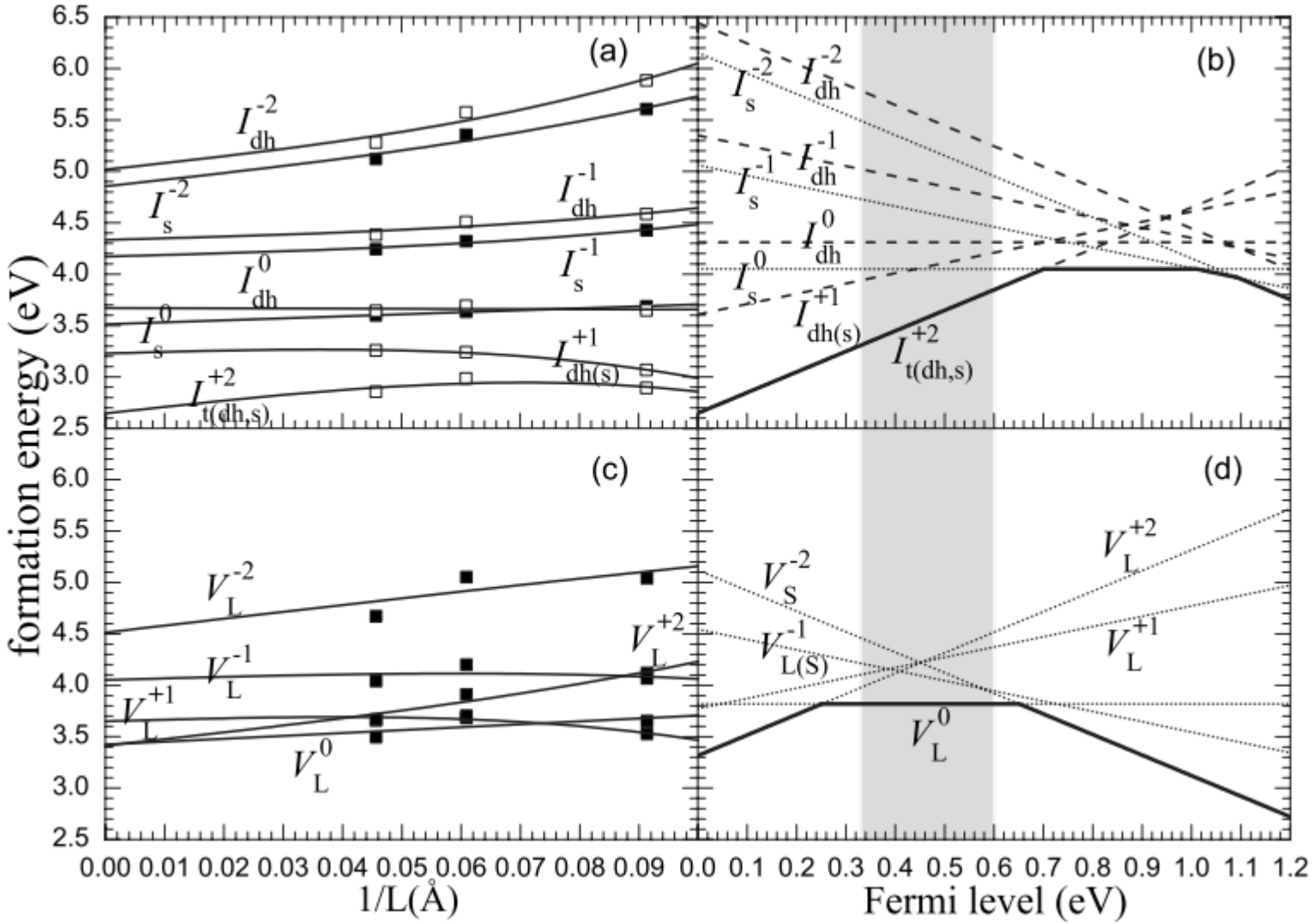
n-type: high E_f => absorption from occupied states into CB

Defects created close to opposing band edge!

Finally explained by defect pool model!

Pierz, JNCS (1987)

Excursion I: Defects in c-Si

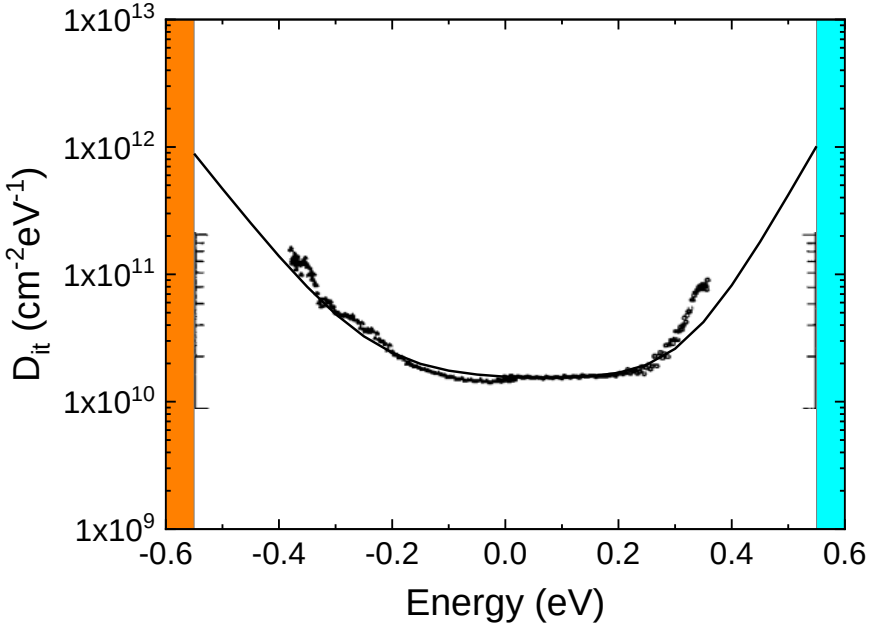


different slopes: singly and doubly charged defects

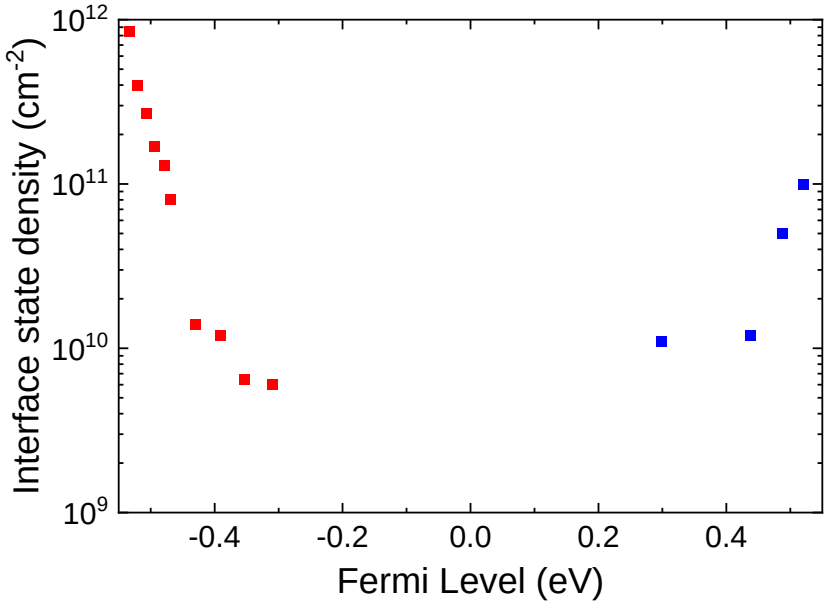
Ma, PRB (2010)

Excursion II: Defects at the Si/SiO_2 interface

Interface state density (weakly doped, measured by DLTS)



Total interface state density vs doping

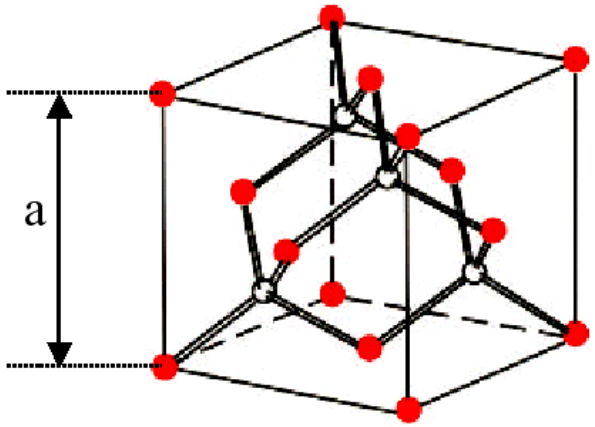


Aberle, JAP (1992)
Snel, SSE (1981)

Excursion III: Defects in CIGS

Diamond (element semiconductors: Ge and Si)

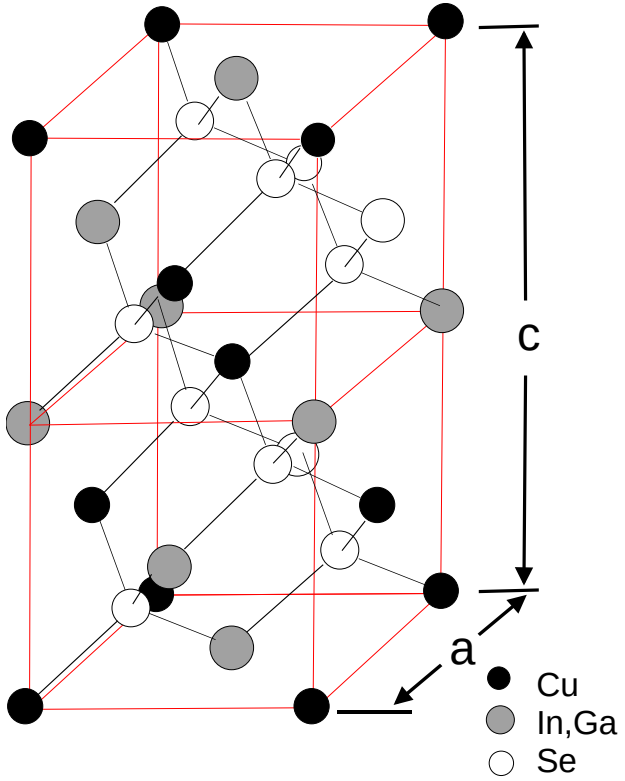
Zincblende (optoelectronic materials: GaAs, InP, GaN)



Photovoltaic materials:

CdTe (Zincblende)

$CuInSe_2$ (Chalcopyrite)

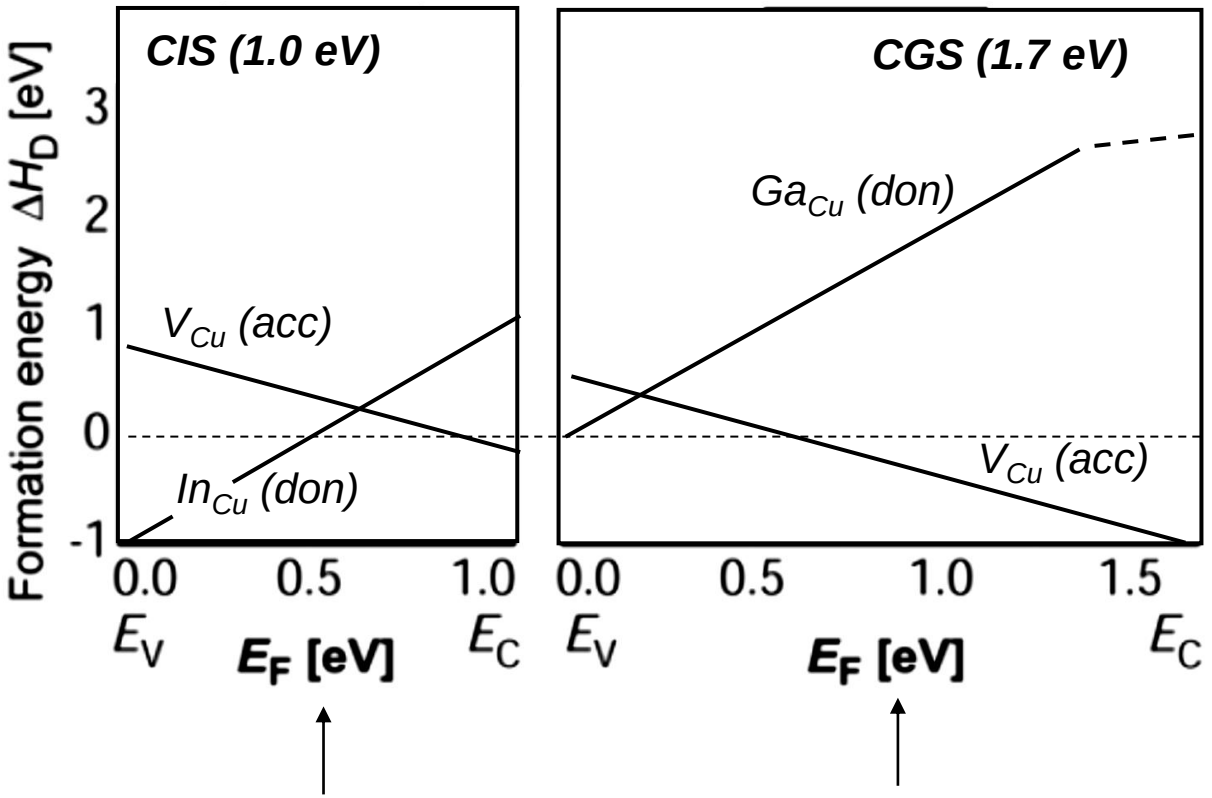


Most common defects in $Cu(In,Ga)Se_2$

- V_{Cu} (copper vacancy):
  leaves behind one unpaired back bond
  => acceptor type defect

- III_{Cu} (In or Ga anti-site)
  two bonding electrons too much
  => (double) donor type defect

Defect formation energies in chalcopyrites



Material not intentionally doped: expect intrinsic material with midgap E_F:

CIS: Formation of In_{Cu} donors needs little energy => natural *n*-material

CGS:. V_{Cu} acceptors form spontaneously => natural *p*-material

Band structure calculation
Zhao, APL 85(24), p5860 (2004)