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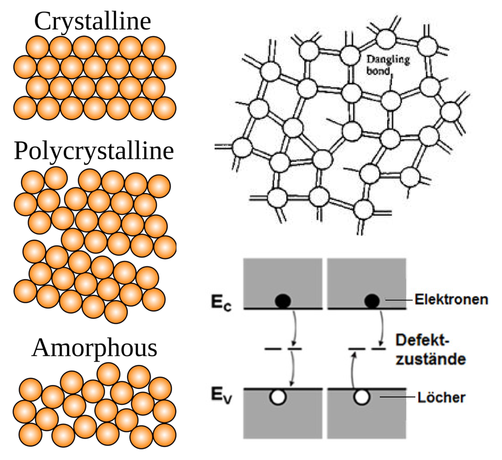
IMPROVING THE DETECTION LIMIT OF QUANTITATIVE EPR ON SILICON DANGLING BOND DEFECTS BY RAPID SCAN EPR

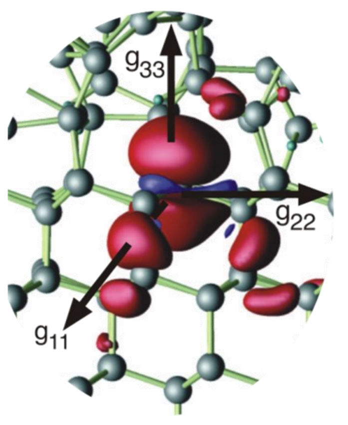
STRUCTURAL DEFECTS IN THIN-FILM SILICON

Thin-film Si solar cells: a-Si, µc-Si, poly-Si
- Reduce material cost to increase price efficiency

Electronic defects limit solar cell efficiency
- Currently 9-12 % for TF devices (c-Si wafer: 25 %)

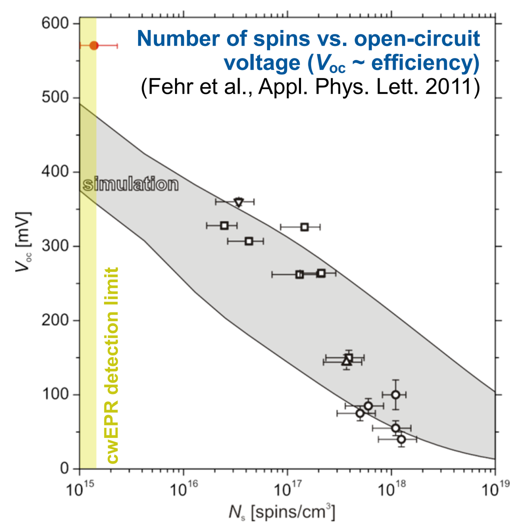
Amorphous silicon: dangling bond defect
- Broken bond: three-fold coordinated Si atom
- Recombination center for charge carriers (voltage and current losses → efficiency decrease)





Dangling bond: paramagnetic
- EPR signal at g_{db} = 2.0055

Use EPR for defect analysis
- Quantitative EPR for spin counting
- Link defect density to efficiency
- Microscopic structure of defects



CW EPR: DEFECT COUNTING

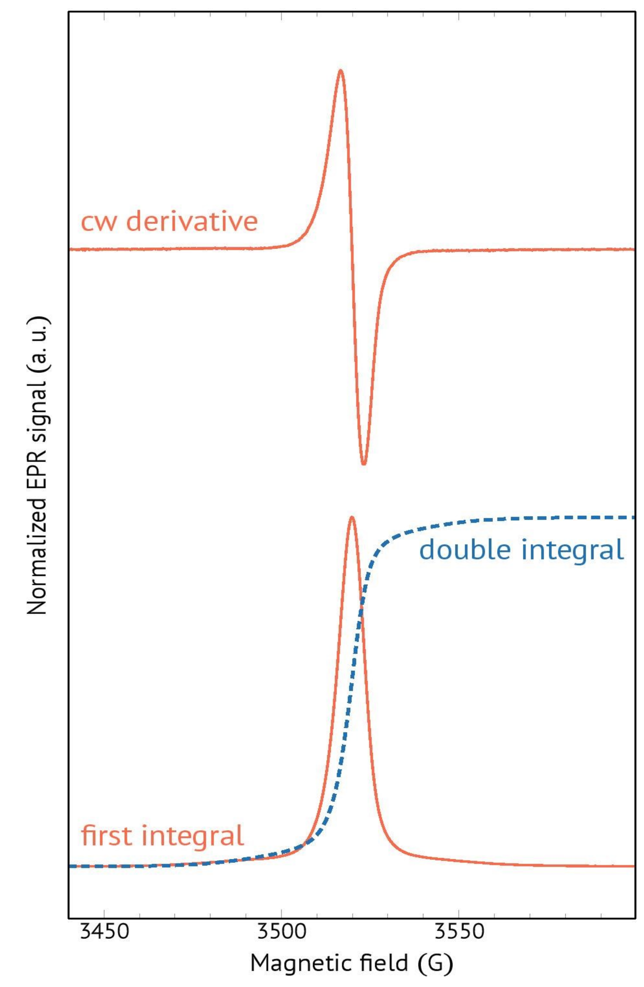
Signal intensity from cwEPR signal
- Field modulation: derivative spectrum
- Signal intensity from double integral

Quantitative EPR: number of spins
- Double integral prop. to number of spins

$$DI = c \cdot \frac{\sqrt{P} \cdot B_{\mathrm{m}} \cdot Q \cdot n_{\mathrm{B}} \cdot S(S+1)}{f(B_1, B_{\mathrm{m}})} \cdot N_S$$

Reference sample for calibration
- Sample with known number of spins (e.g. a-Si:H)

Problem: sensitivity limit of cwEPR
- Currently 10^{11}-10^{12} spins detectable (12 h)
- Enhanced material quality: increase sensitivity
- Alternative: **rapid scan EPR**

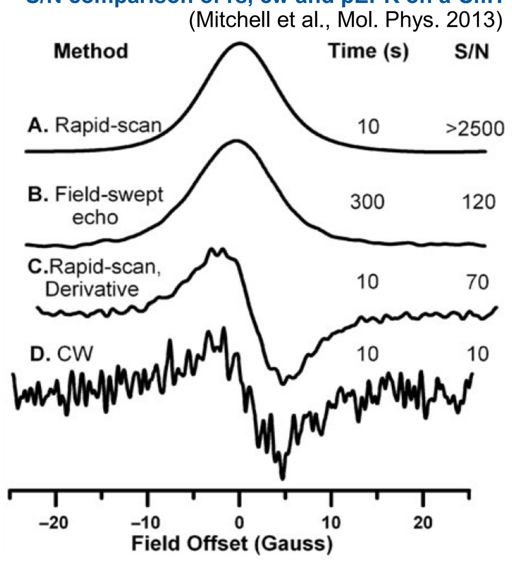


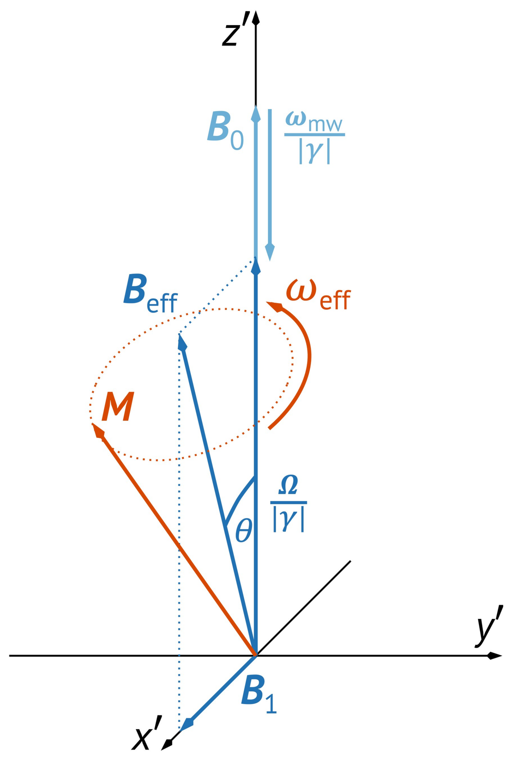
RAPID SCAN EPR

Motivation: S/N enhancement for a-Si:H
- rsEPR Technique developed by Eaton group
- Large S/N benefit for samples with long relaxation times
- Goal: realize rsEPR in a standard Bruker setup

Principle
- Pass resonance fast with respect to T_1 and T_2 → Change EPR saturation behavior
- Passage effects: "wiggles" following signal

S/N comparison of rs, cw and pEPR on a-Si:H (Mitchell et al., Mol. Phys. 2013)





Vector model
"Rapid": B_{eff} rotation faster than T_1 and T_2

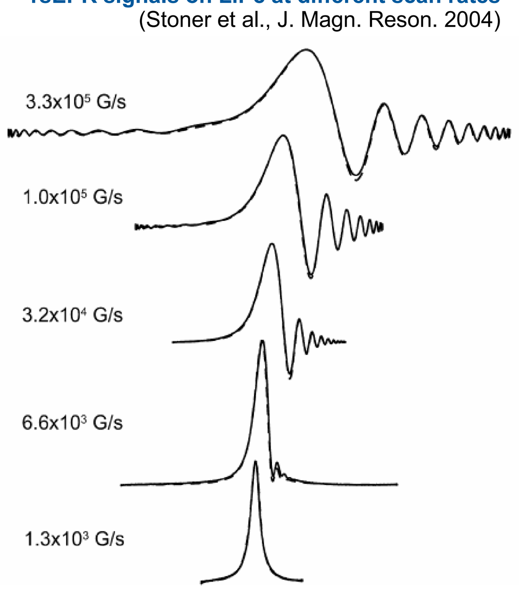
$$\left|\frac{\mathrm{d}\theta}{\mathrm{d}t}\right| = \frac{1}{B_1} \cdot \frac{\mathrm{d}B_0}{\mathrm{d}t} \gg \frac{1}{\sqrt{T_1 T_2}}$$

Non-adiabatic passage

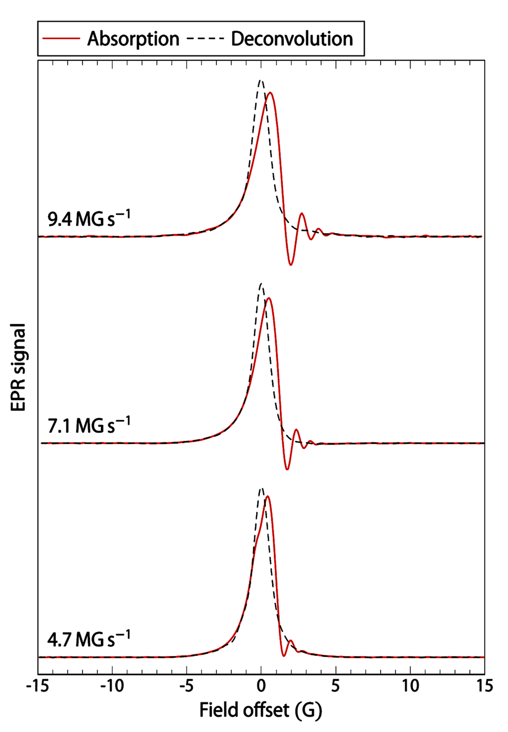
$$\frac{\mathrm{d}B_0}{\mathrm{d}t} \gg |\gamma| B_1^2$$

- Magnetization cannot "follow" magnetic field $\boldsymbol{B}_{\mathrm{eff}}$
- $\boldsymbol{M}$ close to equilibrium value
- Precession in xy-plane (→ wiggles)

rsEPR signals on LiPc at different scan rates (Stoner et al., J. Magn. Reson. 2004)



rsEPR signals and deconvolution on BDPA at different scan rates



Deconvolution
- Signal: convolution of excitation and spin response (FID)

$$r(t) = h(t) * d(t) \Leftrightarrow H(\omega) = R(\omega)/D(\omega)$$

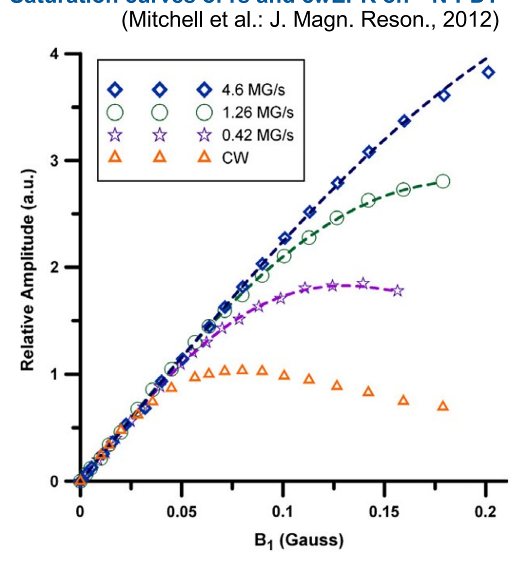
- Driving function (excitation)

$$d(t) = \mathrm{e}^{\,\mathrm{i}\,\phi(t)} = \mathrm{e}^{\,\mathrm{i}\int \Delta\omega(t)\mathrm{d}t}$$

⇒ EPR absorption from FT of rsEPR and driving function

(see Tseitlin et al.: J. Magn. Reson., 2011)

Saturation curves of rs and cwEPR on ^{15}N-PDT (Mitchell et al.: J. Magn. Reson., 2012)



Comparison to cwEPR
- cwEPR: saturation depends on mw power and relaxation
- rsEPR: saturation depends on scan rate
  Use higher mw power in rsEPR: S/N enhancement

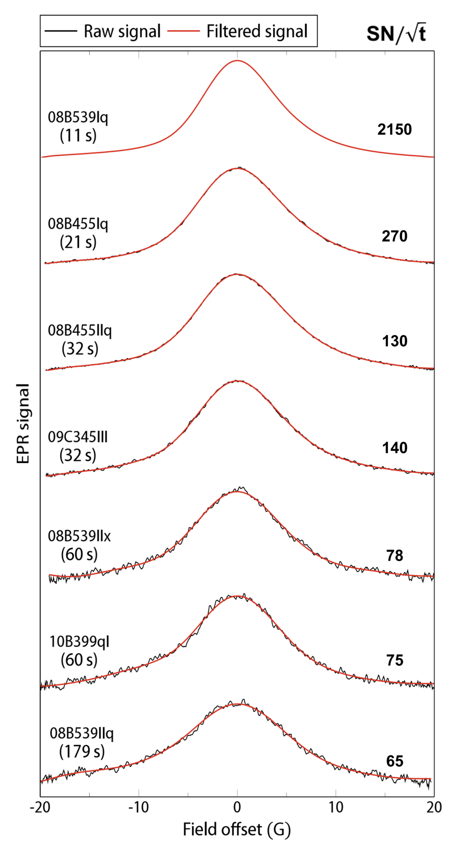
S/N STUDY ON A-SI:H OF VARYING QUALITY

rsEPR vs. cwEPR on a-Si:H
- Compare S/N of a-Si:H samples with different deposition conditions and defect concentrations (10^{12} to 10^{15} spins)
- Use commercial pulse spectrometer (Bruker Elexsys E580)

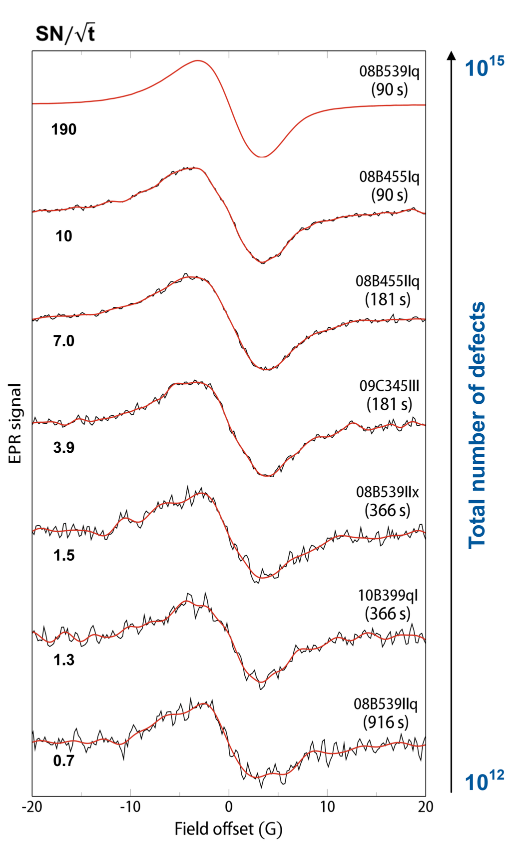
S/N increase by up to a factor of 90
- Factor of 8000 in acquisition time
- Largest benefit for lowest number of spins (highest electronic quality)

⇒ **rsEPR: increased EPR sensitivity for dangling bond defects in silicon**

rsEPR on a-Si:H samples of different electronic quality, recorded at a scan rate of 11.3 MG/s.



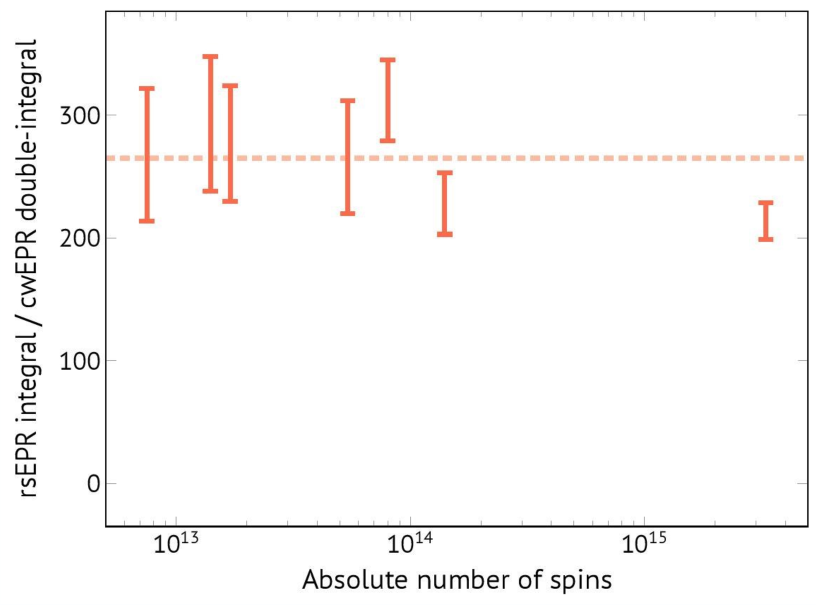
cwEPR on the same a-Si:H samples, recorded with magnetic field modulation of 2 G at 100 kHz



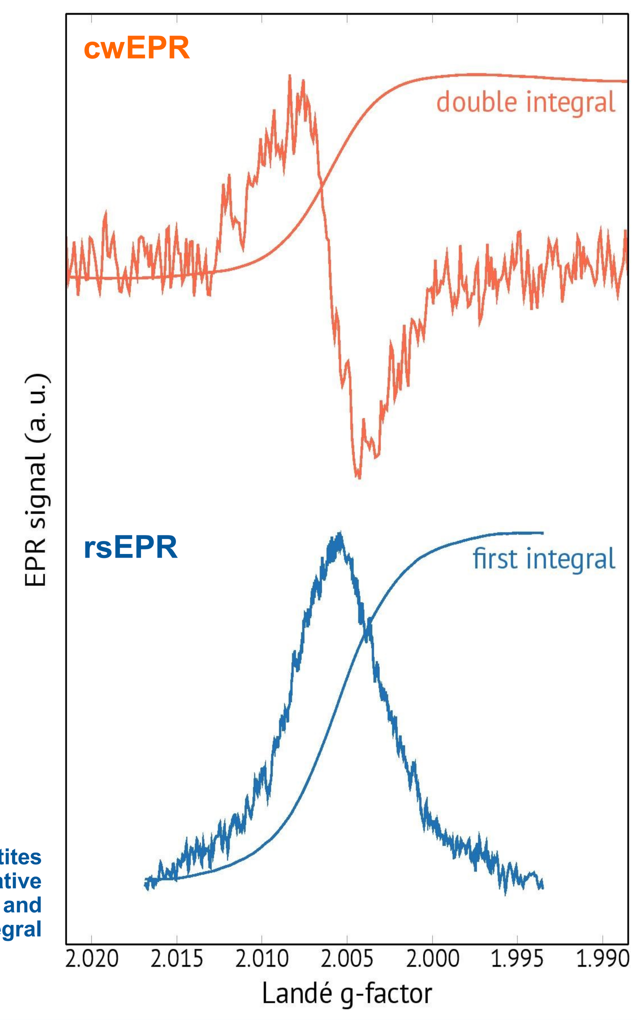
QUANTITATIVE RAPID SCAN EPR

Number of spins from rsEPR signal
- Signal intensity proportional to number of spins?
- Compare cw and rs intensities for seven a-Si:H samples (10^{12} to 10^{15} spins)

rsEPR / cwEPR intensities constant
- Quantitative rsEPR with reference sample



Ratio of rs and cwEPR signal intensities for a-Si:H samples with varying number of dangling bond defects



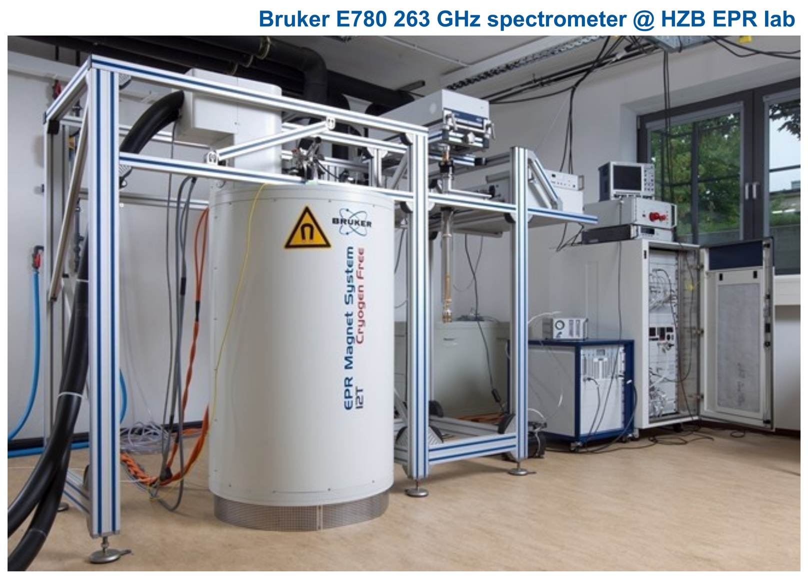
Signal intensities from cw derivative double-integral and rs absorption integral

CONCLUSION AND OUTLOOK

Improved sensitivity of defect counting by rsEPR in a Bruker setup
- rsEPR implemented on Bruker E580 pulse spectrometer without hardware changes
- S/N enhancement for a-Si:H dangling bond by a factor of up to 90
- Use rsEPR intensity for defect counting by comparison with reference sample
- Limitations: sample size (modulation field inhomogeneity), scan rate (max. 40 G, 100 kHz)

Outlook on further developments
- rsEPR at low temperature (increase of relaxation times)
- rsEPR at 263 GHz (longer relaxation times favor rs over cwEPR)
- Frequency-swept rsEPR, possibly at 263 GHz without a resonator

Bruker E780 263 GHz spectrometer @ HZB EPR lab



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