COLORADO SCHOOL OF MINES
EARTH ENERGY ENVIRONMENT

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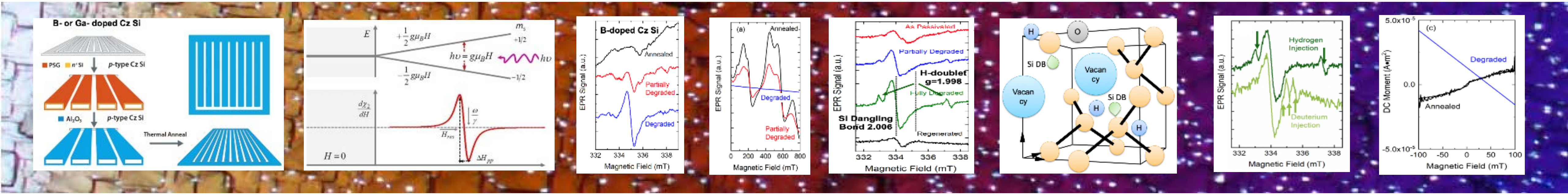
Understanding microscopic mechanisms of LeTID and LID and their unifying features by Electron Paramagnetic Resonance



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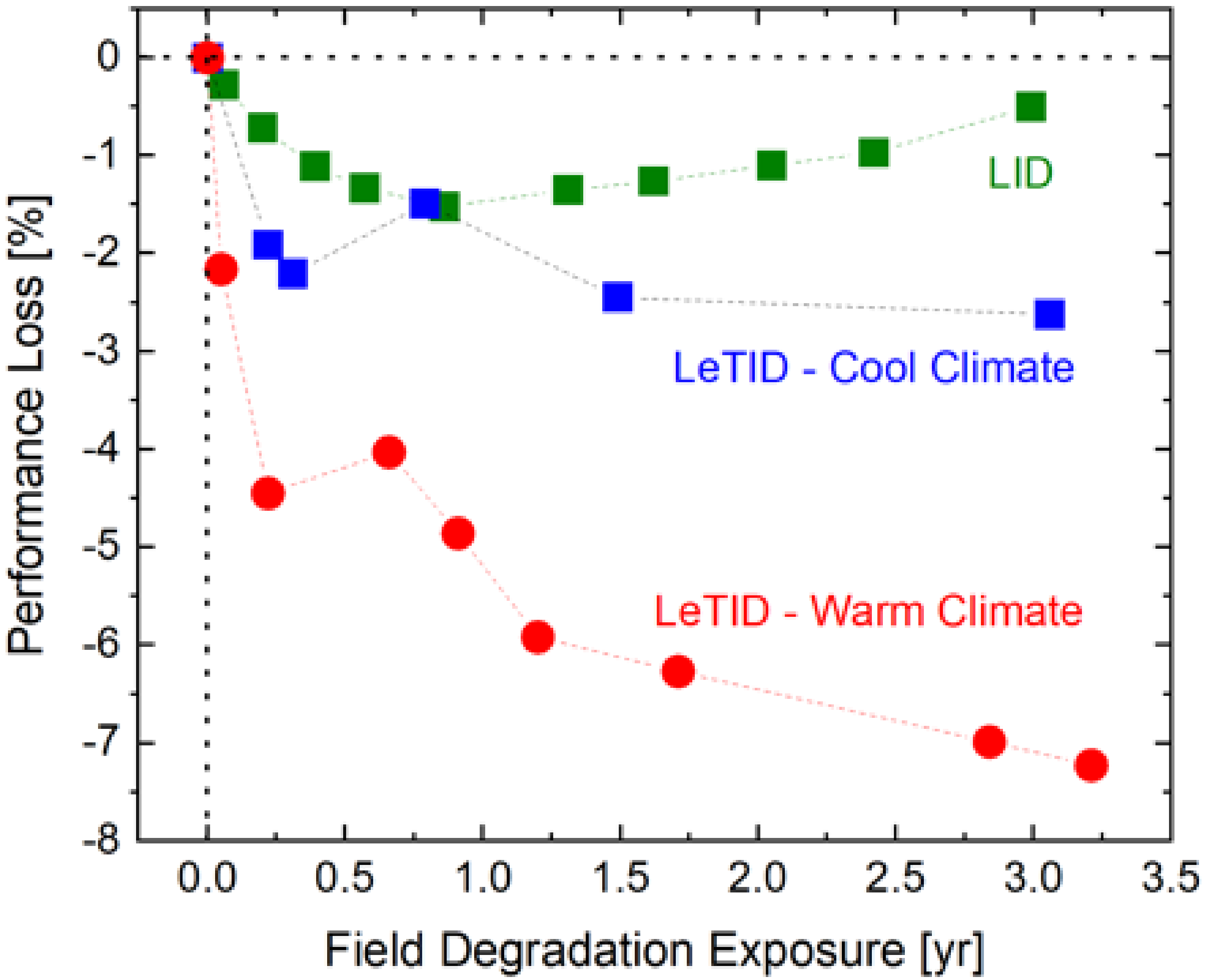
DOE EERE through contract SETP DE-EE0008171 (PVRD2) and contract number DE-AC36-08GO28171. PR-5900-84540.

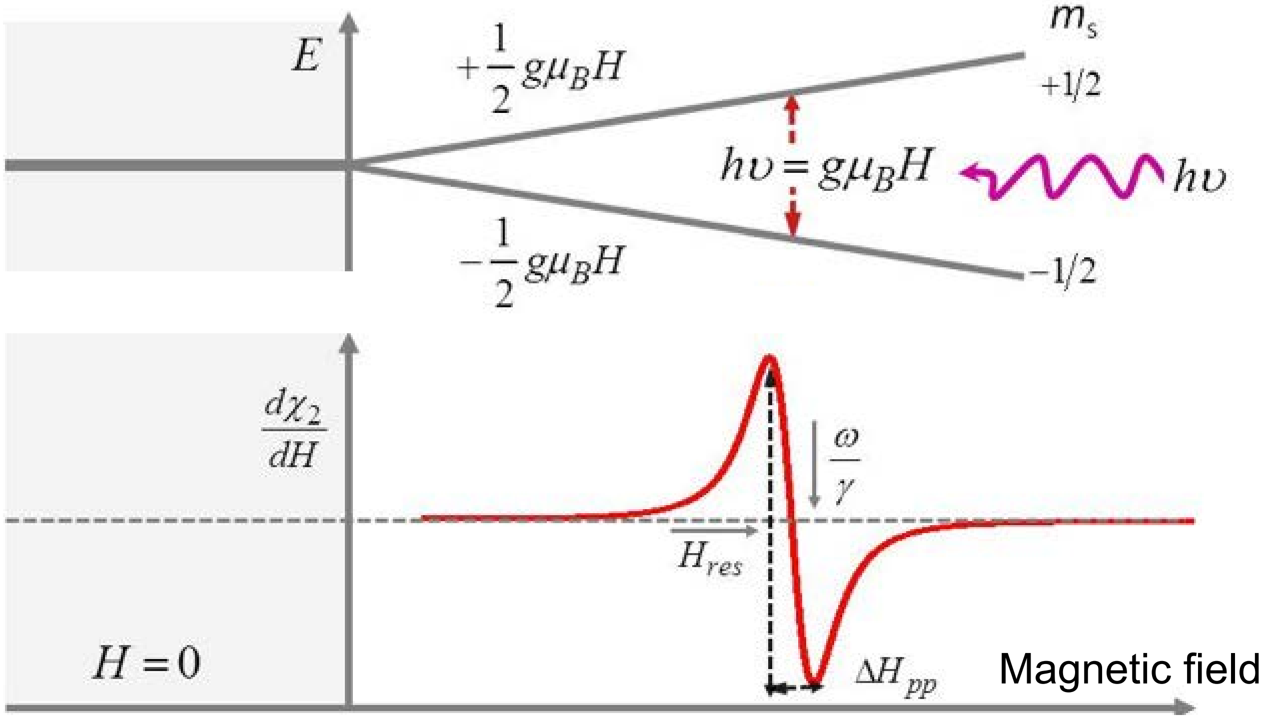
Light-induced degradation (LID) and light- and elevated temperature-induced degradation (LeTID) in p-PERC cells

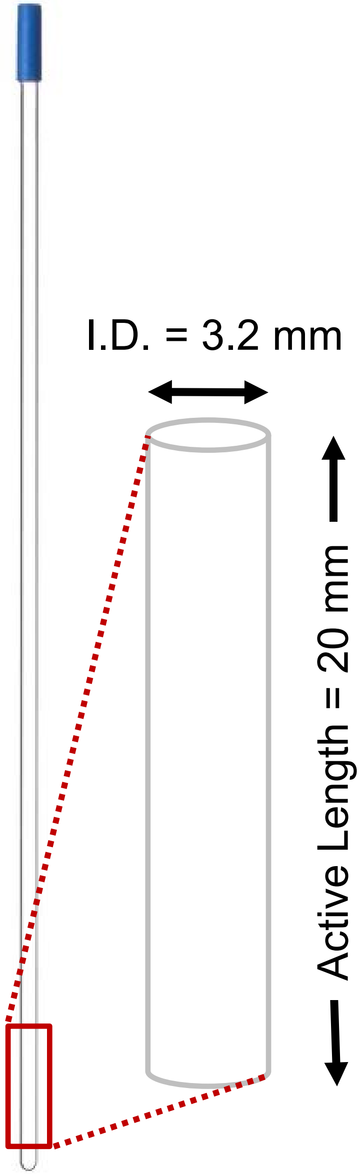


- Both degradation modes cause few relative % cell performance loss; LID can be stabilized in factory or in field; LeTID is much longer-lasting, no field regeneration
- **Both LID and LeTID defects occur in the p-type wafer bulk**
- LID is associated with B dopant and oxygen dimers : $N_{LID} \sim [B]*[O]^2$
- LeTID is not p-dopant atom specific (B, Ga), not related to O; evidence points to excess bulk H introduced upon firing the SiN_x
- Microscopic mechanisms suggested, but role of H less clear

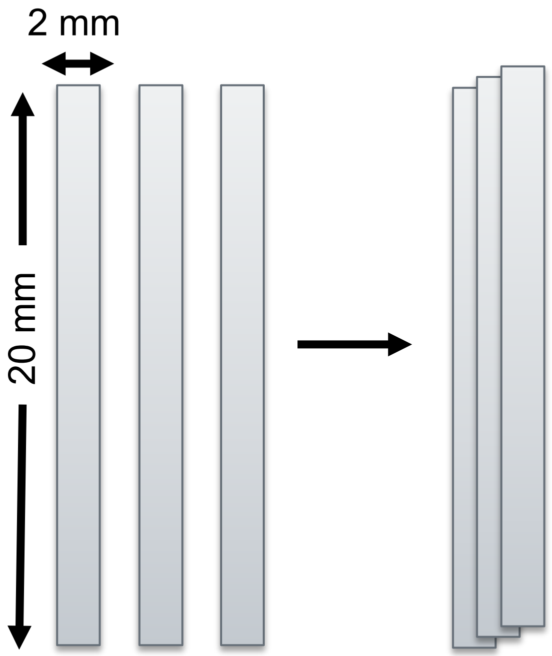
Electron Paramagnetic Resonance Detects Spin-Active Defects

A. R. Meyer *et al.*, *EES,* (2021)





Sample Size and Orientation



EPR : unpaired electrons interact with magnetic field leading to Zeeman splitting.

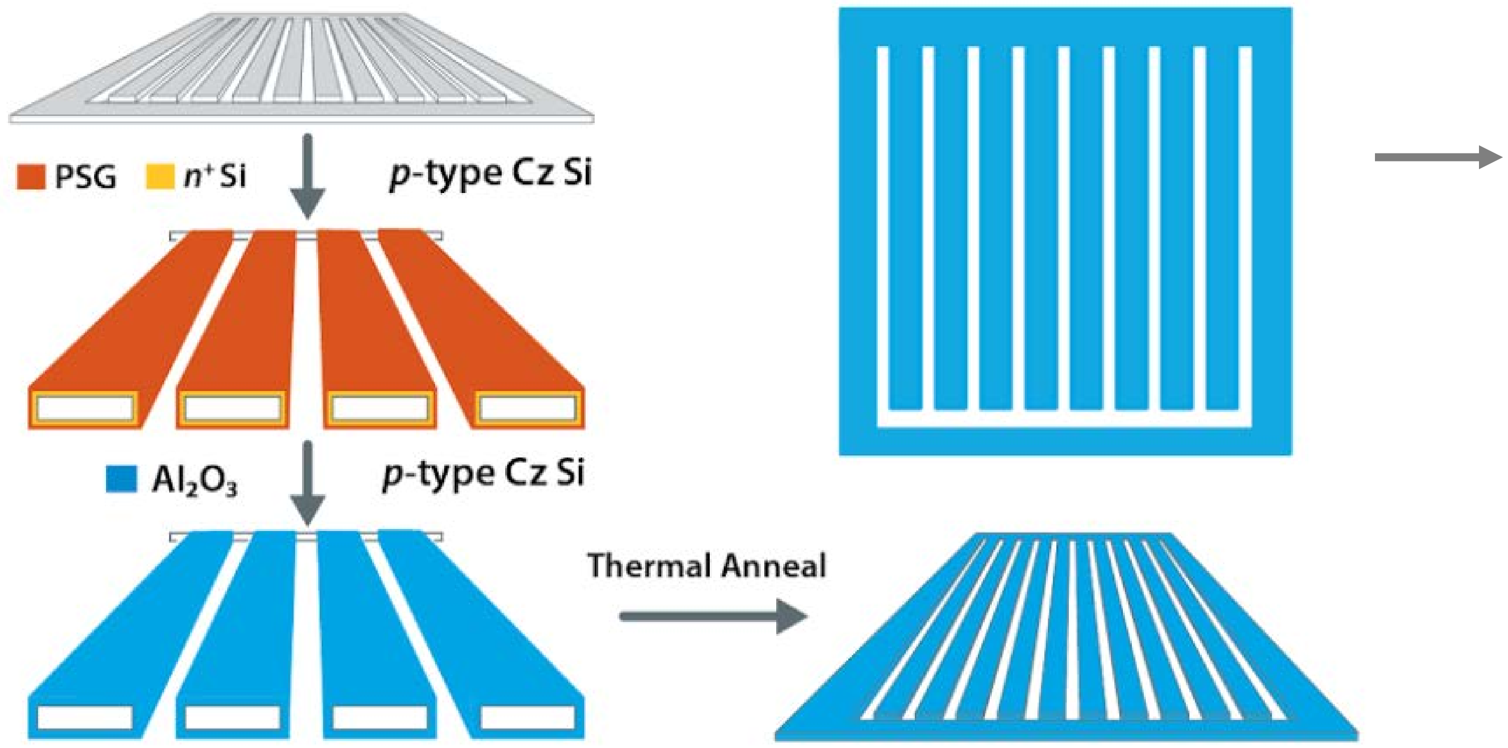
Each defect has a different **g-value** associated with it, which gives insights to the electronic structure of the defect!

~10^{11} spins/cm^3 detection limit in Si wafer samples

M. L. Reed and J. D. Plummer, *Journal of Applied Physics,* (1988) O. Yalçin, *Ferromagnetic Resonance Theory and Applications,* (2013)

Sample preparation for EPR: laser scribing, gettering, etch, passivation

B- or Ga- doped Cz Si



Light-induced degradation
- 1 Sun Illumination
- LID Room T (LeTID 75 °C)
- Up to 24 hours

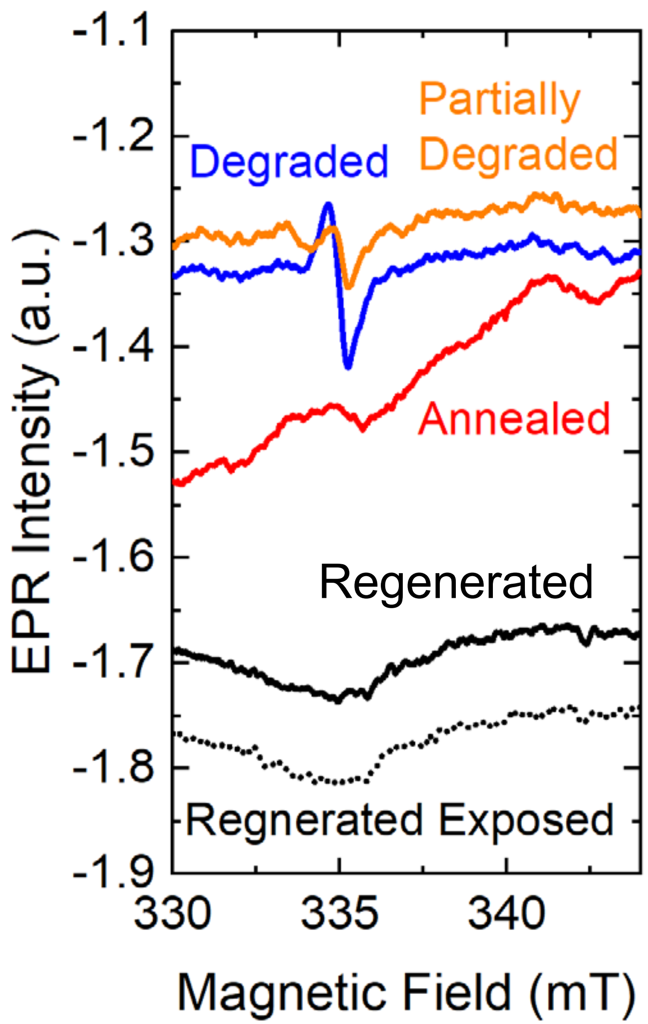
Dark-Annealing
- 200 °C
- 20 min

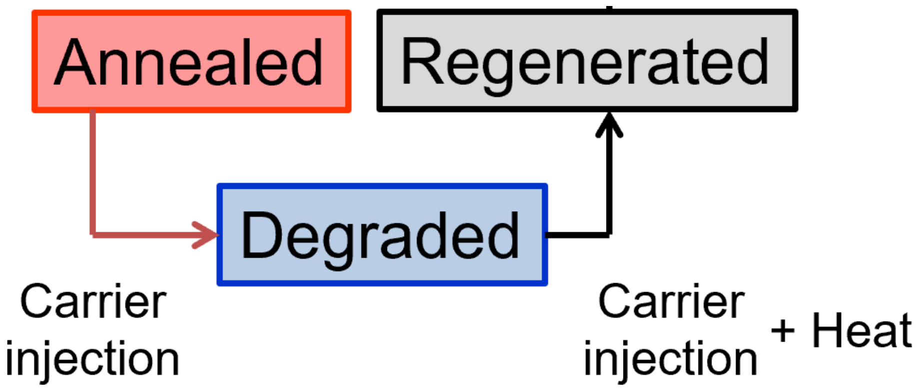
Regeneration (after firing)
- 1 Sun Illumination
- 175 °C
- 2 hours

LeTID: same sample preparation, but gettering optional; SiNx + firing; removal of SiNx; passivation by Al_2O_3

Lifetime samples – same processing

LID Exhibits EPR Defect Signature in Narrow Magnetic Field Scans





Annealed

Regenerated

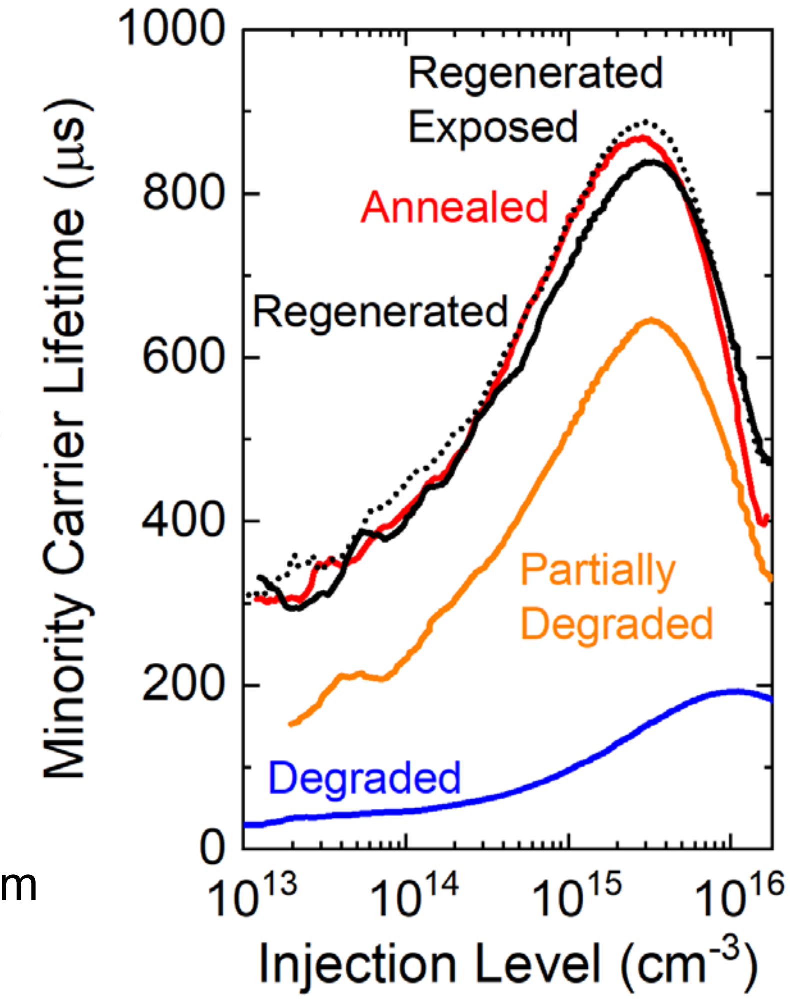
Degraded

Carrier injection

Carrier injection + Heat

Narrow EPR spectrum depends on what state of LID the sample is in

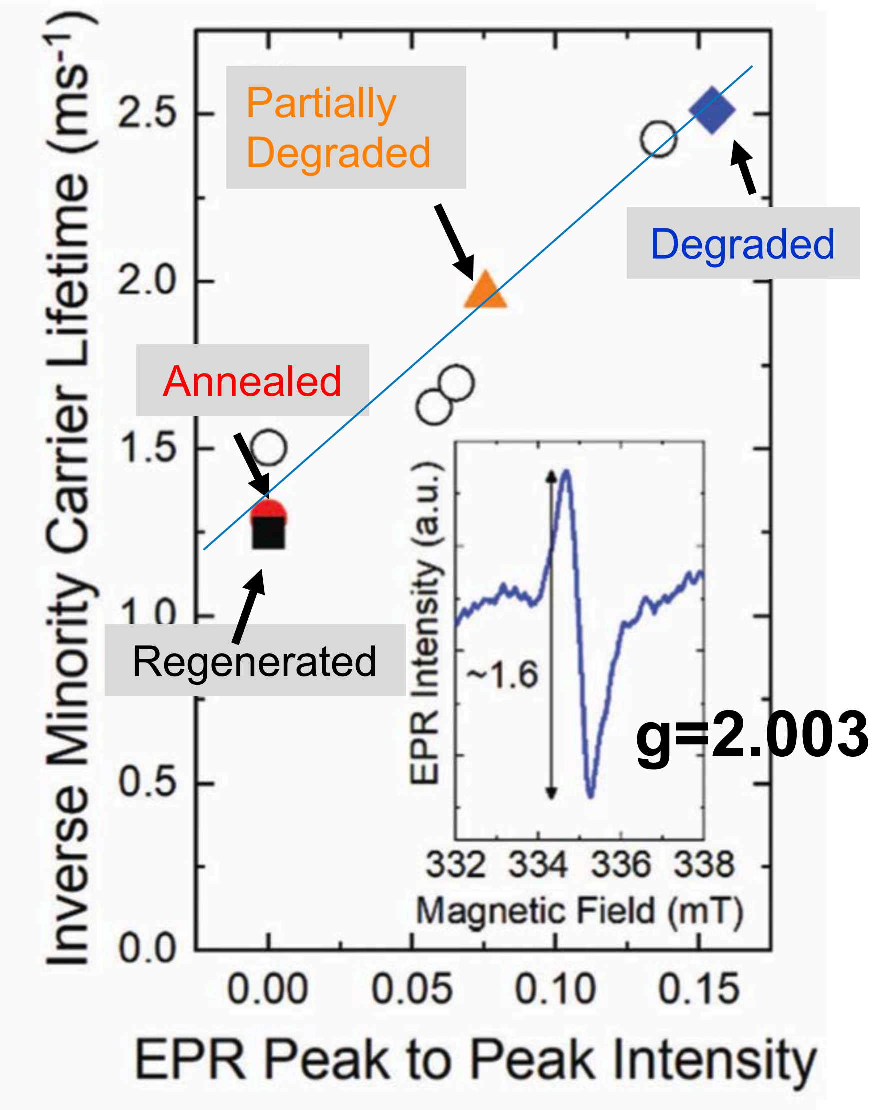
- Annealed – featureless EPR spectrum
- Degraded – EPR signature at 335 mT
- Regenerated – featureless EPR spectrum



Light-degraded state in *p*-type Cz Si shows strong, sharp defect signature (*g*-value = 2.003) compared to samples in the annealed state

A. R. Meyer *et al.*, *EES*, (2021)

Results Suggest Two or More Oxygen Involved



1. Inverse minority carrier lifetime correlates to EPR peak-to-peak intensity in all three states of LID.
2. EPR signature *g*-value 2.003 is closer to the free electron than the Si dangling bond (2.0055). This is typically an effect of nearby oxygen.
    - Suggests that two or more oxygen atoms are involved in the wavefunction

A. R. Meyer *et al.*, *EES,* (2021)

EPR results suggest involvement of two or more oxygen atoms on the wavefunction of the BO LID defect.

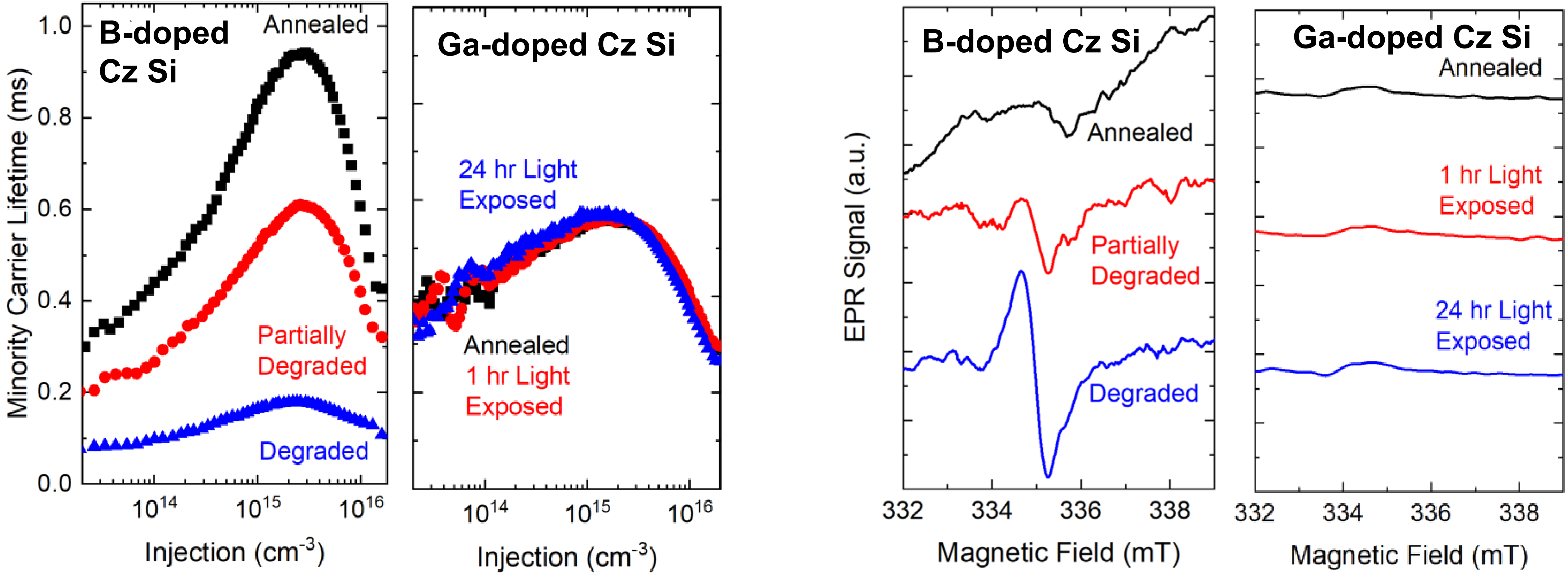
Is there Light Induced Degradation in Ga-Cz Si?

A. R. Meyer *et al.*, *ACS App.En.Mat.*, (2022)

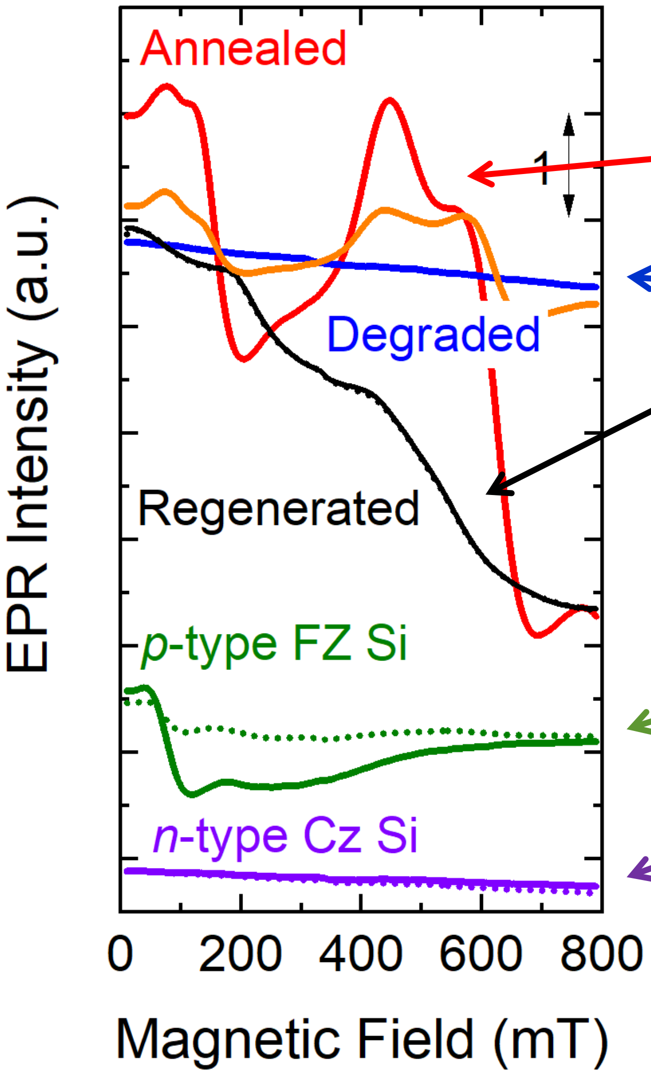
Industry has rapidly transitioned from B-doped Cz Si to Ga-doped Cz Si

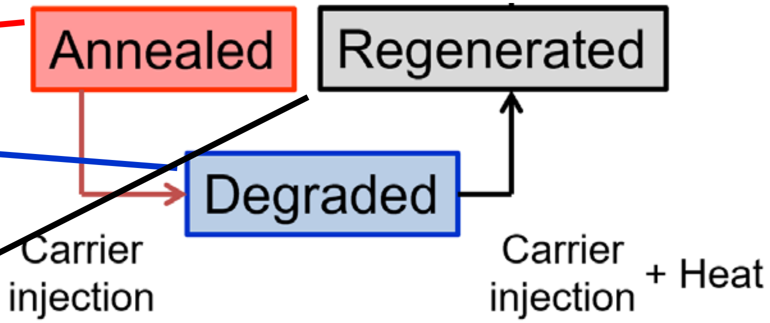
- Higher lifetime and no light induced degradation

No LID in Ga-doped Cz Si: neither in lifetime nor in EPR



LID in fine structure of EPR: besides ~ 10^{12} cm^{-3} deep defects, LID creates > 10^{16} cm^{-3} shallow trap states: all B-acceptor spins disappear




Annealed

Regenerated

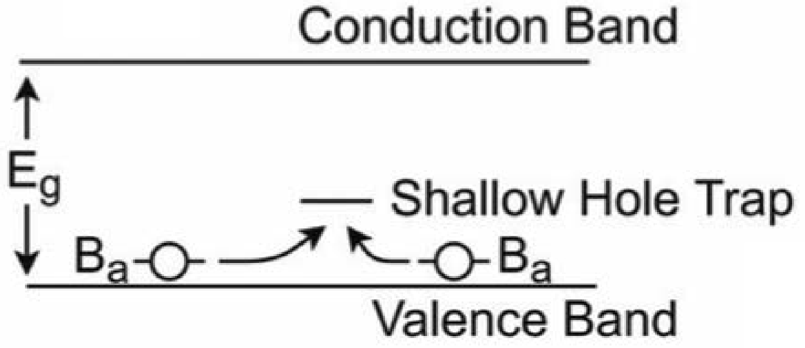
Degraded

Carrier injection

Carrier injection + Heat

EPR fine structure depends on the state of LID and the doping and oxygen concentration

- Annealed – Large paramagnetic signal
- Degraded – Diamagnetic EPR signal
- Regenerated – Paramagnetic signal
- *p*-type FZ Si – Paramagnetic before and after light-exposure
- *n*-type Cz Si – No B_a EPR signatures



A. R. Meyer *et al.*, *EES,* (2021)

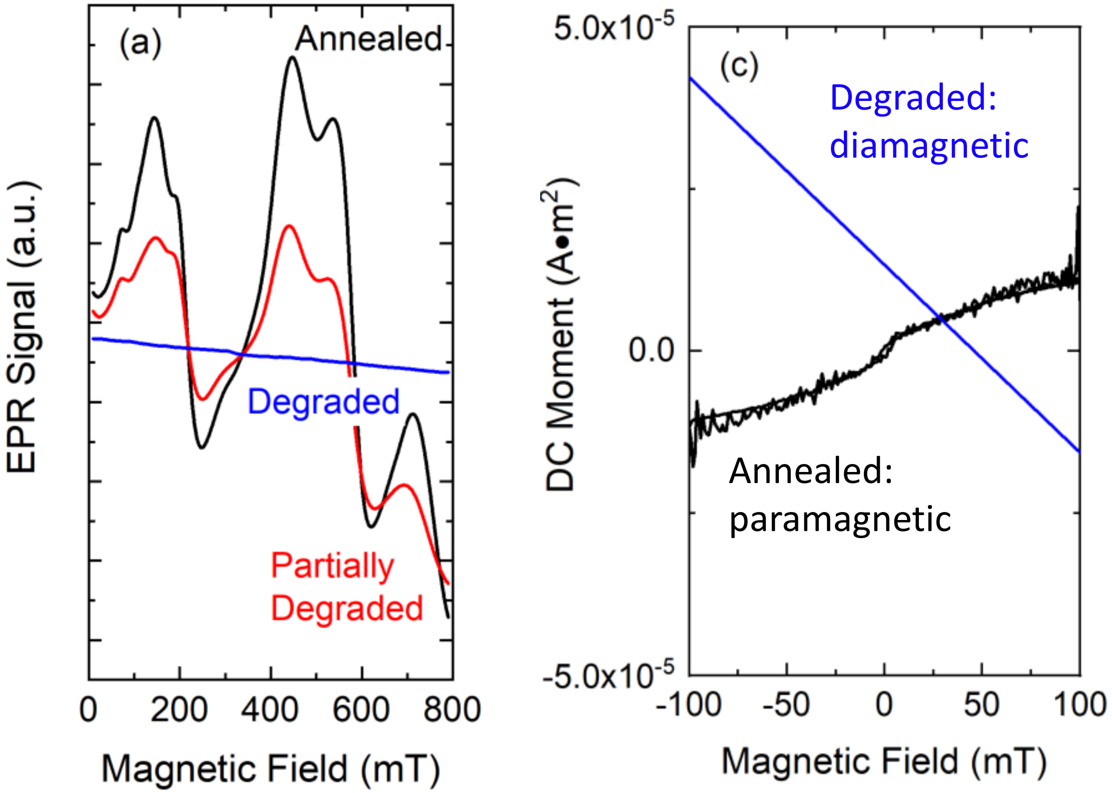
Light exposure affects all B_a atoms as the EPR signal transitions from paramagnetic to diamagnetic

Broad EPR Spectrum in Ga-Cz – Remains Paramagnetic

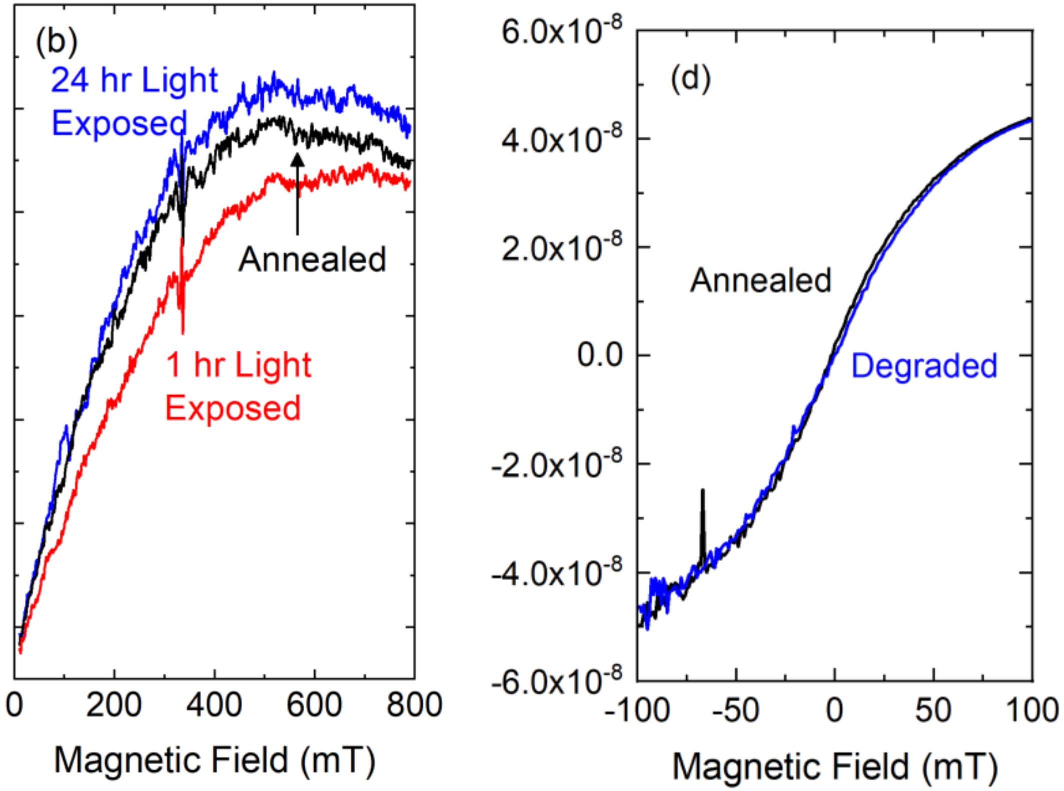
- Ga-doped Cz Si fine structure remains paramagnetic after light exposure
  1. Negative-U center might form but shallower than Ga acceptor – doesn't act as a trap
  2. Negative-U centers do not form upon light exposure

A. R. Meyer *et al.*, *ACS App.En.Mat.*, (2022)

B-doped Cz Si

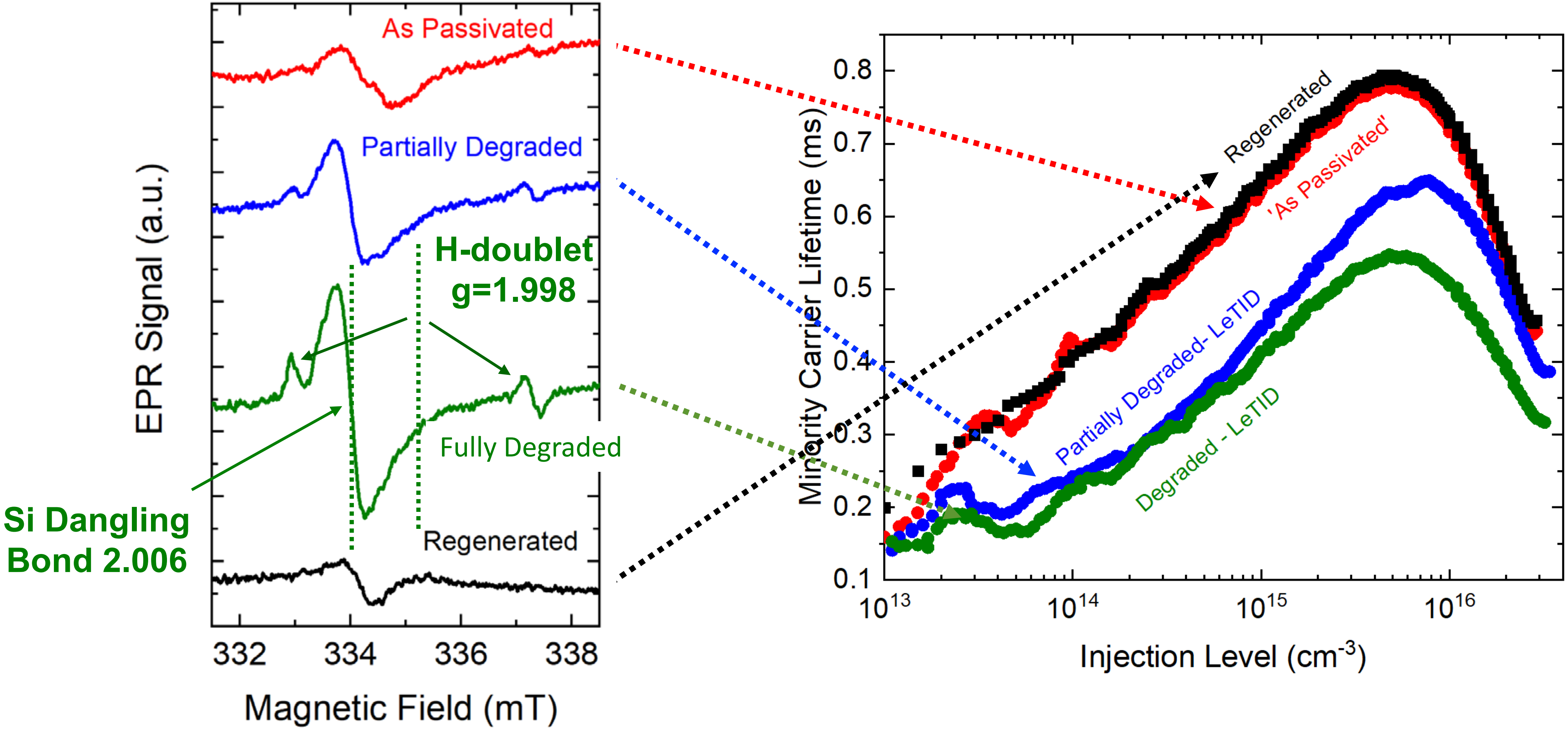


Ga-doped Cz Si



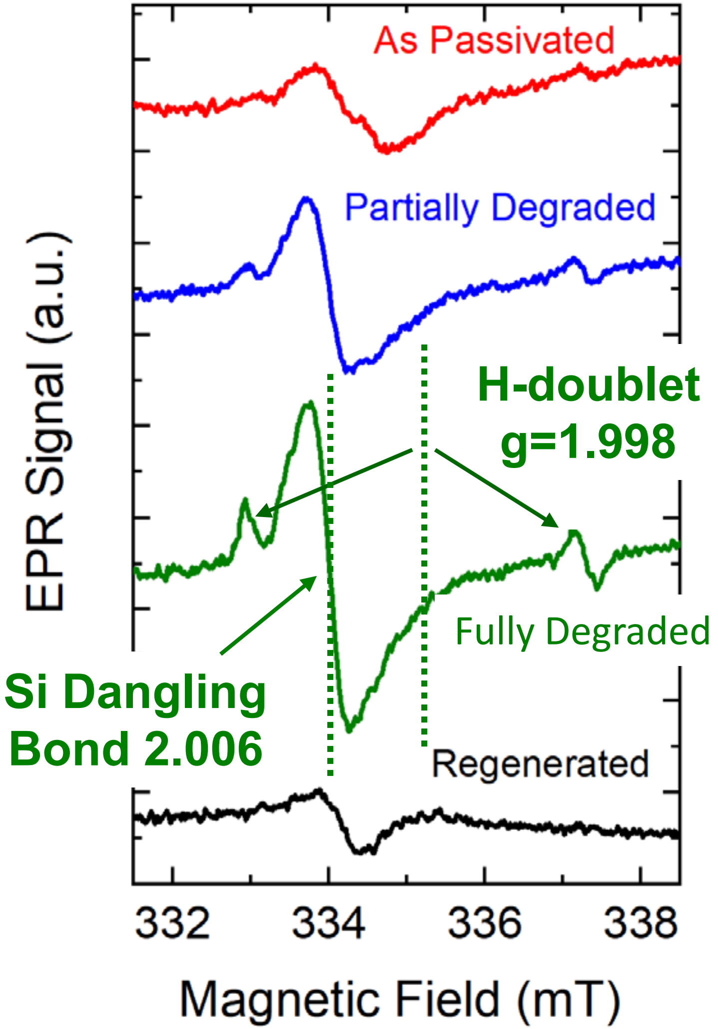
Ga-doped Cz Si remains paramagnetic after light exposure – results in absence of LID

LeTID: Two EPR signals: Si DB and Hydrogen Hyperfine Doublet

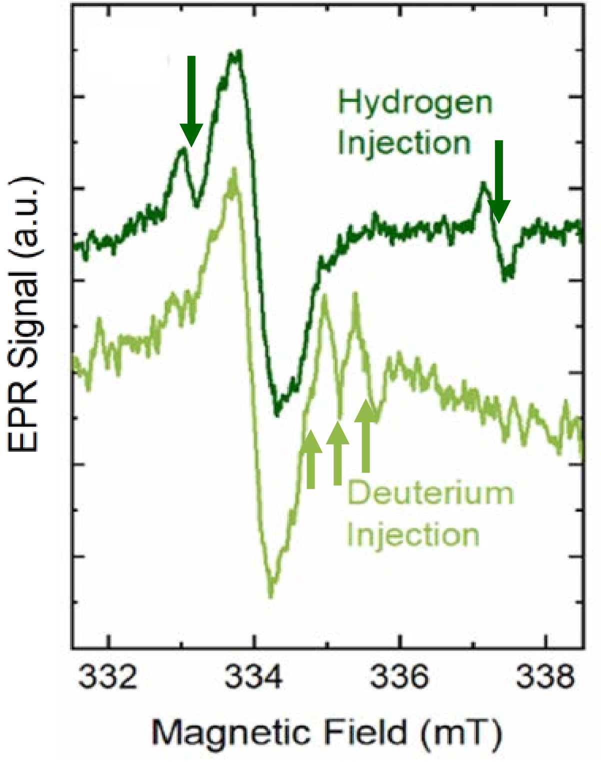


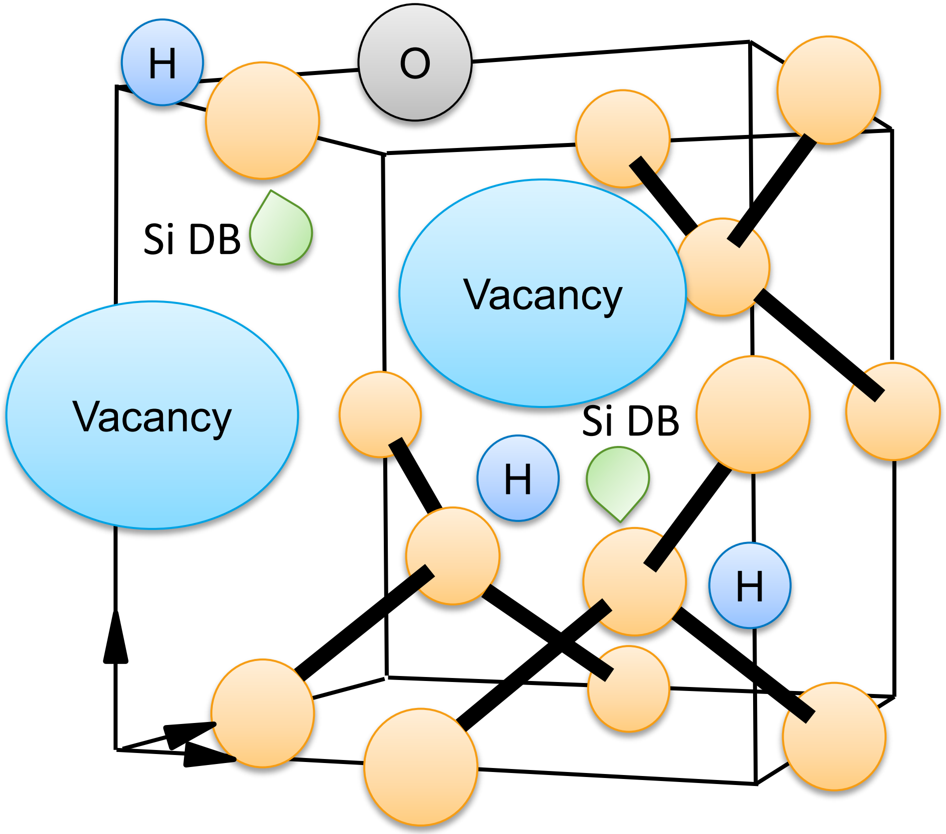
Do these two signals belong to the same defect?

Si Dangling Bond Signal Increases with Increasing LeTID



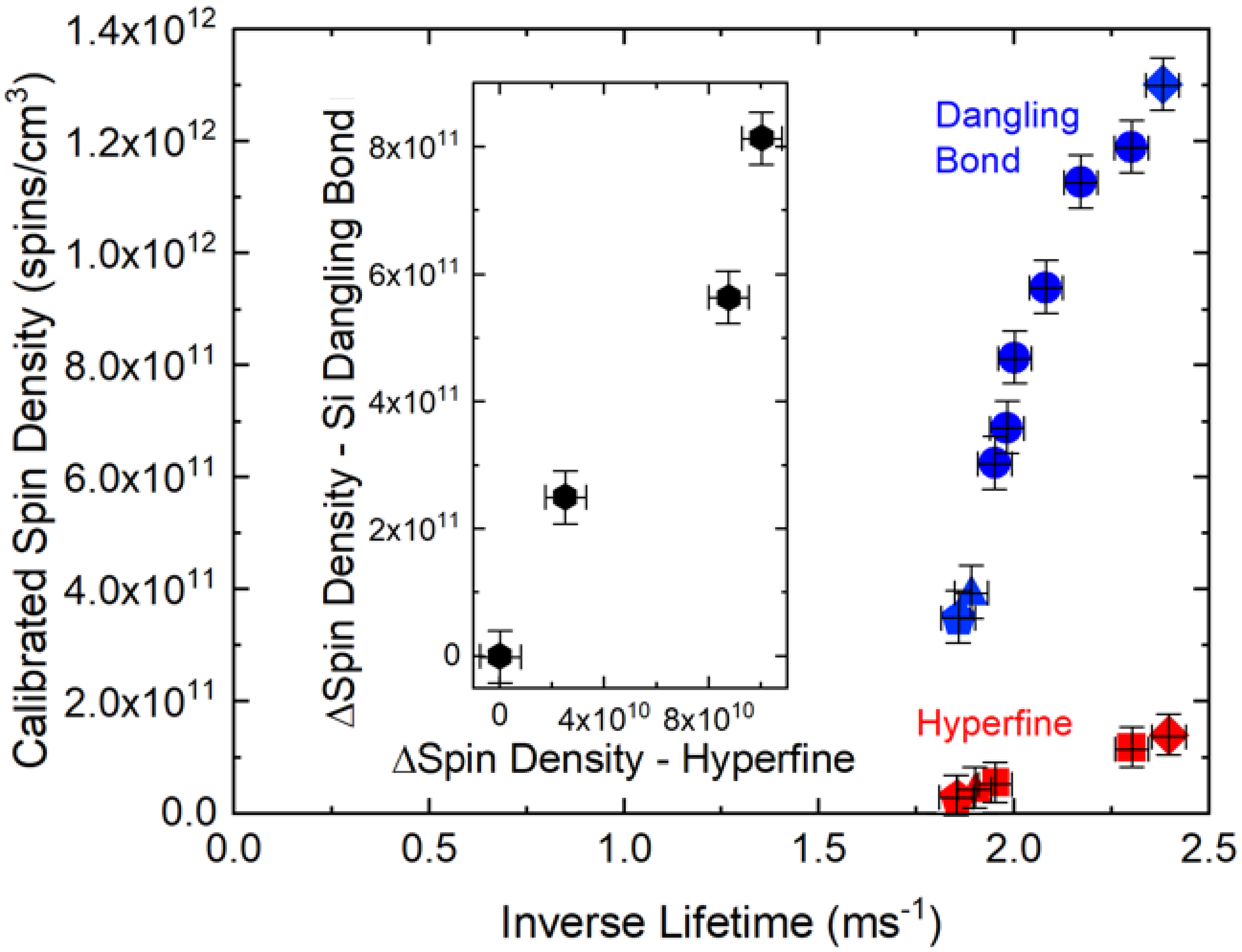
Isotopic replacement H → D
Confirms H involvement





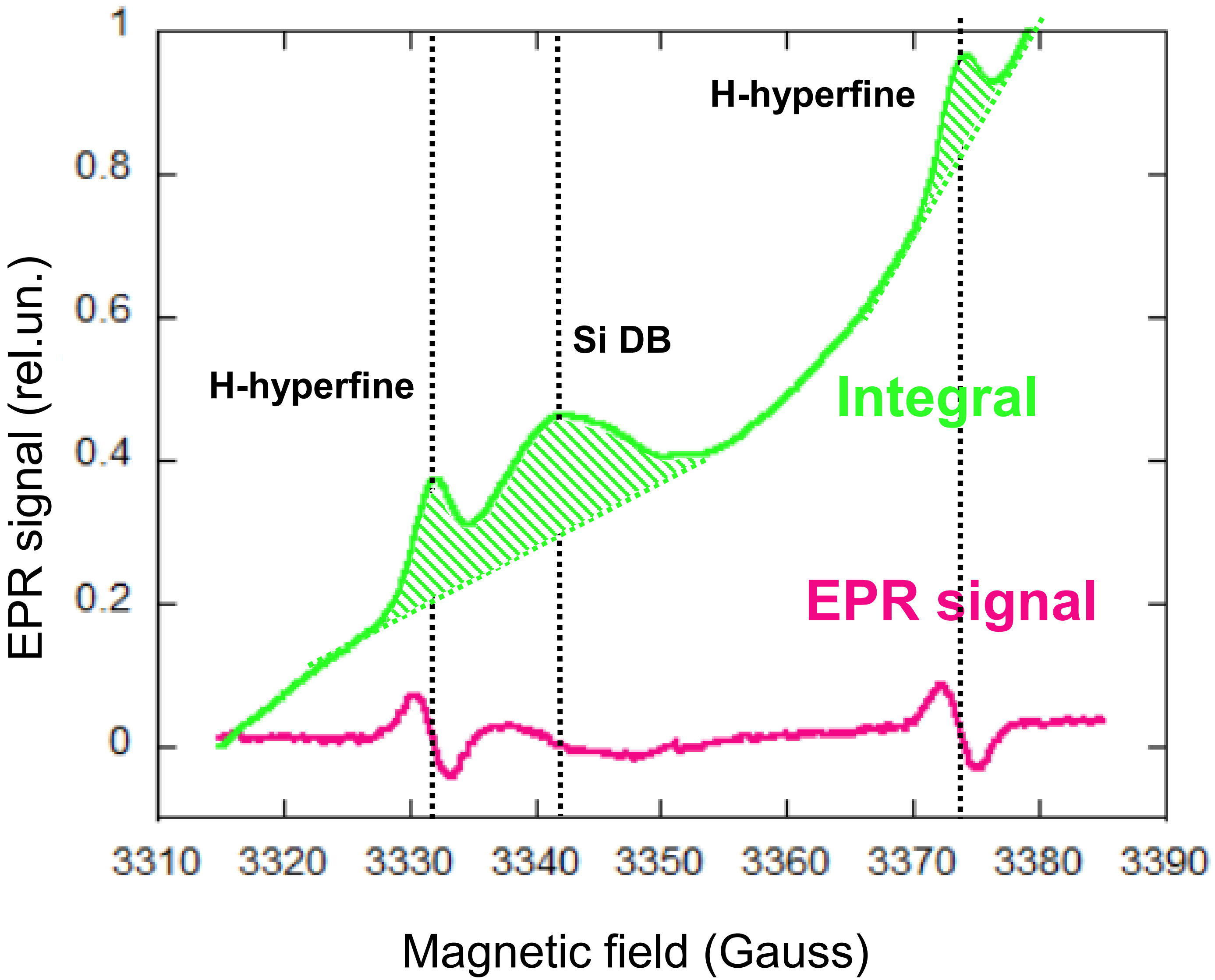
Defect precursor for LeTID is partially hydrogenated vacancy or multivacancy

Two EPR Signatures Correlate – One Defect Responsible for LeTID



Both Si dangling bond and H EPR signatures involved in defect responsible for LeTID

Latest Results (Chirag Mule) : H-Hyperfine and Si DB Spin Numbers are ~ Equal



- Light application at T = 15K enhances and saturates H-hyperfine signals
- May indicate charged defects that becomes spin active due to recombination traffic
- Estimated spin density in H-hyperfine to Si DB ratio about ½ to 1

Conclusions

- **LID degradation** involves not only creation of **~ 10^{12} cm^{-3} recombination centers**, but also **>10^{16} cm^{-3} shallow negative-U traps**
- In Ga-doped Si, LID EPR defects don't appear, but some traps are still created.
- **LeTID: Si DB and H-hyperfine EPR signatures.** We postulate that the defect responsible for LeTID is a partially hydrogenated (multivacancy) with a Si dangling bond and H in the vicinity. O involvement is possible yet unclear.
- We prove that H is related to the structure of the LeTID defect with isotope experiments and its EPR signal is comparable and linear with the Si DB signal upon LeTID degradation.
- Working on simulating these results with DFT to obtain more detailed defect structure.

US DOE EERE under the Photovoltaic Research and Development 2 (PVRD2) program of the Solar Energy Technology Office under Award Number DE-EE0001871 and under contract number DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Solar Energy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.