Australian National University

Iron in crystalline silicon solar cells: fundamental properties, detection techniques, and gettering

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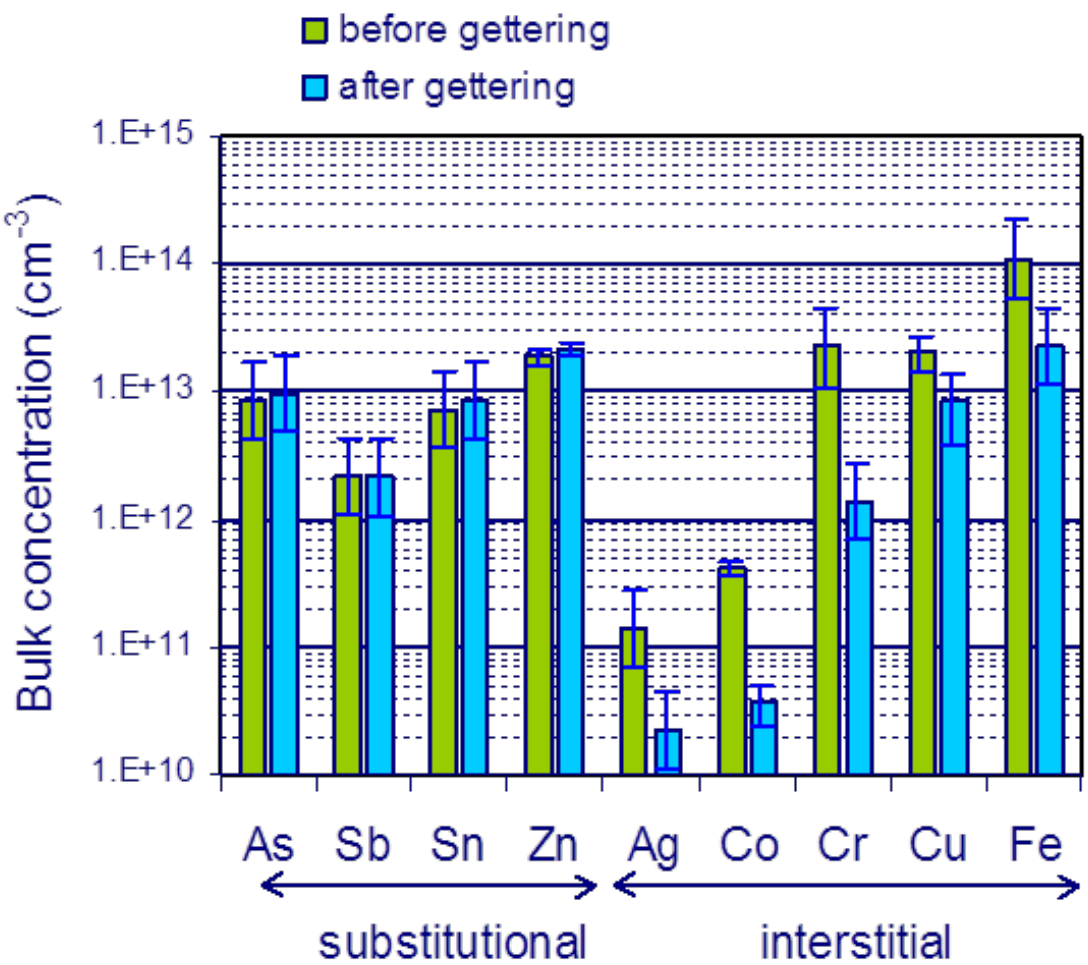
Outline

- Origins of Fe in multicrystalline Si ingots
- Chemical states and recombination activity of Fe in silicon
- Measuring [Fe_i] by QSSPC and PL imaging
- Gettering of Fe during ingot growth and cell fabrication:
  - Internal gettering – at GBs, dislocations and within grains
  - External gettering by P, Al and B diffusions

Origins of Fe in multicrystalline Si ingots

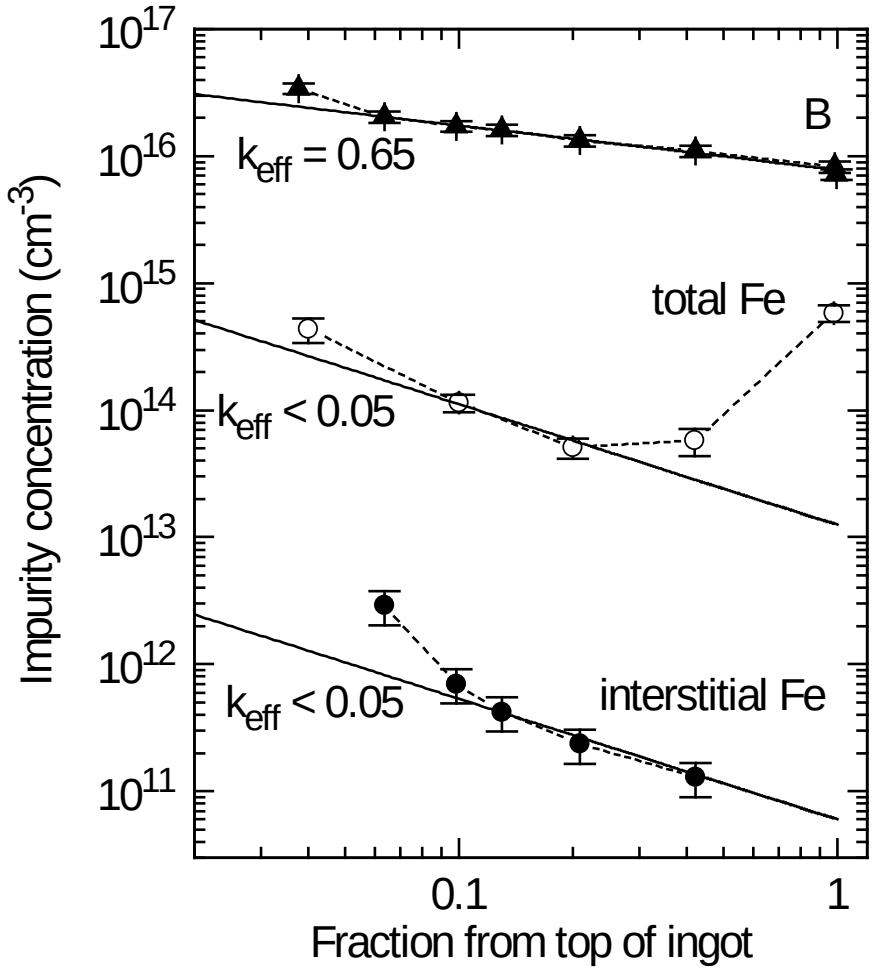
- One of the most common metal contaminants
- **Total** Fe concentration, measured by NAA before and after P gettering
- Comes from the crucible, not the feedstock
- Typically between 10^{12} -10^{15} cm^{-3}



Macdonald *et al.* 29th IEEE PVSC New Orleans (2002)

Origins of Fe in multicrystalline Si ingots

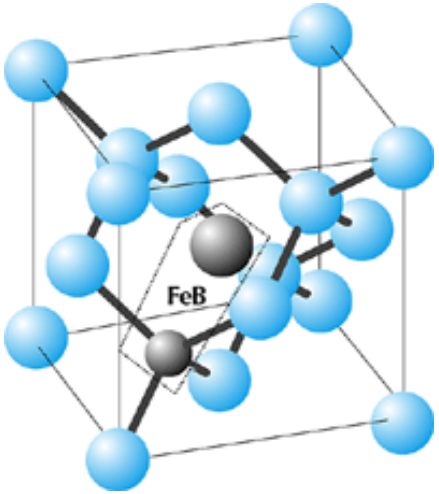
- Concentration increases towards top - segregation
- Also increases at bottom – solid-state diffusion from crucible
- Only a small fraction is interstitial - around 1%
- Remainder is precipitated (or substitutional)
- The dissolved fraction has a much larger impact on lifetime



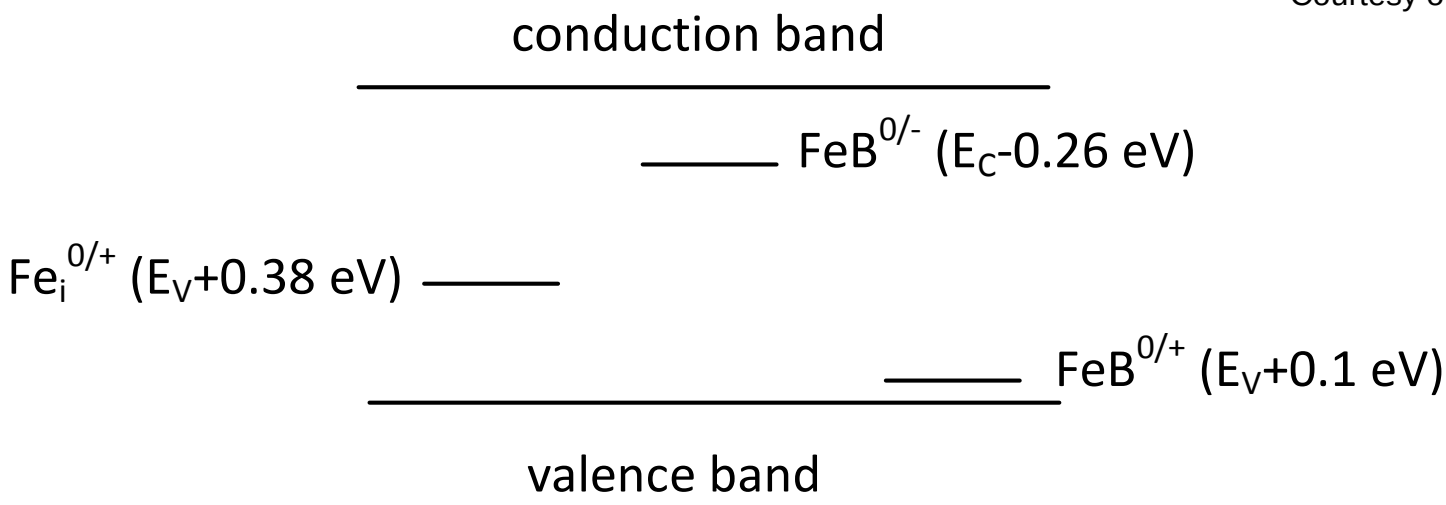
Macdonald *et al.* J. Appl. Phys. **97** 033523 (2005)

Recombination activity of interstitial Fe in silicon

- Interstitial Fe (Fe_i) introduces a deep donor level
- Positively charged in p-type Si - mobile at RT - forms pairs with ionised acceptors.
- Two FeB levels – acceptor and donor
- Pairs break under illumination – only Fe_i present in working cells

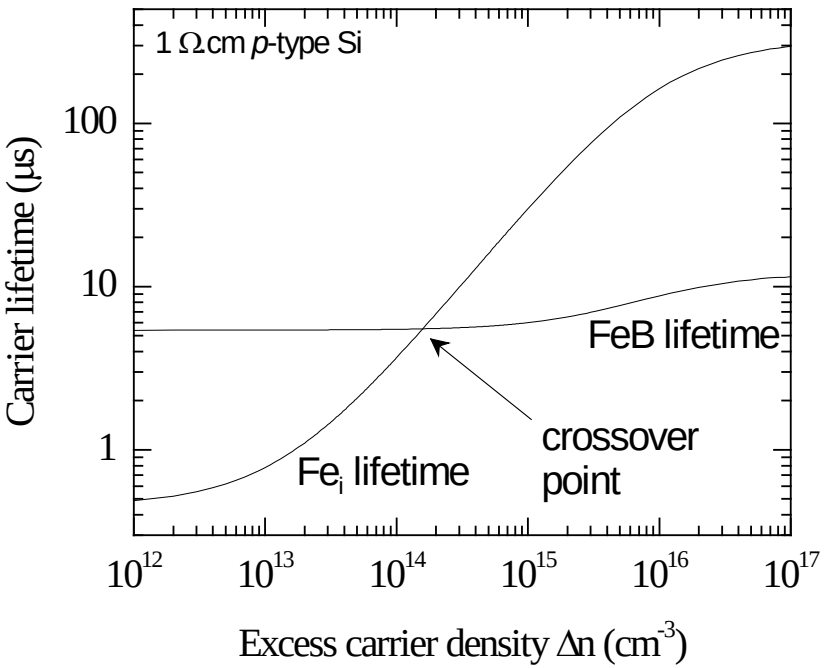


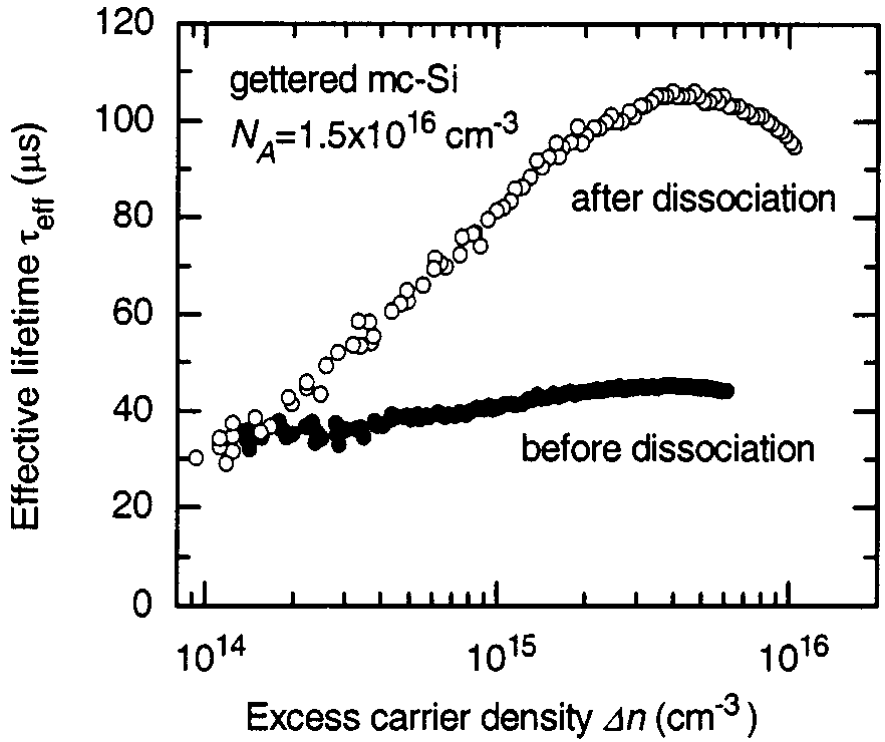
Courtesy of J. Schmidt, ISFH



Recombination activity of Fe in p-type silicon

- Different energy levels and capture cross sections - different lifetime curves
- SRH modelling on left, QSSPC data on right (trapping restricts range)





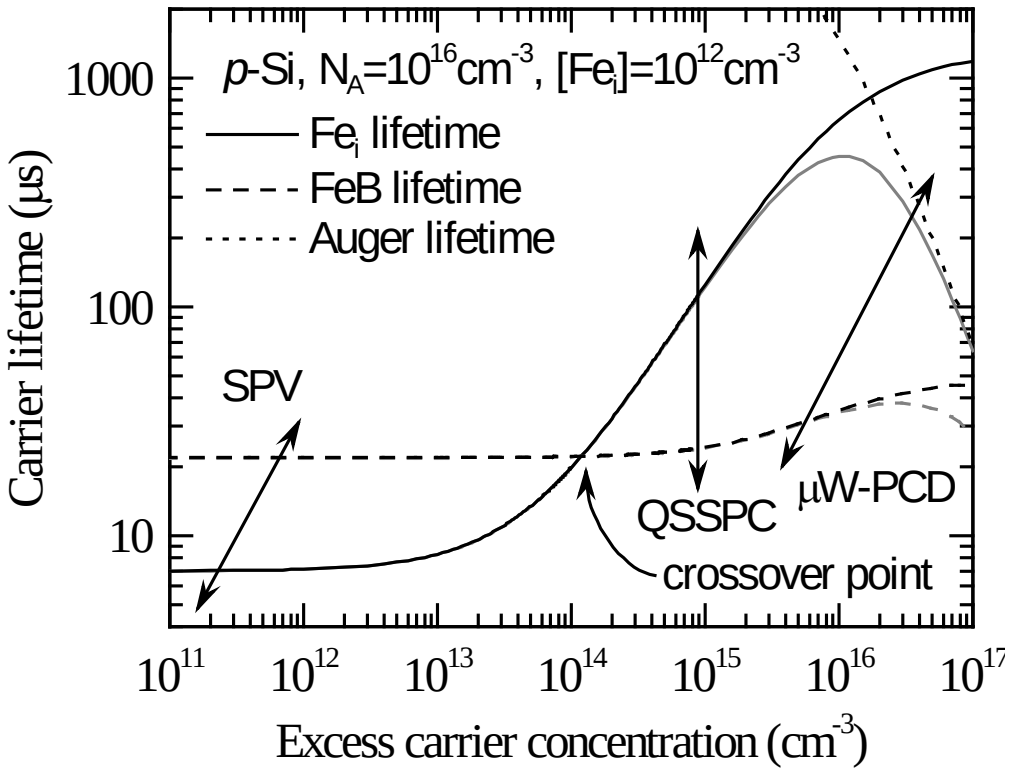
Macdonald *et al.* J. Appl. Phys. **95** 1021 (2004)

Detecting Fe_i using FeB pairing

- Manipulating the SRH equations shows that:

$$[Fe_i] = C \times \left(\frac{1}{\tau_{Fe_i}} - \frac{1}{\tau_{FeB}} \right)$$

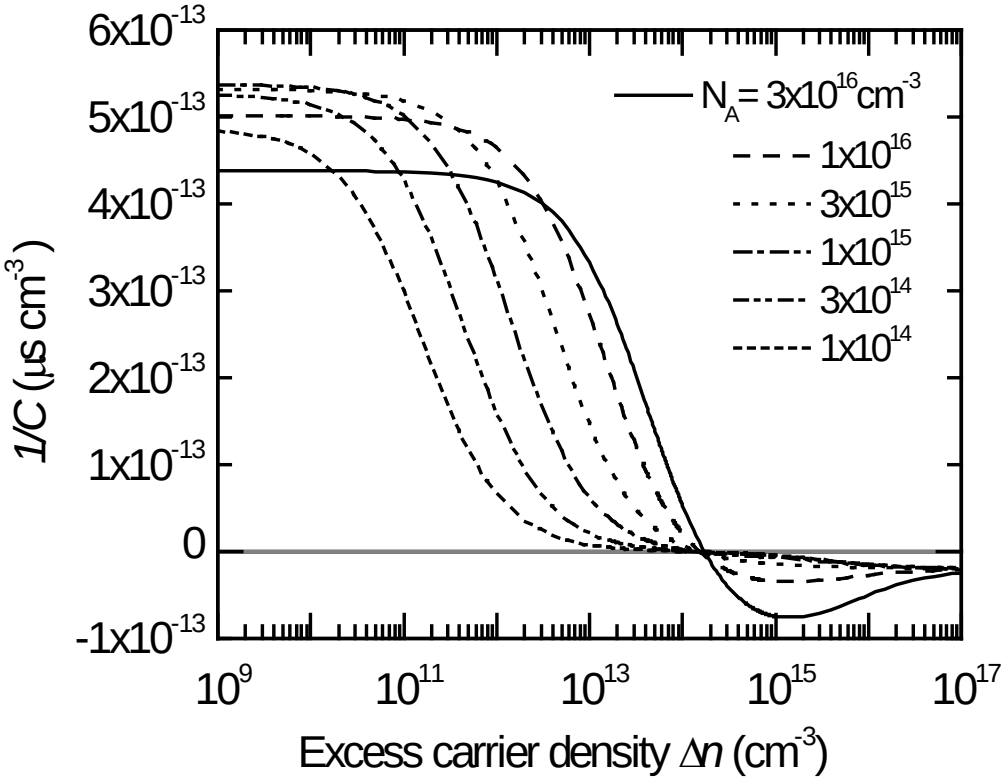
- Zoth and Bergholz developed a famous method based on SPV
- Extended to other methods (uW-PCD and QSSPC)
- Very sensitive (similar to DLTS)
- Only works in p-Si
- Must avoid the crossover point



Detecting Fe_i using FeB pairing

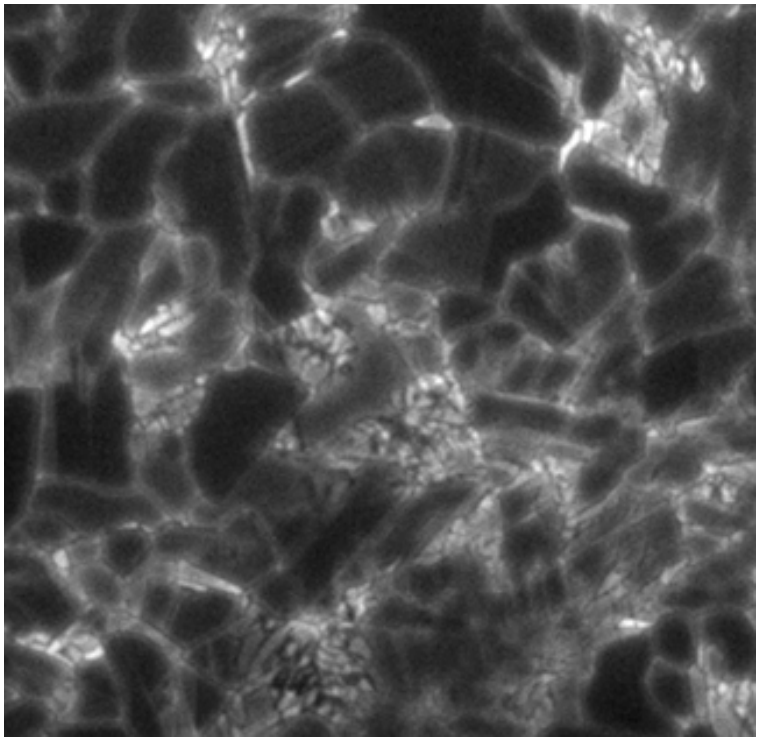
$$[Fe_i] = C \times \left(\frac{1}{\tau_{Fe_i}} - \frac{1}{\tau_{FeB}} \right)$$

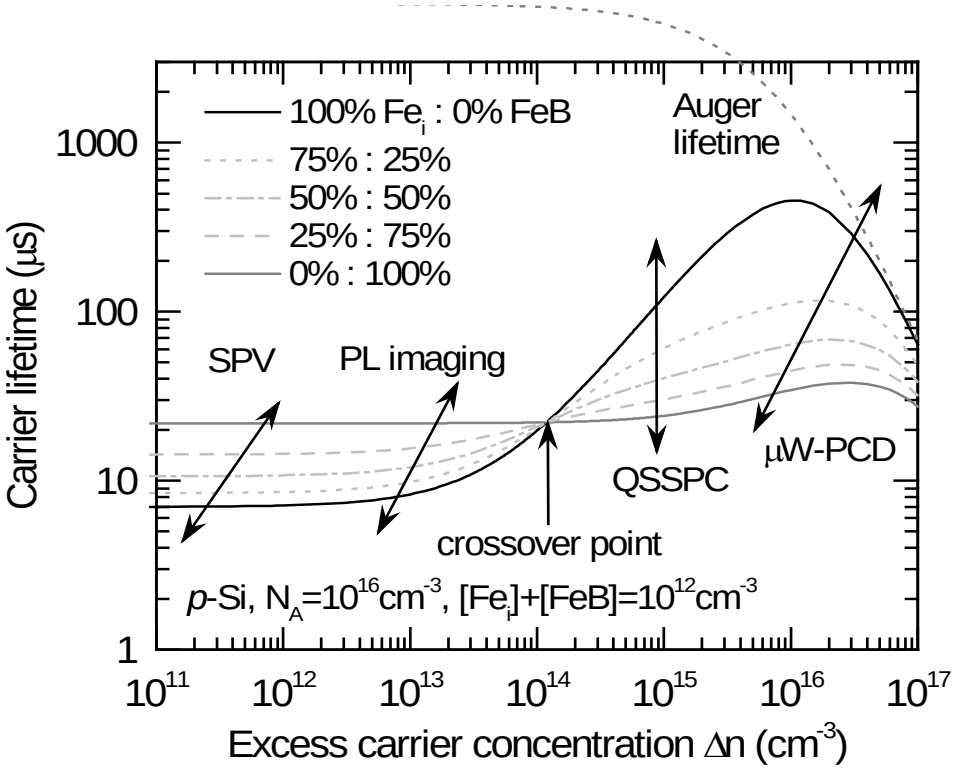
- Pre-factor *C* is a function of doping and excess carrier density.
- In true low injection, *C* becomes constant – ideal measurement region.
- Not accessible to QSSPC or uW-PCD (trapping effects).



Iron imaging with photoluminescence (PL)

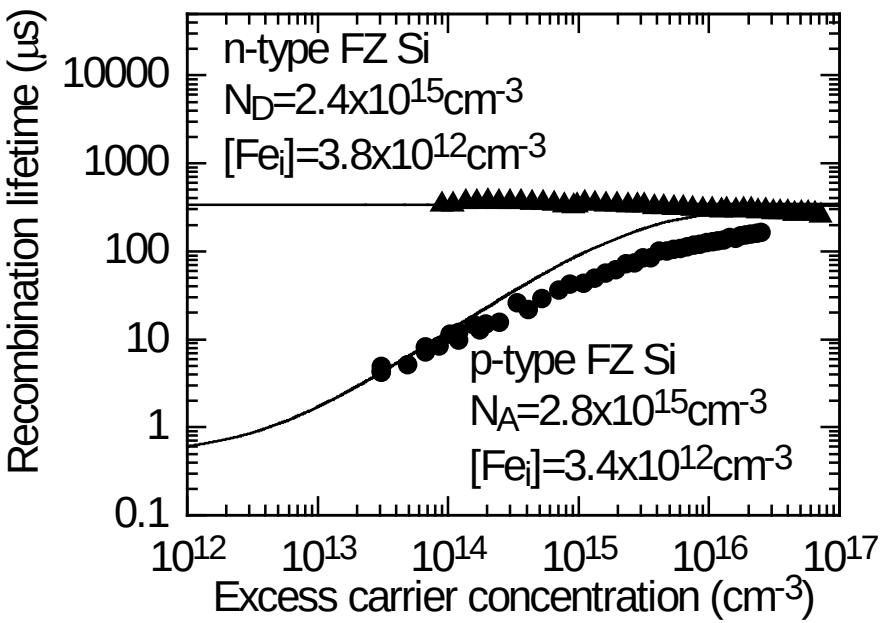
- Band-to-band PL imaging - rapid and highly-resolved method for low-injection lifetime imaging – no trapping effects.
- Allows low-injection Fe imaging - similar to original SPV technique
- Two PL images required, before and after breaking FeB pairs.

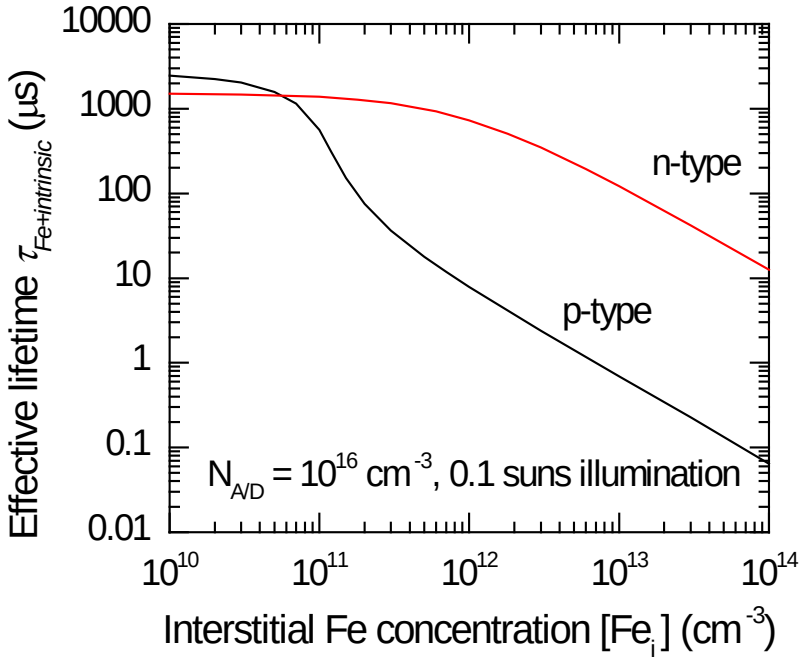




Recombination activity of Fe in n-type silicon

- Neutral charge state in n-type – less attractive for minority carriers compared to p-type.
- Higher lifetime in n-type in low- to mid-injection.
- Possible incentive for using n-type substrates…

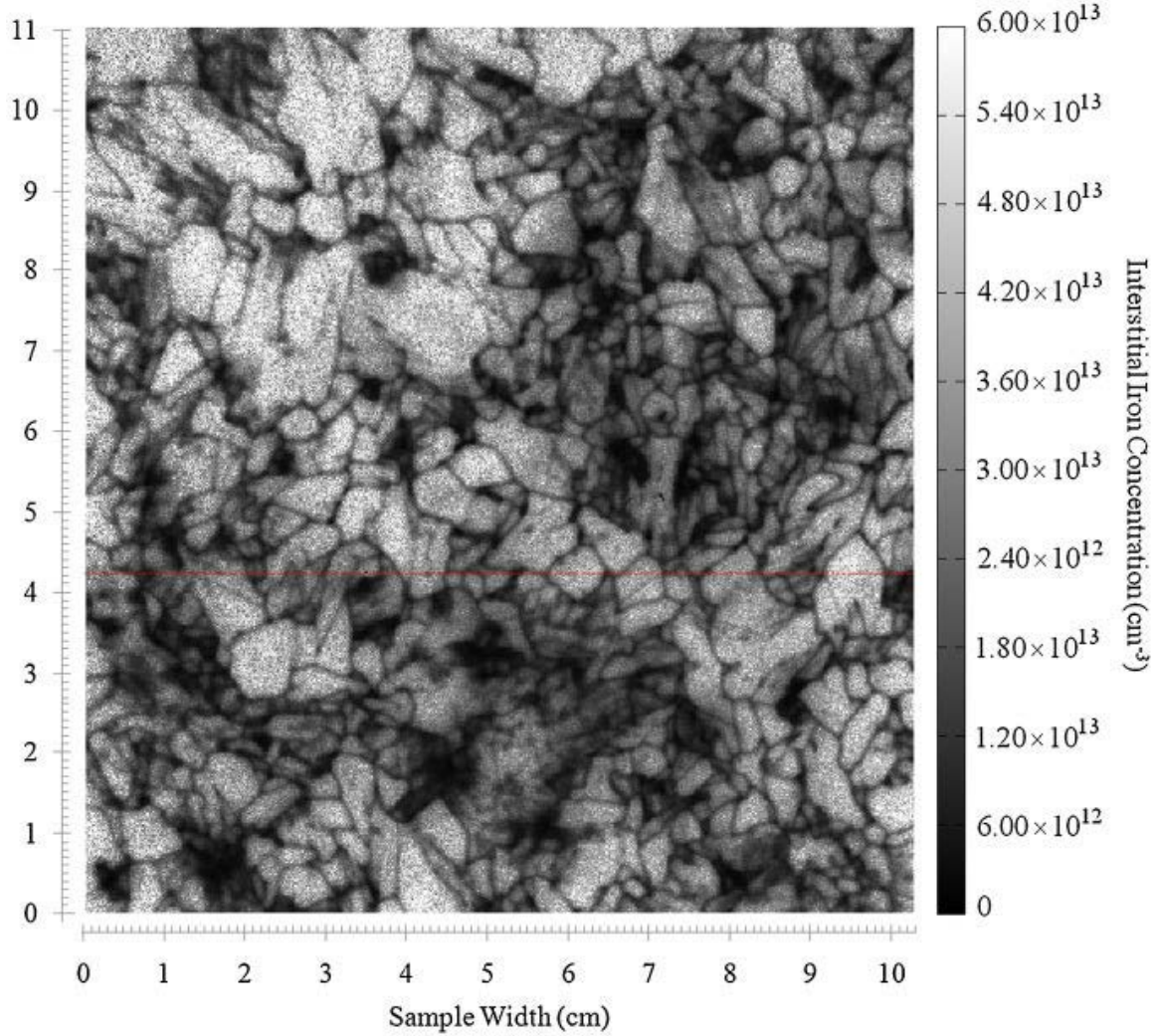




Macdonald and Geerligs, Appl. Phys. Lett. **85** 4061 (2004)

Fe images on mc-Si

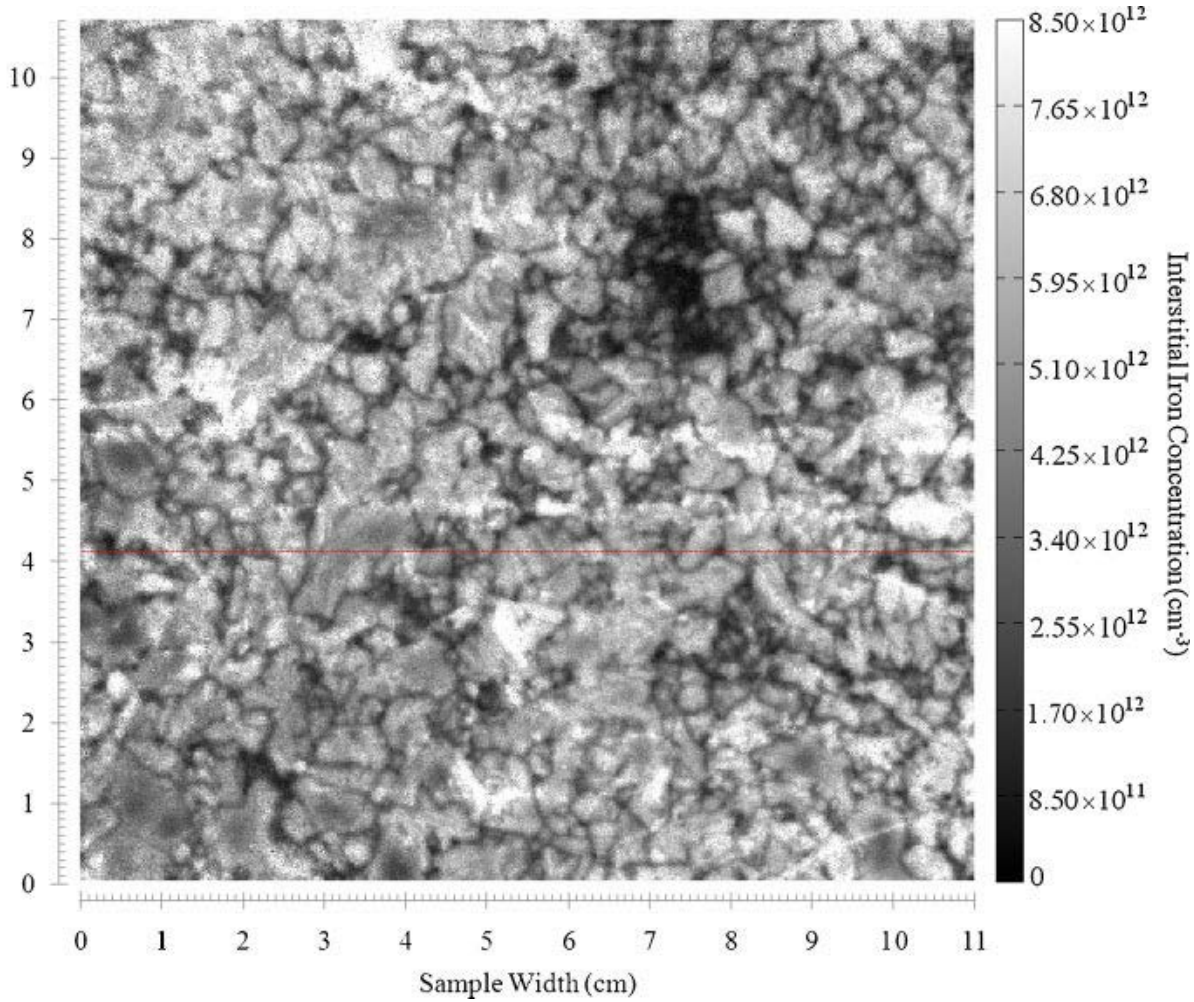
- Wafer 20% from bottom of ingot
- High [Fe_i] (10^{13} cm^{-3})
- Internal gettering of Fe during ingot cooling at GBs, dislocation clusters



Liu *et al.* Progress in PV, **19** 649 (2011)

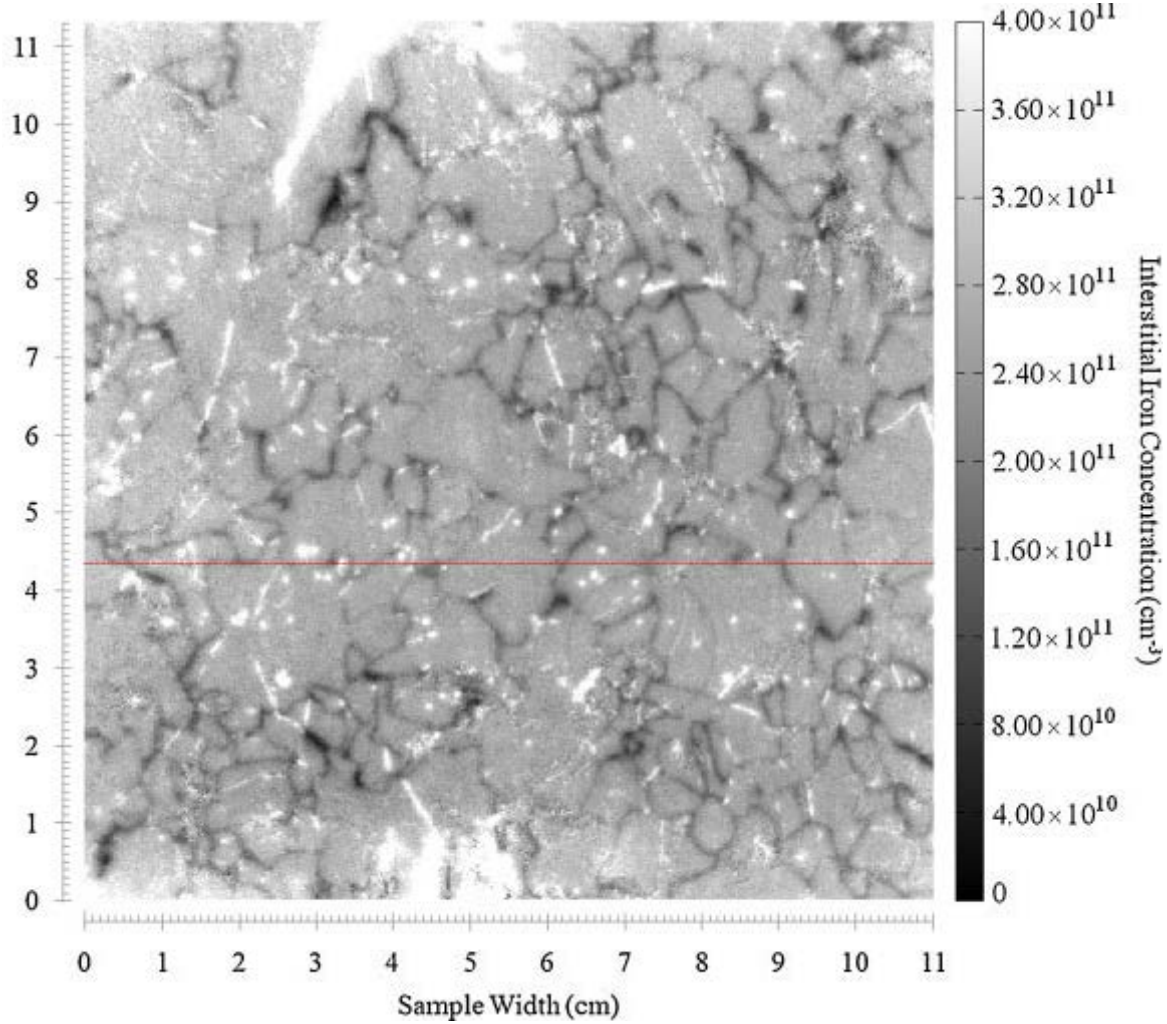
Fe images on mc-Si

- Wafer from near very bottom of ingot
- Moderate [Fe_i] (10^{12} cm^{-3})
- Small grains
- Fewer dislocation clusters
- Lower [Fe_i] *within* grains – presence of precipitation sites



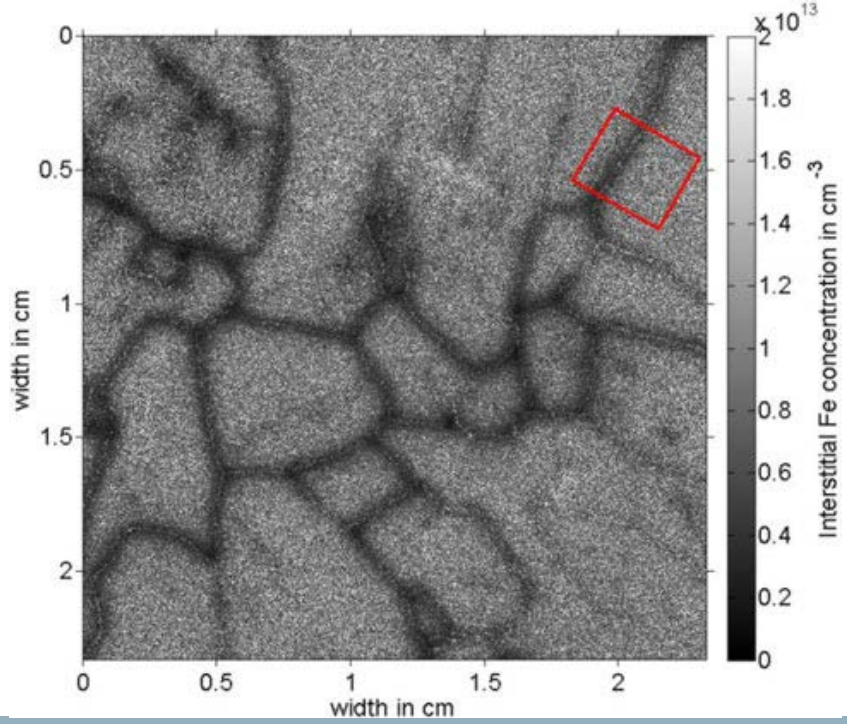
Fe images on mc-Si

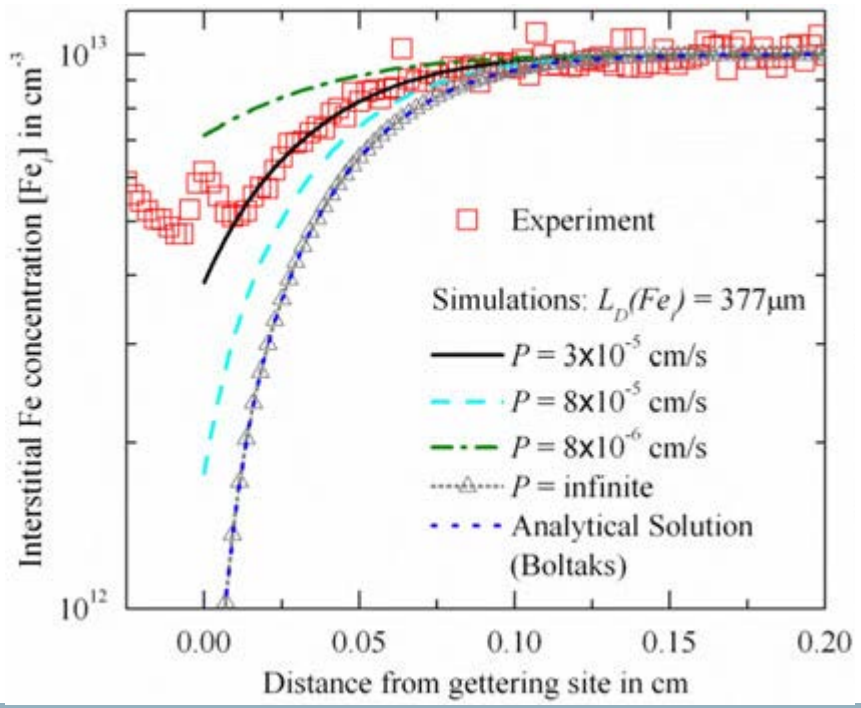
- Wafer from middle of ingot
- Low [Fe_i] (10^{11} cm^{-3})
- Reduced gettering at GBs (due to precipitation starting at lower T)



Internal gettering of Fe at GBs during ingot cooling

- Line-scans of PL images with resolution of 25 microns
- 1D diffusion/capture model – 2 free parameters – diffusion length of Fe_i $L_D(Fe_i)$ and precipitation velocity P of the GB
- Have to take care of PL artifacts!
  - Image smearing in the CCD camera - use point-spread function de-convolution
  - Carrier spreading in the sample – use low-lifetime – i.e. high [Fe_i] samples)

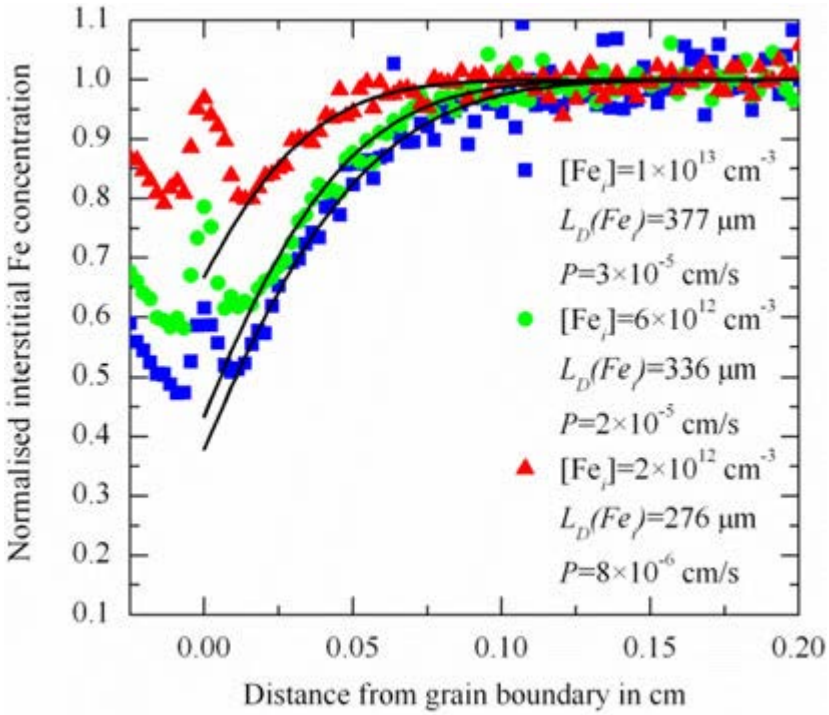


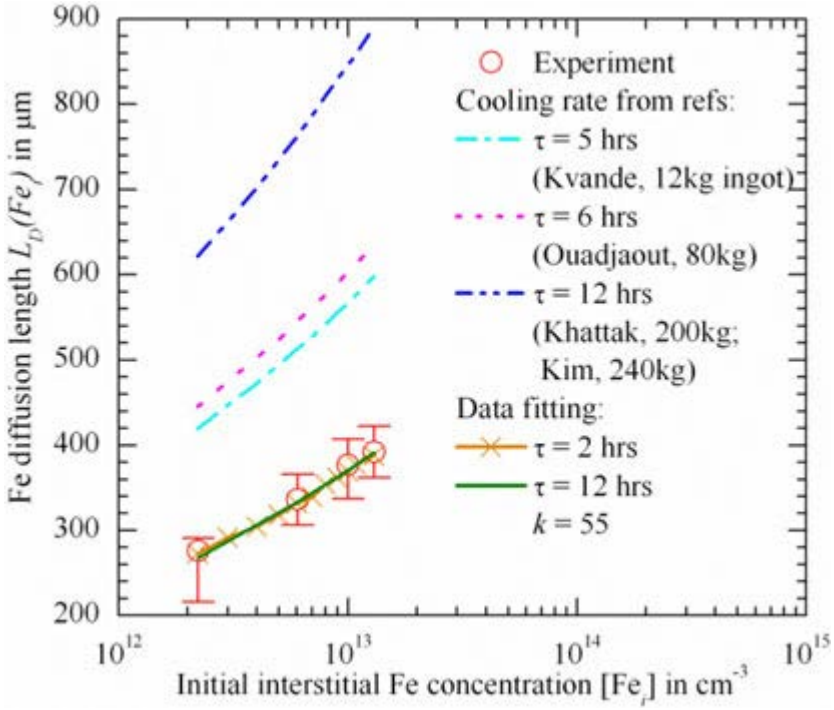


Liu and Macdonald, IEEE JPV **2**, 479, (2012)

Internal gettering of Fe at GBs during ingot cooling

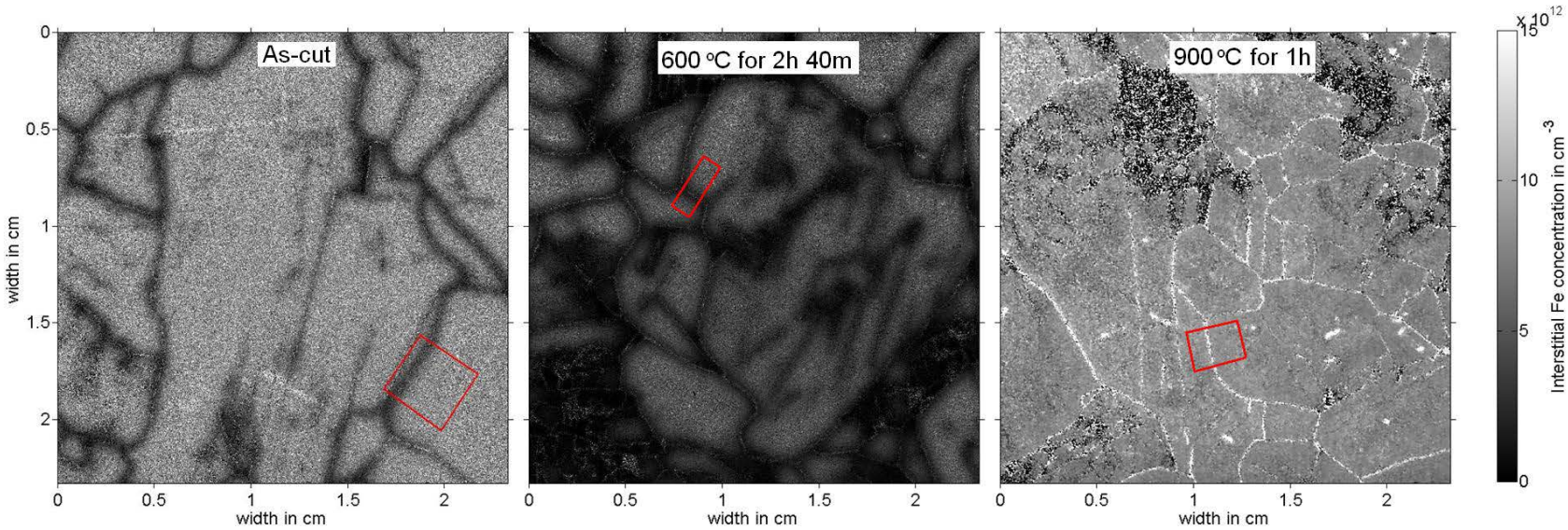
- Same GB on different wafers reveals diffusion length of Fe_i $L_D(Fe_i)$ depends on initial $[Fe_i]$
- Lower $[Fe_i]$ means that precipitation begins *later* during cooling
- Modelling ingot cooling time reveals data can only be explained if precipitation at GBs commences after super-saturation ratio of about 50 is reached!





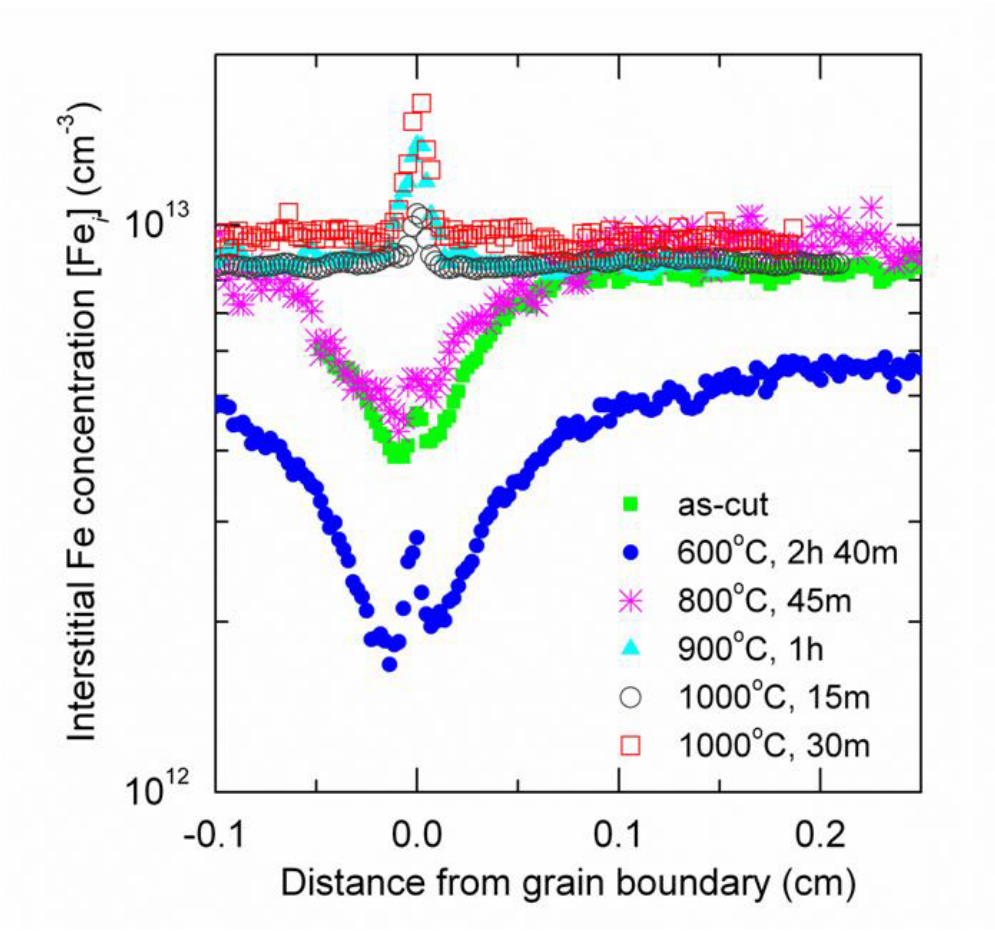
Internal gettering of Fe at GBs during annealing

- Annealing at low temps can drive further precipitation at GBs, and within grains.
- Higher temperatures tend to homogenise the dissolved Fe



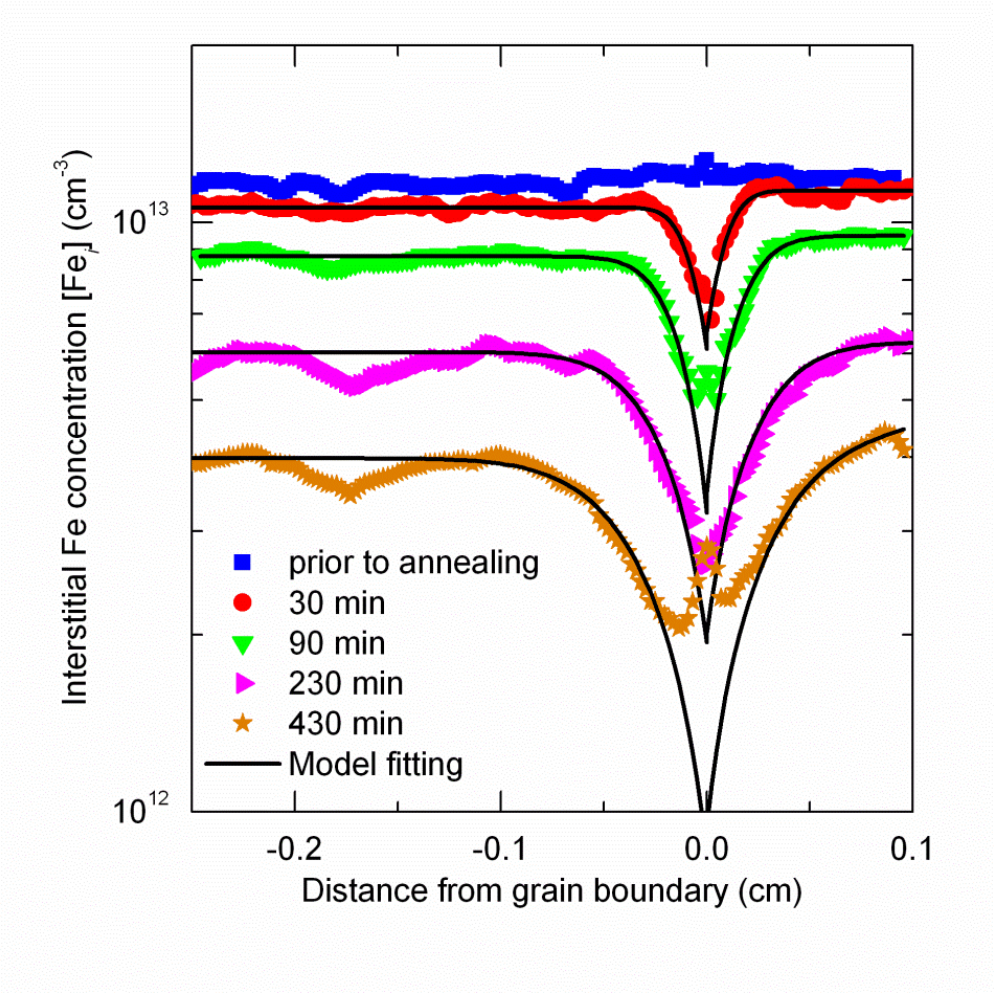
Internal gettering of Fe at GBs during annealing

- At 600 ºC, [Fe_i] is far above solubility limit:
  - Strong super-saturation
  - Drives precipitation at GBs, and within grains
- At 800 ºC, [Fe_i] is approx equal to the solubility limit:
  - No precipitation
- At 900 ºC and above, [Fe_i] is below solubility limit:
  - No precipitation
  - Homogenization by diffusion
  - Dissolution of precipitates also possible



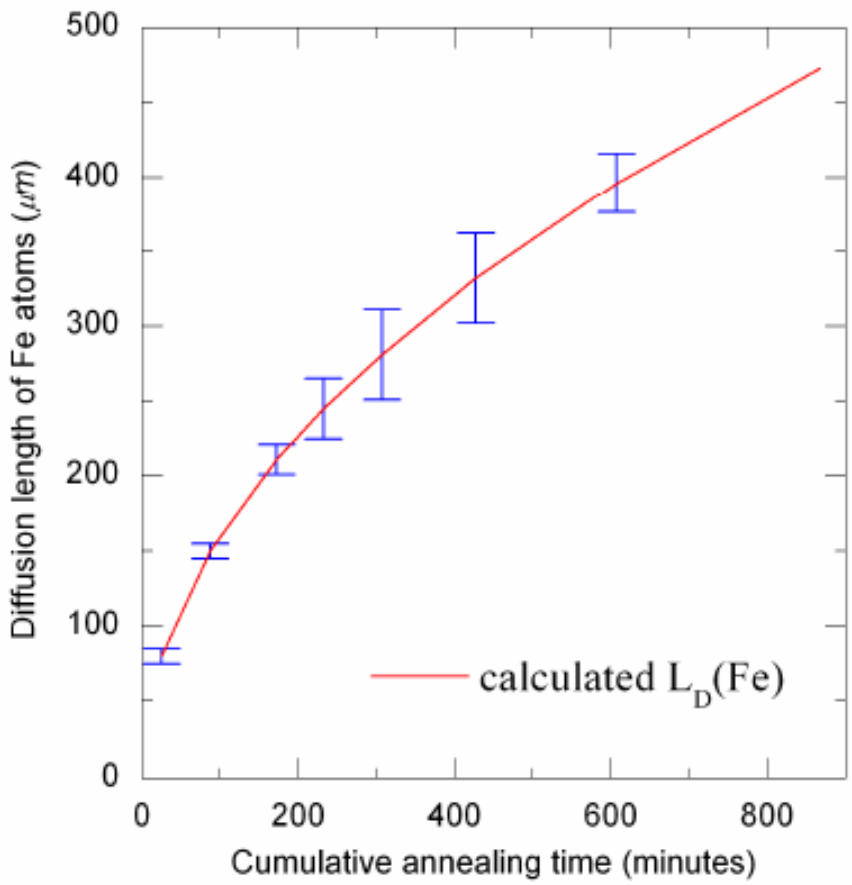
Internal gettering of Fe at GBs during annealing

- 500 C annealing for various times
- 1D diffusion/capture model:
  - Widening denuded zone
  - Reduced intra-grain $[Fe_i]$



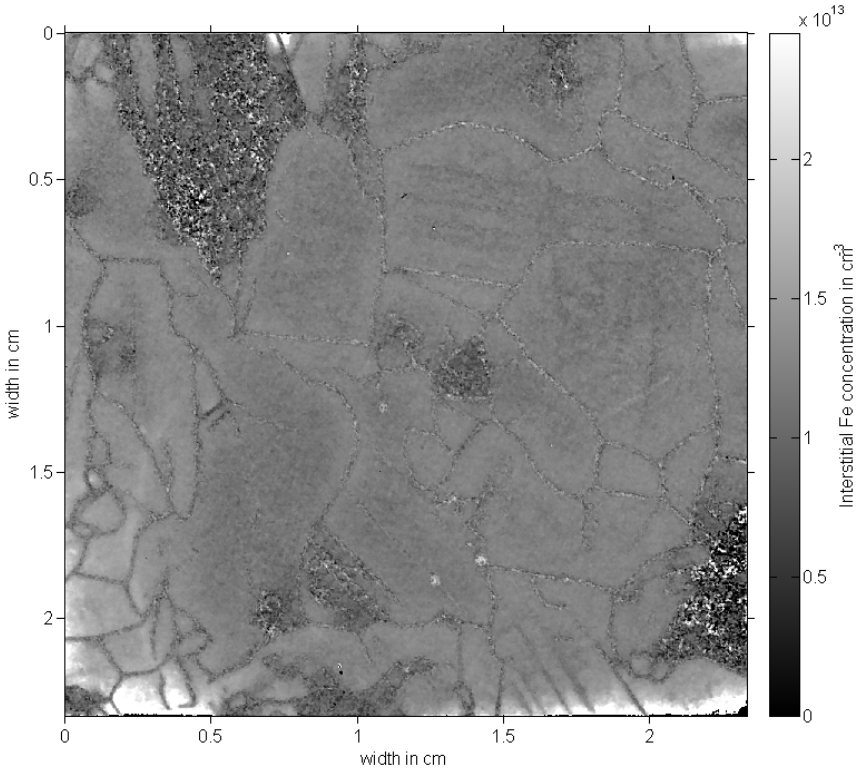
Internal gettering of Fe at GBs during annealing

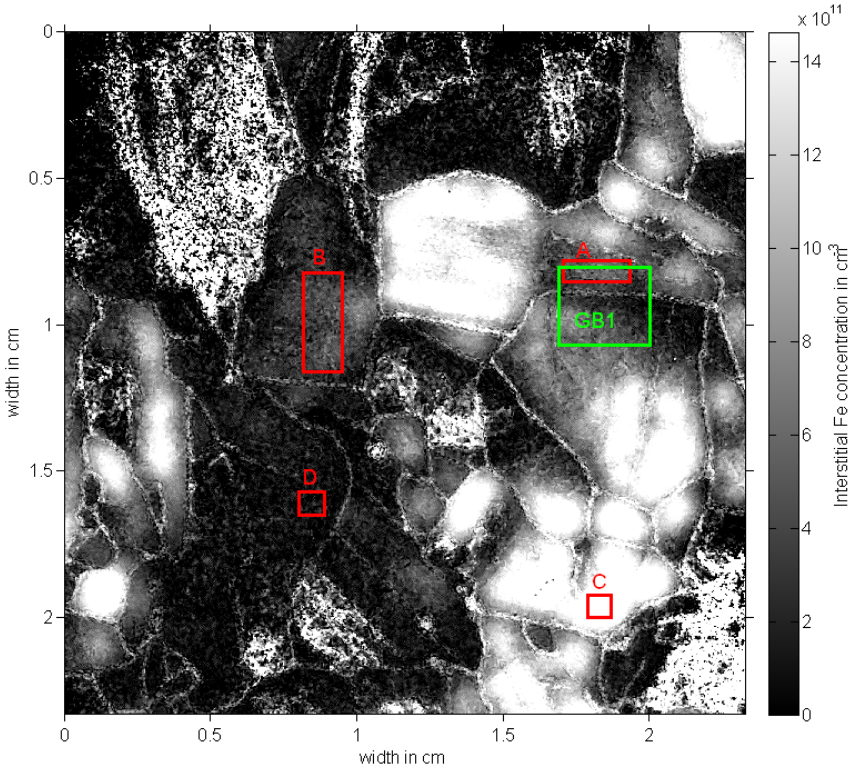
- At fixed temp annealing, diffusion length of Fe can be calculated from literature values.
- Very good agreement with fitted values (500 ºC)
- A method to measure diffusivity?



Internal gettering of Fe *within* the grains

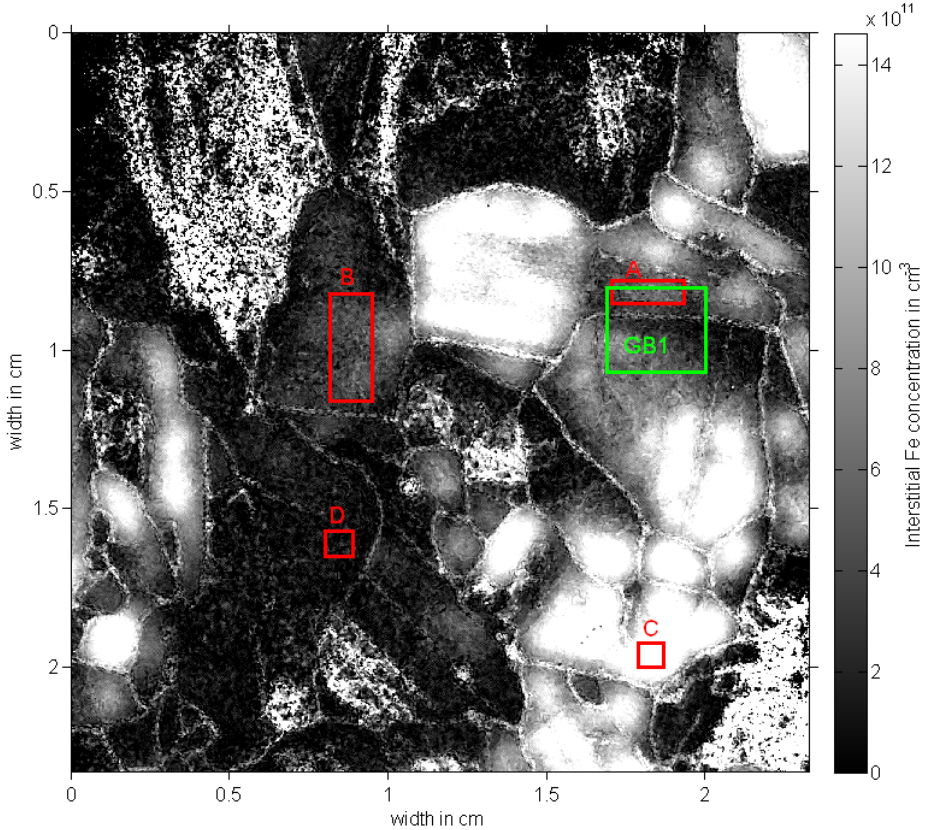
- After homogenization on left, after 14 hour anneal at 500 °C on right.
- Precipitation rate varies from grain to grain.

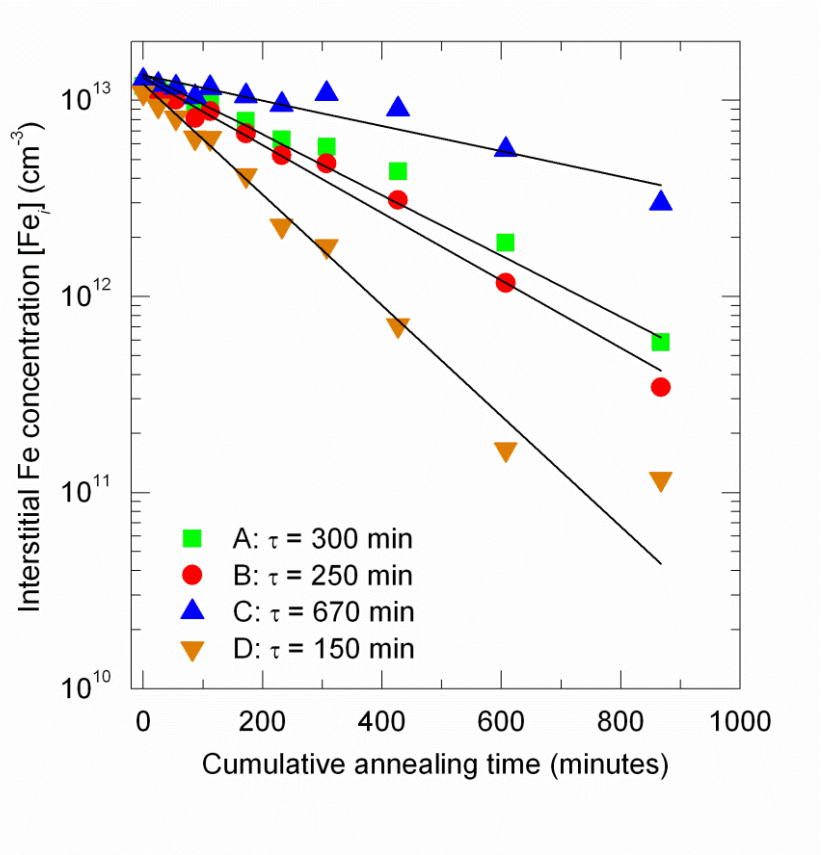




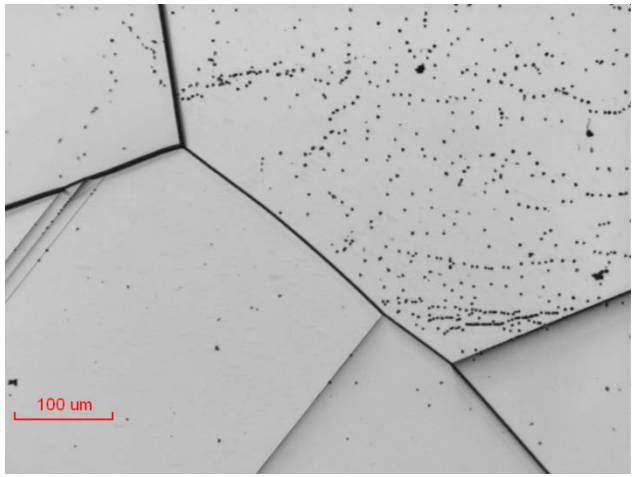
Internal gettering of Fe *within* the grains

- Precipitation rate varies despite initial Fe concentrations being similar

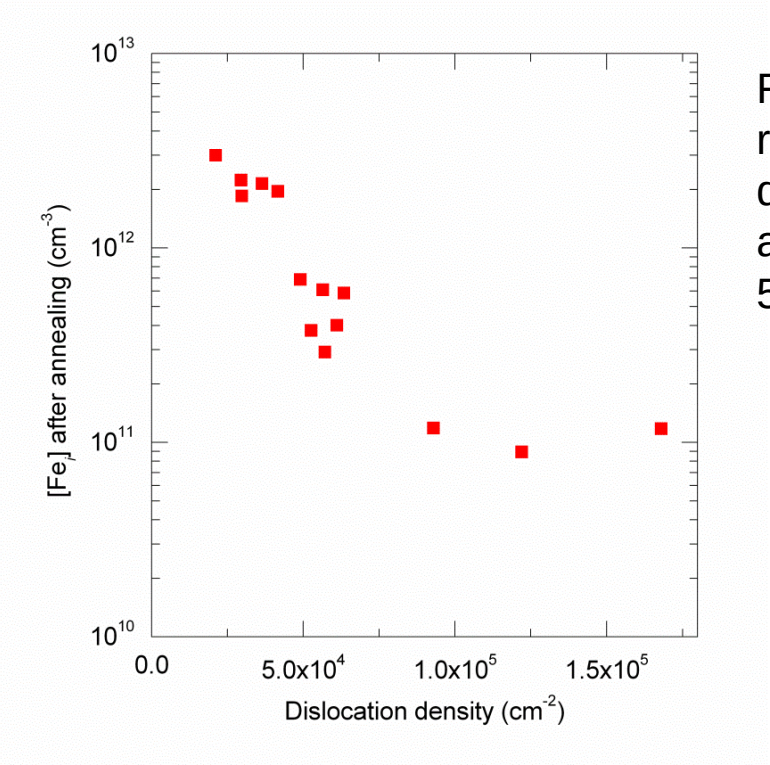




Internal gettering of Fe *within* the grains



Microscope image of a defect etched mc-Si wafer



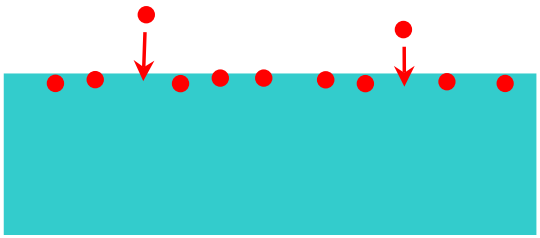
Final [Fe$_i$] with respect to intra grain dislocation density, after annealing at 500°C for 14.5 hours

- Less Fe precipitation in grains of low dislocation density
- Average distance between dislocations is less than Fe diffusion length
- Dislocations act as nucleation sites for Fe precipitation within grains

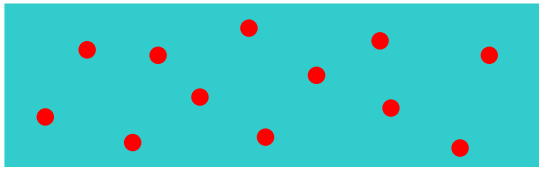
External gettering of Fe_i by P, Al and B diffusions

- Fe-implanted, annealed, mono FZ p-Si, detected by QSSPC.

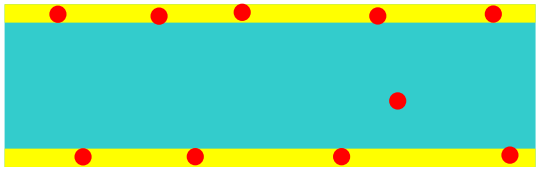
implant Fe



anneal

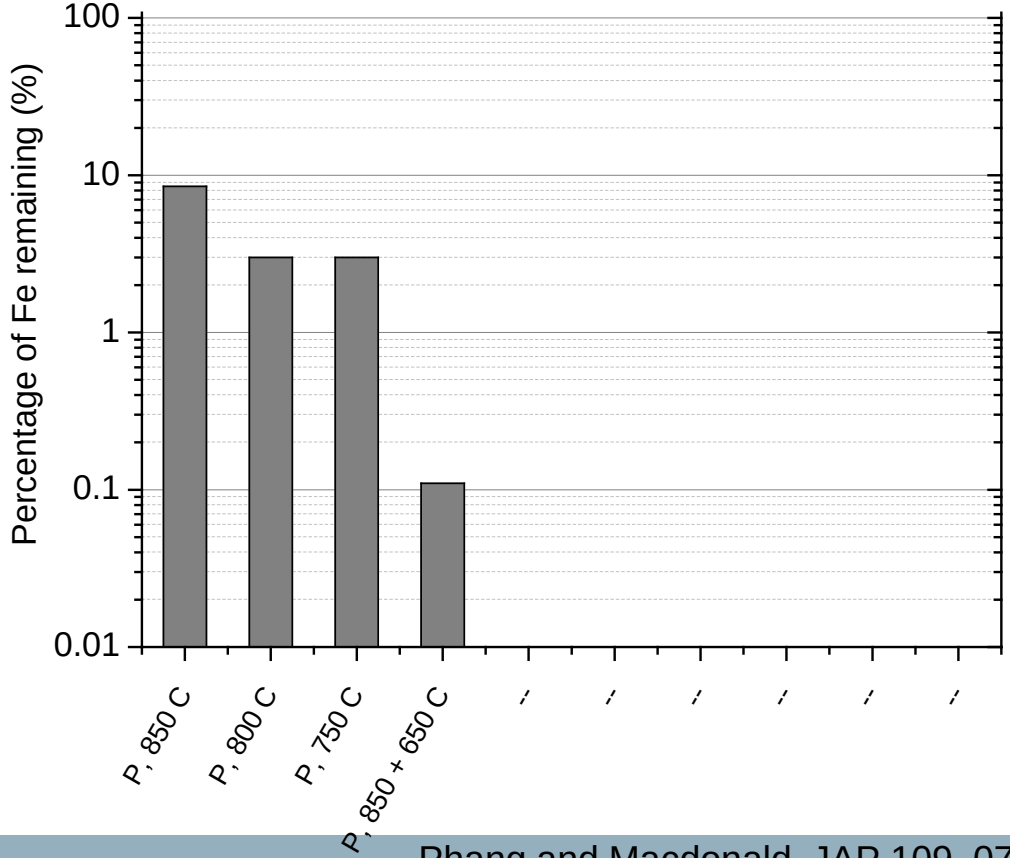


P, B or Al diffusion



Phosphorus gettering of Fe_i

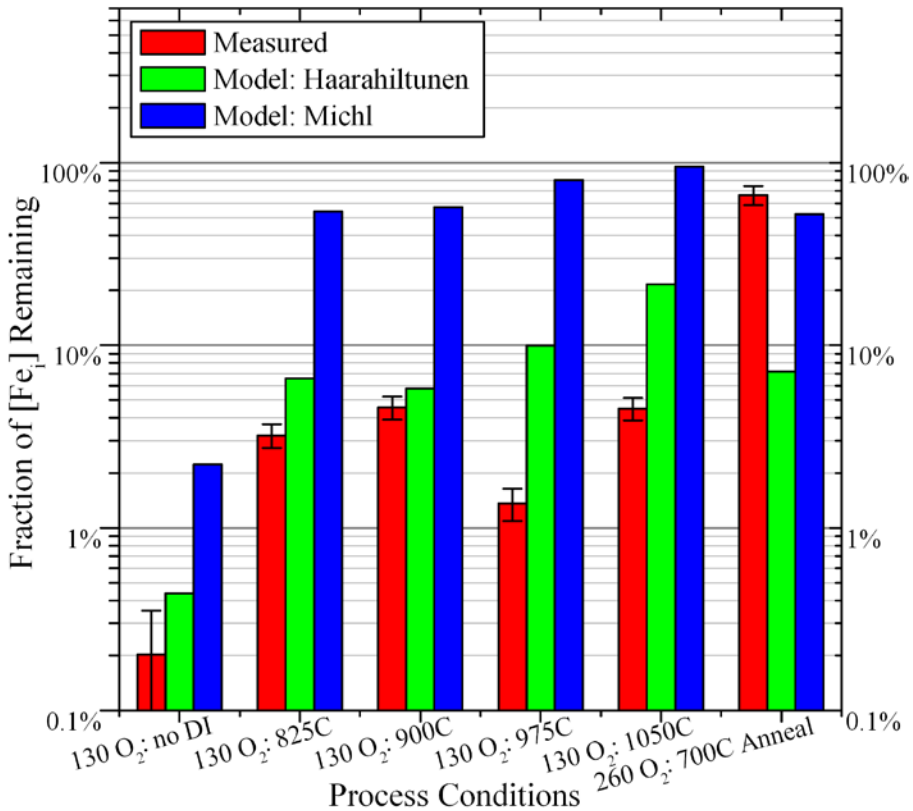
- P gettering removes between 90-99% of Fe – better at lower temp
- Adding a post-getter anneal improves gettering further – segregation ratio improves

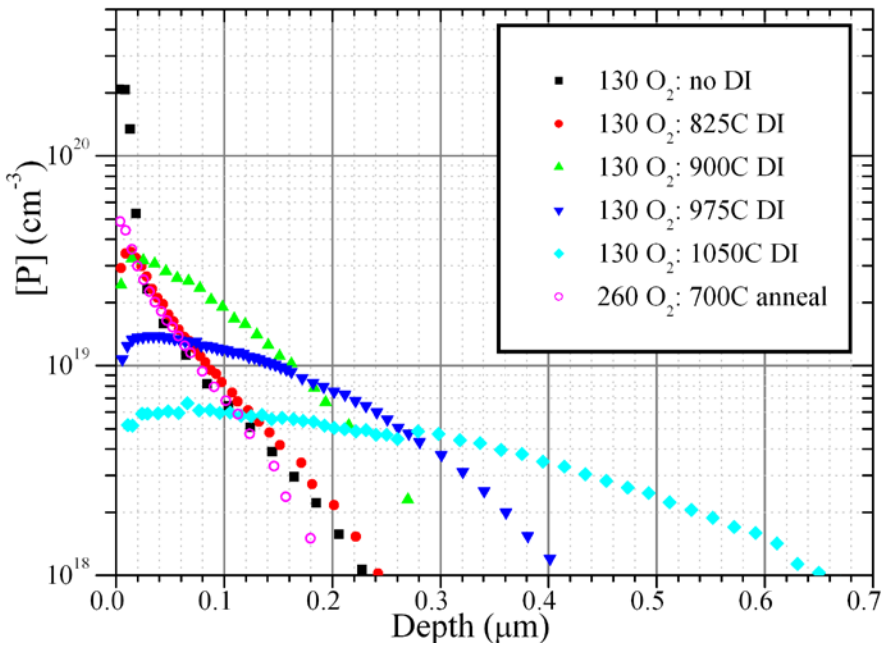


Phang and Macdonald, JAP 109, 073521 2011

Phosphorus gettering of Fe_i

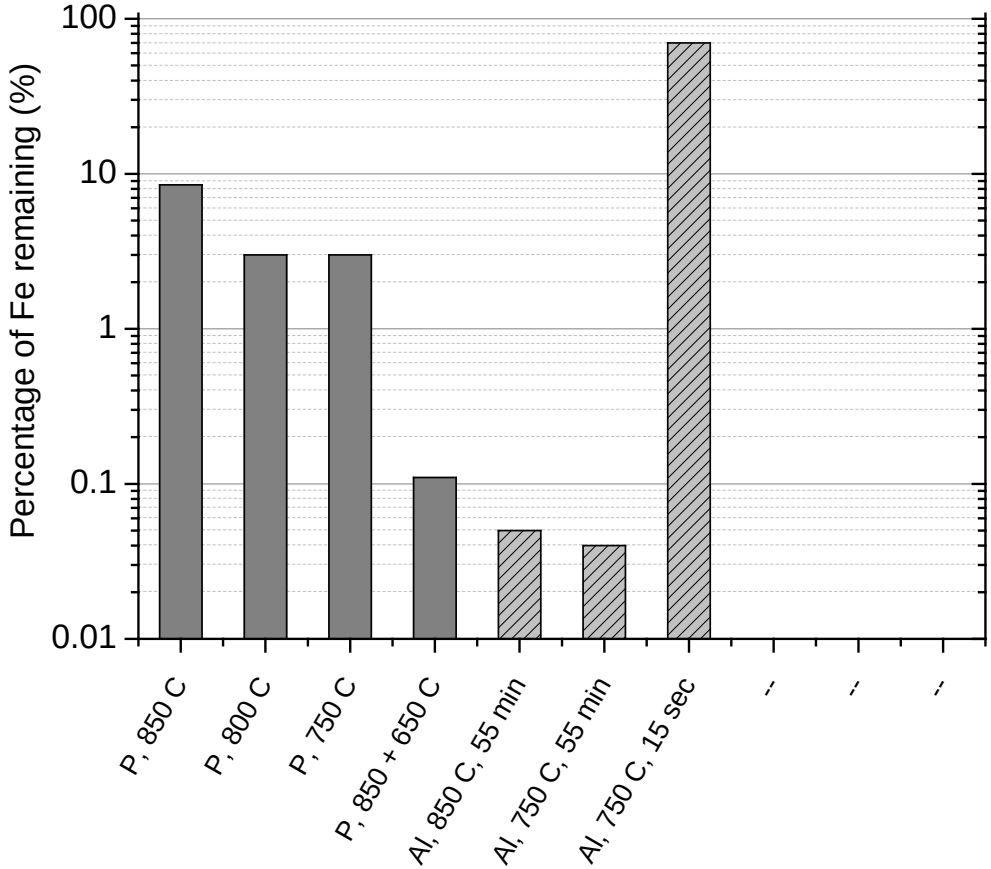
- Driving in P diffusion reduces gettering effectiveness
  - Very heavily doped region (>10^{20} cm^{-3}) required for best gettering

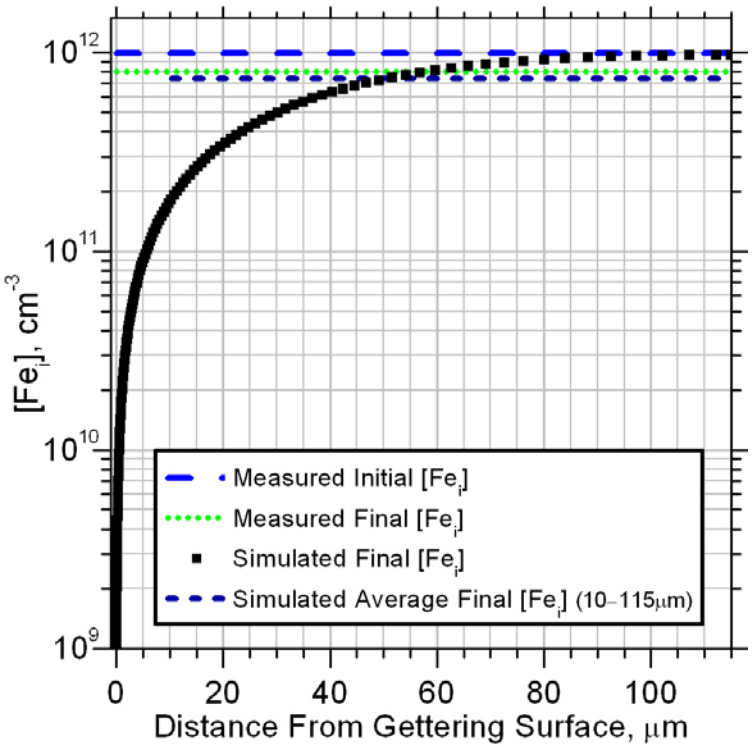




Aluminium gettering of Fe_i

- Al gettering removes more than 99.9%!
- However, typical BSF firing is too short for Al gettering to rear side…

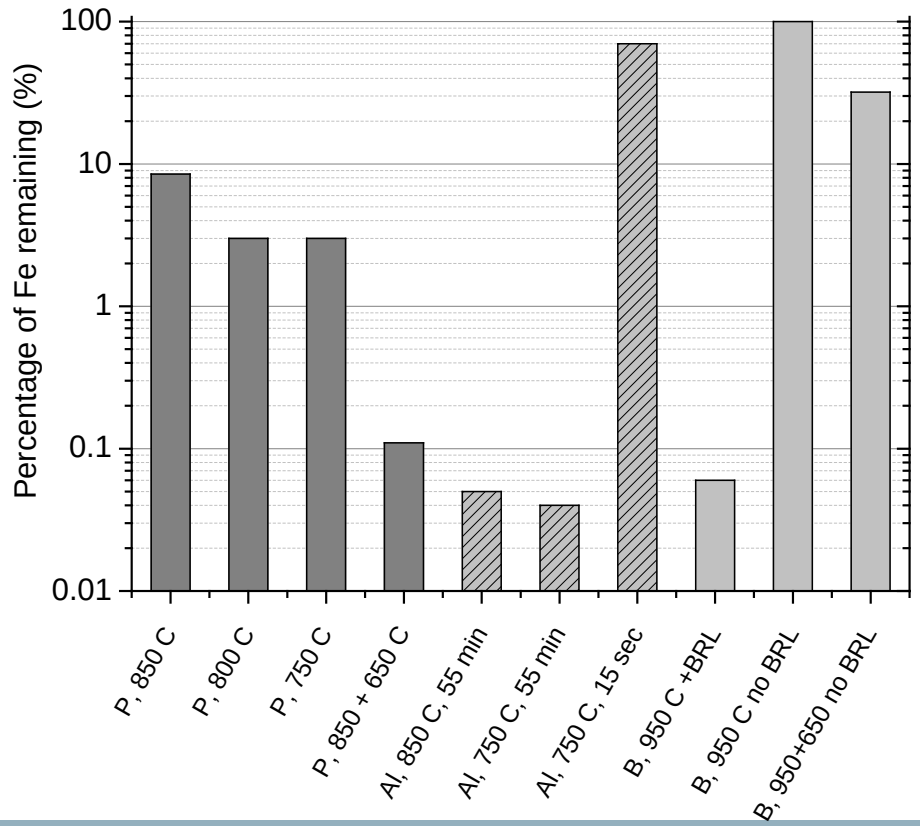


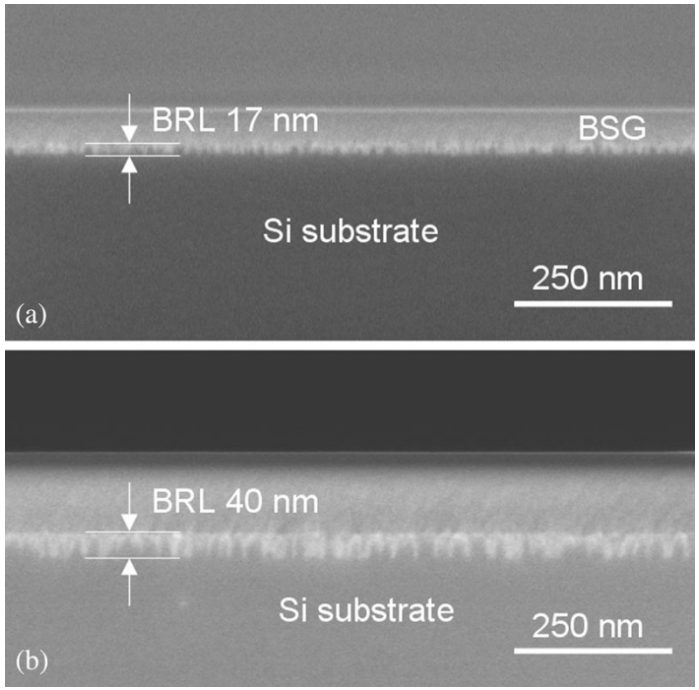


Phang and Macdonald, JAP 109, 073521 2011

Boron gettering of Fe_i

- B gettering very effective if Boron Rich Layer (BRL) is present.
- However, BRL is oxidised *in-situ* to allow low J_{oe} - re-injects Fe into base.
- Even a low temp anneal does not help much…

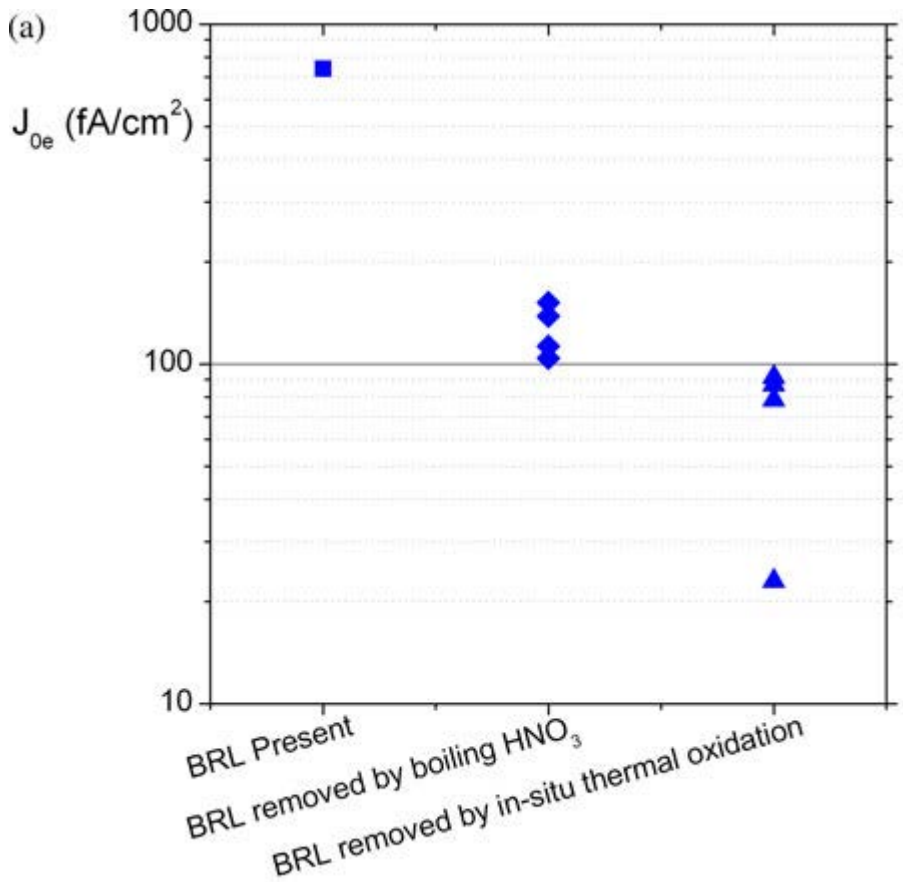




Phang *et al.*, IEEE JPV 3, 261, 2013

Boron gettering of Fe_i

- One solution is to remove the BRL at low temp by etch-back
  - Preserves gettering
  - Allows lower J_{oe}



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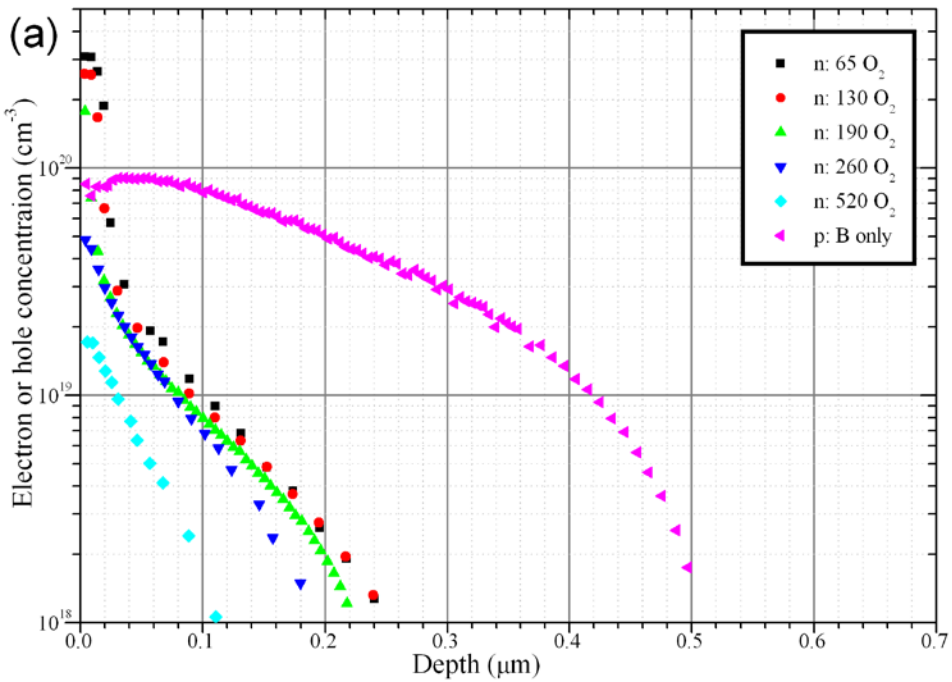
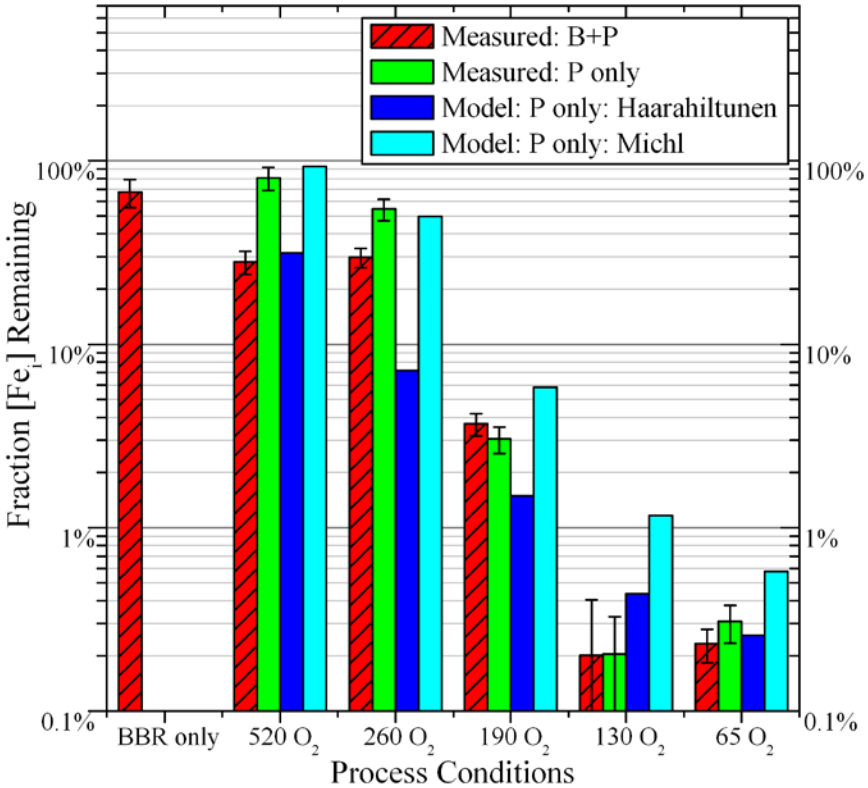
Boron gettering of Fe_i

- Another idea is to overlay a light phosphorus diffusion – ‘buried emitter’.
- Gives very good gettering





Conclusions

- Fe is common in mc-Si wafers, both dissolved and precipitated
- Dissolved iron more active in p-type than n-type due to charge state
- QSSPC allows very sensitive [Fe_i] measurements
- PL allows spatially resolved Fe imaging
- Gettering of dissolved Fe is critical for mc-Si cells
  - Internal gettering at GBs, dislocations and in intra-grain regions
    - Strong super-saturation required
  - External gettering via P, B or Al diffusions can be very effective
    - Al and B more effective than P
    - However, B diffusions require the presence of a BRL

Acknowledgements: this work has been supported by the Australian Research Council (ARC).