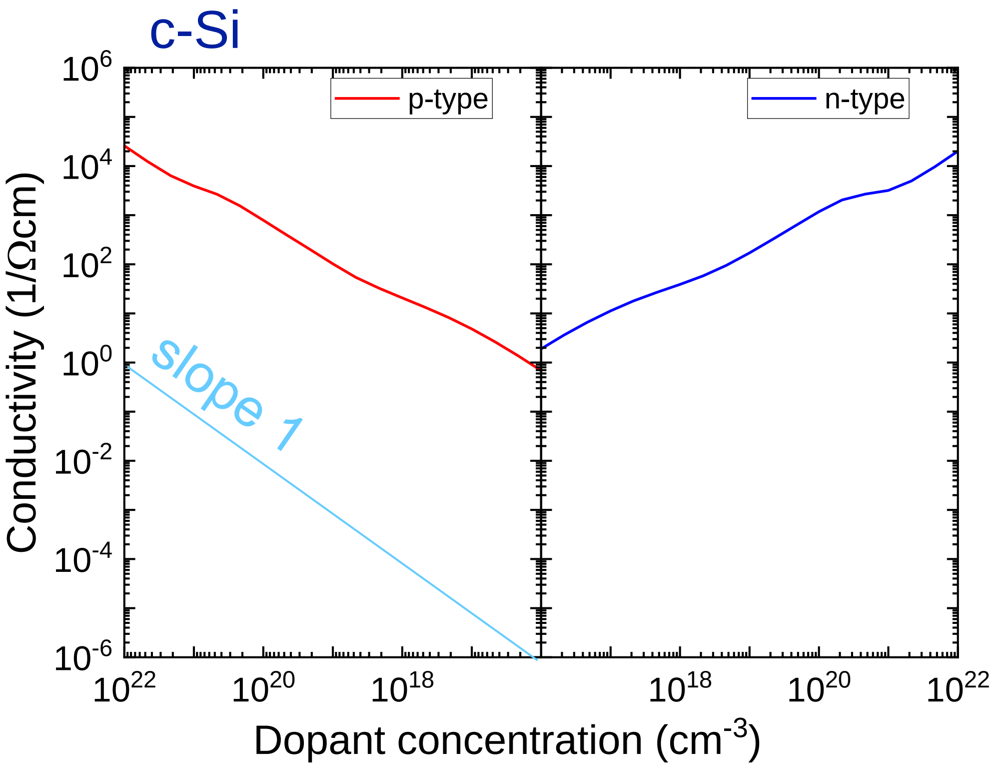
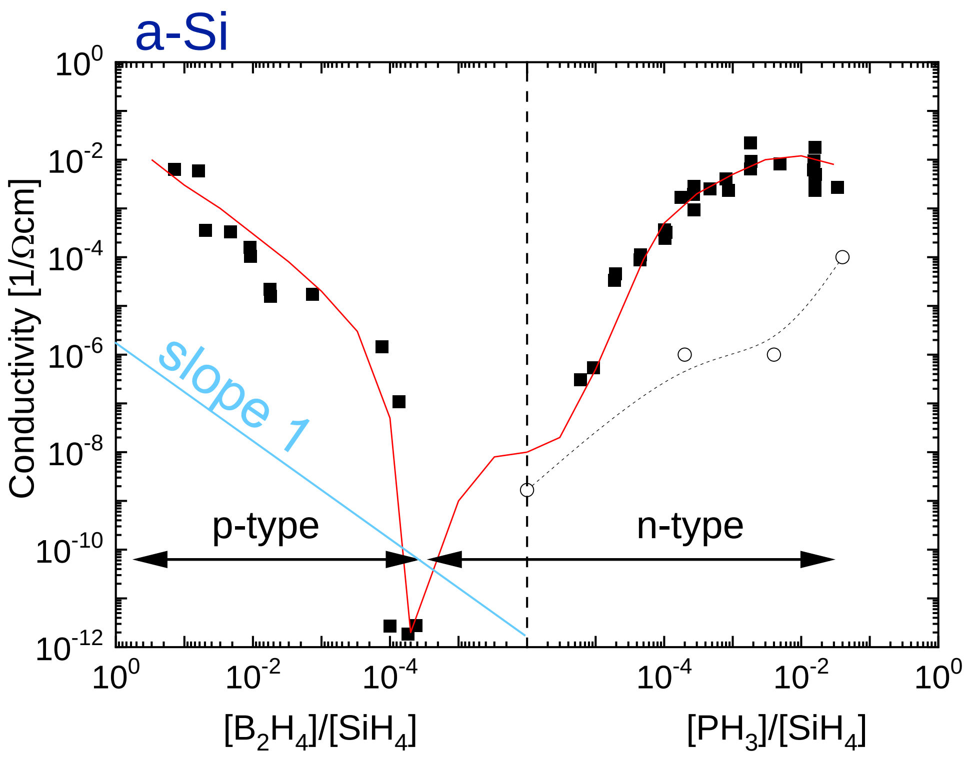
Defects in a-Si:H

Doping efficiency

Very early observation: conductivity tends to saturate (esp. n-type)





Interpretation: strong doping creates many defects that capture free charges

Spear, SSC 17, p1193 (1975)

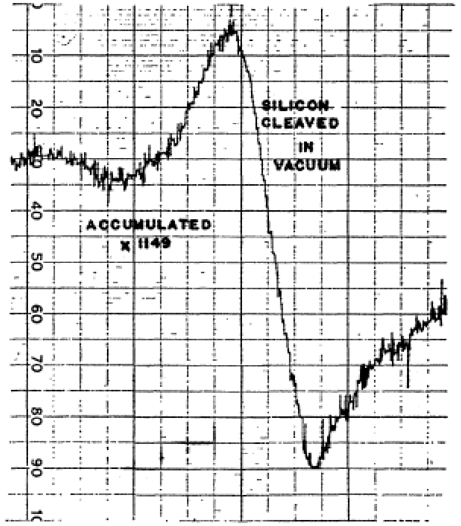
Electron spin resonance (ESR)

F.-J. Haug

A dangling bond contains a single electron

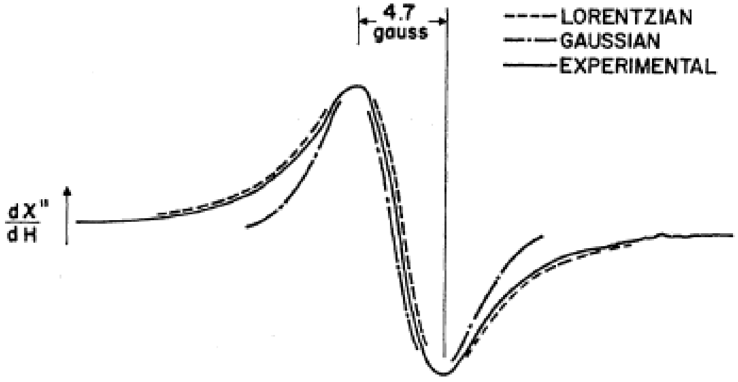
The electron spin of a single electron resonates with an alternating magnetic field (ESR)

cleaved c-Si:
few DBs at
surface
(noisy signal)



Haneman, PR 170(3), p705 (1968)

a-Si



Brodsky, PRL 23(11), p581 (1969)
Brodsky, JNCS 32, p432 (1979)

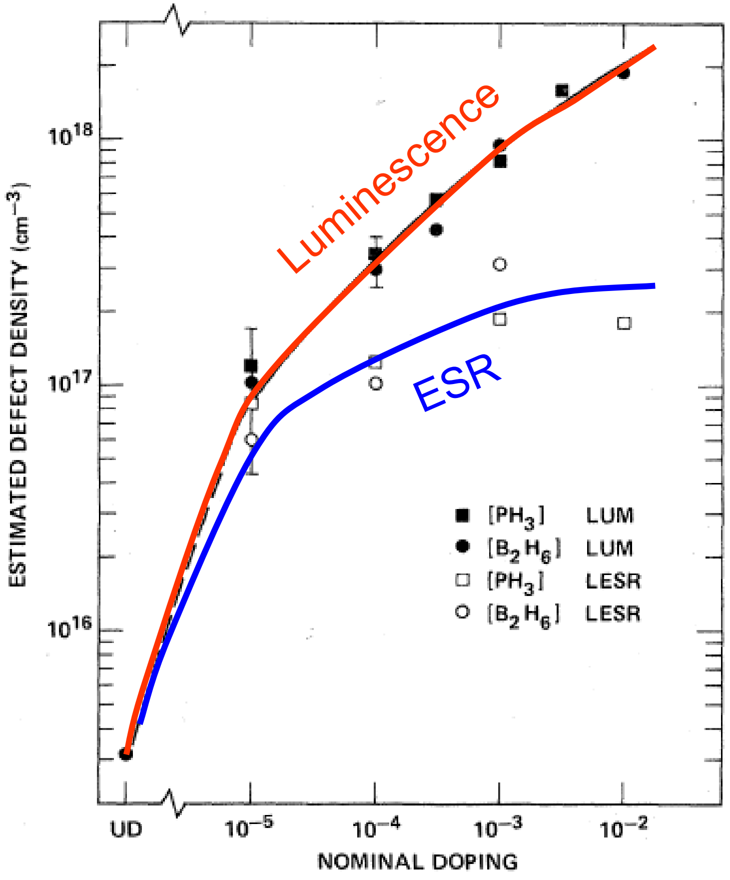
a-Si shows an ESR signal similar to the dangling bonds of cleaved Si

Spin densities ~10^{19} - 10^{20} cm^{-3} (sputtered a-Si)
~10^{15} - 10^{16} cm^{-3} (PE-CVD)

(like on the surface, DBs in PECVD-Si are passivated by hydrogen)

PV-lab
IEM NEUCHATEL

Photoluminescence (PL)



Street, PRB 24(2), p969 (1981)

Two competing recombination mechanism:

- recombination by radiation of a photon (PL)
- recombination at defects w/o radiation (SRH)

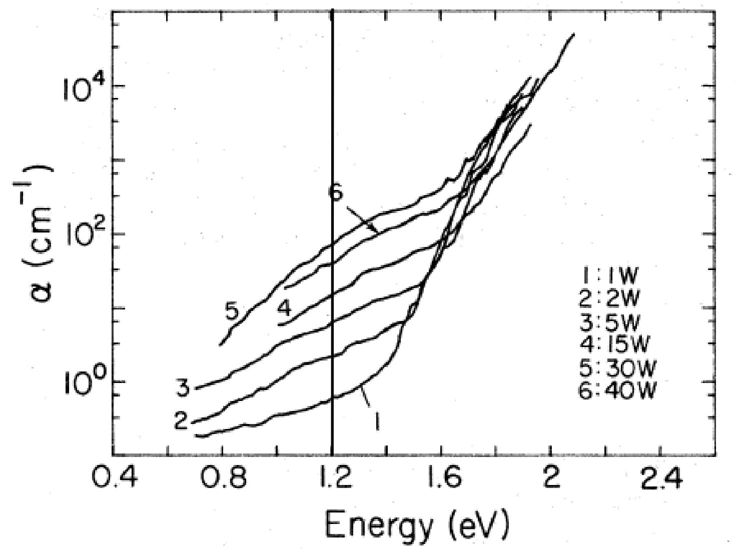
Observation: PL is weaker and decays faster in films with high defect density (more non-radiative recombination)

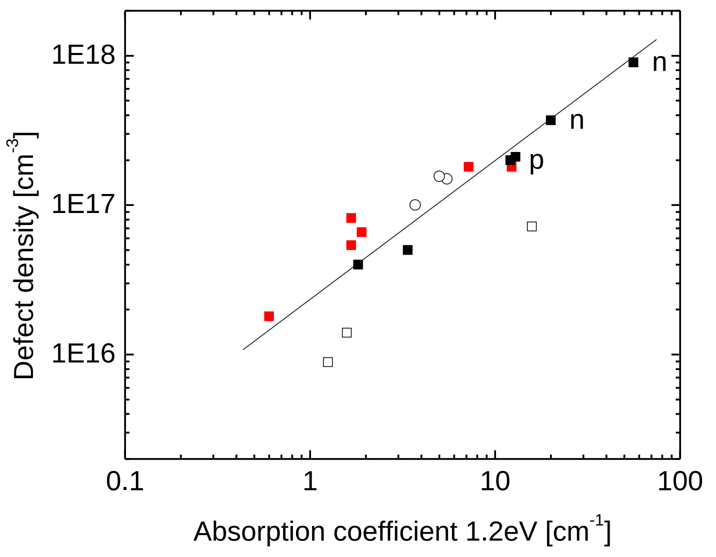
- Doping (of both types) apparently adds defects
- For high doping: ESR seems to underestimate defect density

Hindsight explanation:

- Doping creates charged defects with no or double occupation
- Empty and paired orbitals are **not** visible in ESR

Defect absorption (below Urbach tail)





Indirect method, use value at α ≈ 1.2 eV and calibrate with ESR measurement

Calibration factor:

N_D [cm^{-3}] = 1.5×10^{16} x $\alpha_{1.2\ eV}$ [cm^{-1}]

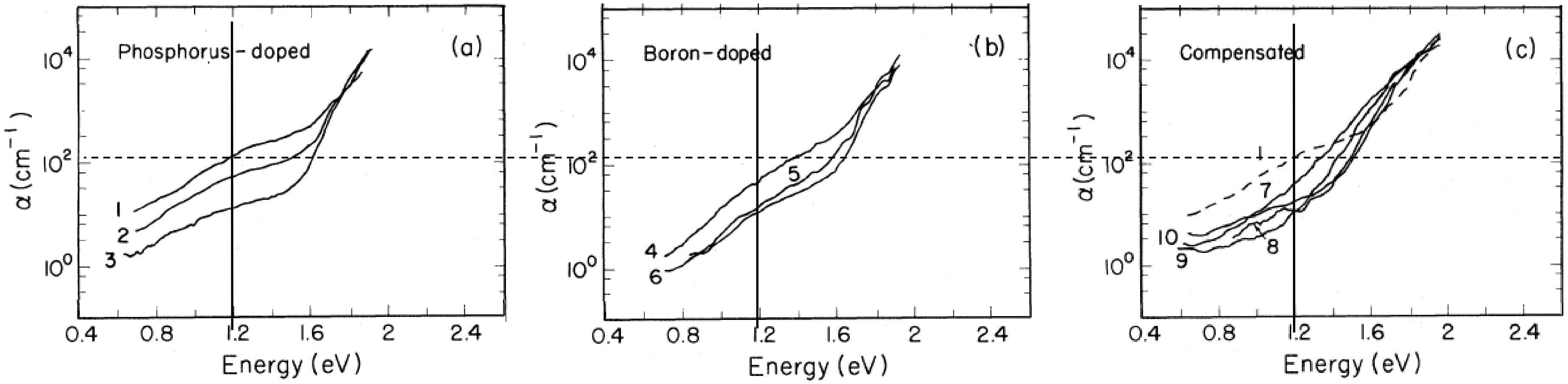
Jackson, PRB 25(8), p5559 (1982)

Jackson, APL 42(1), p105, (1983)
Wyrsch, JNCS 137/138, p347 (1991)
Cabarrocas, J. Phys. I, p1979 (1982)
Günes, JAP 81(8), p3526 (1997)

Defect absorption in doped layers

Increased sub-gap absorption in doped layers

P-doped | B-doped | compensated



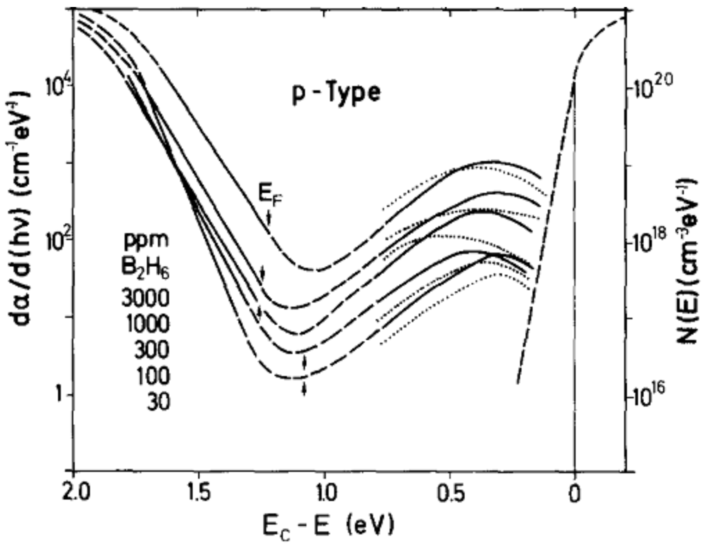
Doping gas ratio:

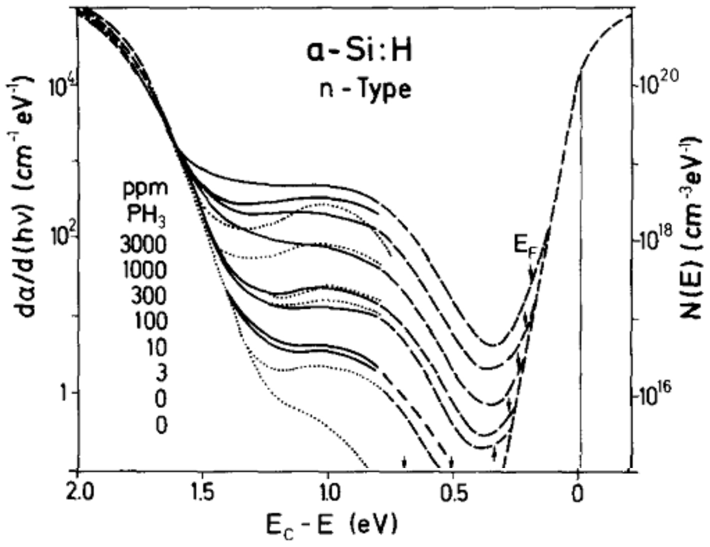
P-doped	B-doped	compensated
1: $1x10^{-3}$	4: $1x10^{-3}$	$1x10^{-3}$ PH_3
2: $3x10^{-4}$	5: $3x10^{-4}$	+ varying B_2H_4
3: $1x10^{-5}$	6: $1x10^{-4}$	

Interpretation of improvement in compensated material:
not the dopants, but Fermi-level shift creates defects

Jackson, PRB 25(8), p5559 (1982)

Energetic distribution of defects





p-type: low E_F => absorption from occupied VB into free defect states

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

Defects created close to the band edge opposed to dopant states!

Especially puzzling for n-type: expect defect band at higher energy due to repulsive correlation energy U in doubly charged defects

Pierz, JNCS (1987)

Specific for a-Si:H - light induced defects

F.-J. Haug

Defect creation

defects are created by illumination (evidenced in photo-conductivity)

=> Staebler-Wronski effect!

further observations

- forward biasing of devices can also create new defects (even in dark!)
- reverse biasing reduces the impact of illumination
- energy of the illuminated photons does not matter much

Conclusion:

Recombination processes are responsible for defect creation

Defect curing

the **initial** defect density can be restored by annealing (e.g. 30 min, 180°C and exponentially slower at lower T)

Staebler and Wronski, APL 31(4), p292, (1977)
Staebler, APL 39(9), p733, (1977))

Equilibrium

Initial idea of equilibrium defect density:

- recombination of carriers creates defects
- the origin of the carriers does not matter (light, bias, etc.)

Thus:

- recombination of thermally activated carriers should also create defects
- there is an equilibrium between creation and curing at high temperature
- During cool-down, the equilibrium is eventually too slow to follow the cooling ramp; the defect density is **frozen in**

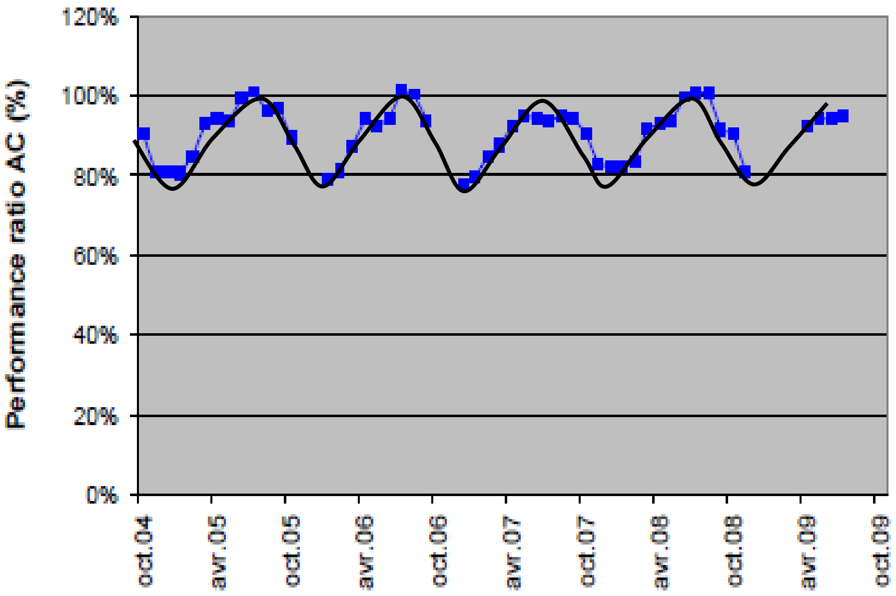
Thus: dangling bond defects (occupied by one e^-) are inherent to a-Si:H, they form in an **equilibrium process** at high temperature

$$\mathrm{Si-Si} \rightleftharpoons 2\mathrm{D}^0$$

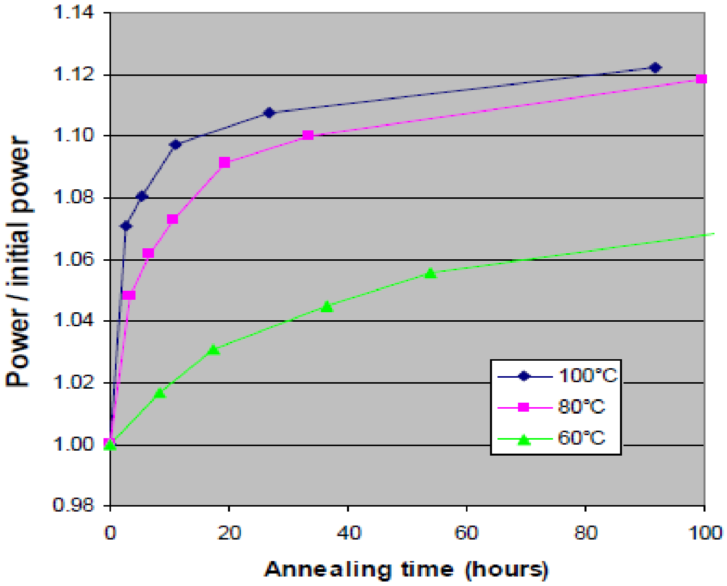
Smith, PRB 32(8) p5510 (1985)
Smith, PRL 59(6) p688, (1987)

Defect dynamics in devices

Outdoor performance



Annealing kinetic into initial state



Solar module efficiency oscillates throughout the year

equilibrium between

defect formation (light) and annealing (heat)

Fischer, Proc. EU-PVSEC (2009)