Seminar at the School of Photovoltaic and Renewable Energy Engineering
University of New South Wales, Australia

WARWICK

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Bulk minority carrier lifetime issues in silicon materials for photovoltaics

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EPSRC
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EPSRC-funded UK silicon PV materials activity

SuperSilicon PV project
(EP/M024911/1)

Tony Peaker, Bruce Hamilton, Matthew Halsall, Vladimir Markevich

- DLTS.
- Bulk passivation.

John Murphy, Nick Grant

- Bulk lifetime issues.

Peter Wilshaw, Sebastian Bonilla, Phill Hamer

- Surface and bulk passivation.
- Characterisation (EBIC, atom probe).

Bulk lifetime issues in PV

- Motivation for working on (silicon) PV is clear.
- Recent advances in surface passivation mean that bulk lifetime can limit the efficiency of some of the best cells.
- There is a need to understand the physics of the recombination process which occur in PV substrates.
- Need to be able to quantify lifetime and study it during cell processing, and ideally need to develop processes to improve it.

Outline of talk

1. Injection-dependent lifetime analysis approach
2. Recombination at oxygen-related extended defects
3. Internal gettering in mc-Si
4. High lifetime silicon materials (if time allows)

Co-workers for this talk

- Robert Falster, Vladimir Voronkov
- Karsten Bothe, Rafael Krain
- Mohammad Al-Amin, Alex Pointon, Nick Grant
- Rachel McGuire
- Dan Macdonald, Fiacre Rougieux

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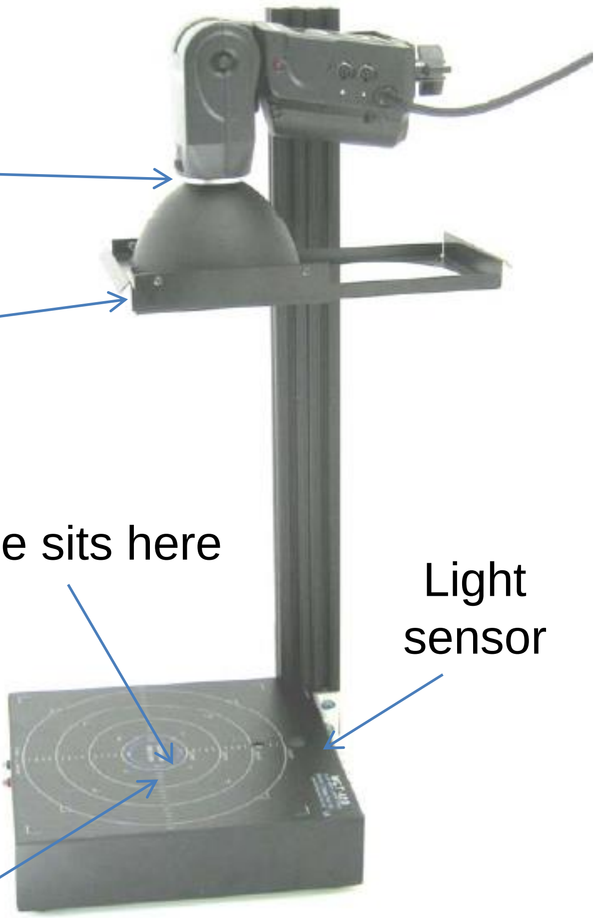
Injection-dependent lifetime measurements



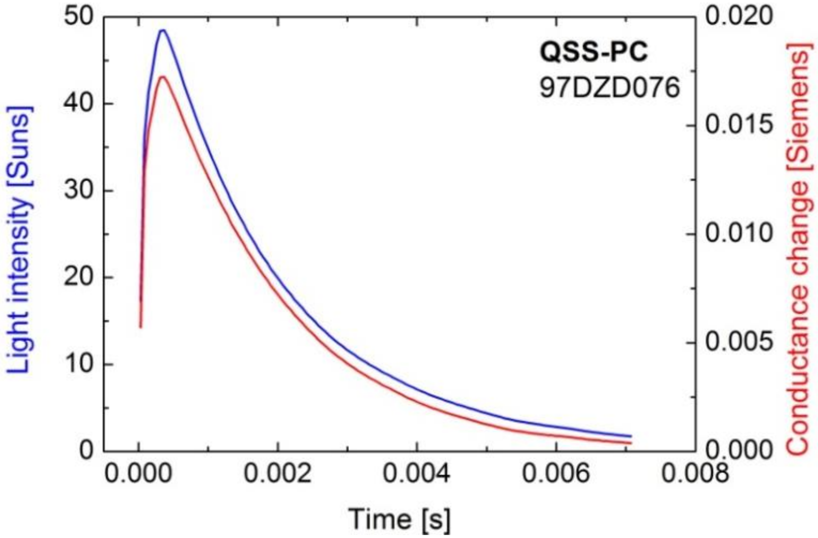
Flash

Filters

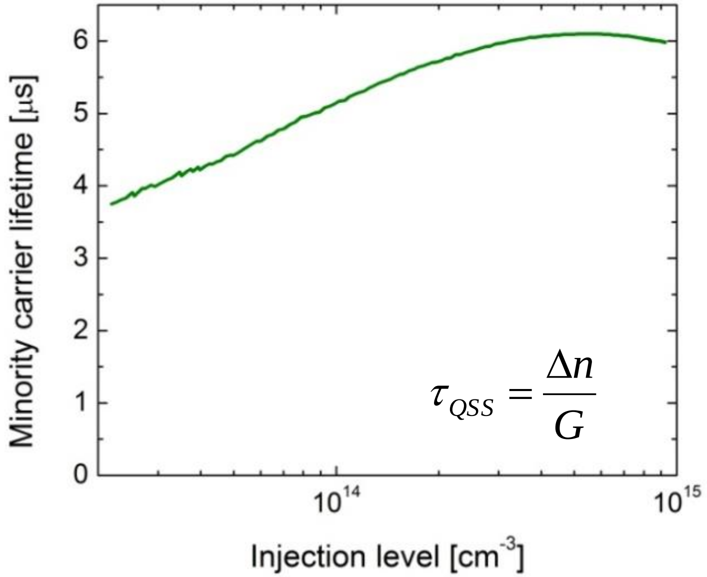
Sample sits here

Light sensor

Eddy current sensor



$$\Delta n = \frac{\Delta\sigma}{q\left[\mu_n(\Delta n, N_A, N_D) + \mu_p(\Delta n, N_A, N_D)\right]}$$



$$\tau_{QSS} = \frac{\Delta n}{G}$$

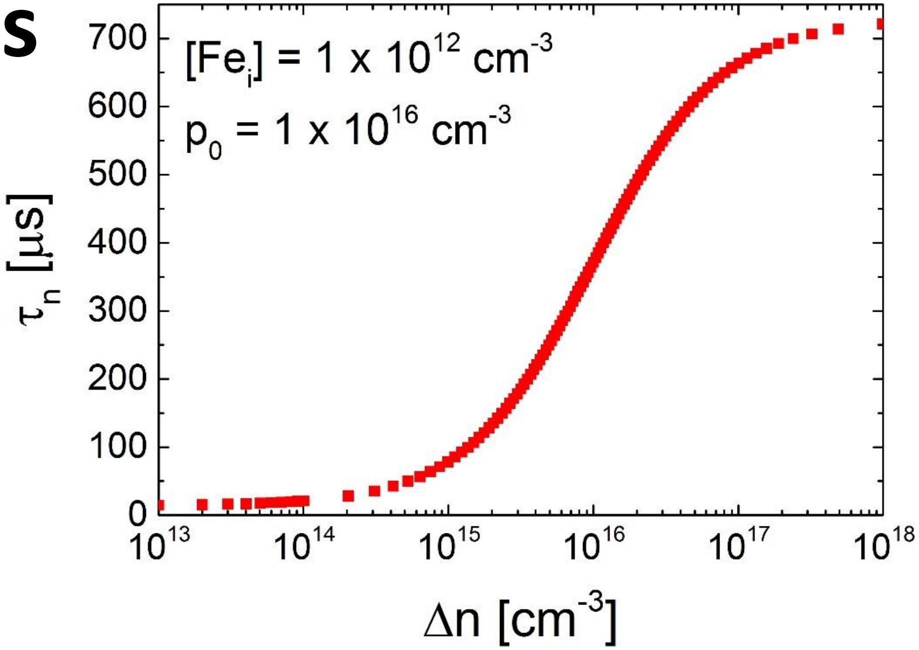
Plotting lifetime curves

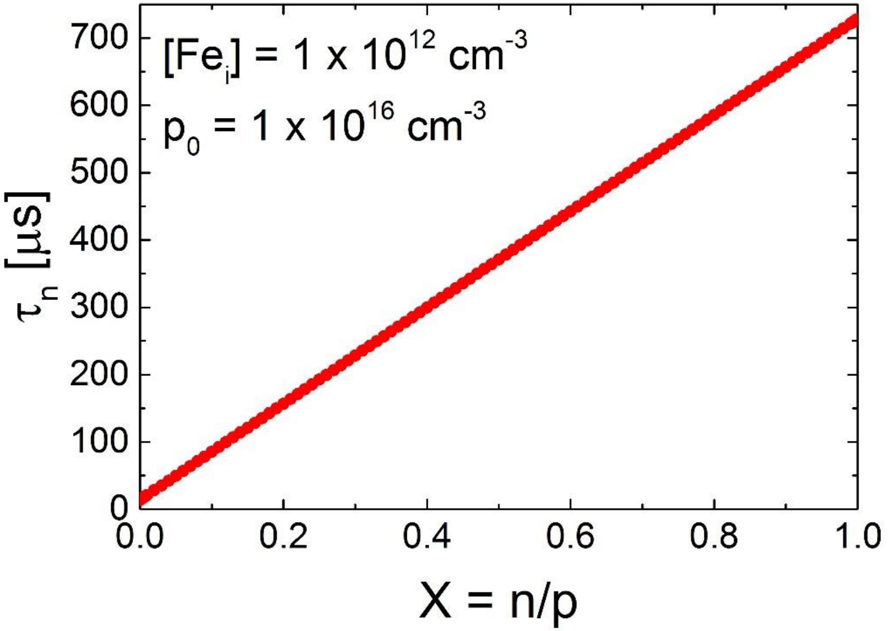
- Usually people consider lifetime as a function of the excess minority carrier density, *i.e.* plot τ versus Δn for *p*-type or Δp for *n*-type.

- Instead plot lifetime versus X = n/p:

$$X = \frac{n}{p} = \frac{n_0 + \Delta n}{p_0 + \Delta p}$$

- In this example, an apparently complicated Δn response becomes simple.





Assumes Δn = Δp (no trapping)

Linear formulation of SRH statistics

See: Murphy *et al.*, *J. Appl. Phys.*, **111** 113709 (2012)

Instead of the usual SRH expression:

$$\tau_{\mathrm{n}} = \frac{1}{N}\left(\frac{\frac{1}{\alpha_n}(p_0 + p_1 + \Delta n) + \frac{1}{\alpha_p}(n_0 + n_1 + \Delta n)}{p_0 + n_0 + \Delta n} \right)$$

$$p_1 = N_V \exp\left(-\frac{(E_T - E_V)}{kT} \right)$$

$$n_1 = N_C \exp\left(-\frac{(E_C - E_T)}{kT} \right)$$

We use a linear form (derivation given in the reference above):

$$\tau_n = \frac{1}{\alpha_n N}\left[\boxed{1 + \frac{Qn_1}{p_0} + \frac{p_1}{p_0}} + \boxed{X\left(Q - \frac{Qn_1}{p_0} - \frac{p_1}{p_0} \right)} \right]$$

$$Q = \frac{\alpha_n}{\alpha_p}\left(= \frac{\sigma_n}{\sigma_p} \right) \qquad X = \frac{n}{p} = \frac{n_0 + \Delta n}{p_0 + \Delta p}$$

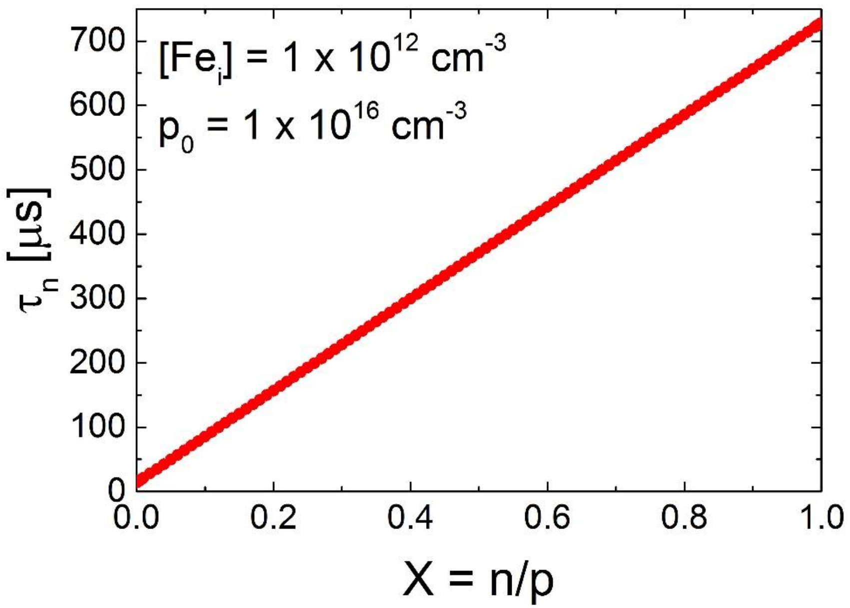
First term: independent of injection level

Second term: linearly dependent on n/p

Extracting defect parameters

$$\tau_n = \frac{1}{\alpha_n N}\left[1+\frac{Qn_1}{p_0}+\frac{p_1}{p_0}+X\left(Q-\frac{Qn_1}{p_0}-\frac{p_1}{p_0}\right)\right]$$

- The gradient and intercept as X → 1 can be trivially determined from the experimental lifetime plot versus X = n/p.



- Do this for samples with different doping levels (p_0) and use:

$$\left.\frac{d\tau_n}{dX}\middle/\tau_{n\,X\to1}\right. = \boxed{\frac{Q}{1+Q}} - \frac{1}{p_0}\boxed{\left(\frac{Qn_1+p_1}{1+Q}\right)}$$

Intercept ⇒ $Q = \alpha_n / \alpha_p = \sigma_n / \sigma_p$

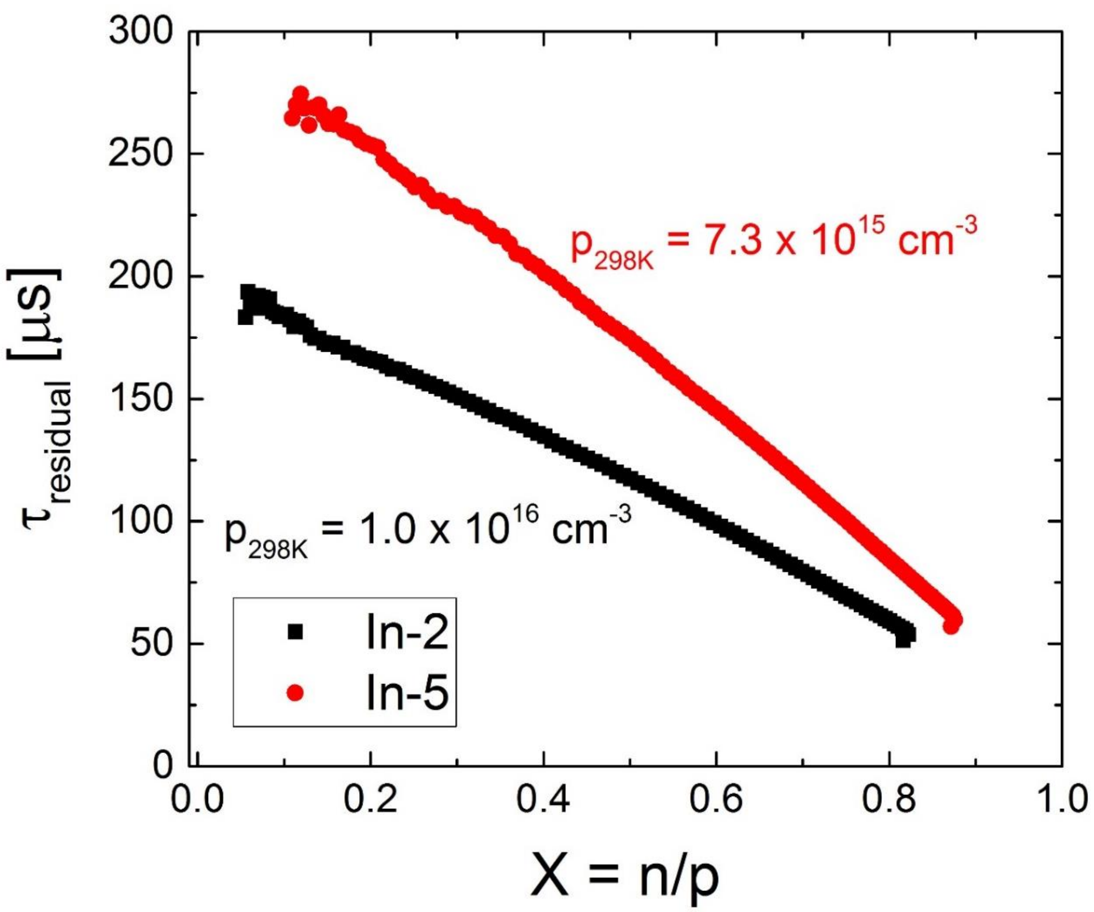
Gradient ⇒ $Qn_1 + p_1$

- Also look at X → 1 limit:

$$\tau_{n\,X\to1} = \frac{1}{\boxed{\alpha_n N}}[1+Q]$$

- Term proportional to state density.

Application to indium doped silicon



1. Passivate the surfaces well (S = 4 cm/s in this case)

2. Strip out other known recombination processes

$$\tau_{\text{residual}} = \left(\frac{1}{\tau_{\text{measured}}} - \frac{1}{\tau_{\text{intrinsic}}} \right)^{-1}$$

e.g. intrinsic recombination (we use Richter *et al.*, Phys. Rev B., **86** 165202 (2012).

3. Apply injection-dependent approach.

Extracting defect parameters for indium

$$\tau_n = \frac{1}{\alpha_n N}\left[1 + \frac{Qn_1}{p_0} + \frac{p_1}{p_0} + X\left(Q - \frac{Qn_1}{p_0} - \frac{p_1}{p_0}\right)\right] \qquad Q = \frac{\alpha_n}{\alpha_p}\left(= \frac{\sigma_n}{\sigma_p}\right) \qquad X = \frac{n}{p} = \frac{n_0 + \Delta n}{p_0 + \Delta p}$$

First term: independent of injection level

Second term: linearly dependent on n/p

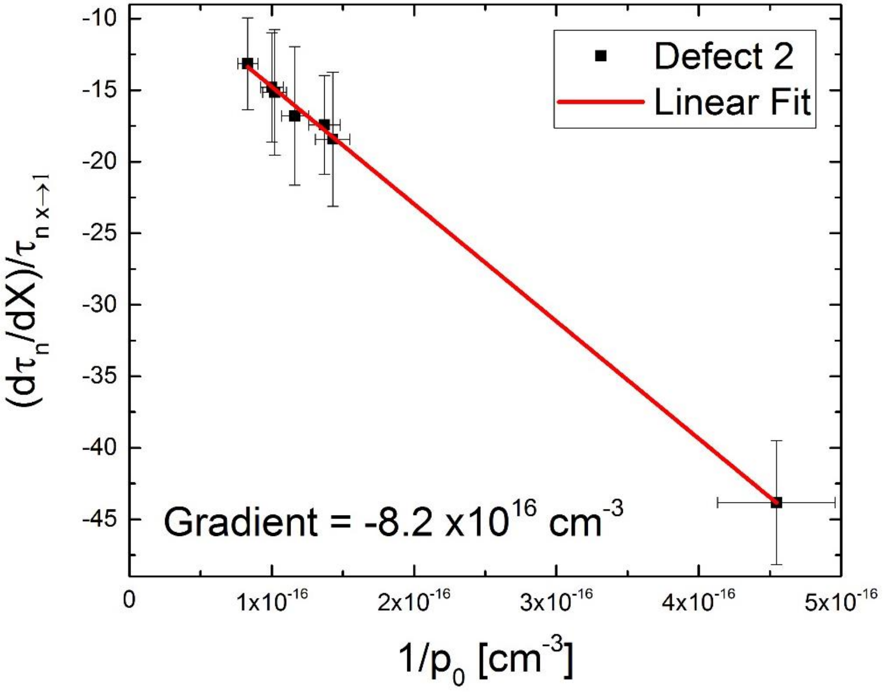
$$\frac{d\tau_n}{dX}\Big/\tau_{n\,X\to 1} = \frac{Q}{1+Q} - \frac{1}{p_0}\left(\frac{Qn_1 + p_1}{1+Q}\right)$$

Intercept $\Rightarrow Q = \alpha_n / \alpha_p = \sigma_n / \sigma_p$

Gradient $\Rightarrow Qn_1 + p_1$

Assume close to valence band

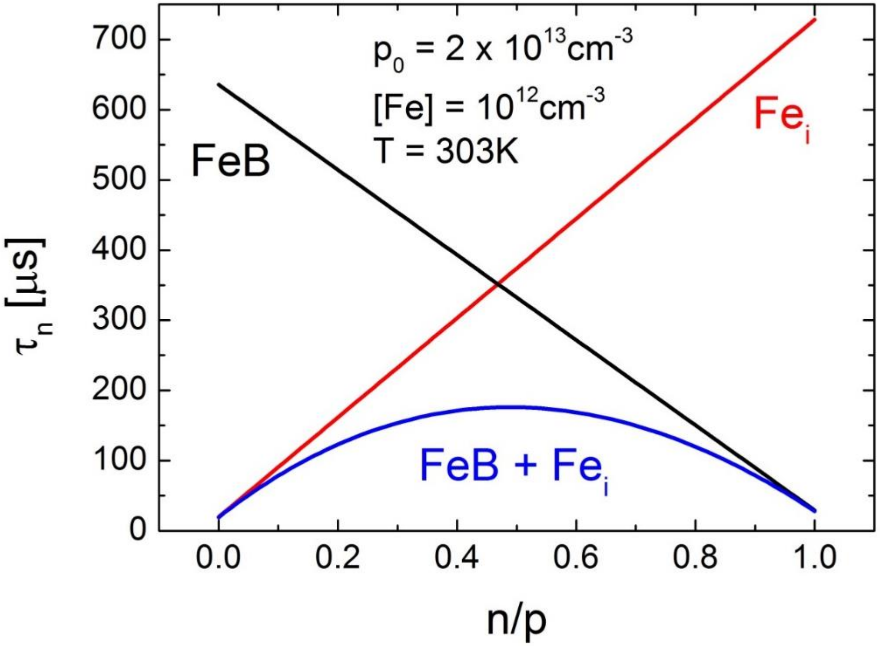
$\Rightarrow \quad E_V + 0.152\ eV$



More complicated cases…

Two independent SRH centres

$$\frac{1}{\tau_n} = \frac{1}{\tau_1} + \frac{1}{\tau_2}$$



The defect parameters can then be extracted by using the same approach as before twice.

One defect with two energy levels

Derived in Murphy *et al.*,
J. Appl. Phys., **111** 113709 (2012)

$$\tau_n = \frac{1 + \left(\dfrac{\dfrac{Q_1 n_1 (1-X)}{p_0} + 1}{Q_1 X + \dfrac{p_1 (1-X)}{p_0}} \right) + \left(\dfrac{X + \dfrac{p_2 (1-X)}{Q_2 p_0}}{\dfrac{n_2 (1-X)}{p_0} + \dfrac{1}{Q_2}} \right)}{N \left[\dfrac{\alpha_{n1}}{Q_1 X + \dfrac{p_1 (1-X)}{p_0}} + \dfrac{\alpha_{p2}}{\dfrac{n_2 (1-X)}{p_0} + \dfrac{1}{Q_2}} \right]}$$

Used by Niewelt *et al.* in LID work (PSS RRL, **6** 692 (2015)

Summary of the linear SRH approach

- The physics is the same as the “normal” approach, but the linear approach provides a neat way of visualising what is going on.

- Key points:

  - A single lifetime measurement cannot tell you very much about the SRH properties of the defect.

  - Varying with majority carrier concentration (doping level) easily allows information on the energy level and ratio of cross sections to be extracted if the samples are well controlled.

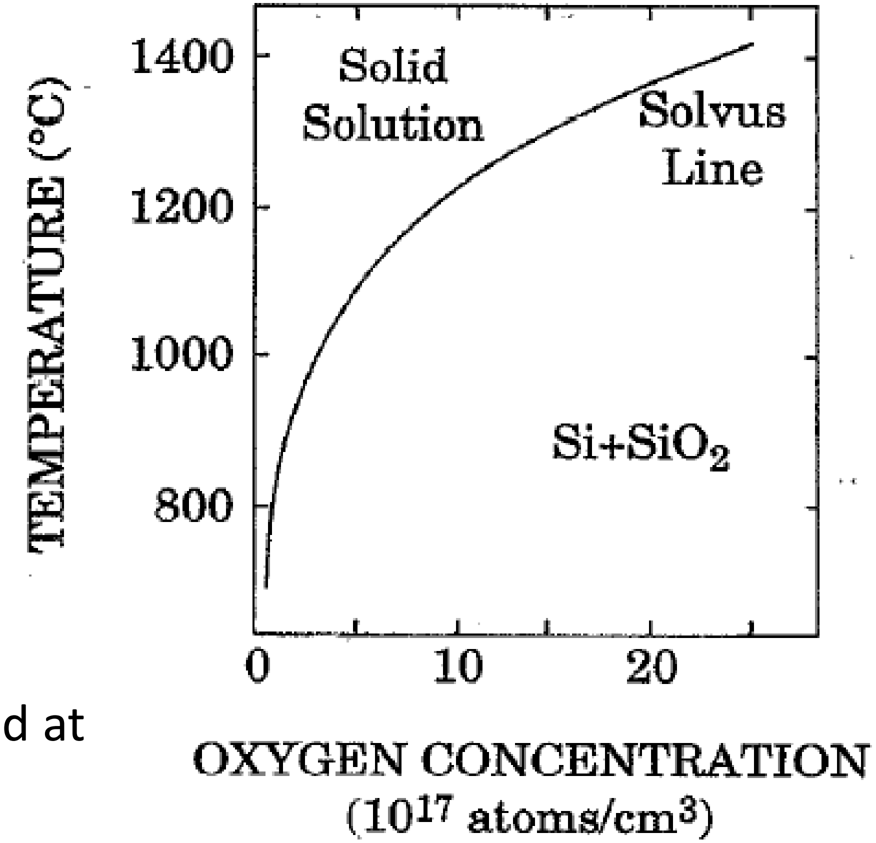
  - Getting the state density in isolation from lifetime measurements is not possible as it is always multiplied by the capture coefficient (cross-section).

Outline of talk

1. Injection-dependent lifetime analysis approach
2. Recombination at oxygen-related extended defects
3. Internal gettering in mc-Si
4. High lifetime silicon materials

Oxygen in silicon

- Oxygen in Cz-Si and mc-Si comes from the silica crucible which contains the melt.
- Well known to be linked to light induced degradation, but there is another problem…
- Typical levels of oxygen are supersaturated at cell processing temperatures.
- Silicon dioxide precipitates are thermodynamically stable, but need to nucleate.



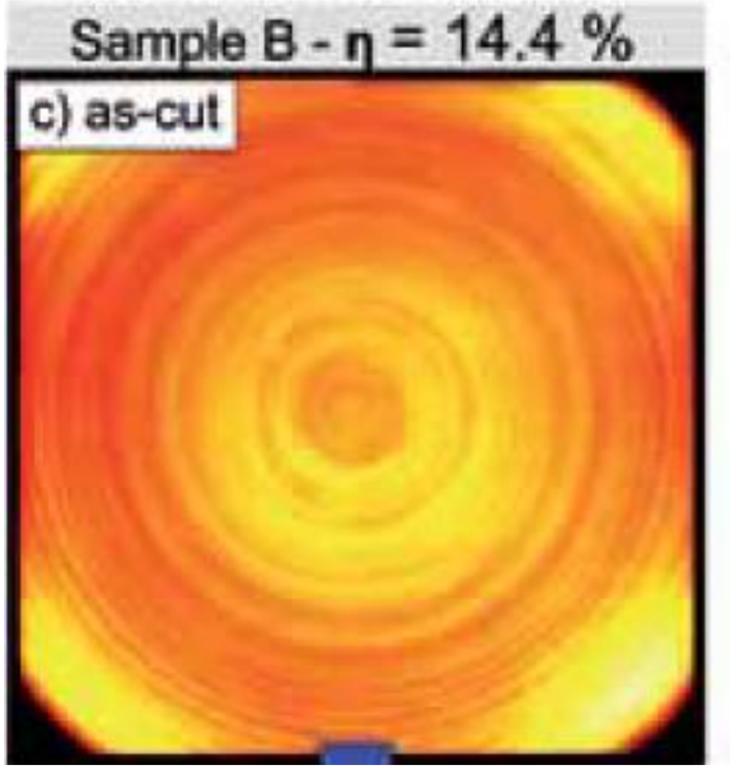
From Borghesi *et al.*,
J. Appl. Phys., **77** 4169 (1995)

- Cz-Si ingots for PV are often pulled too fast! ⇒ sub-optimal v/G ratio* ⇒ high concentration of vacancies ⇒ nucleation centres for oxide precipitates.

* See Voronkov, *J. Cryst. Growth*, **59** 625 (1982)

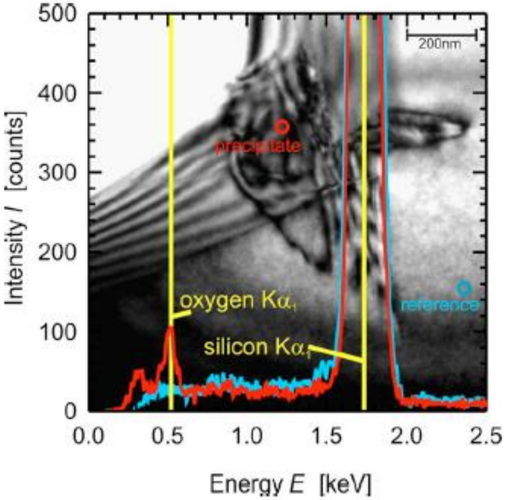
Oxygen-related extended defects in silicon

mono-Si

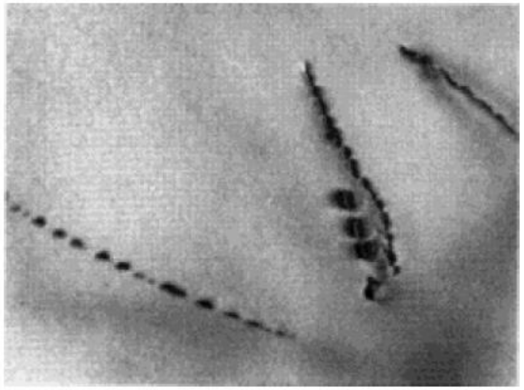


Haunschild *et al.*,
Photovoltaics International (2012)

mc-Si



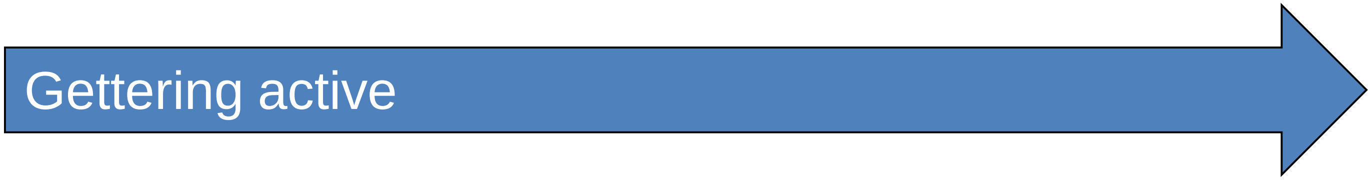
Bothe *et al.*, *J. Appl. Phys.*, **106** 104510 (2009)



Möller *et al.*, *Phys. Stat. Sol. (a),* **171** 175 (1999)

Oxide precipitate growth in silicon

See R. Falster, V.V. Voronkov *et al.*, Proceedings of the Electrochemical Society, *High Purity Silicon VIII*, **200405** 188 (2004)



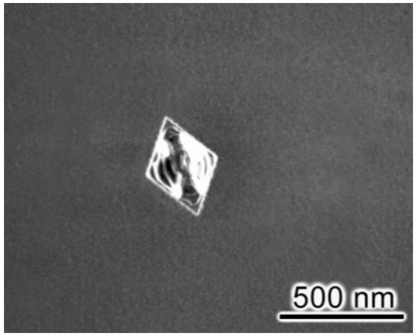
Gettering active

1. Unstrained

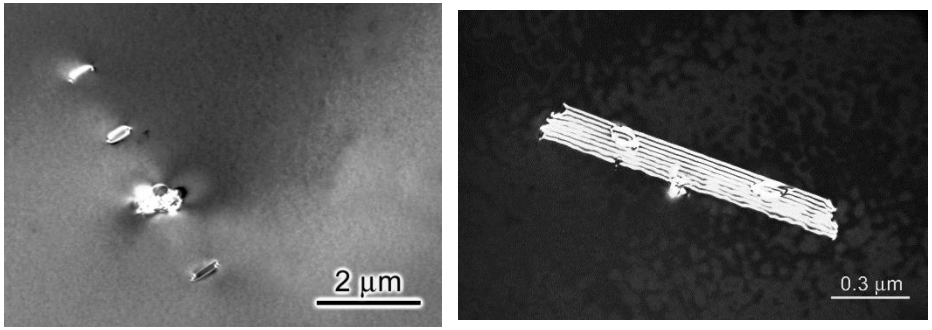
?

Not detectable
by etching/ TEM

2. Strained



3. Strained + dislocations/ SFs

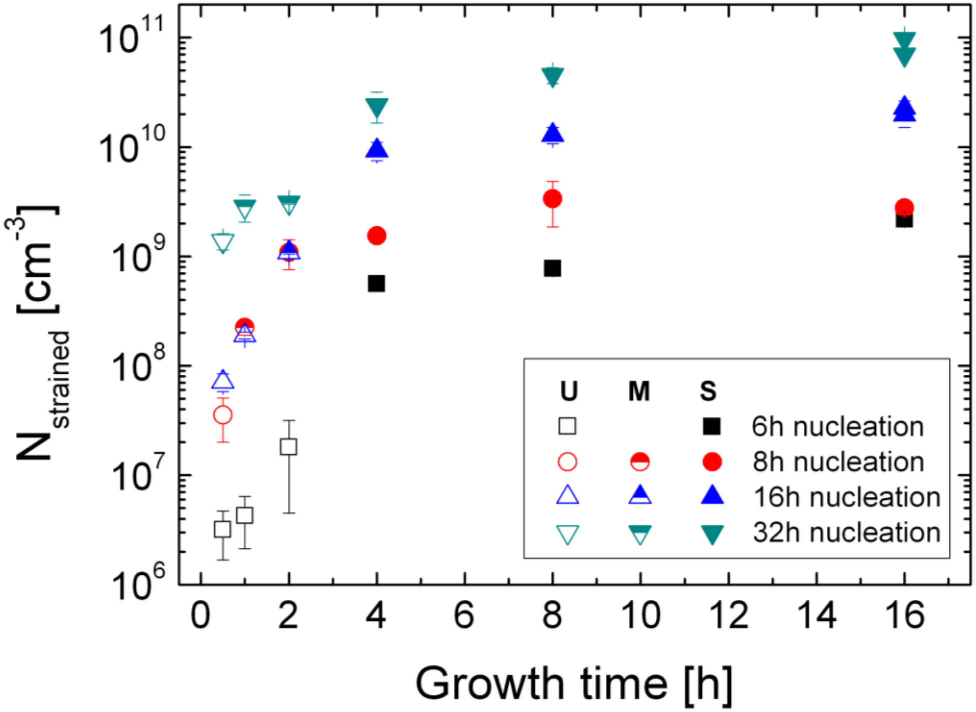


- The rate of transformation of unstrained “ninja” particles depends strongly on oxygen concentration, density of growing precipitates and growth temperature
- How recombination-active are the different precipitate structures?

Specimen preparation for lifetime study

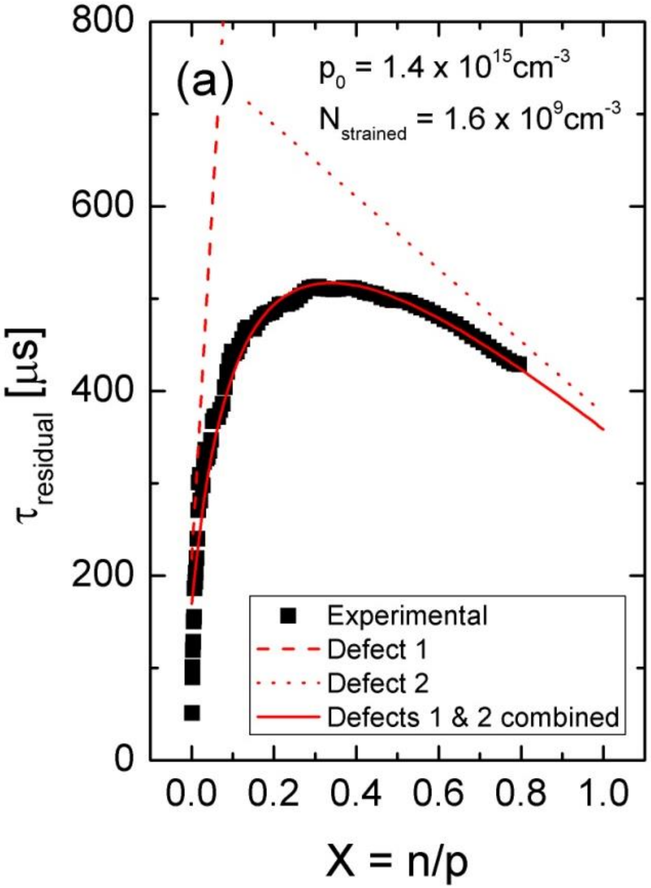
- ~100 high-purity (001)-orientation Cz-Si wafers.
  - Oxygen concentration: 5.9 to 9.6 x 10^{17} cm^{-3}
  - p-type: [B] = 0.39 to 8.2 x 10^{15} cm^{-3}
  - n-type: [P] = 0.05 to 1.0 x 10^{15} cm^{-3}

- Four-stage precipitation treatment:
  - 15 min at 1000°C to dissolve grown-in precipitates
  - **Nucleation** at 650°C for range of times (6 to 32h)
  - 'Drift' anneal at 800 °C for 4h to grow nuclei
  - **Growth** anneal at 1000 °C for range of times (0.5 to 16h)



- Strained oxide precipitate densities determined by Schimmel etching

Typical p-type lifetime curve



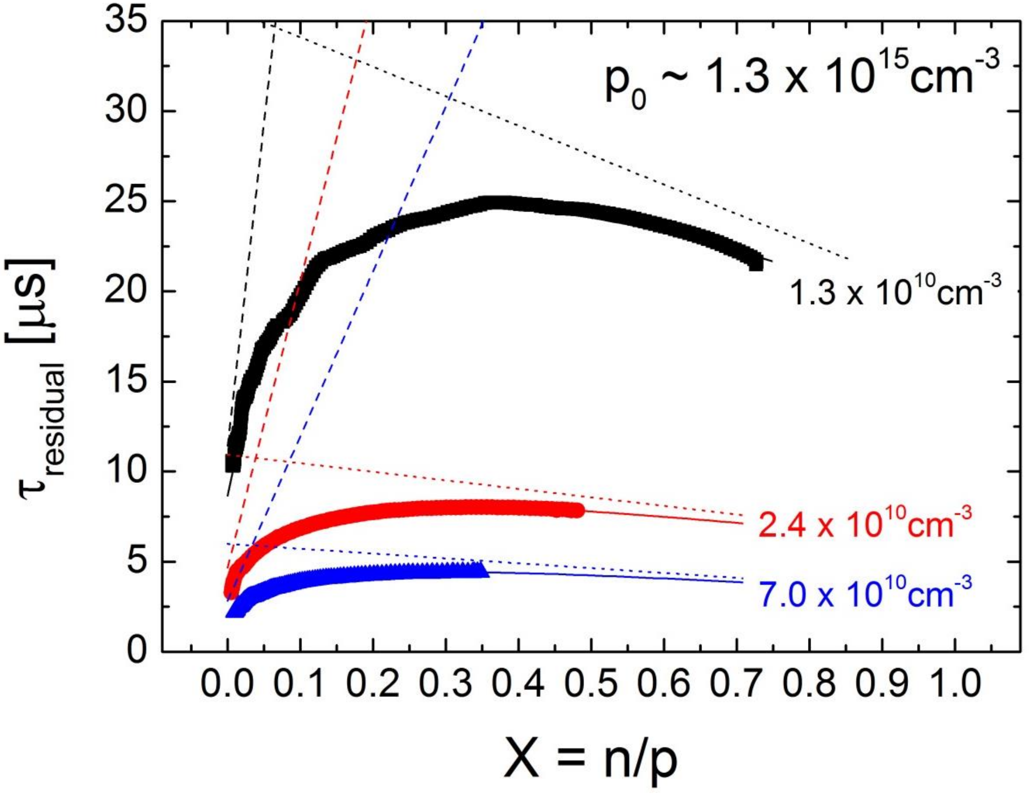
- Lifetime measured with FeB pairs and boron-oxygen defects dissociated.
- Low Fe_i concentration ($< 4 \times 10^{11}\text{cm}^{-3}$)

$$\frac{1}{\tau_{\text{residual}}} = \frac{1}{\tau_{\text{measured}}} - \left(\frac{1}{\tau_{\text{band-to-band}}} + \frac{1}{\tau_{\text{CE Auger}}} + \frac{1}{\tau_{\text{Fe}_\text{i}}} \right)$$

- Recombination clearly not via a single one-level defect

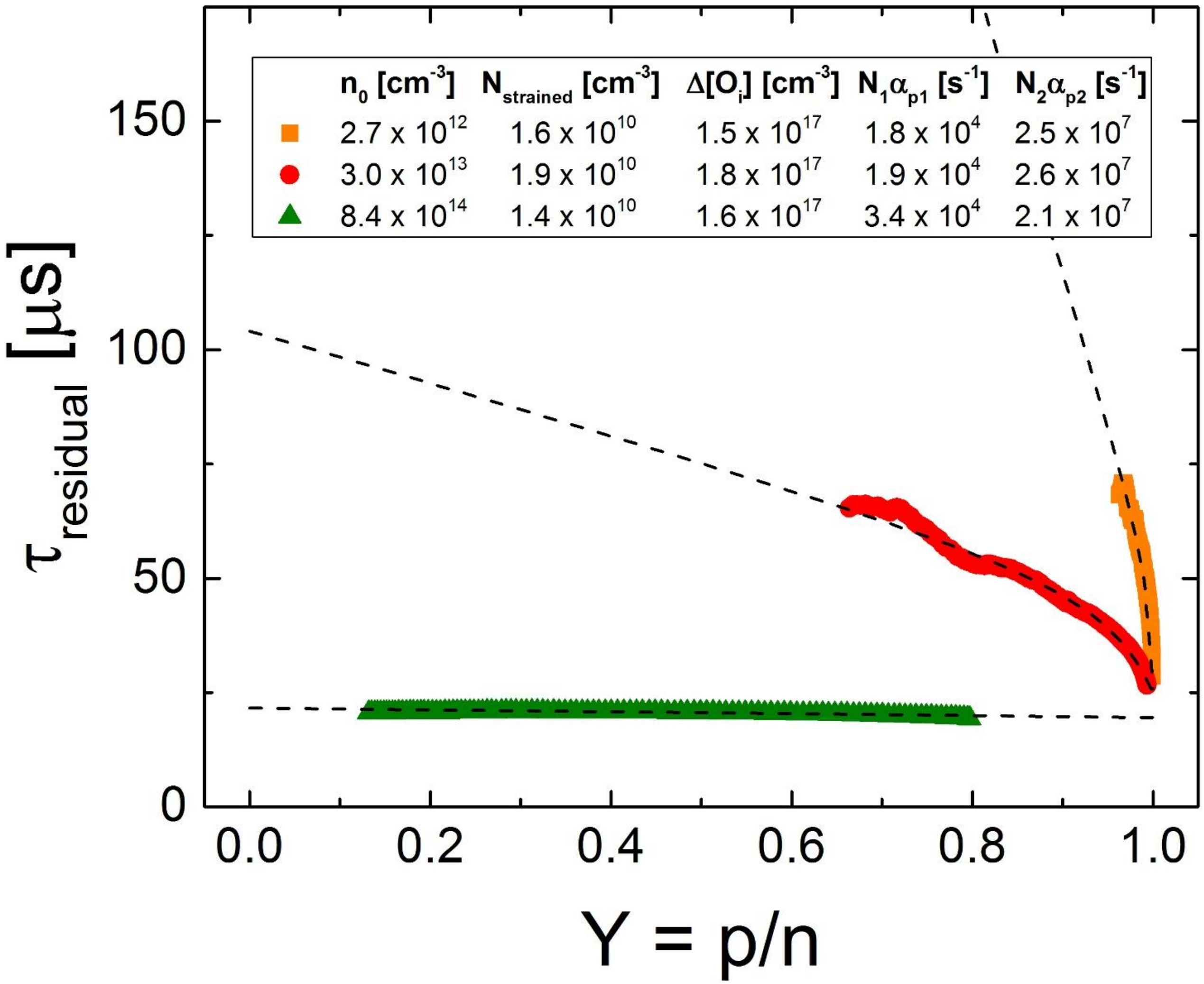
Murphy *et al.*, J. Appl. Phys., **111** 113709 (2012)

Dependence on precipitate density (p-type)



- Similar n/p dependence in > 50 p-type wafers
- In all cases the data can be fitted by just two independent centres
- We call these “Defect 1” and “Defect 2”

Dependence on doping (n-type)



- Very similar precipitate densities, but substantially different doping levels.
- Similar SRH fitting parameters ($N\alpha_p$).
- Parameterisation valid in n-type as well as p-type.

Murphy *et al.*, J. Appl. Phys., **118** 215706 (2015)

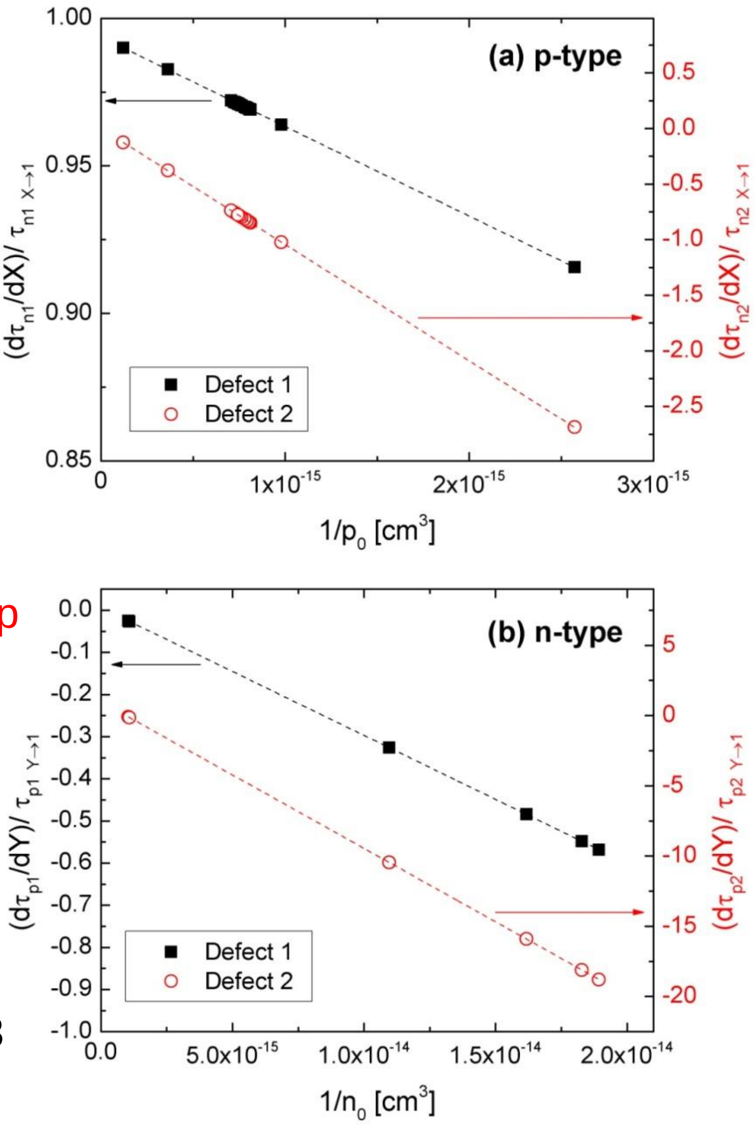
Extraction of SRH parameters

$$\tau_n = \frac{1}{\alpha_n N}\left[1+\frac{Qn_1}{p_0}+\frac{p_1}{p_0}+X\left(Q-\frac{Qn_1}{p_0}-\frac{p_1}{p_0}\right)\right]$$

$$\frac{d\tau_n}{dX}\Big/\tau_{n\,X\to1} = \frac{Q}{1+Q}-\frac{1}{p_0}\left(\frac{Qn_1+p_1}{1+Q}\right)$$

Intercept ⇒ $Q = \alpha_n / \alpha_p = \sigma_n / \sigma_p$

Gradient ⇒ $Qn_1 + p_1$



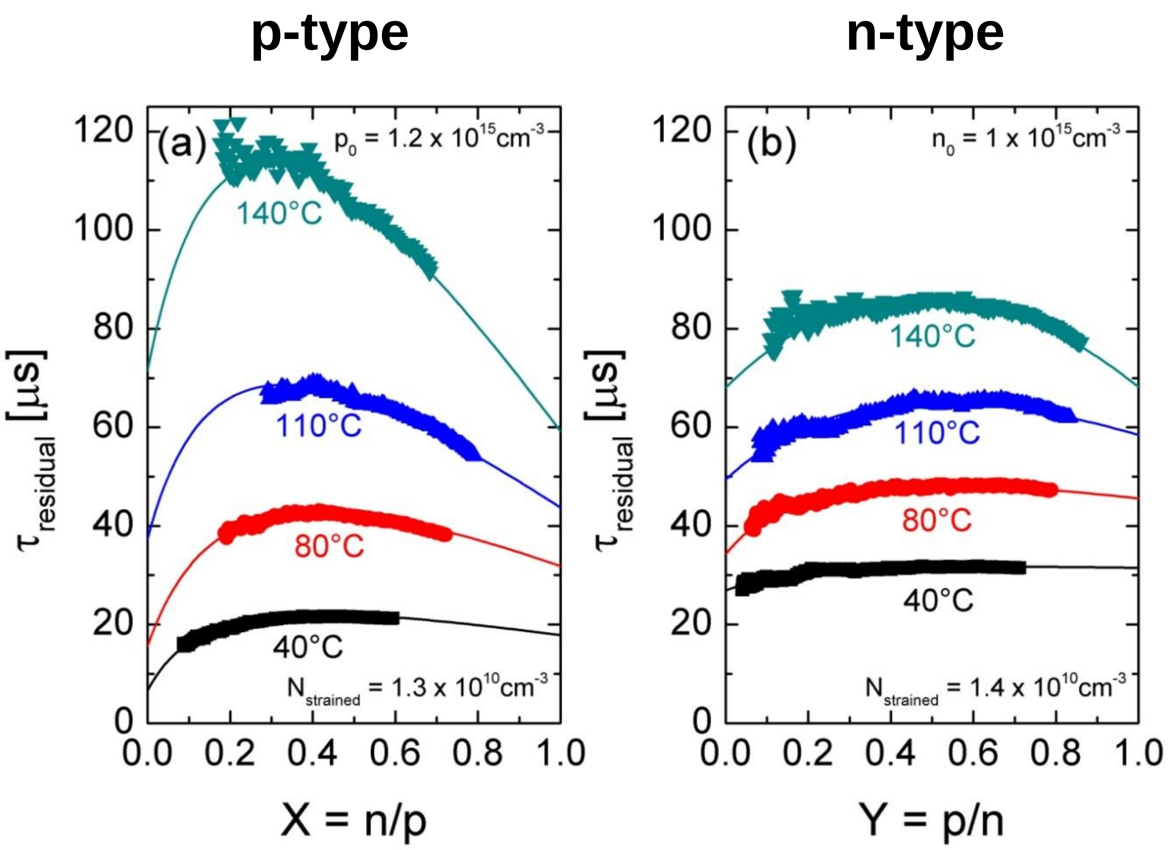
Defect 1:

$Q_1 = 157$, $Q_1n_1 + p_1 = 4.8 \times 10^{15}\text{cm}^{-3}$

Defect 2:

$1/Q_2 = 1200$, $Q_2n_2 + p_2 = 1.0 \times 10^{15}\text{cm}^{-3}$

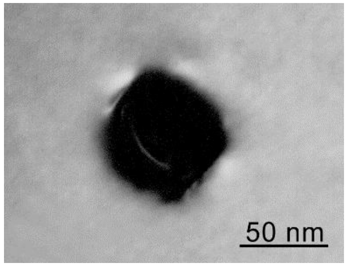
Temperature-dependence of lifetime

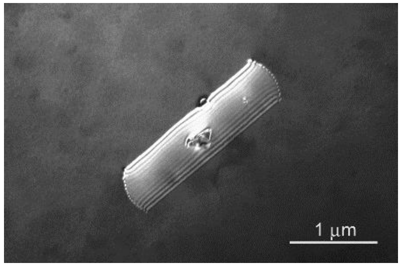


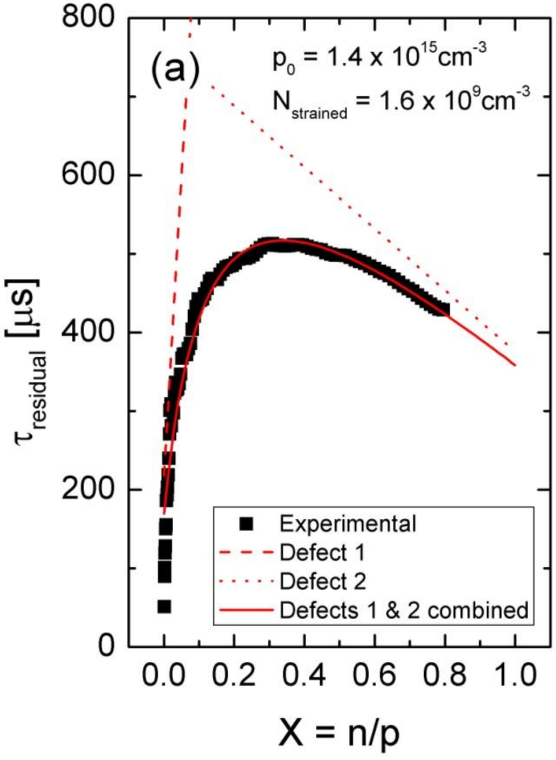
- Lifetime increases with increasing temperature
- Temperature-dependence allows proximity to valence/ conduction band to be determined
  - Defect 1: $E_V + 0.22$eV
  - Defect 2: $E_C - 0.08$eV
- Activation energies for capture coefficients
  - α_{p1}: 0.20 eV
  - α_{n2}: 0.14 eV

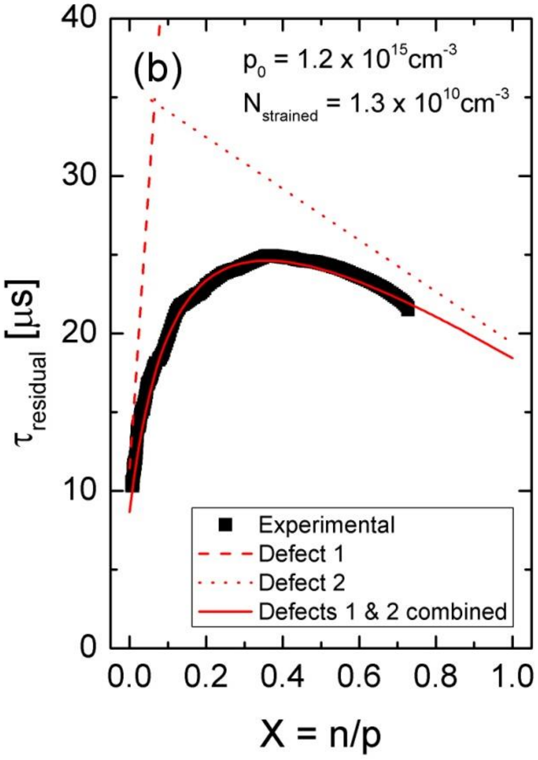
Murphy *et al.*, J. Appl. Phys., **111** 113709 (2012)

The role of dislocations and stacking faults









- Same injection response.
- No new levels associated with dislocations and stacking faults.

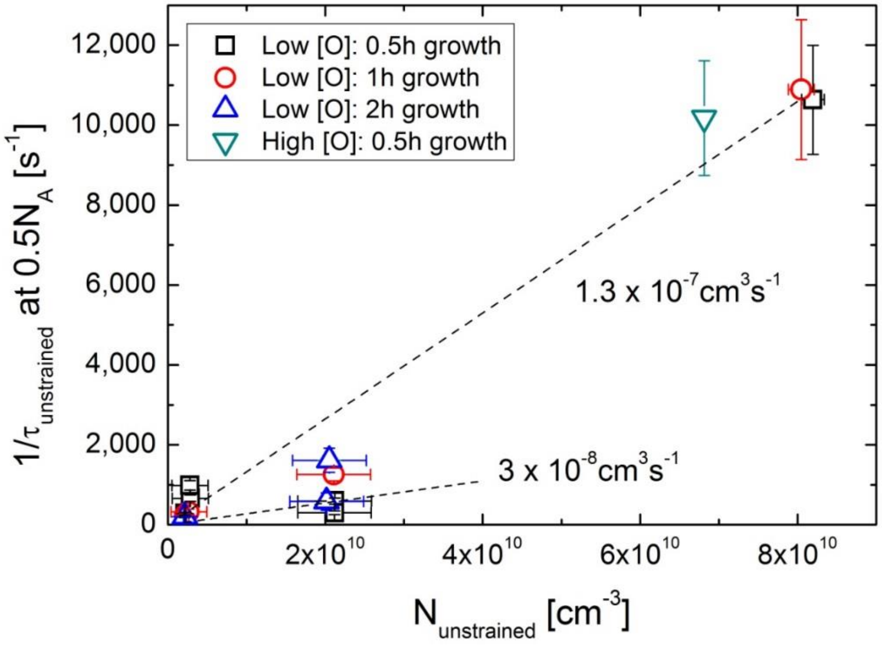
TEM images from V.Y. Resnik (Moscow)

Murphy *et al.*, J. Appl. Phys., **111** 113709 (2012)

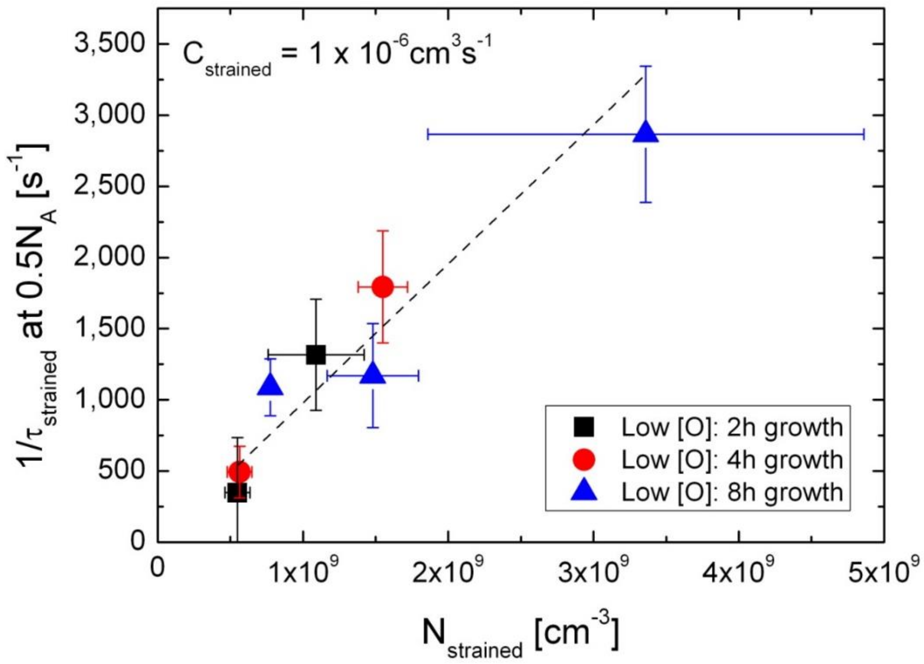
Unstrained (“ninjas”) versus strained

$$N_{\text{unstrained}}(\text{n,g}) = N_{\text{strained}}(\text{n,16h}) - N_{\text{strained}}(\text{n,g})$$

Unstrained



Strained (no dislocations/ SFs)



- Recombination at unstrained precipitates ~10 to ~30 weaker than at strained ones.

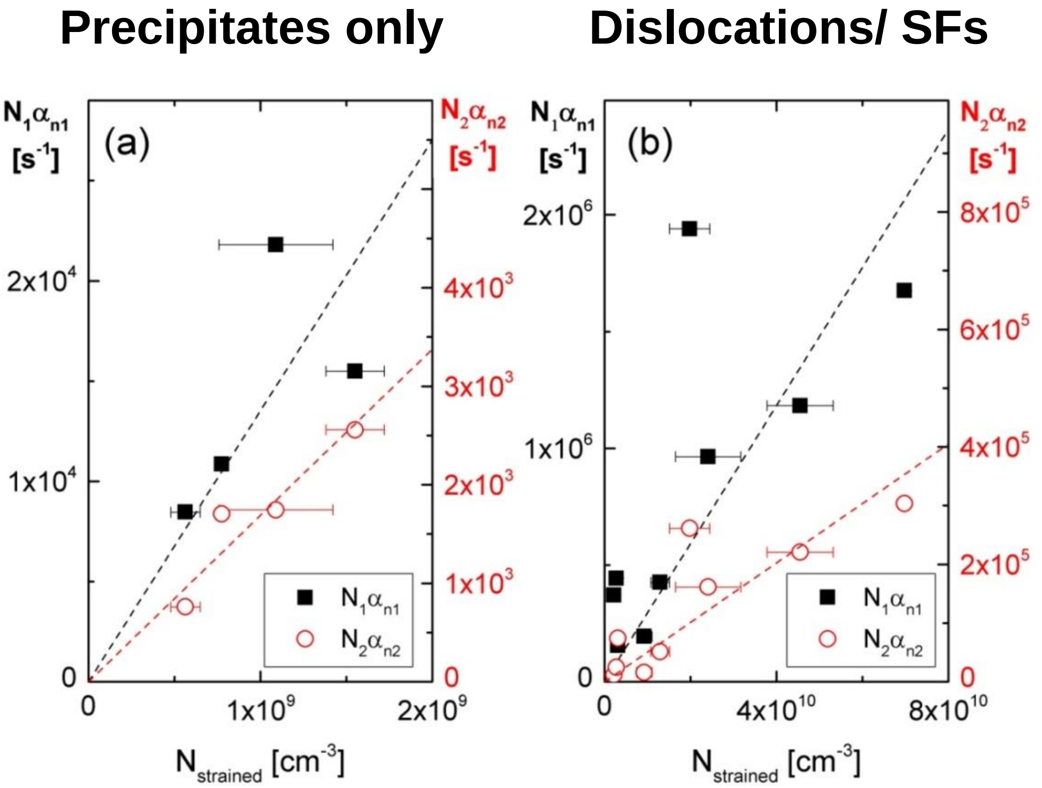
Murphy *et al.*, *J. Appl. Phys.*, **110** 053713 (2011)

Density dependence?

$$\tau_n = \frac{1}{\alpha_n N}\left[1 + \frac{Qn_1}{p_0} + \frac{p_1}{p_0} + X\left(Q - \frac{Qn_1}{p_0} - \frac{p_1}{p_0}\right)\right]$$

$$X \rightarrow 1 \qquad \tau_n = \frac{1}{\boxed{\alpha_n N}}\left[1 + Q\right]$$

- State density coupled to capture coefficient



Precipitates only

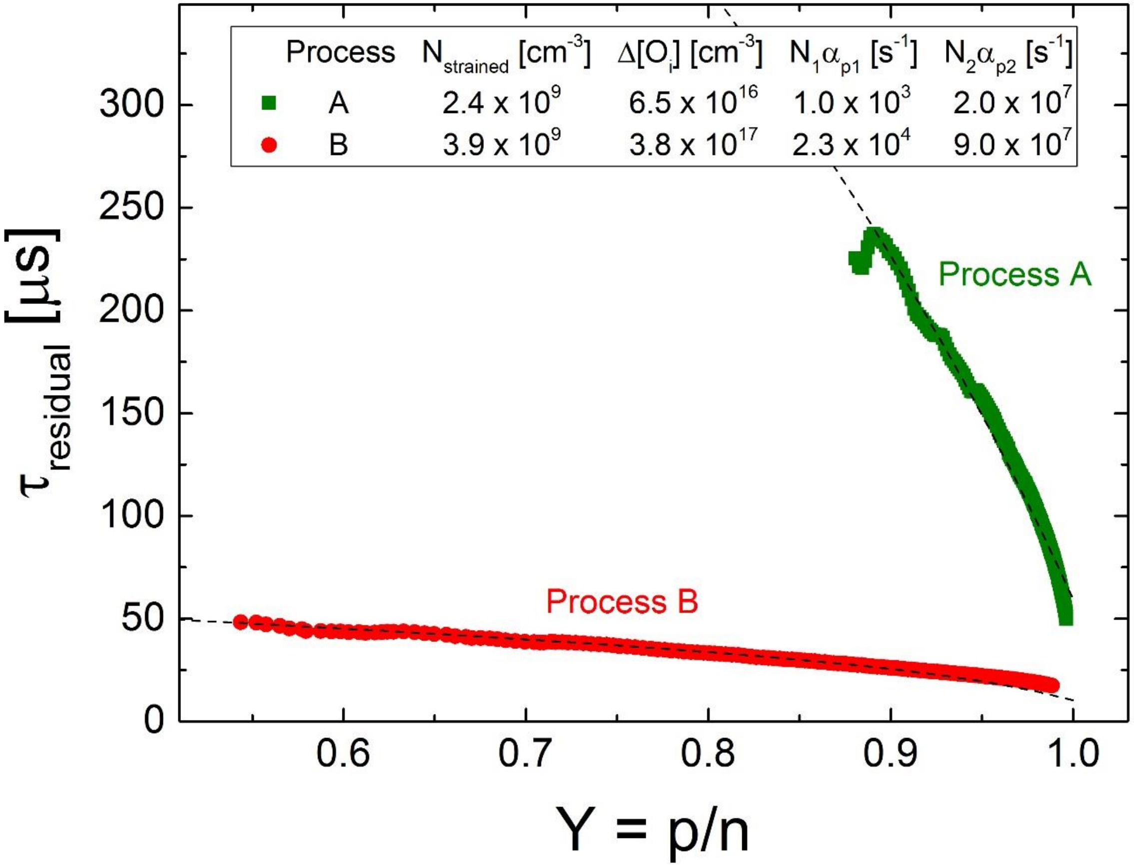
Dislocations/ SFs

- Relationship between $\alpha_n N$ and precipitate density ~ linear

- Gradient ~2x to 3x higher when precipitates are surrounded by dislocations and stacking faults

Murphy *et al.*, J. Appl. Phys., **111** 113709 (2012)

Changing the size of the precipitates



- Use a vastly different thermal process to create samples with similar densities of precipitates with different sizes.
- Process B has >10 high temperature steps from a baseline temperature steps (900 ° C to 1175 °C).
- Estimate precipitate sizes from interstitial oxygen loss data (from IR measurements).

Murphy *et al.*, J. Appl. Phys., **118** 215706 (2015)

Density vs surface area dependence

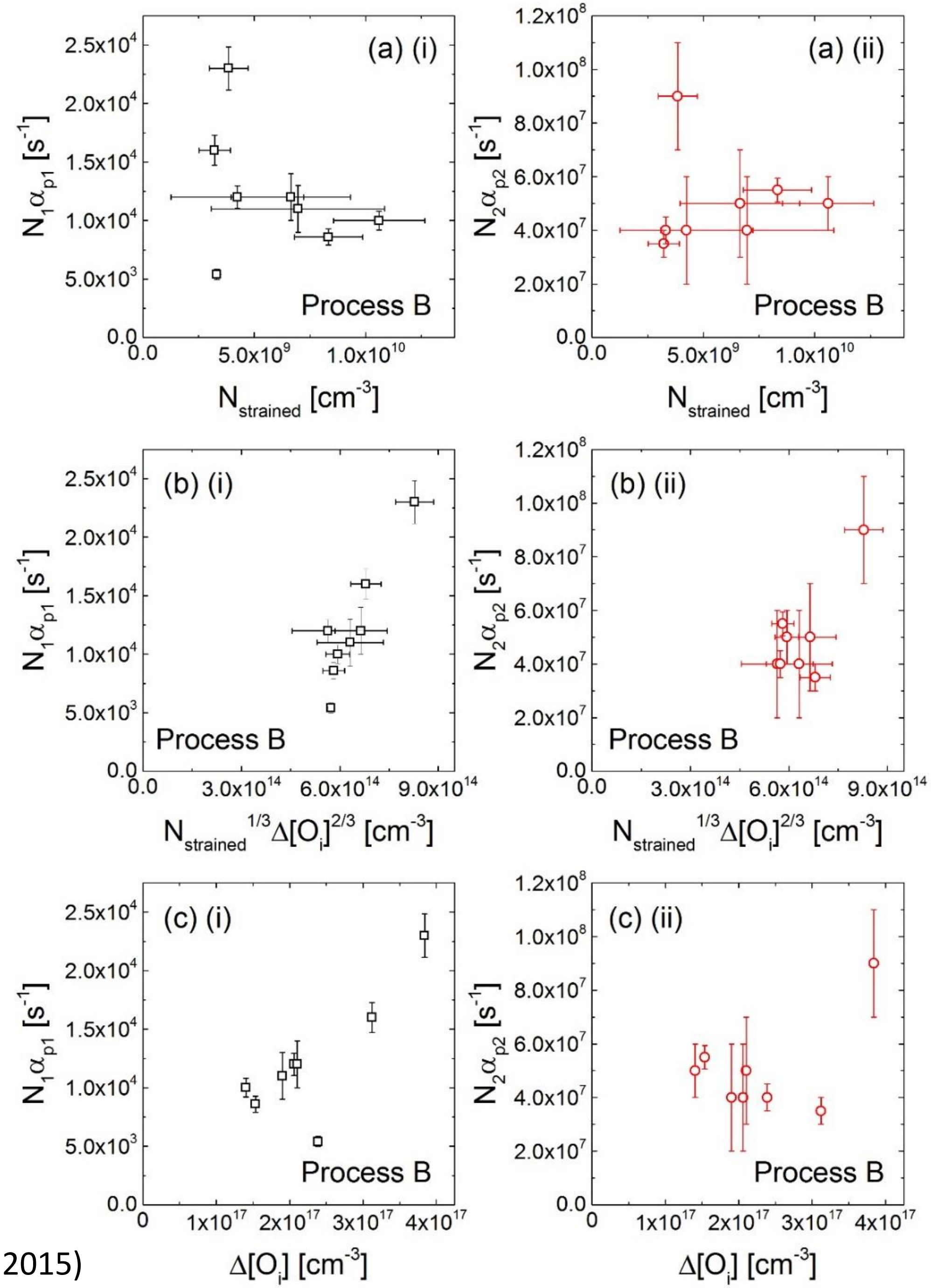
For spheres:

$$N_i\alpha_{pi} = \eta_i\alpha_{pi}(4\pi N_{\text{strained}})^{\frac{1}{3}}\left(\frac{3(\Delta[\mathrm{O_i}]-[\mathrm{O_{unstrained}}])}{\rho}\right)^{\frac{2}{3}}$$

For platelets:

$$N_i\alpha_{pi} = \eta_i'\alpha_{pi}\frac{2}{\rho d}(\Delta[\mathrm{O_i}]-[\mathrm{O_{unstrained}}])$$

Recombination activity likely to be dependent on surface area of precipitates and not density

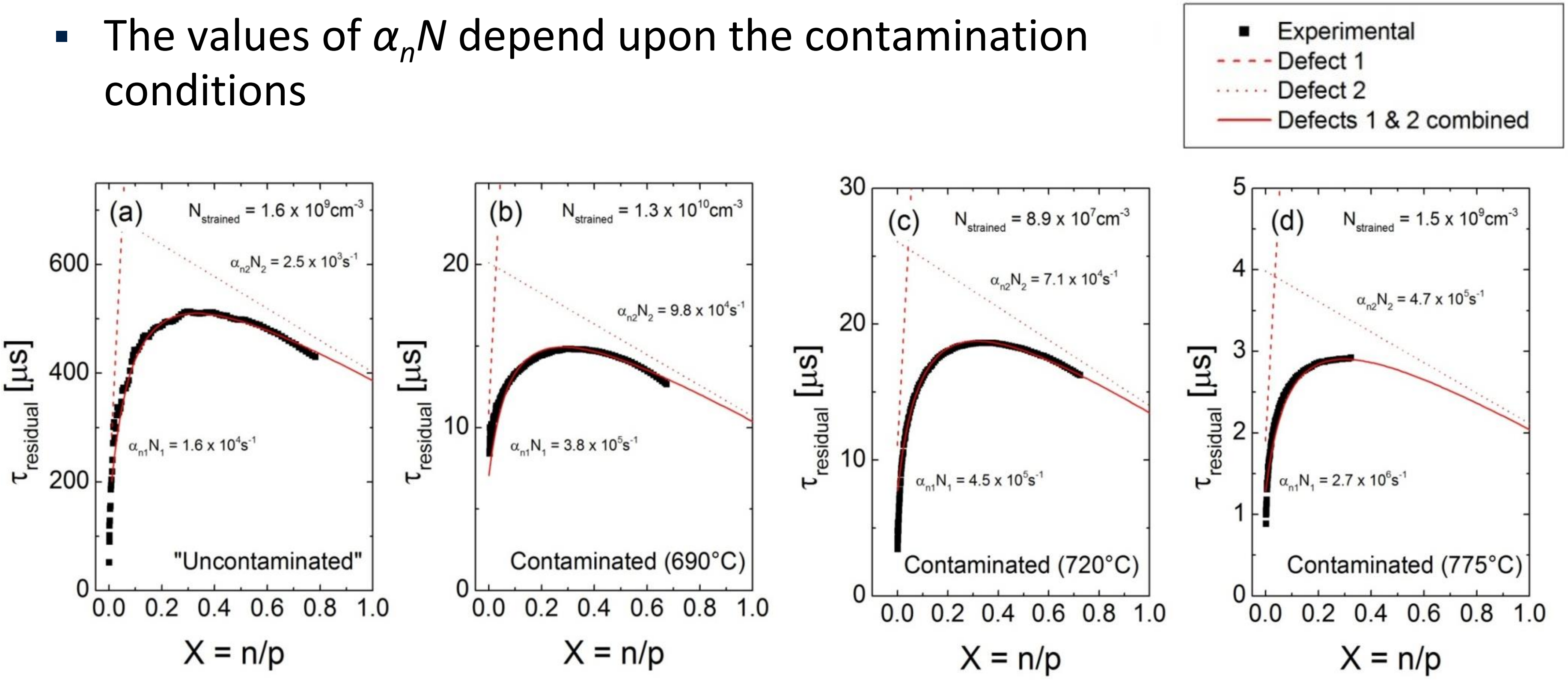


Murphy *et al.*, J. Appl. Phys., **118** 215706 (2015)

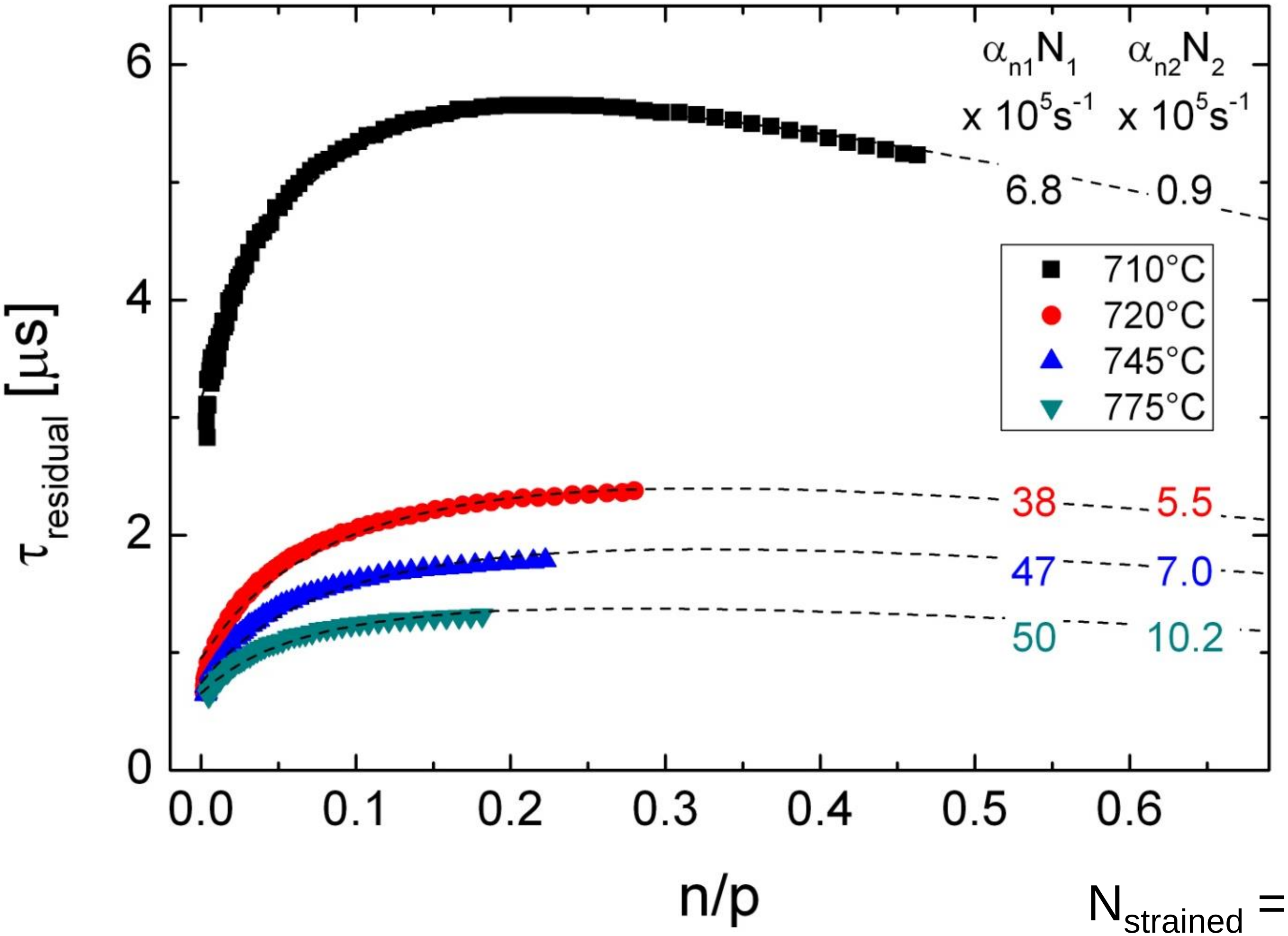
Iron contamination

- “Uncontaminated” and contaminated samples have the same form of injection-dependence

- The values of $\alpha_n N$ depend upon the contamination conditions



Same wafer, different contamination temperatures

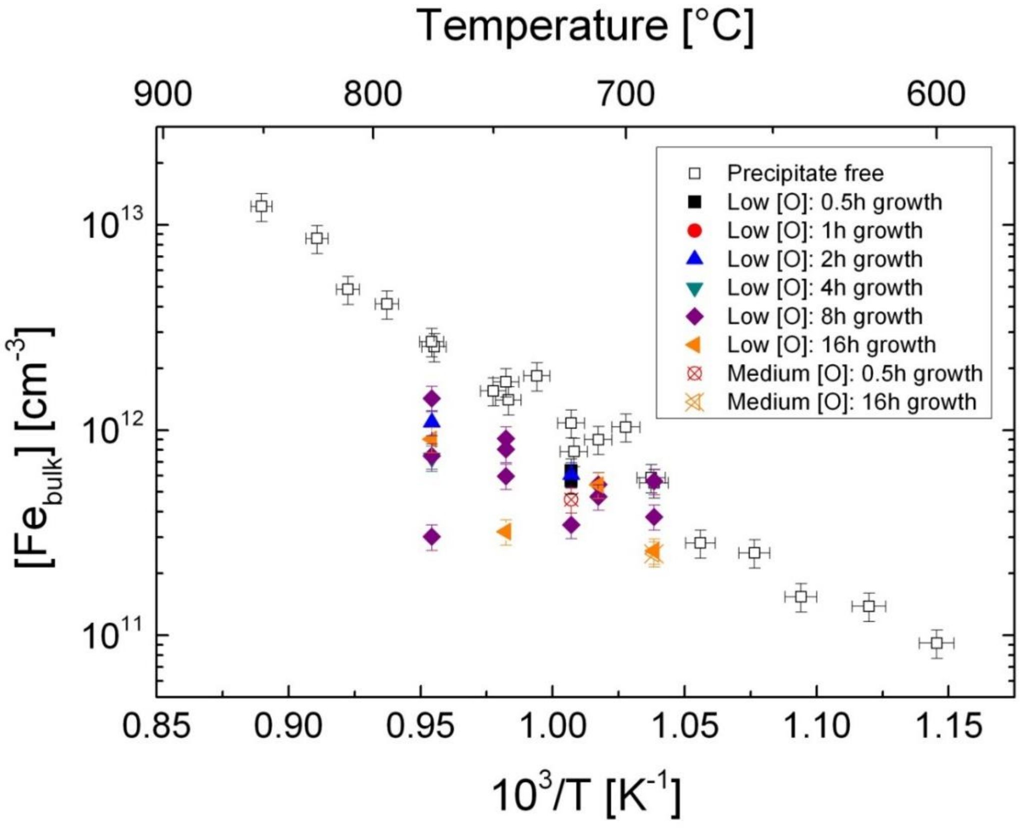


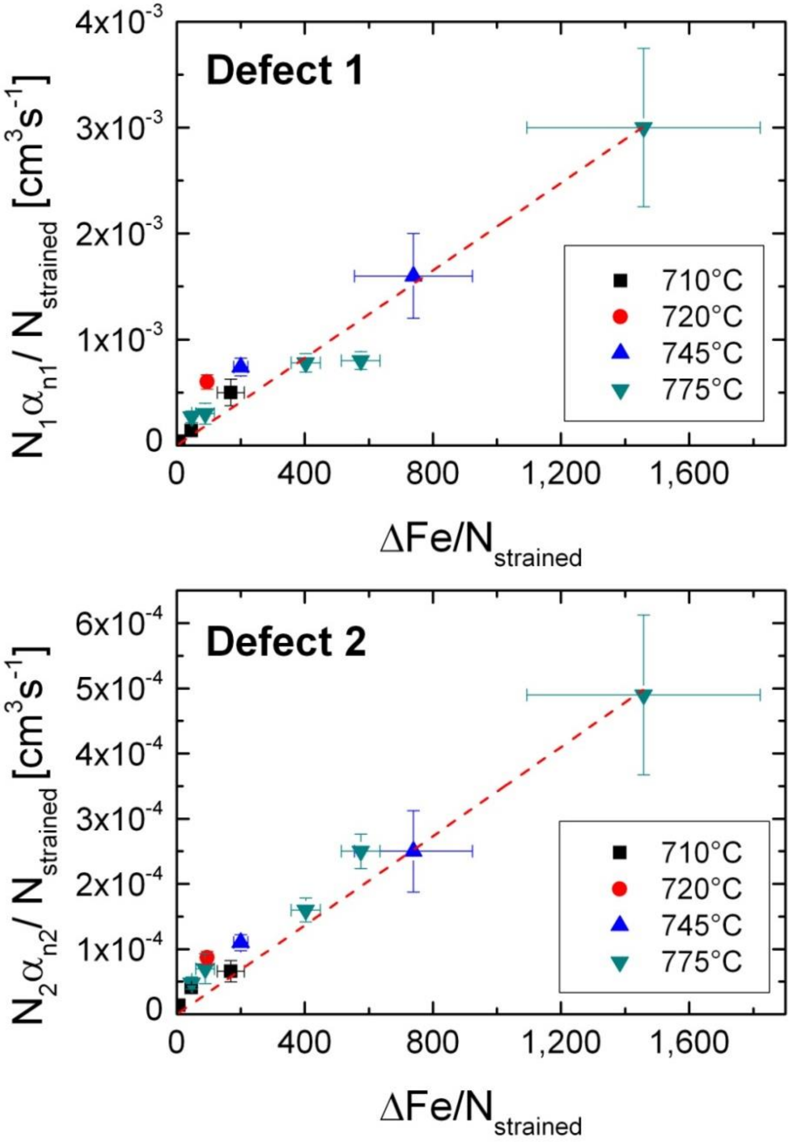
$N_{strained} = 6.4 \times 10^9 cm^{-3}$

Murphy *et al.*, Appl. Phys. Lett., **102** 042105 (2013)

State density is proportional to interstitial iron lost to precipitates

Murphy *et al.*, Appl. Phys. Lett., **102** 042105 (2013)





At least some (and possibly all) recombination activity at oxide precipitates is due to impurities

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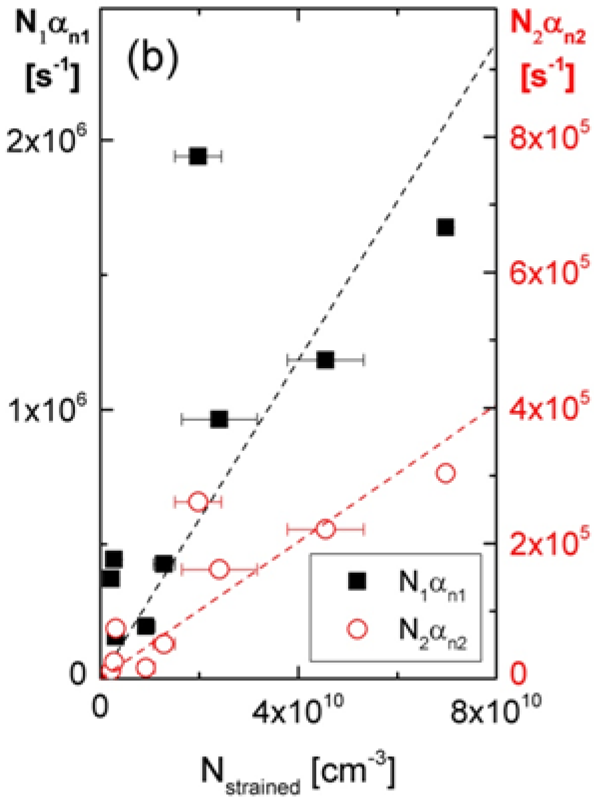
How much iron would need to be at an "uncontaminated" precipitate?

"Uncontaminated"



$N_1\alpha_{n1}/ N_{strained} = 2.9 \times 10^{-5} cm^3 s^{-1}$

$\Rightarrow \Delta Fe/ N_{strained}$ = 14 Fe atoms/ ppt

$N_2\alpha_{n2}/ N_{strained} = 5.1 \times 10^{-6} cm^3 s^{-1}$

$\Rightarrow \Delta Fe/ N_{strained}$ = 15 Fe atoms/ ppt

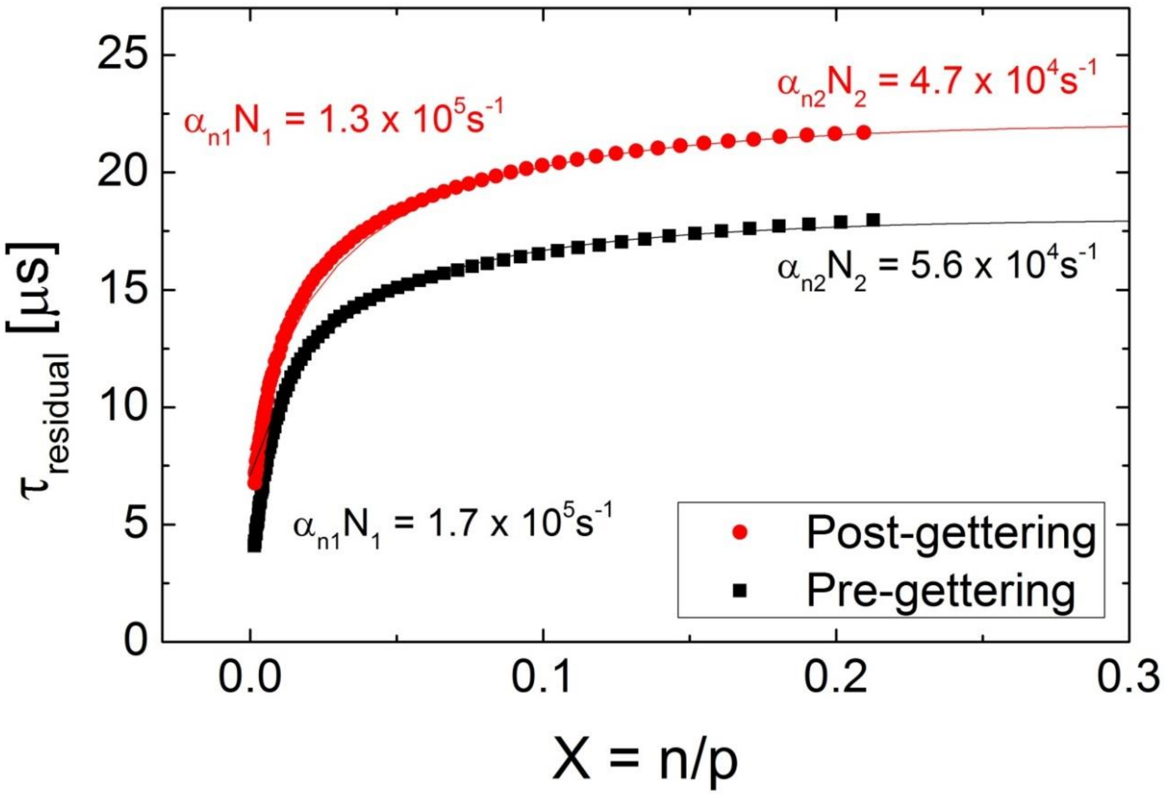
Recombination could be controlled by just ~15 iron atoms per precipitate

$\Rightarrow \sigma_{n1} \approx 1 \times 10^{-13} cm^2$

$\Rightarrow \sigma_{n2} \approx 1.5 \times 10^{-14} cm^2$

Murphy *et al.*, Appl. Phys. Lett., **102** 042105 (2013)

Competitive gettering



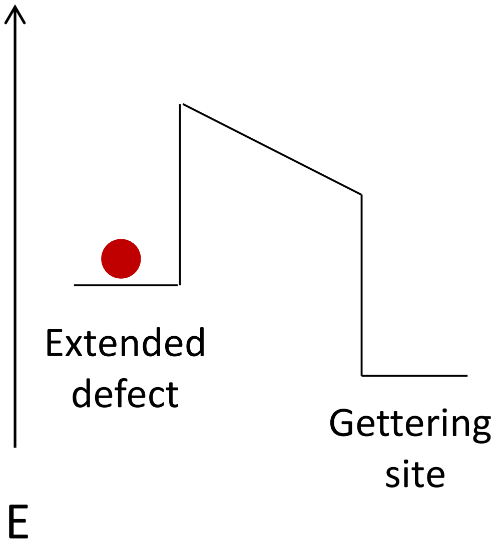
- Standard 850 + 875°C ISFH PDG process.
- Iron more effectively gettered by P-diffused layer than precipitates.
- ~20% reduction in $\alpha_n N$ for each state.

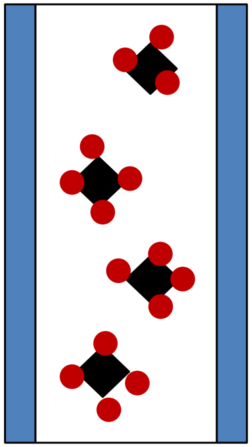
Bulk [Fe]: 1.4 x 10^{12}cm^{-3} → 5.2 x 10^{11}cm^{-3}

Murphy *et al.*, *Solar Energy Materials and Solar Cells*, **120** 402 (2014)

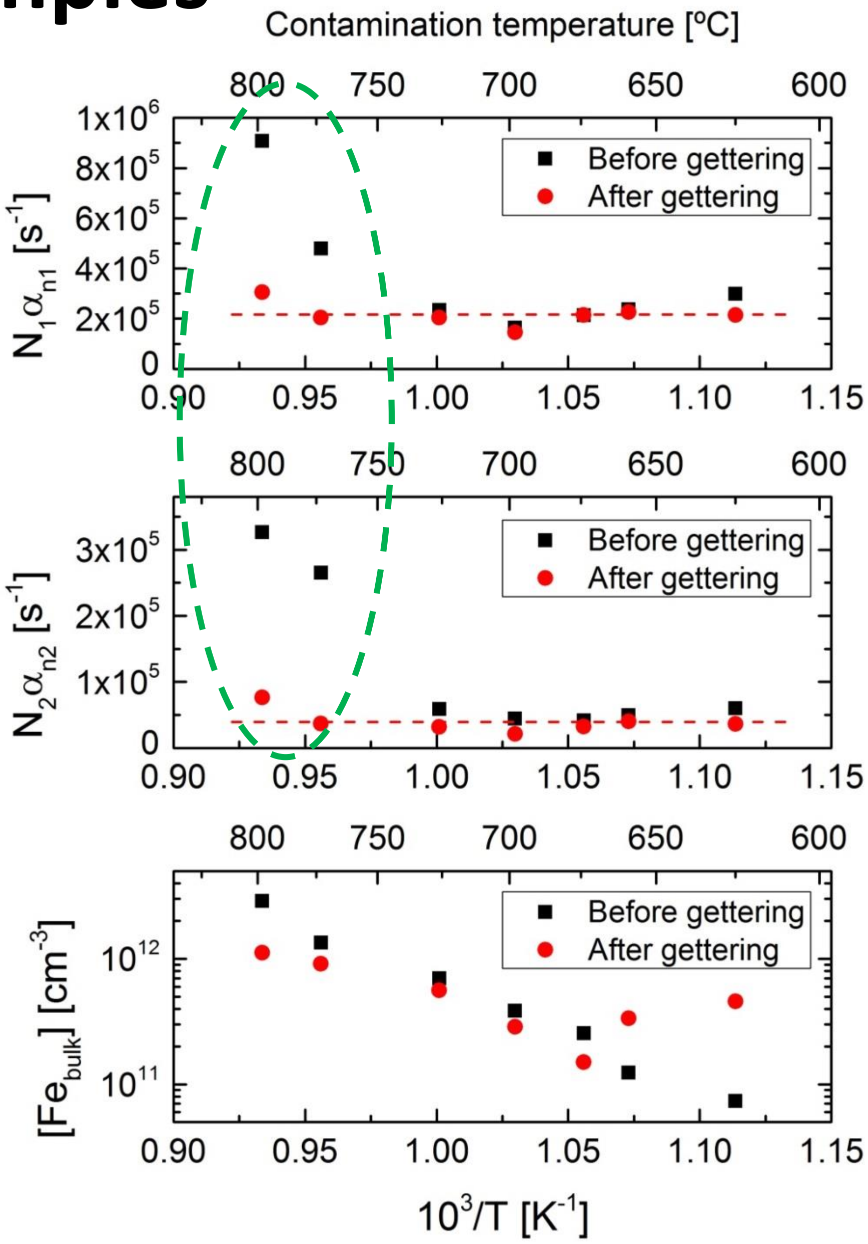
PDG of contaminated samples

- PDG removes iron from precipitates for contamination temperature < 850 °C.





- Above 850 °C (solubility: 1.2 x 10^{13} cm^{-3}) the iron becomes ungetterable. Co-precipitation?



Murphy *et al.*, *J. Appl. Phys.*, **116** 053514 (2014)

Summary of Part II (oxide precipitates)

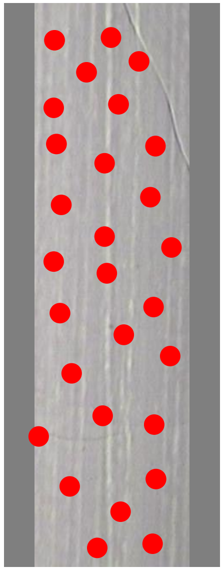
- Injection-dependent lifetime measurements on samples with different doping levels reveal two independent SRH centres:
    - "Defect 1" at $E_V + 0.22$eV, with $Q_1 = \alpha_{n1}/ \alpha_{p1} = 157$
    - "Defect 2" at $E_C – 0.08$eV, $1/Q_2 = \alpha_{p2}/ \alpha_{n2} = 1{,}200$
- In "uncontaminated" materials, the density of states is dependent on the total surface area of the precipitates (not density).
- Iron decorated oxide precipitates have the same centres with density being proportional to interstitial iron loss. Possible that all recombination activity is due to impurities.
- Reasonable levels of iron can be gettered away from oxide precipitates , although very high levels of iron at oxide precipitates is not getterable.

Outline of talk

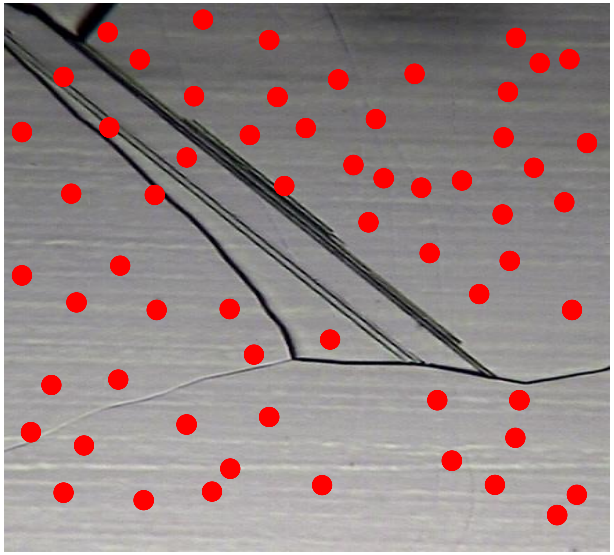
1. Injection-dependent lifetime analysis approach
2. Recombination at oxygen-related extended defects
3. Internal gettering in mc-Si
4. High lifetime silicon materials

Gettering in mc-Si

- External gettering requires transport of impurities to near surface regions (*e.g.* P/B-diffusion, Al, saw damage).
- Internal gettering occurs within the material, for example at dislocations, precipitates or grain boundaries.



External gettering

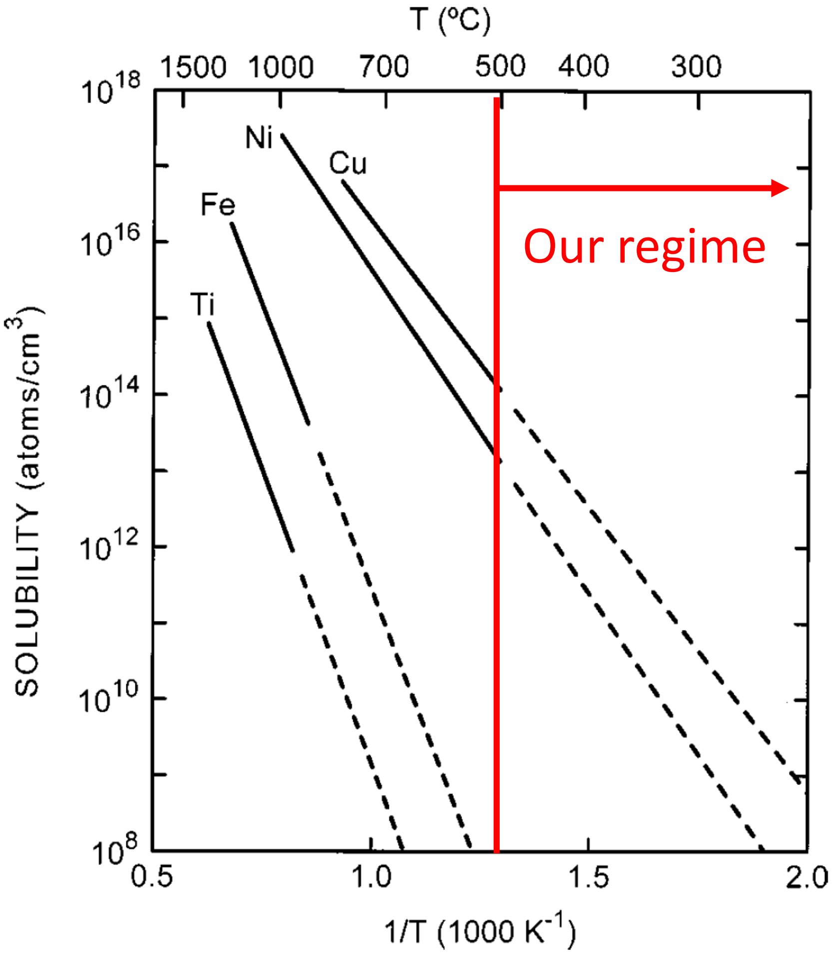


Internal gettering

- Unintentional internal gettering usually occurs during casting/ cell processing. *Intentional* internal gettering?

Low temperature internal gettering

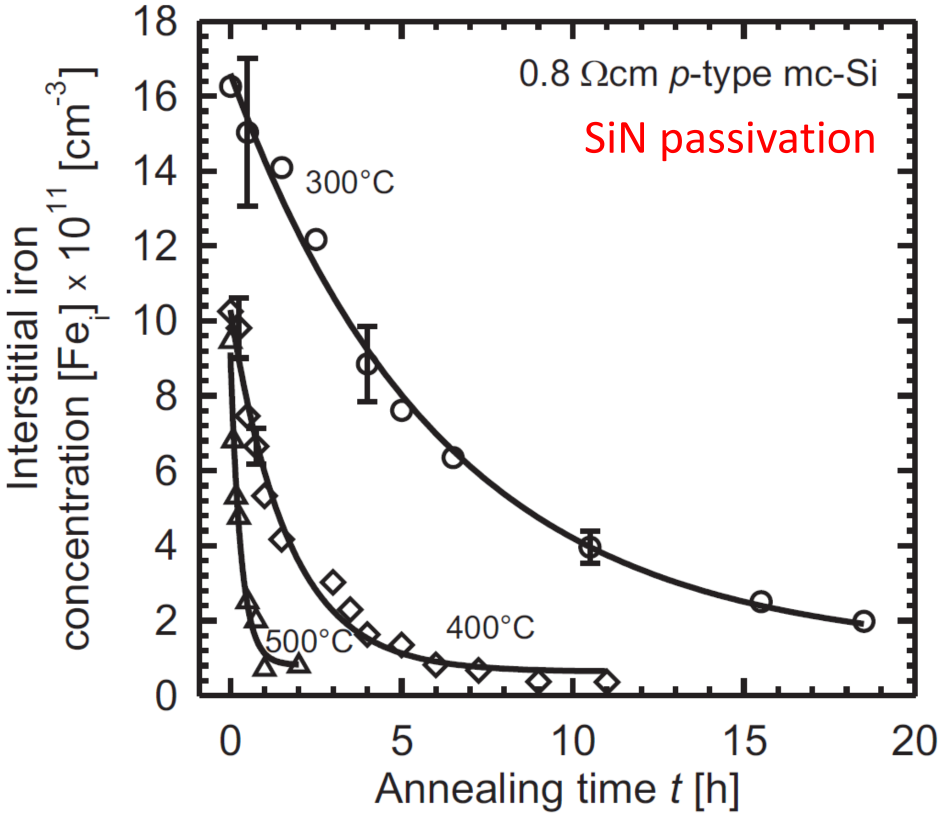
- High temperature processes are relatively expensive and may result in contamination.
- At low temperatures the solubility of transition metals is low.
- Diffusivity is also low, but annealing times can be long and there is no need for (very) clean conditions.
- Compare to toughening anneals of glass (~550 °C for ~1 day)

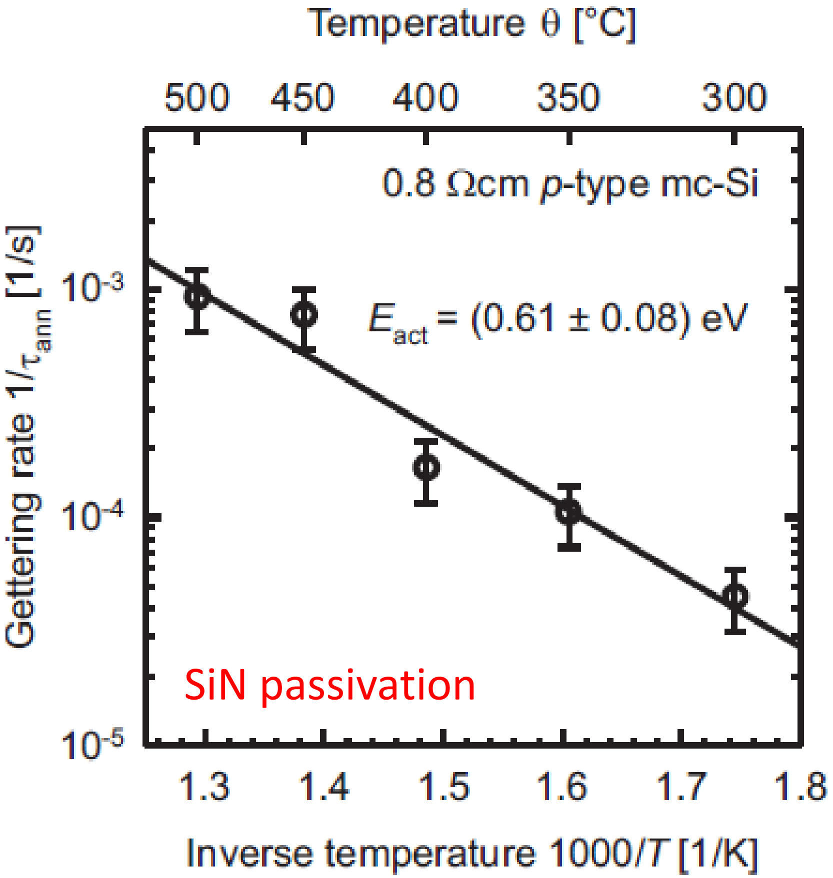


Graph from Myers *et al.*,
J. Appl. Phys., **88** 3795 (2000)

Prior low T internal gettering study

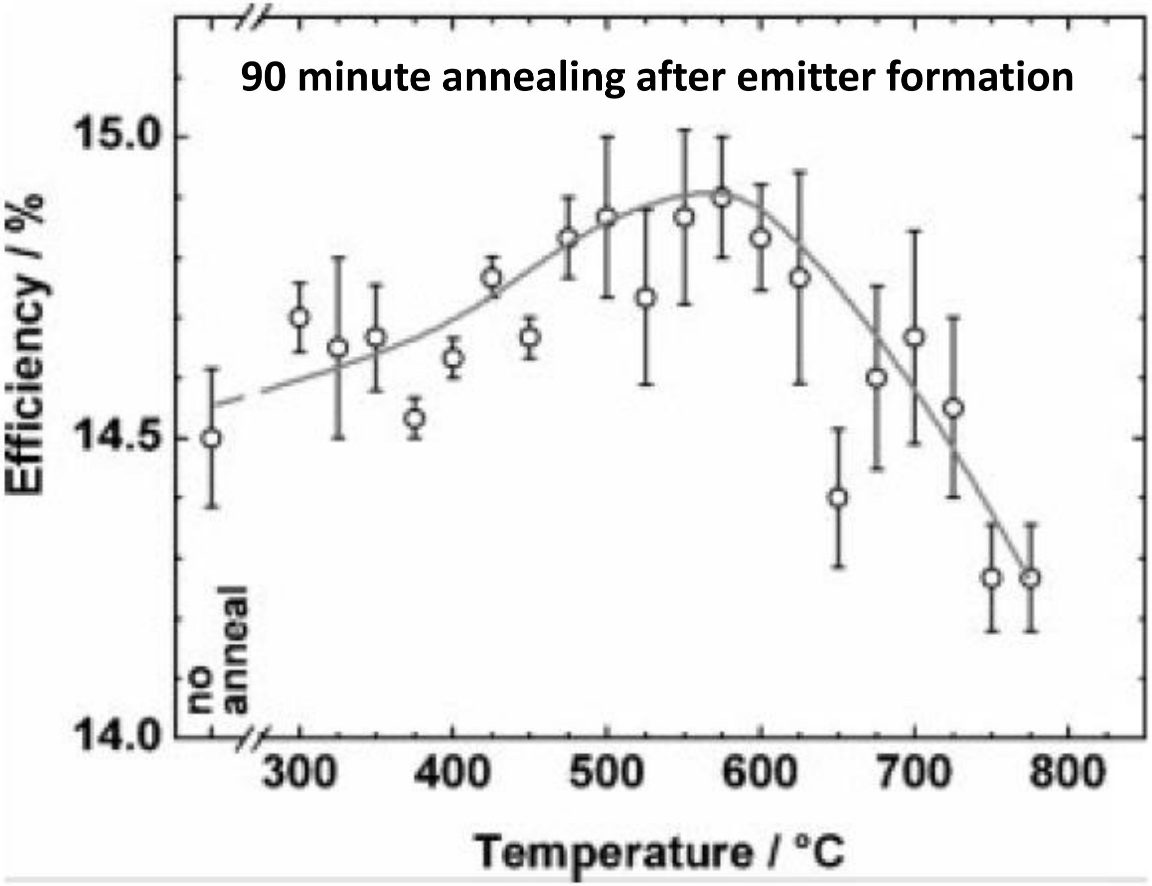
Krain, Herlufsen & Schmidt, *Applied Physics Letters*, **93** 152108 (2008)





- But, what happens to lifetime?
- Is it actually this straightforward?

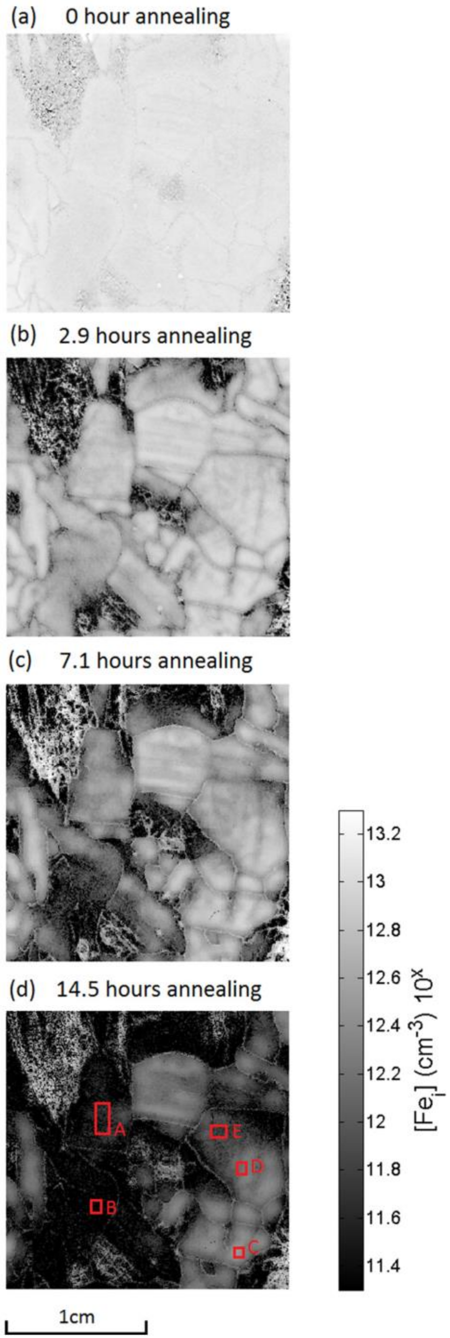
Some other studies



Rinio *et al.*, *Prog. Photovoltaics*, **19** 165 (2011)

- What is really going on?

500 °C after 1000 °C oxidation



Liu and Macdonald,
J. Appl. Phys., **115** 114901 (2014)

Studying internal gettering is difficult. Why?

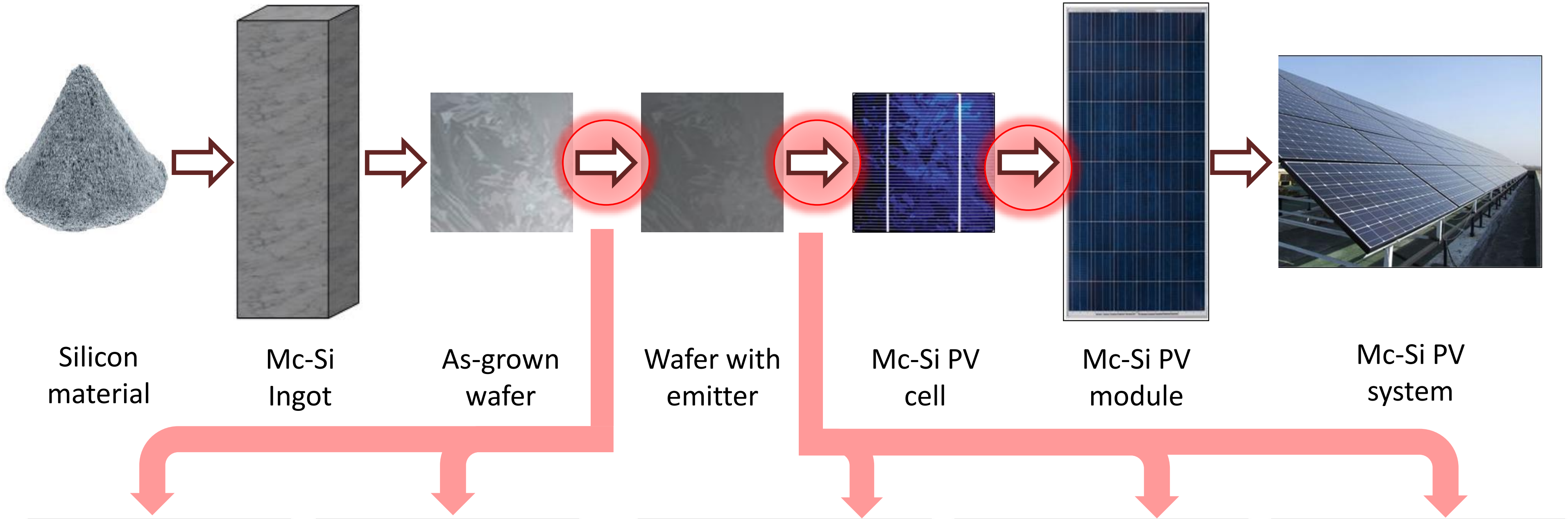
1. Defect distribution changes during surface passivation.
    - Particularly for high temperature oxidations.
    - Also a problem at low temperatures (for SiN, Al_2O_3).

2. Surface passivation can introduce hydrogen.
    - This probably happens for SiN at 350 to 400 °C.
    - Difficult to distinguish between transport and bulk passivation effects.

3. Annealing affects the surface recombination velocity.
    - Difficult to report a consistent bulk lifetime.

In our study we try to overcome the above issues in an attempt better to understand internal gettering in mc-Si.

When in the cell process?



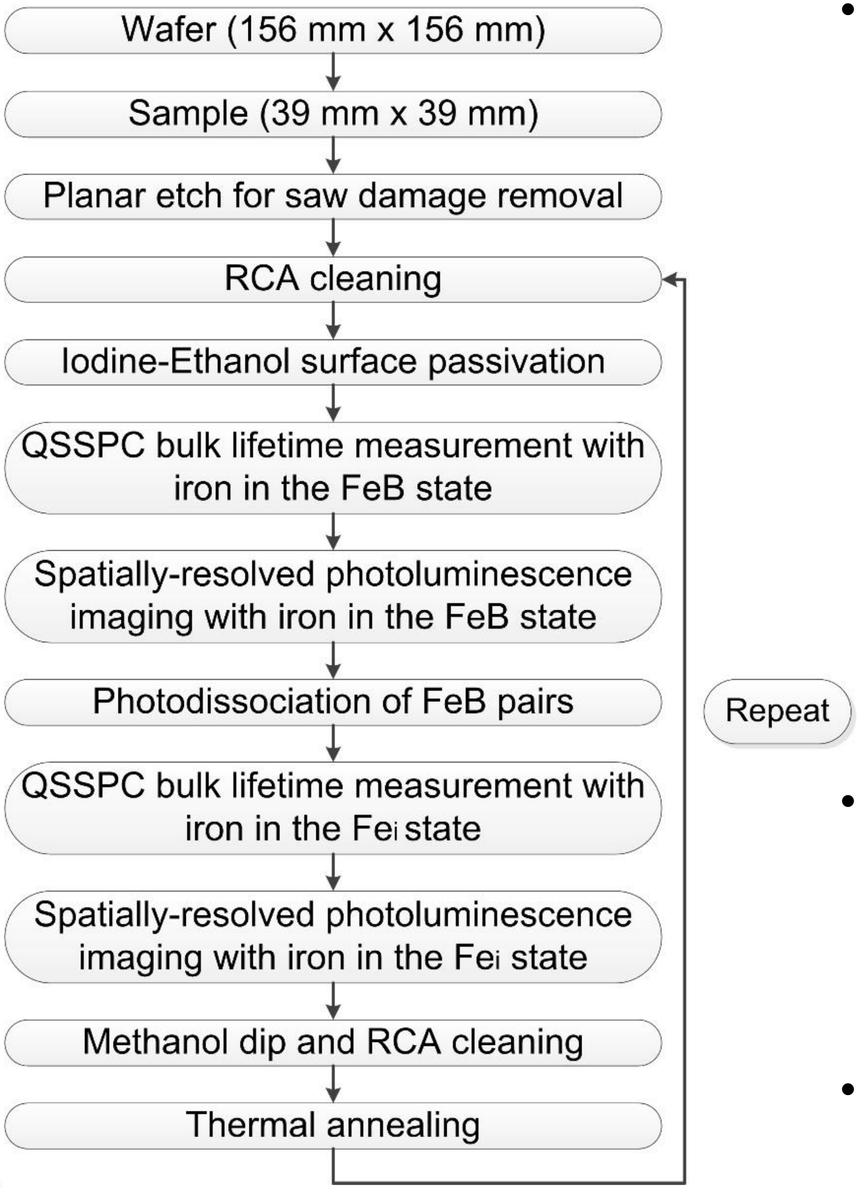
Silicon material → Mc-Si Ingot → As-grown wafer → Wafer with emitter → Mc-Si PV cell → Mc-Si PV module → Mc-Si PV system

Experiment I	Experiment II	Experiment IIIa	Experiment IIIb	Experiment IIIc
• B, MB, MT, T • LTIG (300 - 500 °C) • I-E passivation	• B, MB, MT, T • LTIG (300 - 500 °C) • SiN passivation	• B,MB, MT, T • LTIG (300 - 500 °C) • I-E passivation	• B,MB, MT, T • Emitter off • LTIG(400 °C) • I-E passivation	• B • Emitter off • LTIG (400 °C) • SiN versus I-E passivation

This talk

Experiments in progress

Experiment I: Sample processing sequence



Wafer (156 mm x 156 mm)

Sample (39 mm x 39 mm)

Planar etch for saw damage removal

RCA cleaning

Iodine-Ethanol surface passivation

QSSPC bulk lifetime measurement with iron in the FeB state

Spatially-resolved photoluminescence imaging with iron in the FeB state

Photodissociation of FeB pairs

QSSPC bulk lifetime measurement with iron in the Fe_i state

Spatially-resolved photoluminescence imaging with iron in the Fe_i state

Methanol dip and RCA cleaning

Thermal annealing

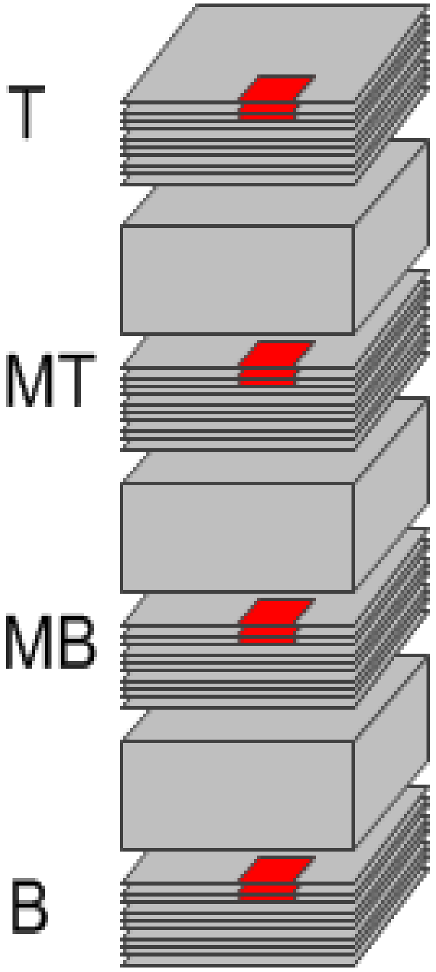
Repeat

- Iodine-ethanol surface passivation.

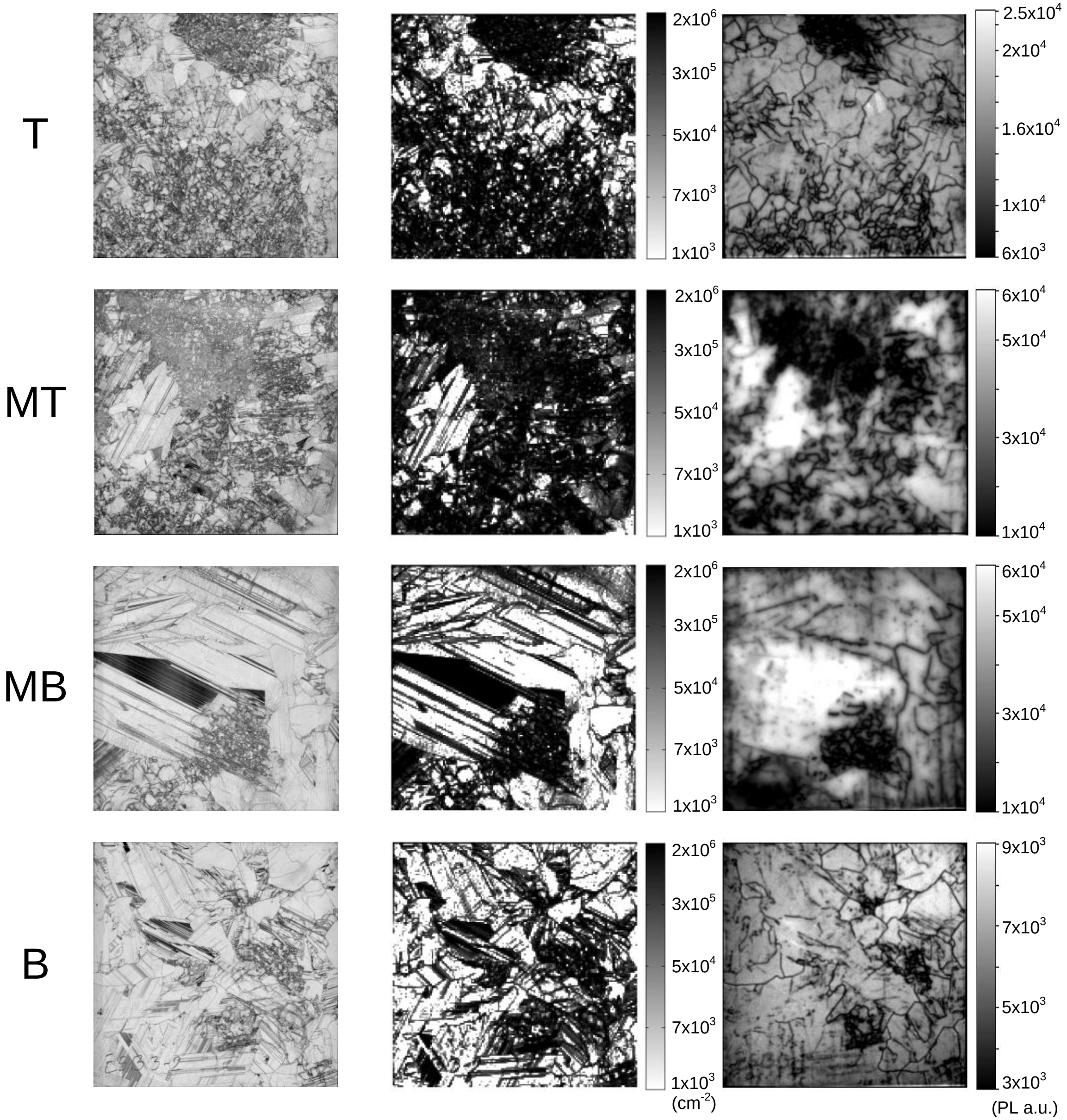
- Annealing performed in a standard laboratory tube furnace (60mm diameter) under nitrogen at 300 °C to 500 °C.

- Samples cooled rapidly (not quenched) by removing boat to air.

mc-Si samples



3.9 cm by 3.9cm



(a) Scanned images

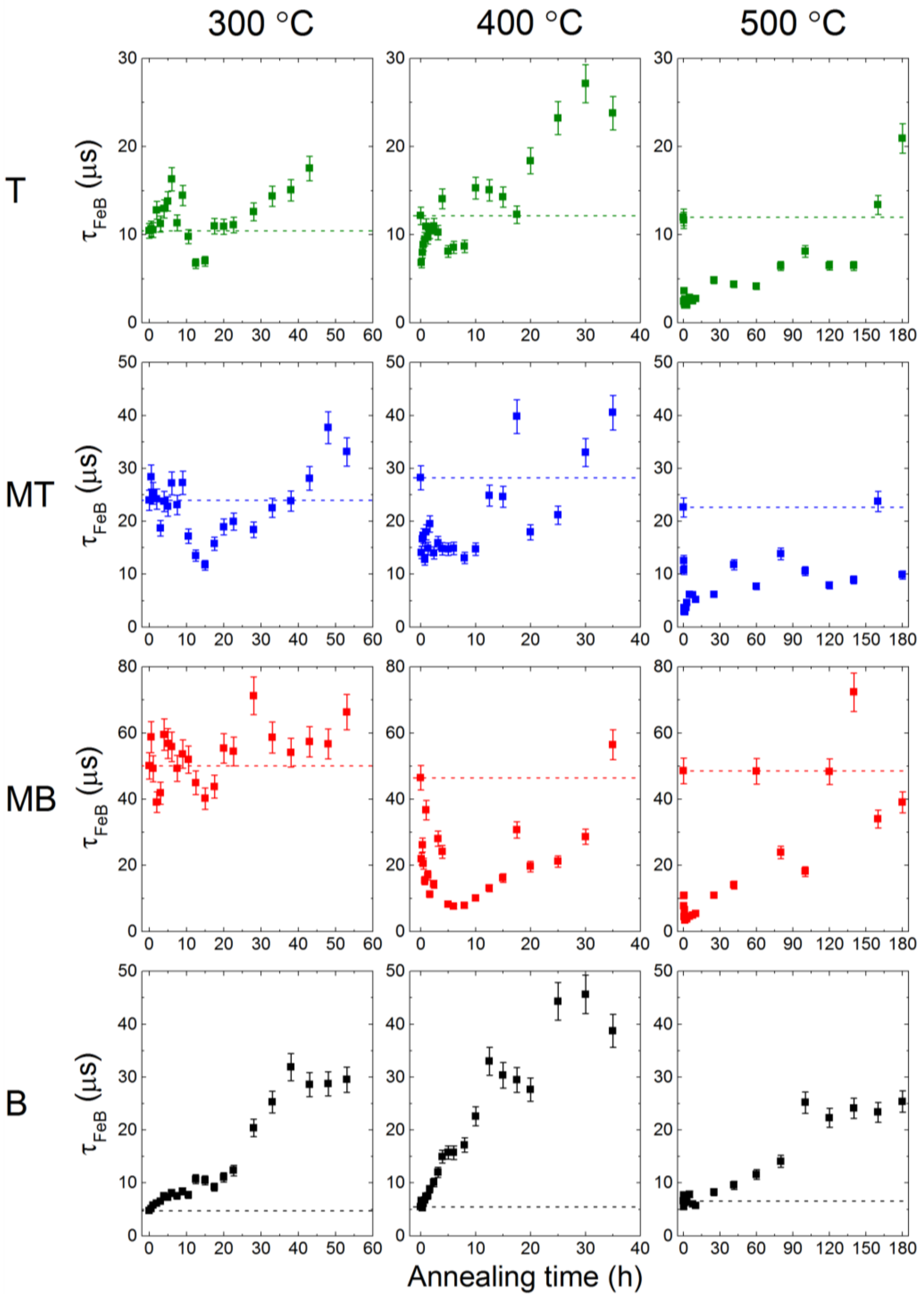
(b) Dislocation density mapping

(c) Photoluminescence images

Dislocation density maps use algorithm from Needleman *et al.*, PSS RRL, **7** 1041 (2013)

Lifetime data (I-E)

- Substantial improvement in bottom wafers (factor of 7).
- Relatively good wafers (middle) get worse with low temperature annealing.



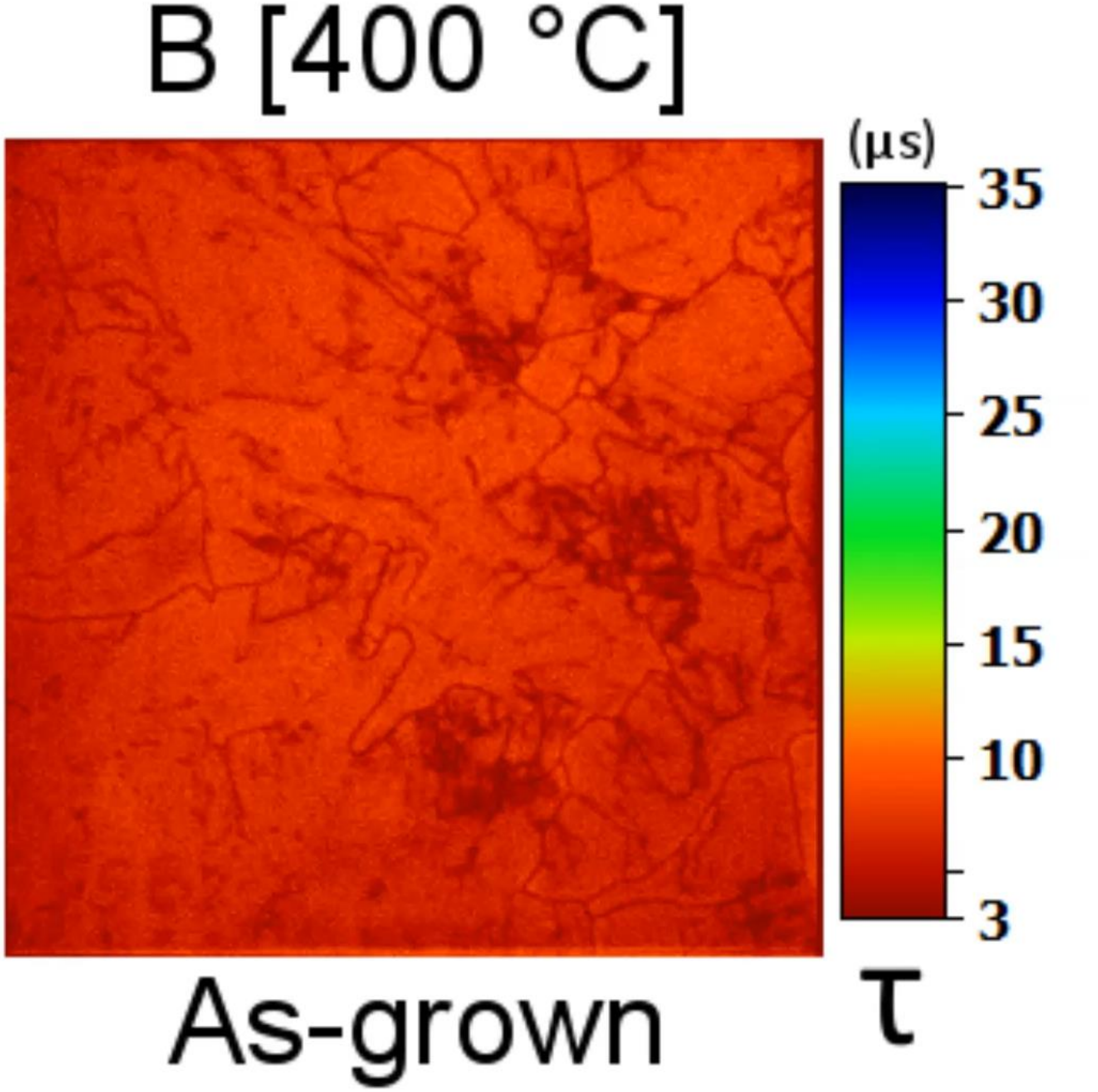
Internal gettering in “bad” wafers at 400 °C

- Sample from bottom of ingot (3.9 cm by 3.9cm).

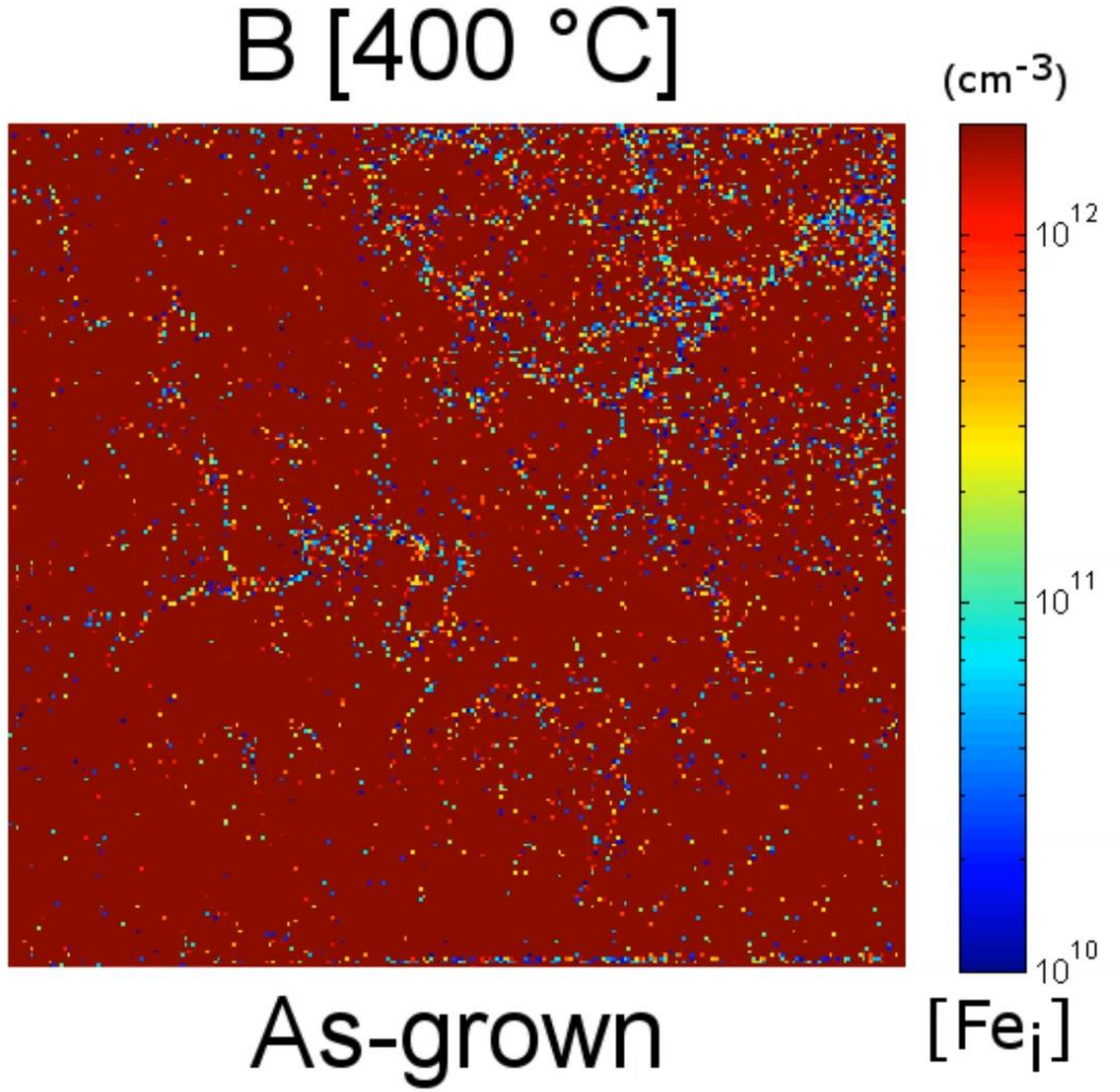
- Illumination of ~0.45 sun for 5s.

- FeB pairs mostly associated.

- Low injection level (10^{13} to 10^{14} cm^{-3}).

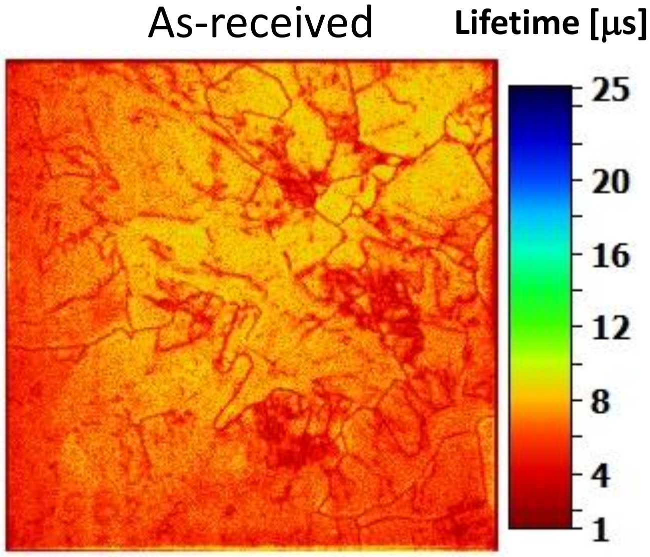


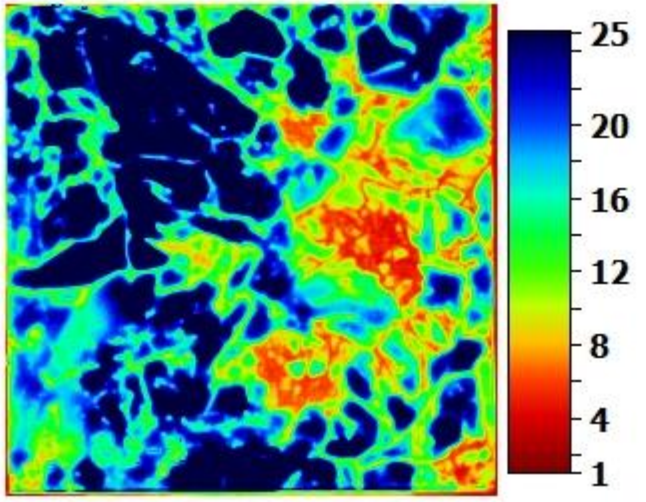
Interstitial iron evolution



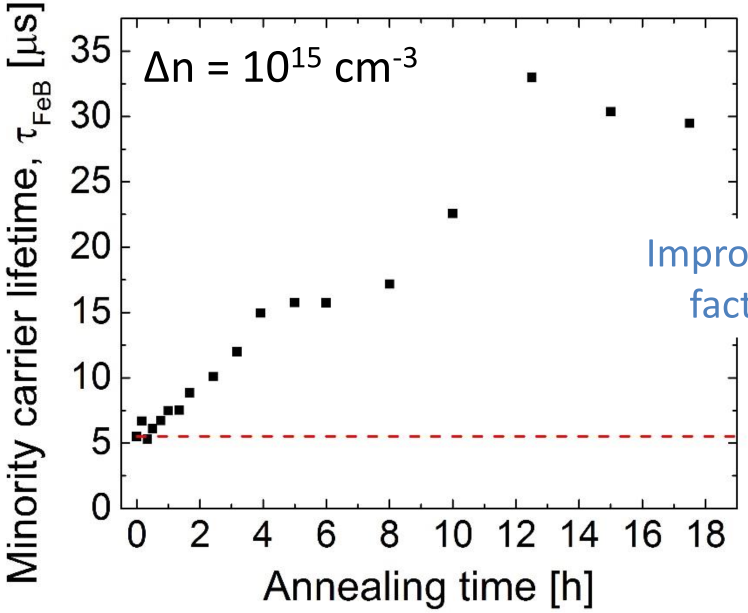
Internal gettering in bottom wafers at 400 °C

As-received

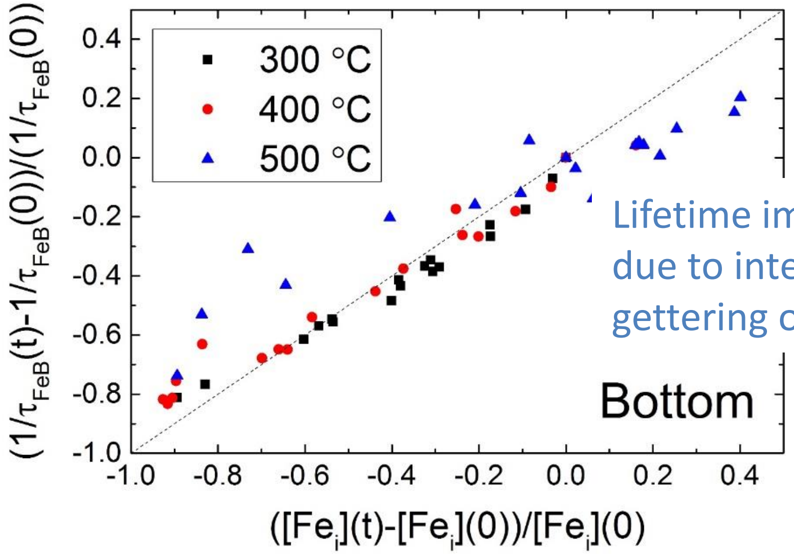




1050 mins = 17.5 h



Improvement by factor of ~6

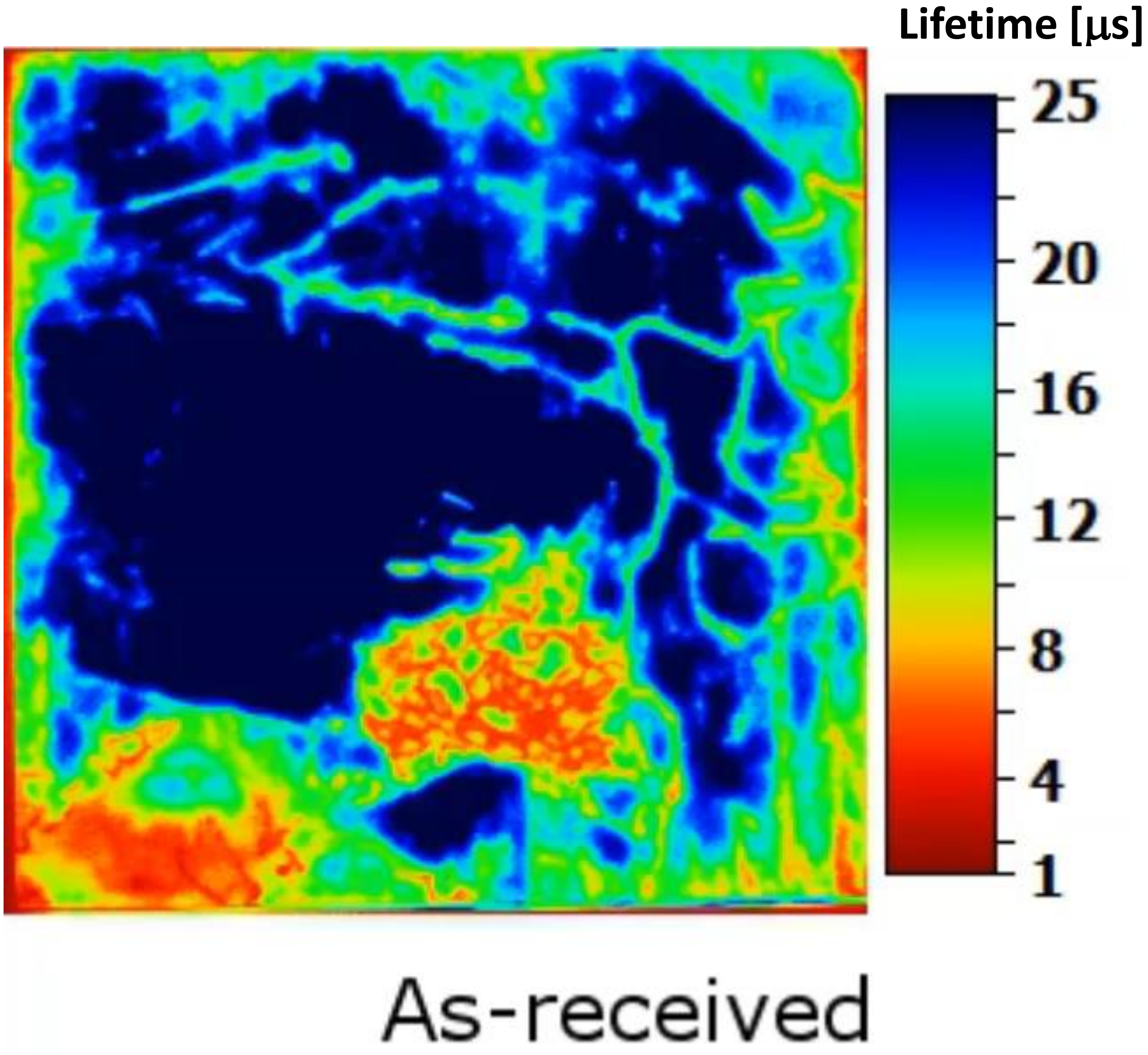


Lifetime improvement due to internal gettering of bulk iron

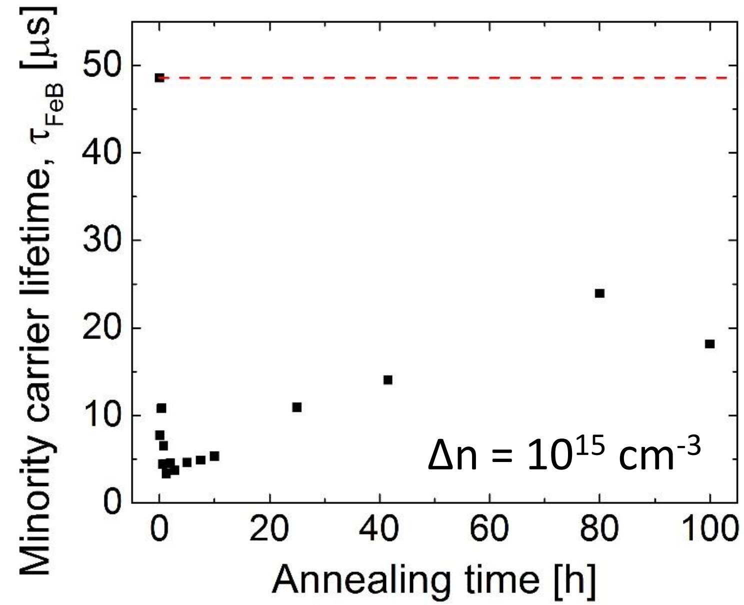
Note: different injection levels for lifetime images and graph

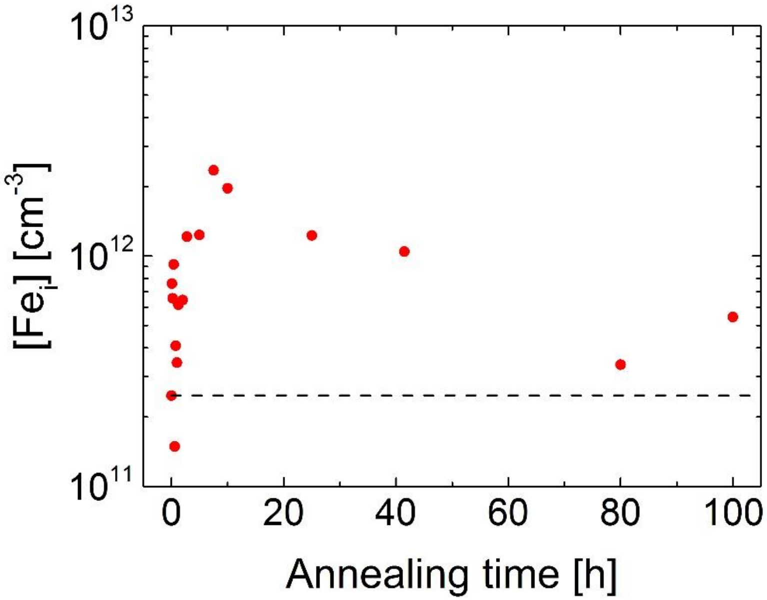
Annealing of “good” wafers at 500 °C (I-E)

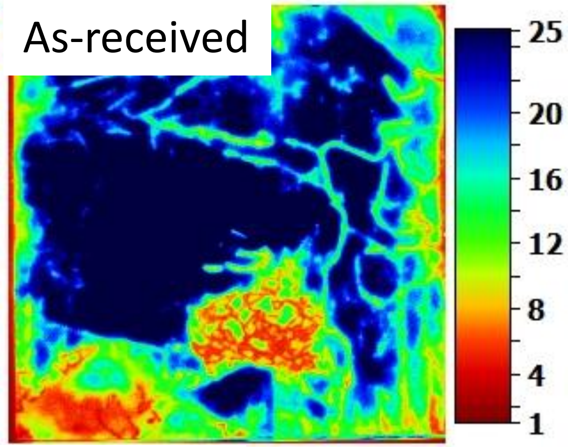
- Sample from middle bottom (MB) of ingot (3.9 cm by 3.9cm).
- Illumination of ~0.45 sun for 5s.
- FeB pairs mostly associated.
- Low injection level (10^{13} to 10^{14} cm^{-3}).

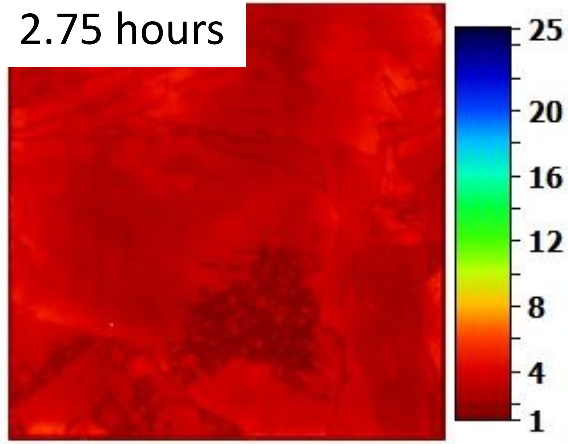


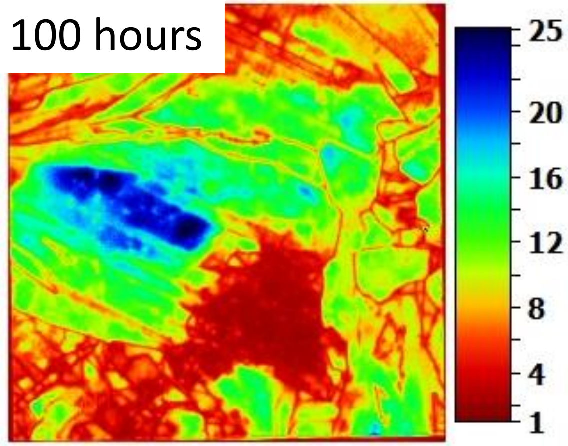
“Good” wafers at 500 °C (MB)






As-received

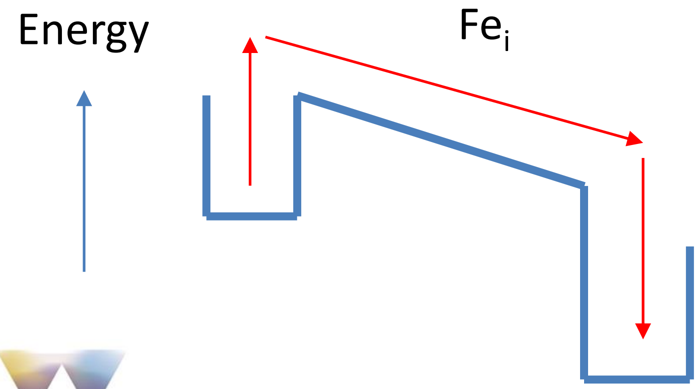

2.75 hours

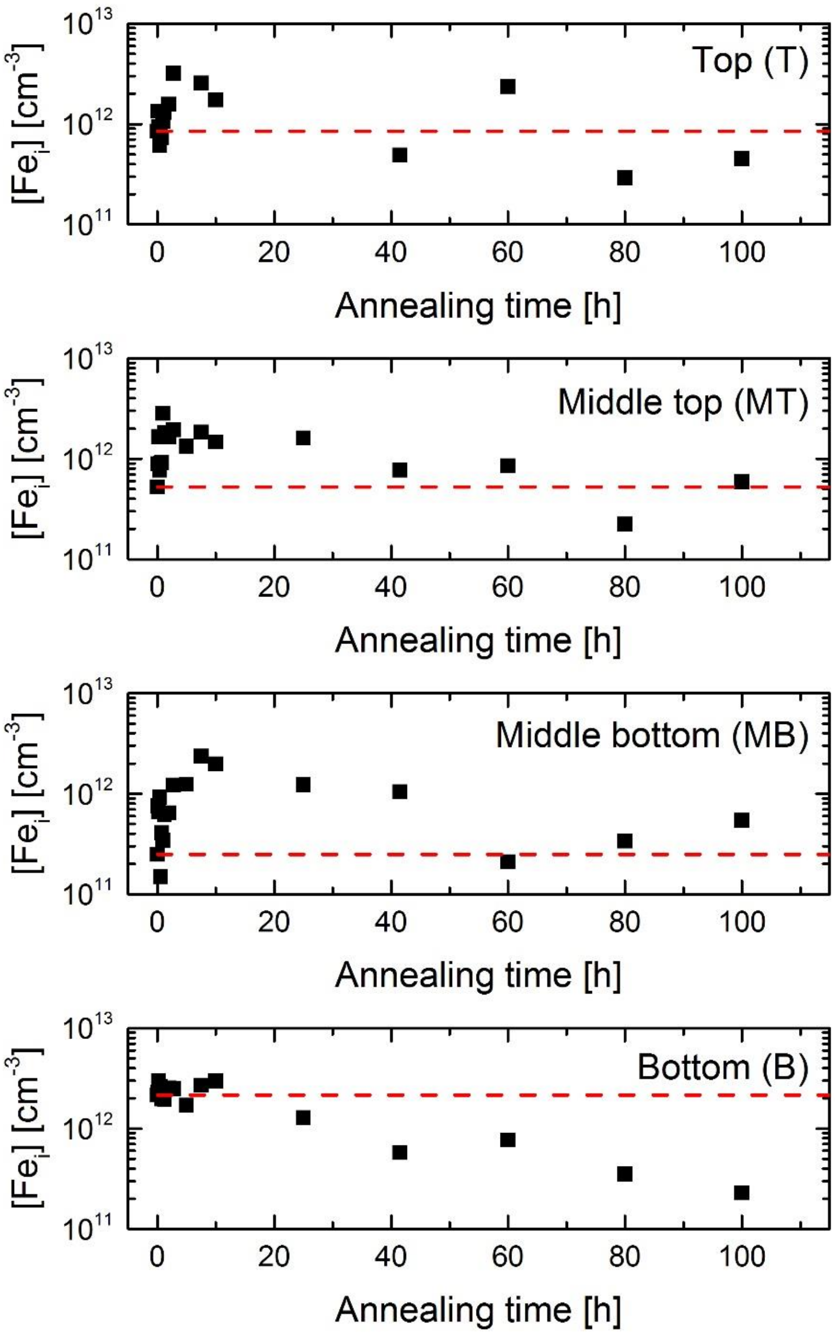

100 hours

Note: different injection levels for lifetime images and graph

Iron release at 500 °C (I-E)

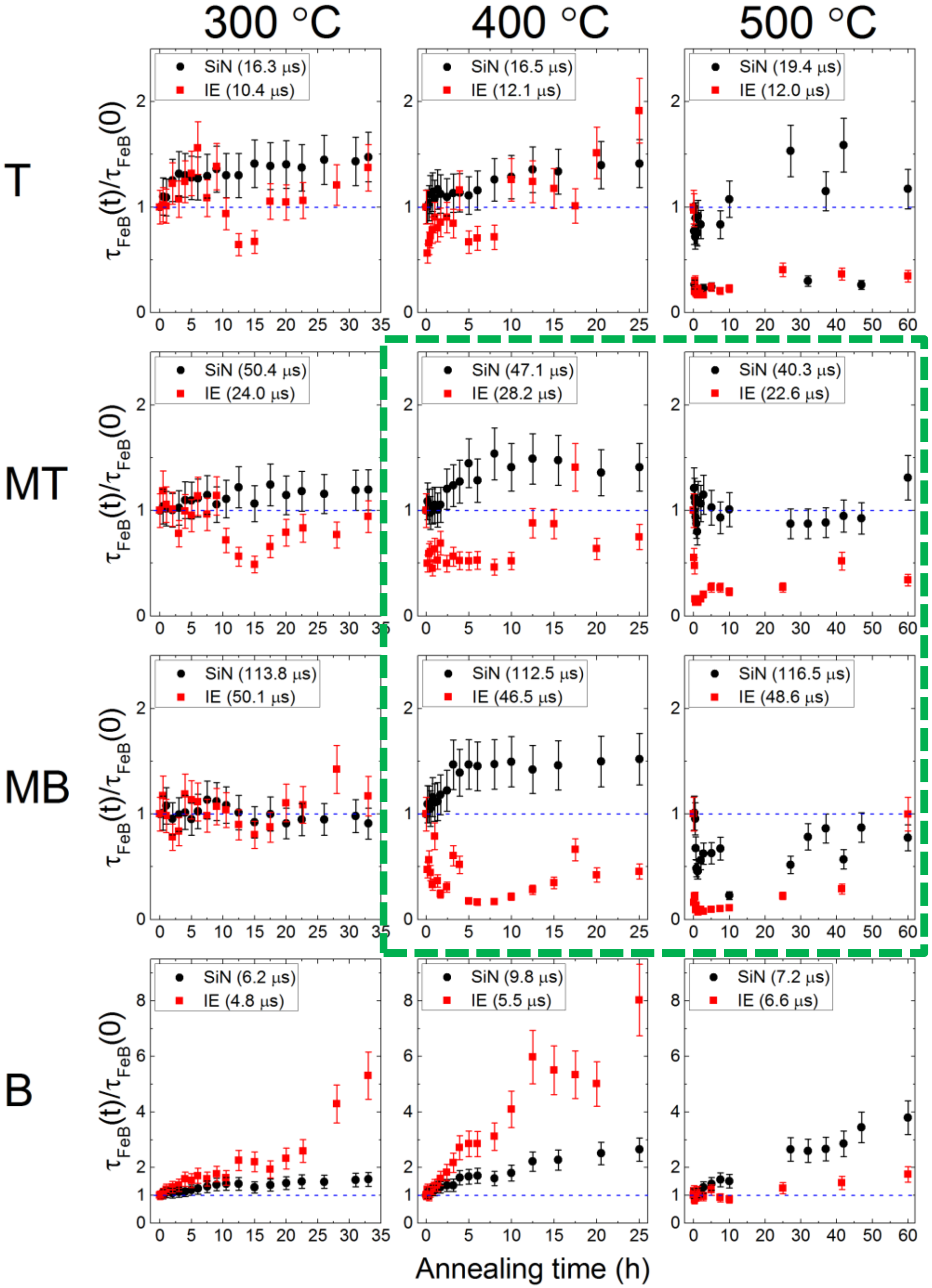
- 500 °C annealing initially increases the interstitial iron concentration to 3 x 10^{12} cm^{-3} in all cases.
- Interstitial iron is released into the bulk from other states (*e.g.* in precipitates/ bound to other defects).
- The interstitial iron then gets recaptured.



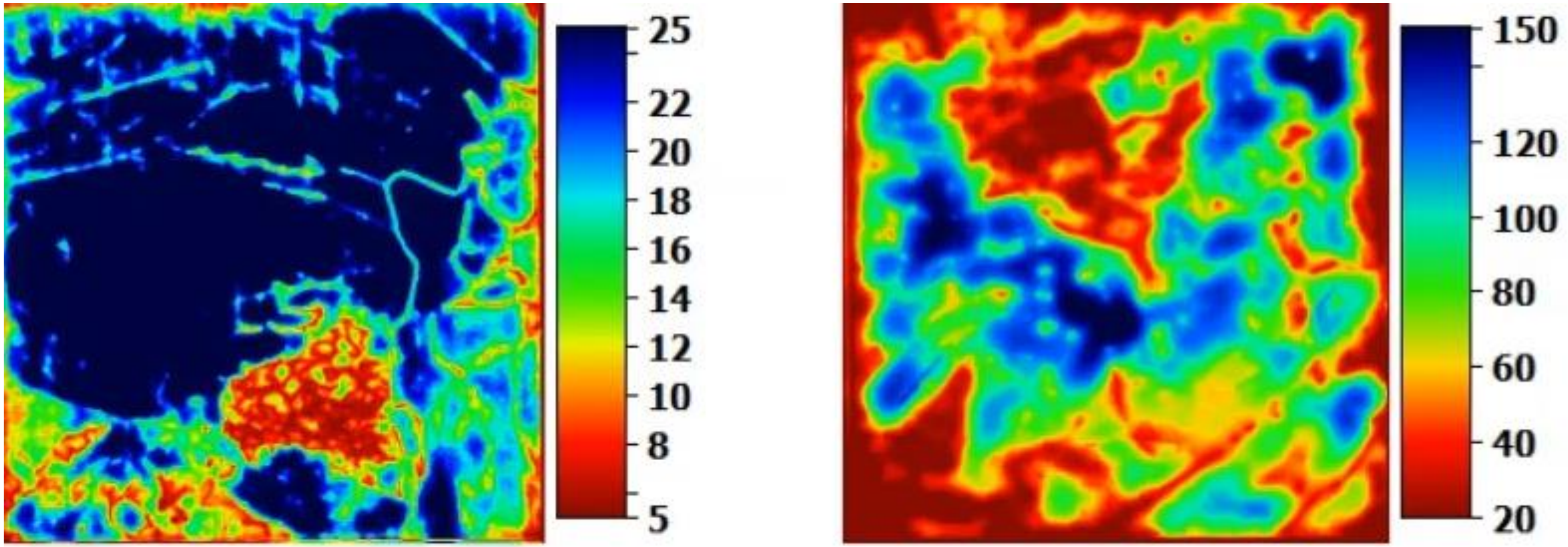


Experiment II (SiN): τ

- In some cases considerable difference between I-E passivation case and SiN passivation case.
- Higher lifetime samples do not seem to degrade (as much) with SiN passivation.
- Bulk hydrogenation effect?



IE versus SiN: MB annealing at 400 °C



Iodine-ethanol

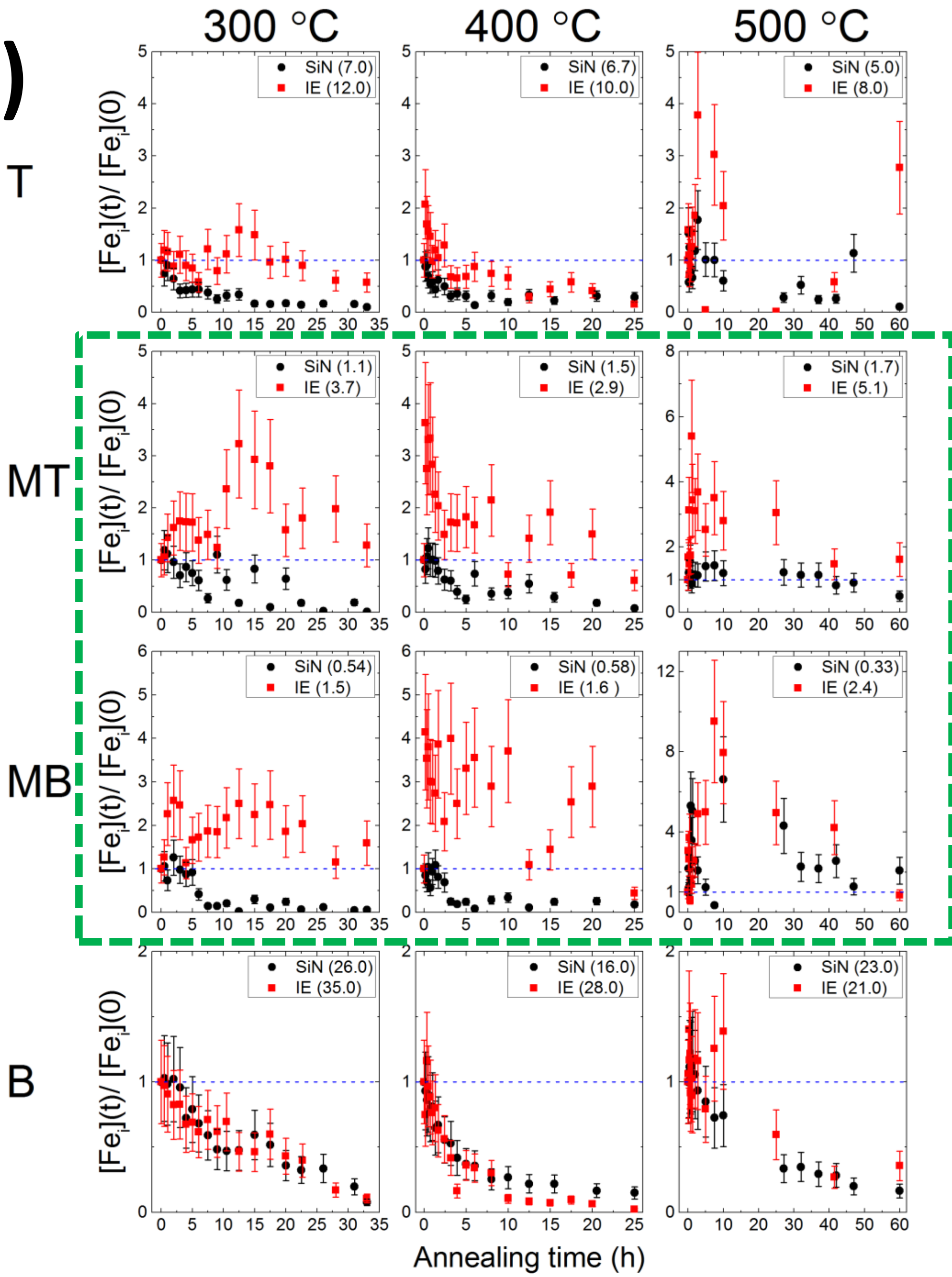
Silicon nitride

As-received

- Initial lifetime higher in SiN case (lower SRV + initial hydrogenation).
- Lifetime of SiN passivated sample much more stable.

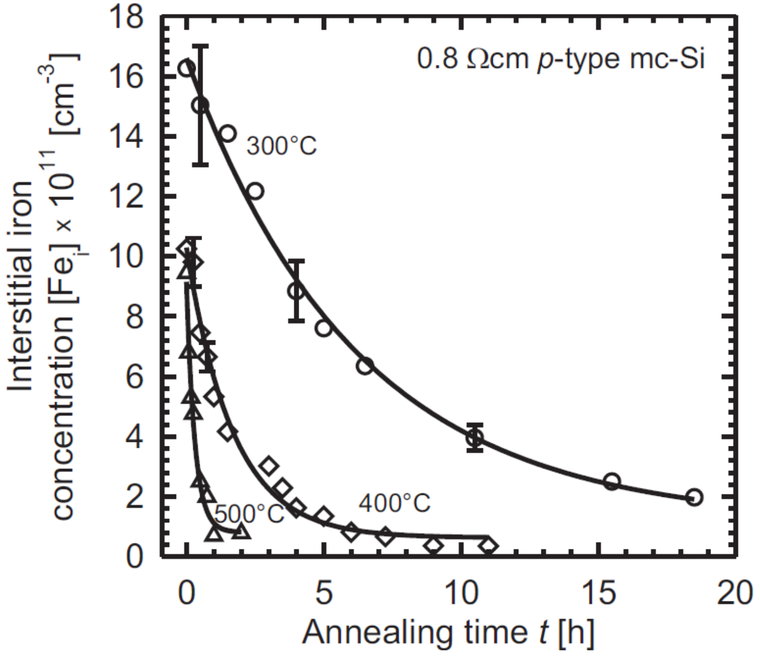
Interstitial Fe (SiN/ I-E)

- In some cases considerable difference between I-E passivation case and SiN passivation case.
- Interstitial iron seems to decay more systematically with SiN than with I-E.
- Possible that hydrogen from SiN interacts with Fe and passivates it or prevents its release from precipitates.

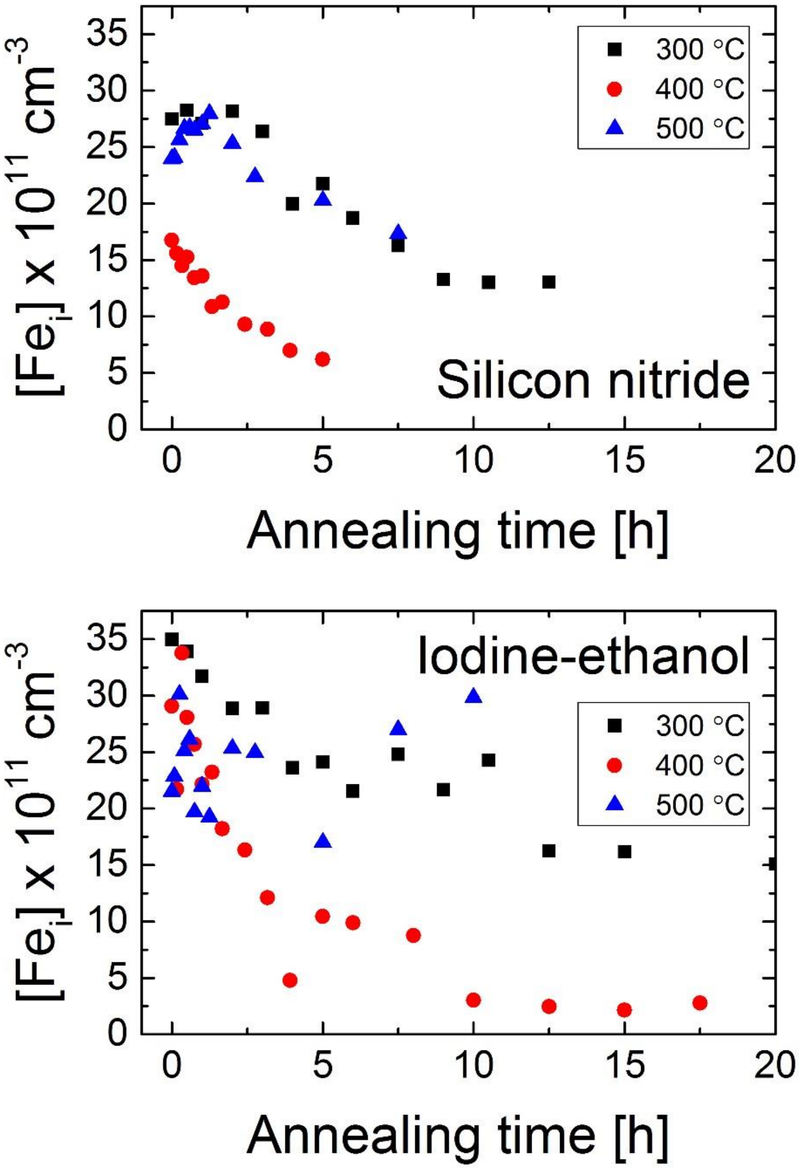


Comparison with Krain *et al.*

Krain *et al.*, *Appl. Phys. Lett.*, **93** 152108 (2008)



Data from our bottom samples



- We find different behaviour to Krain *et al.*'s in most samples with either SiN or IE surface passivation.
- Even bottom samples substantially different at 500 °C.

Summary – low temperature annealing

- Low temperature annealing can improve the carrier lifetime of as-received mc-Si *in certain cases* and hydrogen is <u>not</u> necessary for the effect to occur.
- Low lifetime bottom wafers are always improved (with and without hydrogen) by gettering of iron. Lifetime can improve by a factor of > 6 (so far) by annealing for 10+ hours at 400 °C.
- Low lifetime top wafers are not significantly improved by low temperature annealing.
- Good wafers from the middle are not improved. Iron release into the bulk at 400 °C and 500 °C appears to be prevented by hydrogenation.
- The behaviour of iron in silicon at 300 °C to 500 °C is a complicated problem and needs further investigation.

Outline of talk

1. Injection-dependent lifetime analysis approach
2. Recombination at oxygen-related extended defects
3. Internal gettering in mc-Si
4. High lifetime silicon materials

Float-zone lifetime stability (brief)

- FZ-Si has low oxygen concentration, so might be considered to be an ideal PV substrate (and useful for surface passivation studies).

- Is the lifetime in FZ-Si actually stable with thermal processing?

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Phys. Status Solidi RRL, 1–5 (2016) / DOI 10.1002/pssr.201600080

rrl solar

Thermal activation and deactivation of grown-in defects limiting the lifetime of float-zone silicon

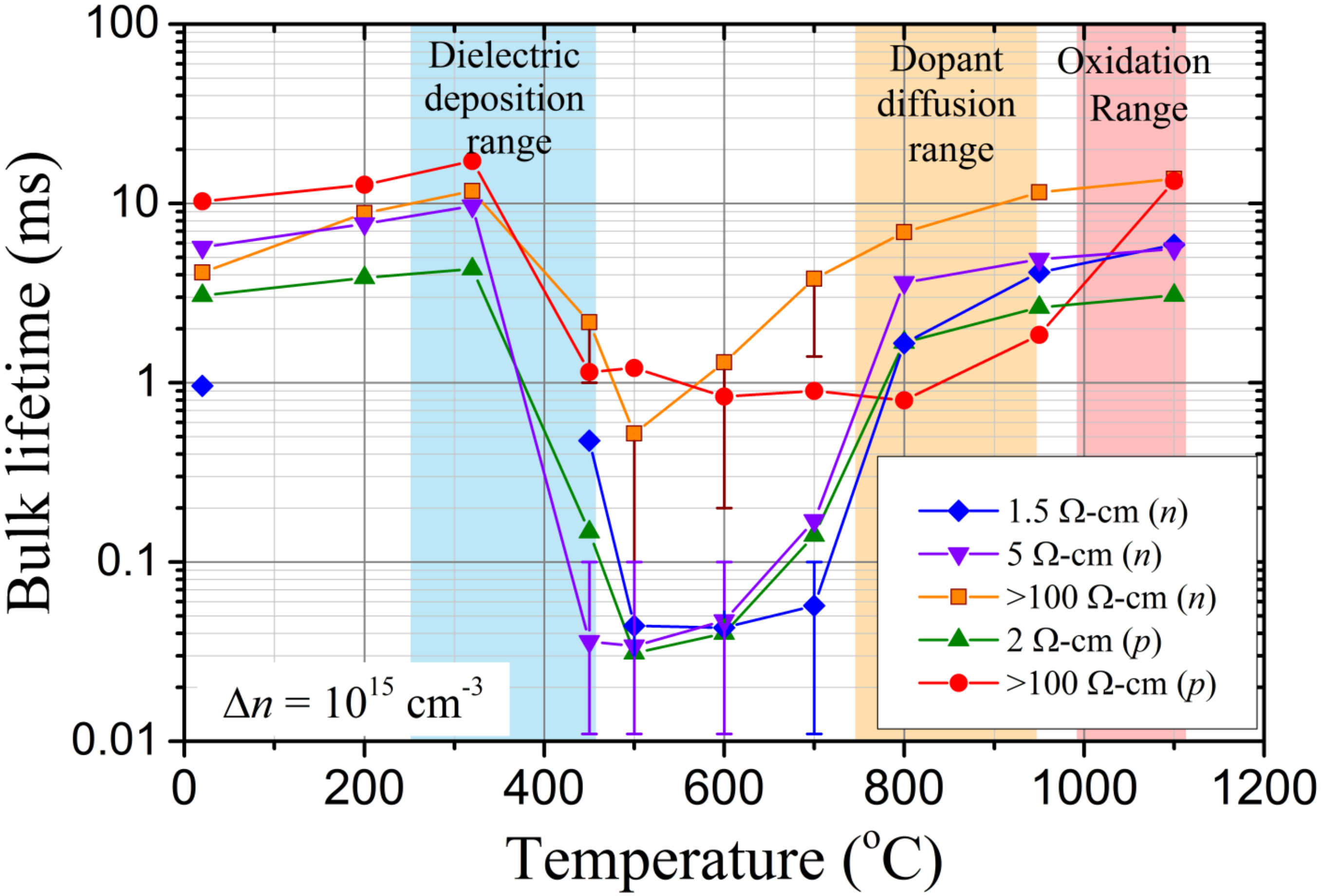
Nicholas E. Grant[*,1], Vladimir P. Markevich[2], Jack Mullins[2], Anthony R. Peaker[2], Fiacre Rougieux[1], and Daniel Macdonald[1]

WARWICK
THE UNIVERSITY OF WARWICK

Thermal stability of float-zone silicon

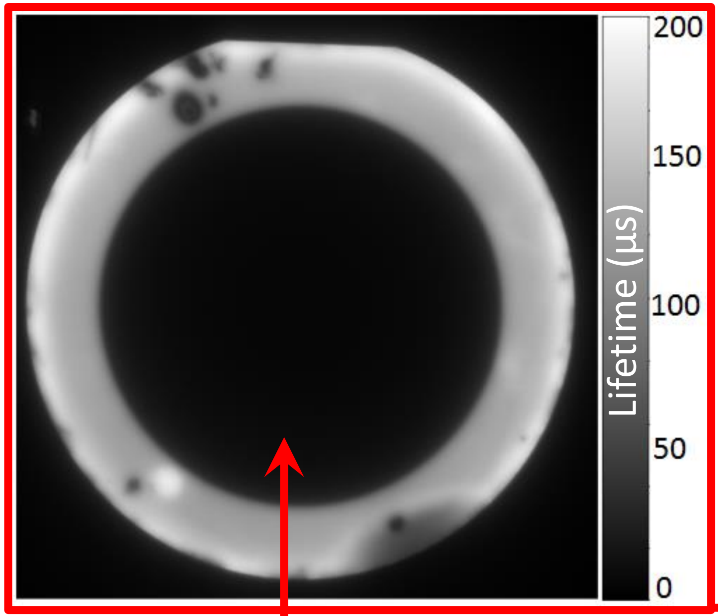
Study to appear in Physica Status Solidi RRL in the next few days

Grant *et al.*, DOI: 10.1002/pssr.201600080

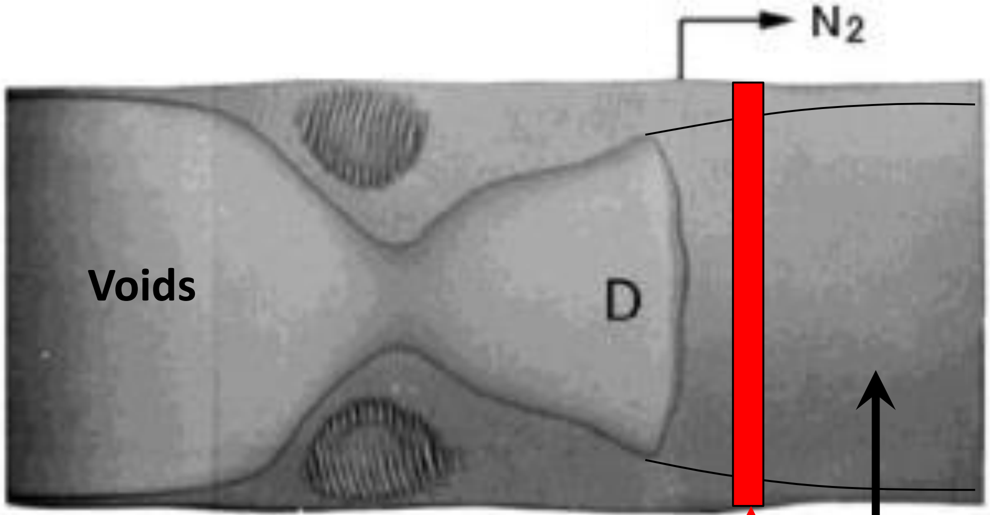


Various manufacturers; each data point a different sample

Thermal instability of FZ-Si: 400–800 °C



X-ray topography map



Un-clustered vacancies

This is only a representation

There is sufficient evidence to suggest that the high recombination region is related to un-clustered vacancies, which have resulted from a fast growth rate and the addition of nitrogen.

Overall summary

- Analysing the injection dependence of lifetime in terms of SRH statistics is relatively straightforward in well-controlled samples (have samples with different doping levels).
- Oxygen-related extended defects cause substantial lifetime reductions. Impurities at precipitates enhance recombination, but can be gettered away to an extent.
- Low temperature internal gettering can result in substantial improvements in lifetime in mc-Si, but the process is complicated.
- Passivation choice strongly affects low temperature annealing behaviour. Hydrogen appears to affect behaviour of iron.
- Any questions?