Characterisation of Individual Defects in Multicrystalline Silicon

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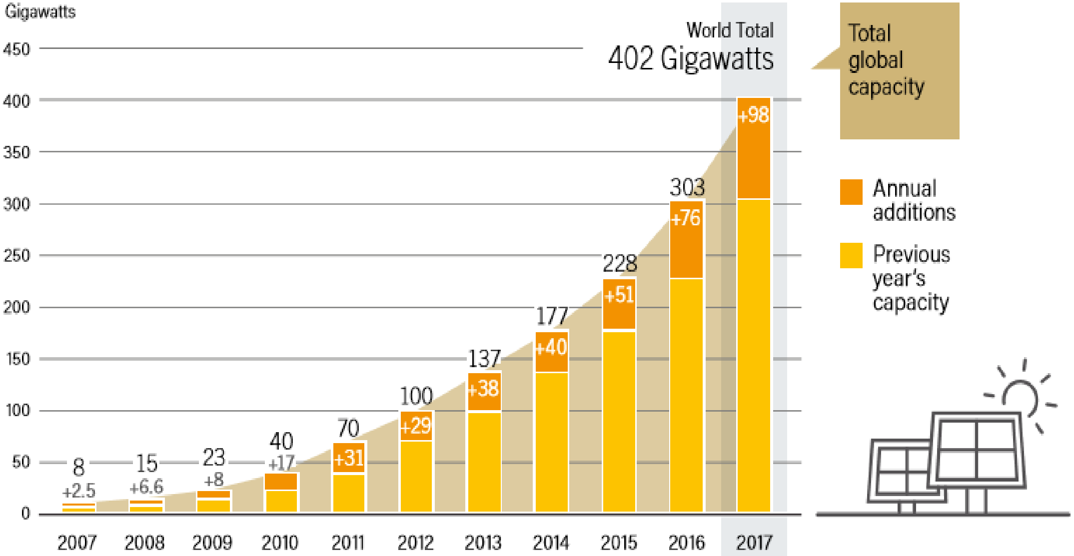
Multicrystalline Silicon (mc-Si) Solar Cells

- The solar industry is **rapidly** increasing its production capacity
- During 2017 photovoltaic capacity increased to 40,000 new solar panels being installed every hour [2]
- Year on year reduction in cost (6% decrease in 2017 to $0.39)
- Low cost mc-Si solar cells are the dominant industrial technology, over 60% of global module production [1]



[1] J. Jin 2015, Top Solar Power and Industry Trends

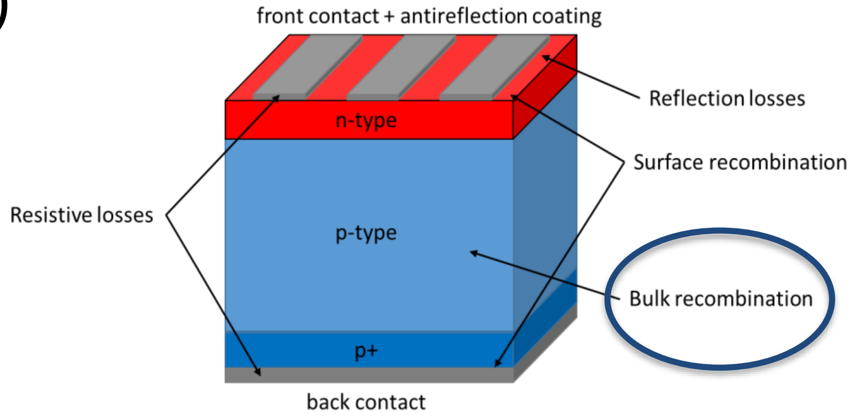
[2] Renewables 2017, Global Status Report

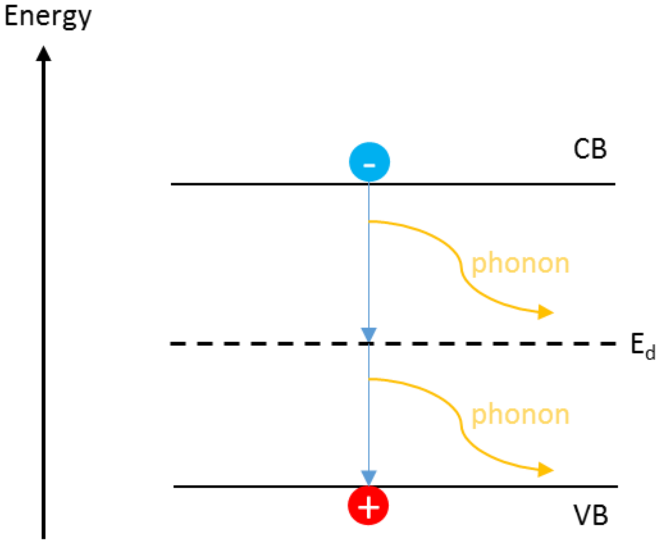
Multicrystalline Silicon (mc-Si) Solar Cells

- Although dominant, multicrystalline silicon is approximately 1% abs efficiency lower than monocrystalline
- Due to crystallographic defects
- These defects result in the formation of recombination active regions in the wafer, which limit the cell performance
- Understanding and characterising these regions is extremely difficult, since recombination can be enhanced by small levels of impurities concentrated at atomic scale defects

➡ Requires advanced microscopy

Photovoltaic cell with losses labelled





Recombination via defect levels

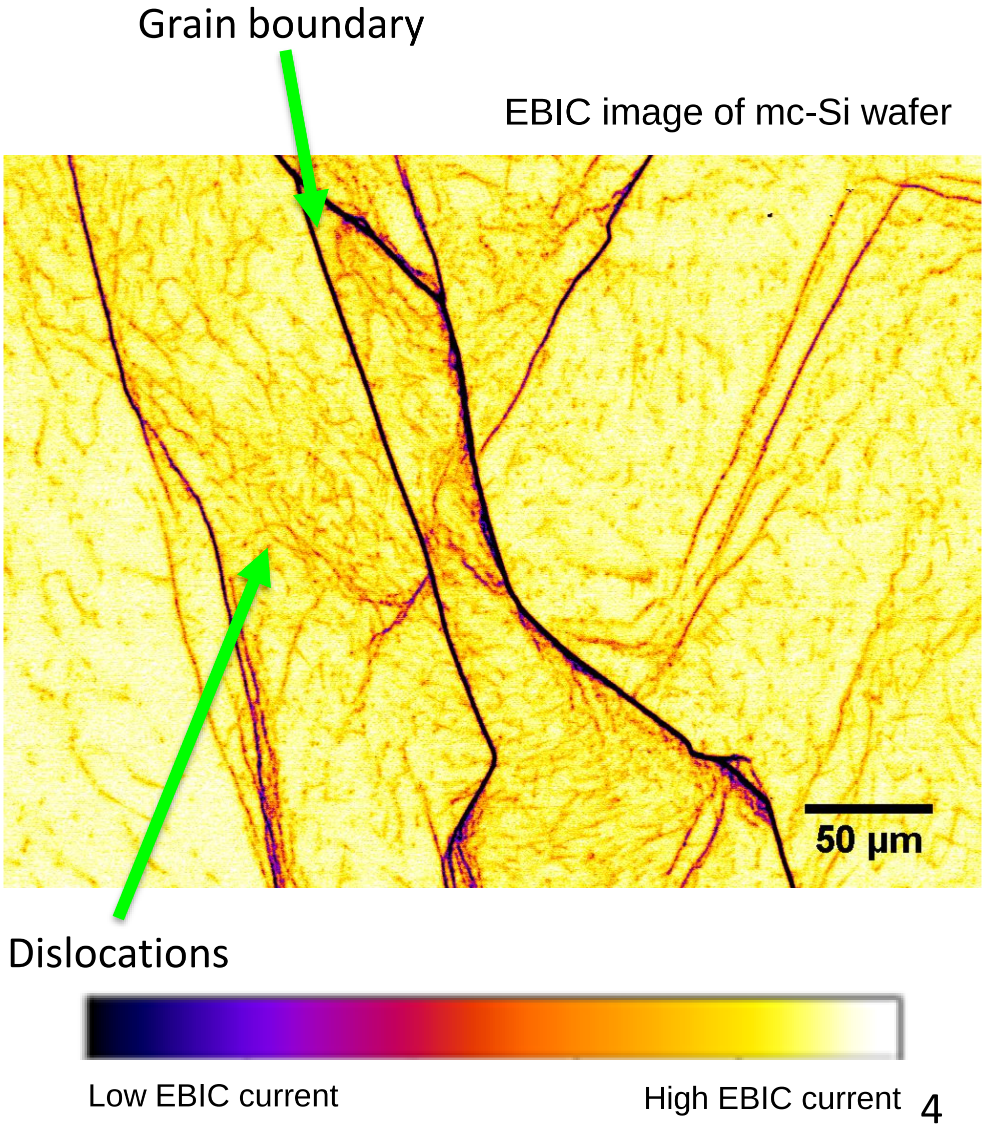
Areas of Recombination

- The recombination active areas consist of regions with a high concentration of crystallographic defects

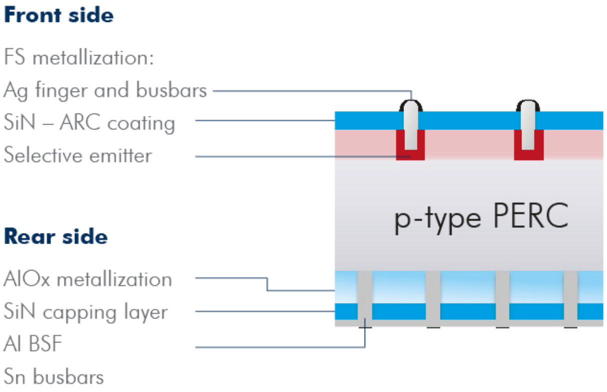
- Electron beam induced current (EBIC) map shows recombination

➡ Large quantities of recombination active grain boundaries and intragrain dislocations

- Small amounts of impurities (e.g. transition metals) decorate these defects and cause recombination



Gettering and Passivation



Industry uses two key treatments to improve the electrical properties of mc-Si:

- **Gettering** is the removal of (some) electrically active impurities to less critical regions
  - e.g. Phosphorus diffusion gettering (PDG), occurs during cell diffusion process and results in impurities being collected immediately adjacent to the cell surface
  - Cleaner dislocations and grain boundaries are less electrically active

- **Hydrogen Passivation** (HP) introduces **atomic** hydrogen which bonds to (some) crystallographic defects and impurities, reducing their recombination activity

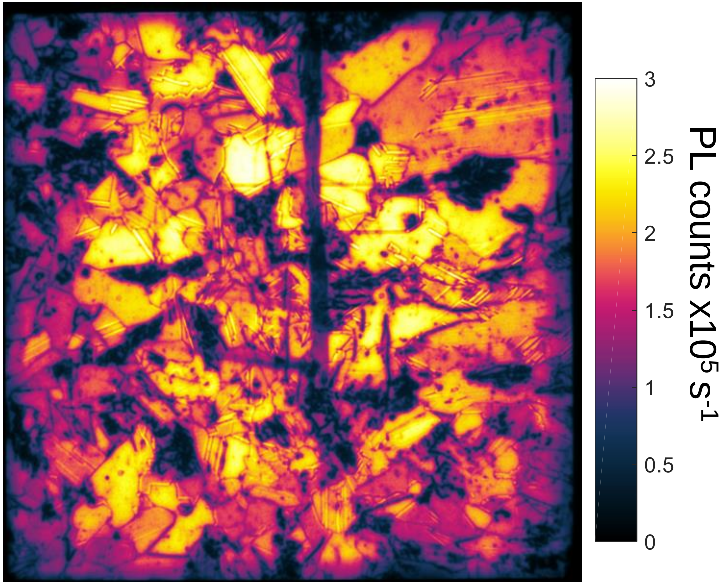
  - e.g. Hydrogen in-diffusion from dielectric layers (SiN and AlO_x) during high temperature firing

Image Courtesy of Institute for Solar Energy Research Hamelin (ISFH)

Aims

- Characterise the crystallographic defects in multicrystalline silicon
- Why is the combination of gettering and hydrogen passivation not always effective?
- Which impurities + defects are especially harmful to cell efficiencies?

➡ Need – a multiscale method which can provide a detailed characterisation of a mc-Si wafer at various stages of processing

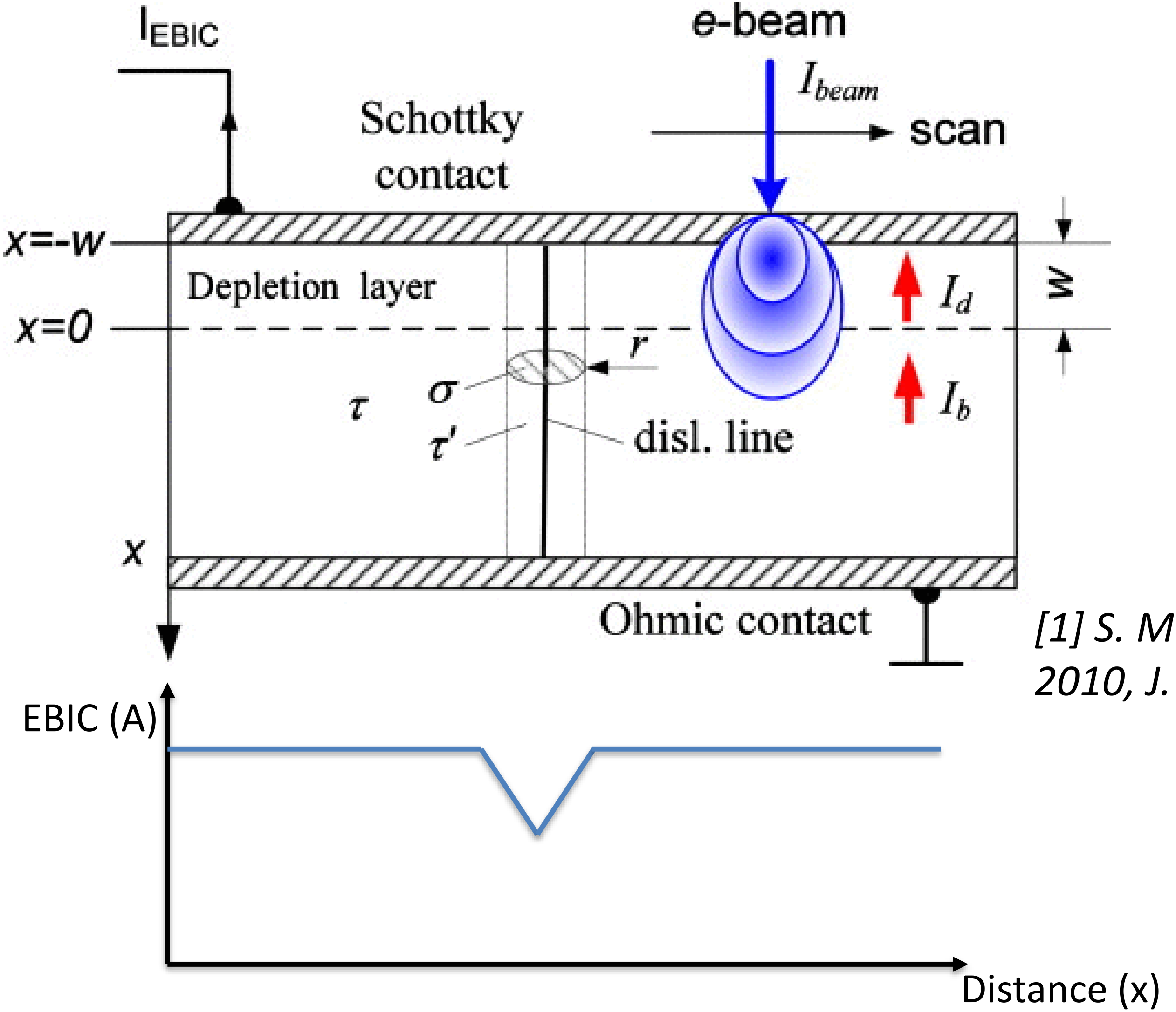


PL image of a p-type wafer post Phosphorus Diffusion Gettering + H passivation

Multi-microscopical approach

- Macroscale:
    - **Bulk Lifetimes**
    - **Photoluminescence (PL)**
    - Total impurity concentration measurements
- Microscale:
    - **Electron Beam Induced Current (EBIC)**
    - Laser Beam Induced Current (LBIC)
    - Micro- photoluminescence (µ-PL)
- Nanoscale:
    - **Transmission Kikuchi Diffraction (TKD)**
    - **Transmission Electron Microscopy (TEM)**
    - **Atom Probe Tomography (APT)**
    - X-Ray Fluorescence (XRF)

Electron Beam Induced Current

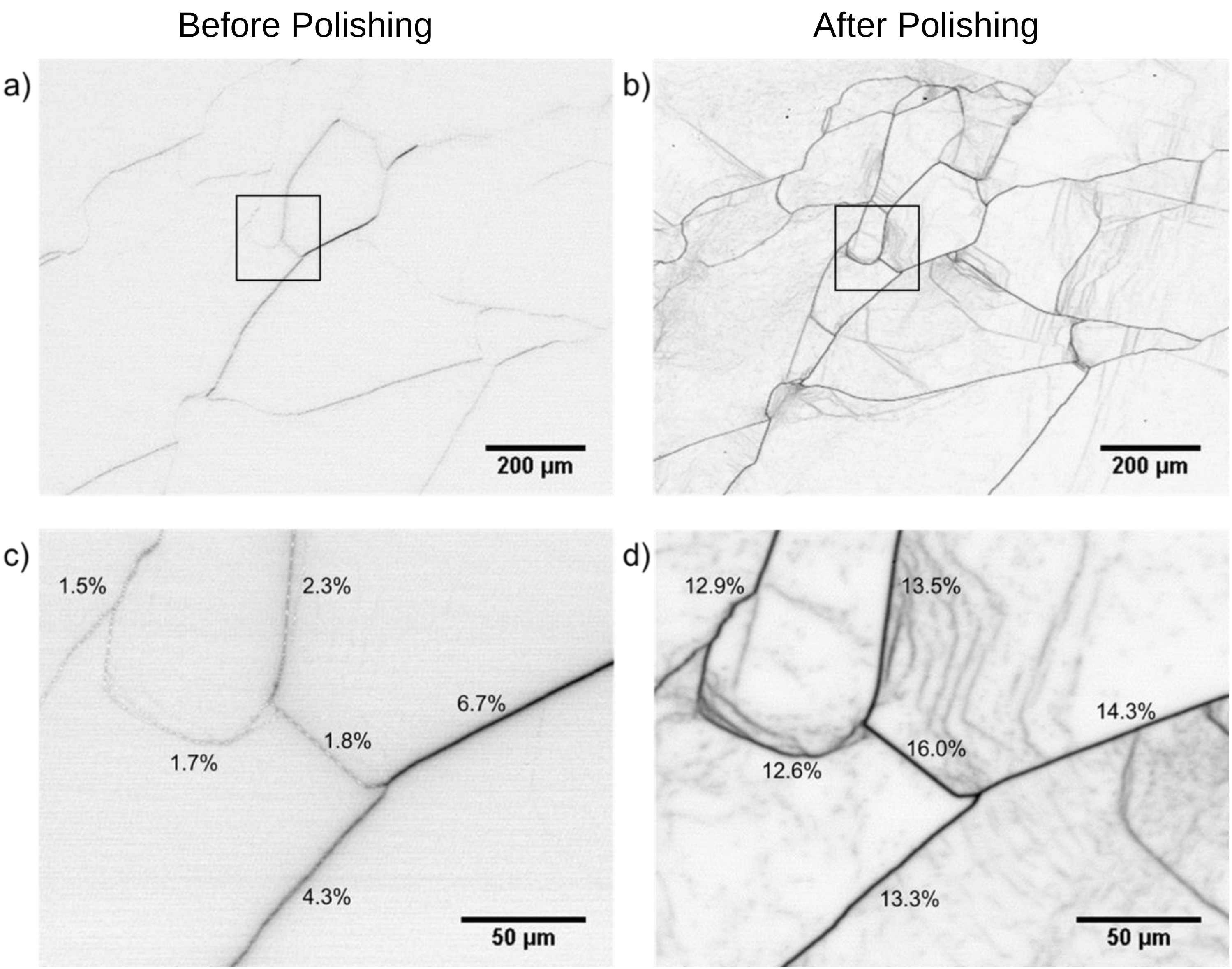


[1] S. Maximenko 2010, J. Appl. Phys.

Colloidal Silica Polishing

- Colloidal silica is a standard technique to produce flat surfaces prior to microscopy such as EBIC and APT
- Sample surface is polished for around 12 hours to ensure a 'mirror finish'
- We found that lifetimes QSS-PC (photoconductance) crashed, as confirmed in PL
- EBIC and APT employed to determine whether room temperature diffusion of impurities has occurred
- Wafer shown before and after polishing

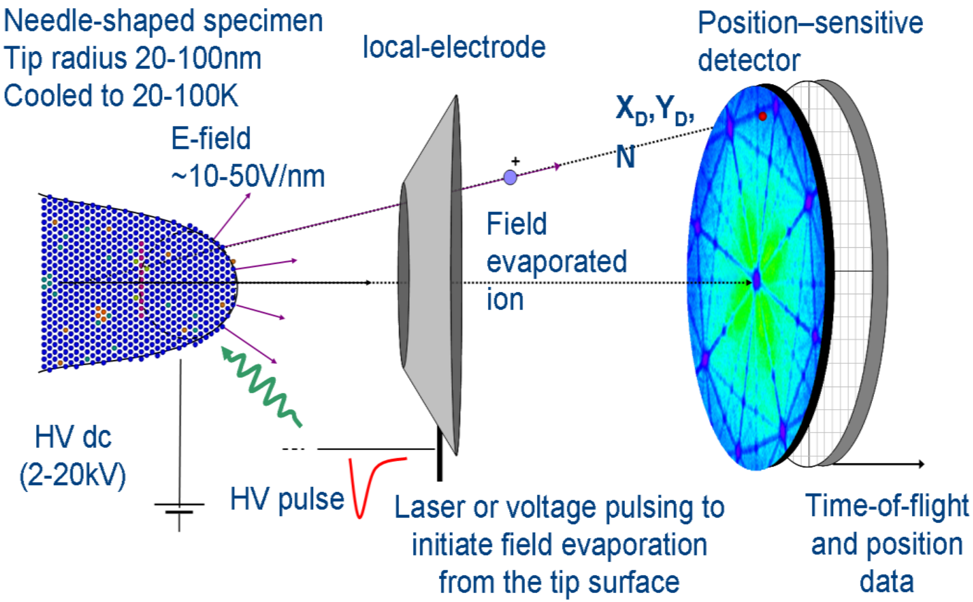
Colloidal Silica Contamination - EBIC



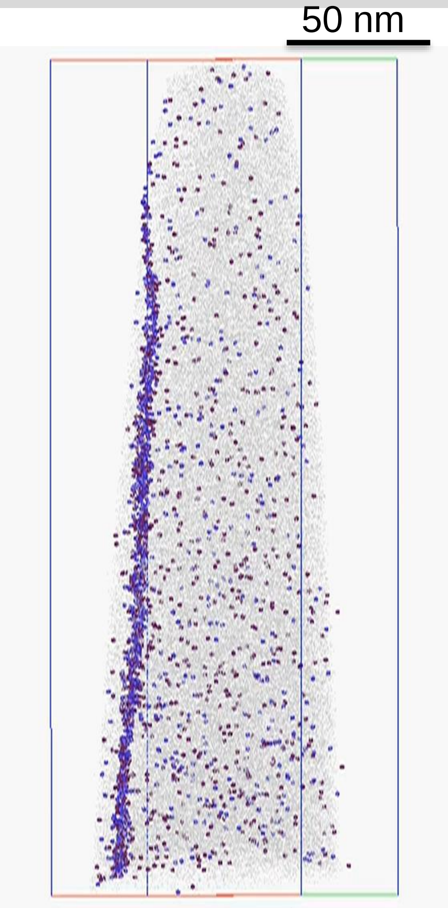
Before Polishing

After Polishing

Atom Probe Tomography



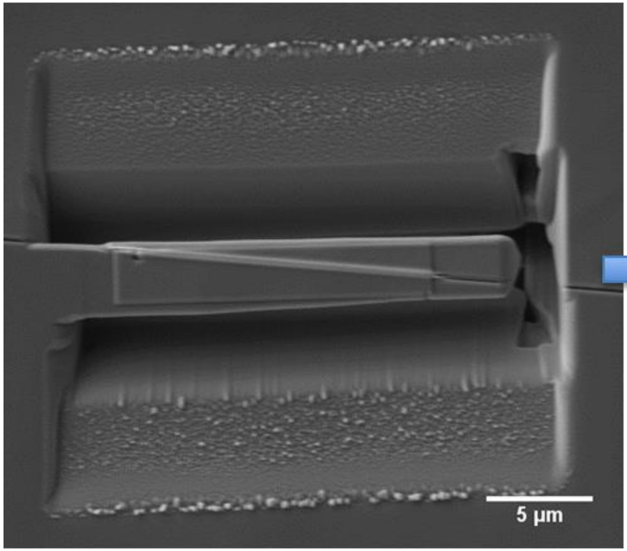
B. Gault, 2010, Micro & Microanal 16(01)



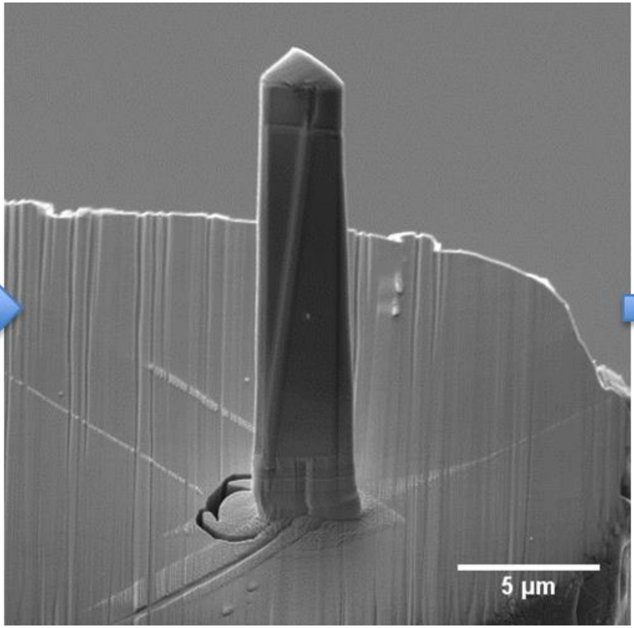
APT is an established technique it allows:

- Atomic scale resolution of atom positions
- Time of flight mass spectroscopy gives chemical species
- Needs a needle specimen of diameter 100nm
- Atoms in the bulk are difficult to separate from background noise

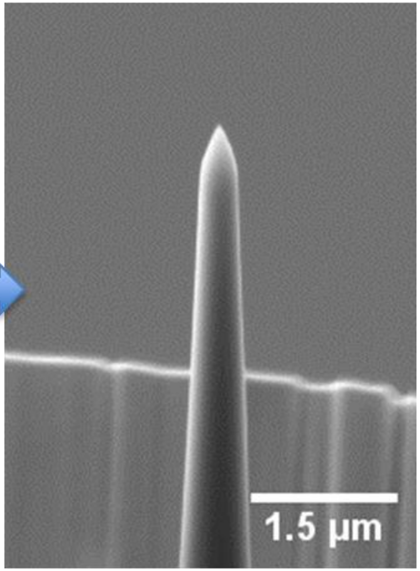
Atom Probe Tomography



Grain boundary (GB) marked by E-beam deposited W and undercut using FIB methods



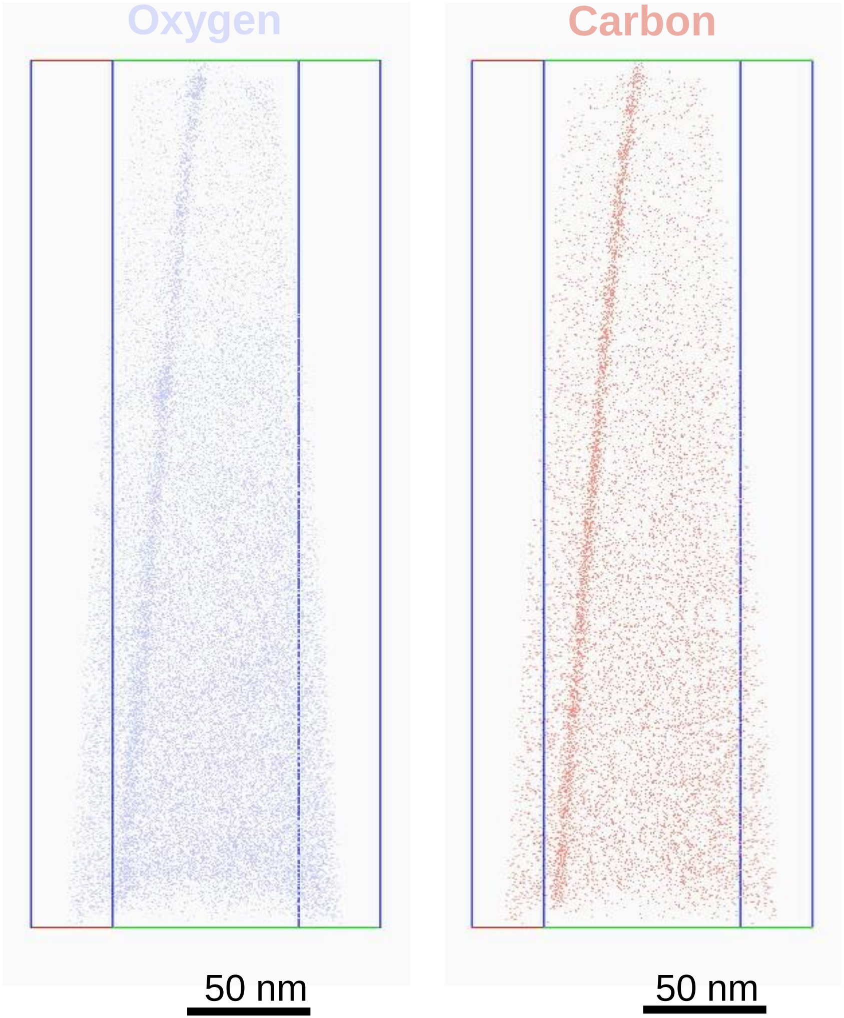
End-on liftout upon a FIB TEM half grid with end flattened using FIB



APT needle (d ≈ 100nm) produced with grain boundary running along the tip

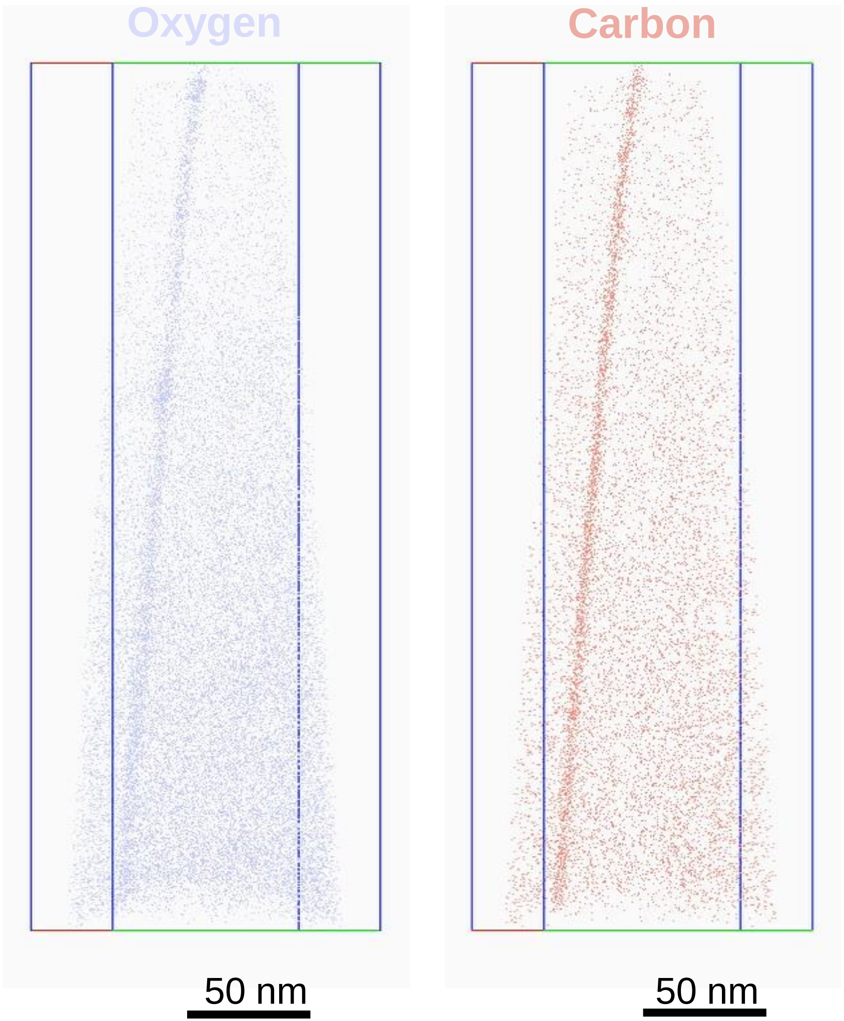
Colloidal Silica Contamination - APT

Before Polishing

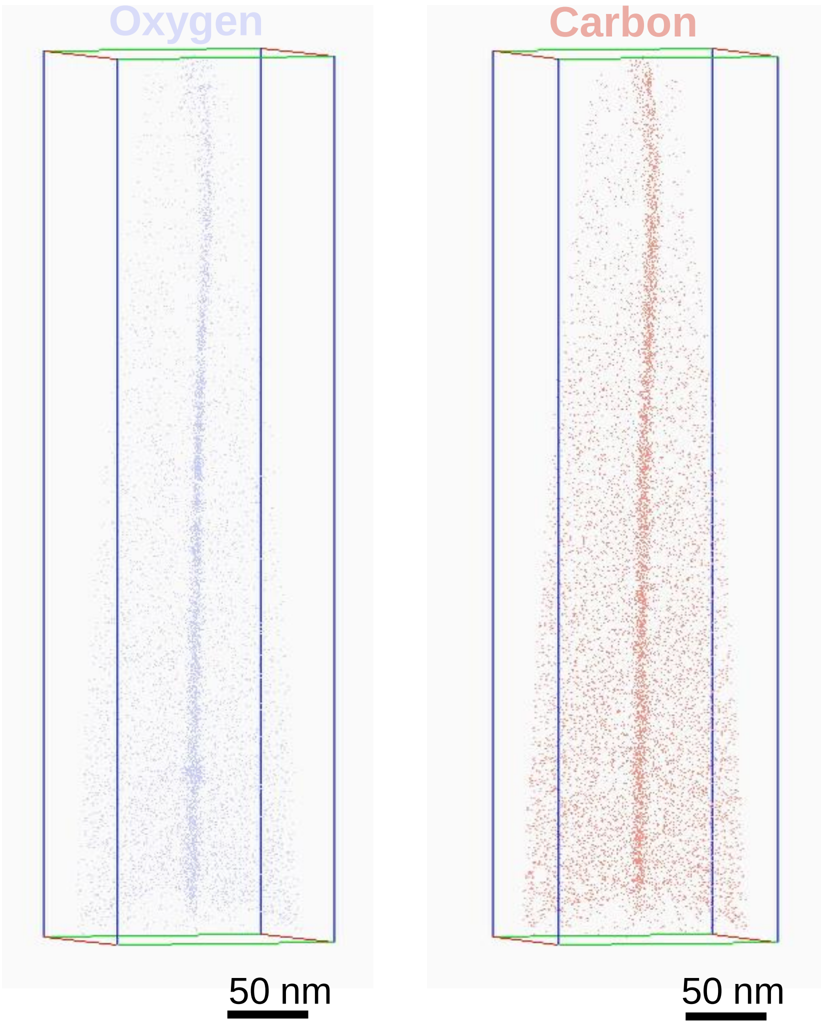


Colloidal Silica Contamination - APT

Before Polishing



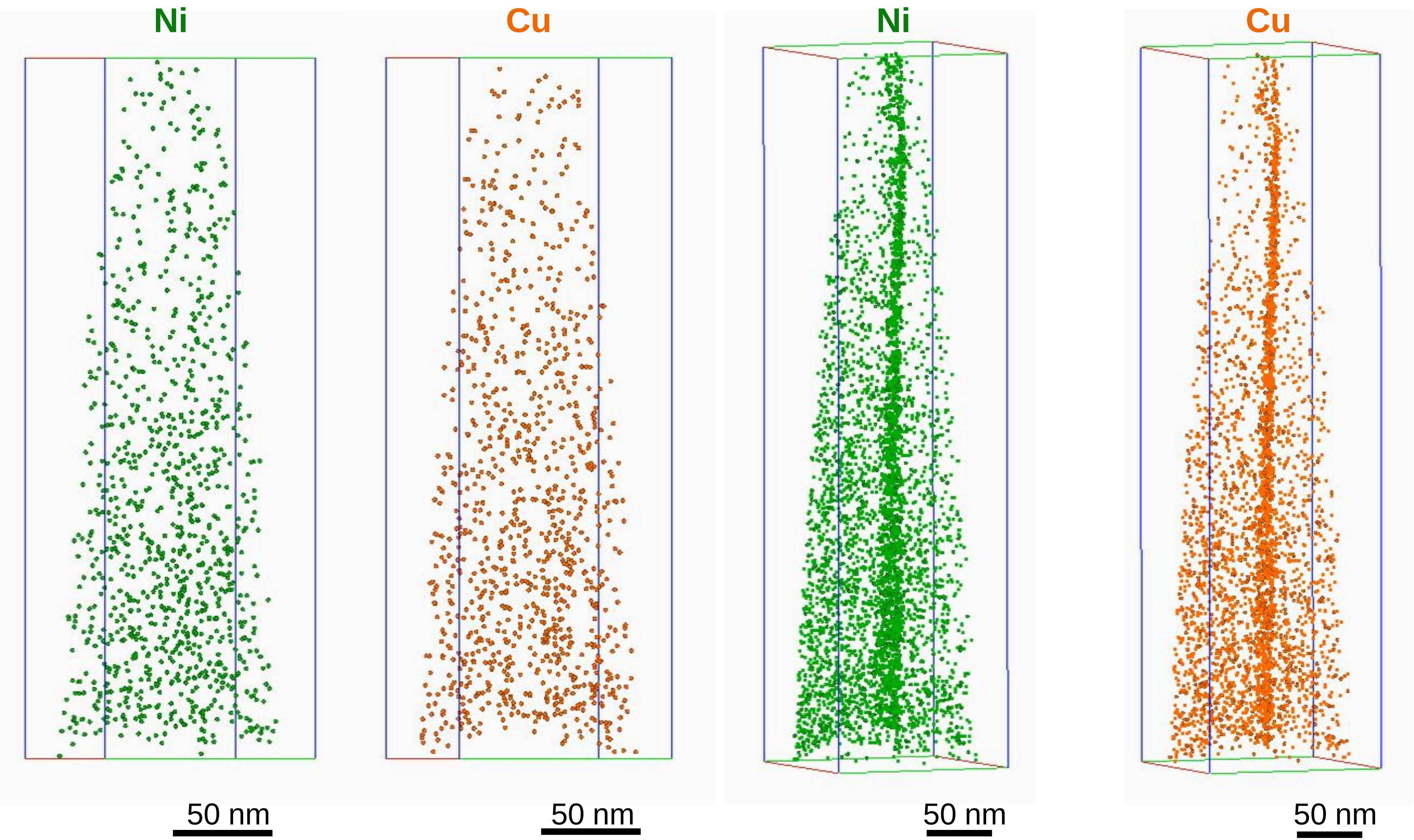
After Polishing



Colloidal Silica Contamination - APT

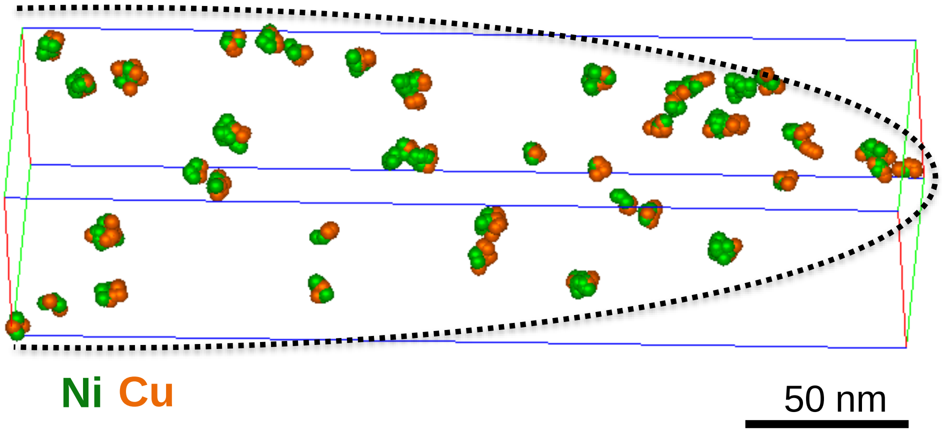
Before Polishing

After Polishing



Colloidal Silica Polishing - Conclusions

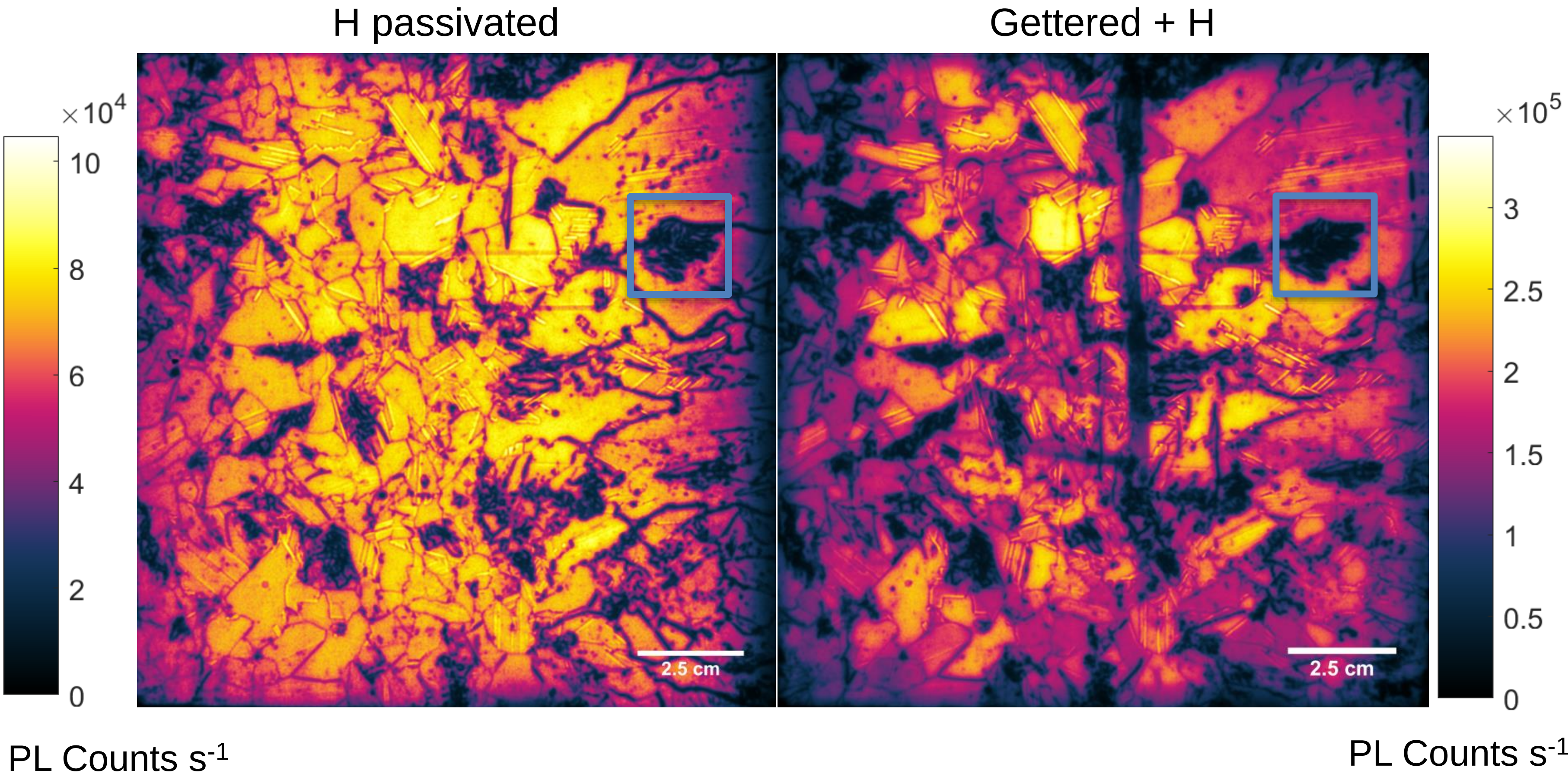
- Colloidal silica - shown to introduce nickel in mc-Si (Yarykin, 2017)
- Issue in our samples →
  - Laboratory contamination
  - Fast diffusion of impurities via crystallographic defects
- Concentration of Ni and Cu high enough to induce clustering



Major study

- HP multi Si p-type sister wafers
- 4 types of wafers:
    1. As-Cast
    2. Phosphorus Diffusion Gettered
    3. Hydrogen Passivated
    4. Phosphorus Diffusion Gettered + Hydrogen Passivation
- Work in progress

Photoluminescence



H passivated

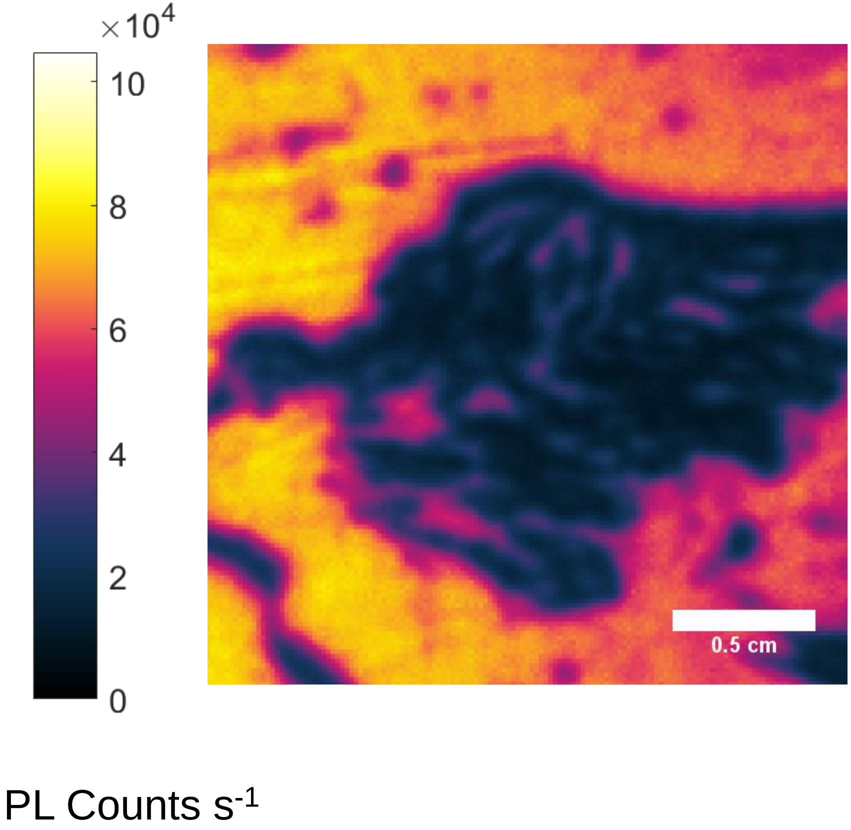
Gettered + H

PL Counts s^{-1}

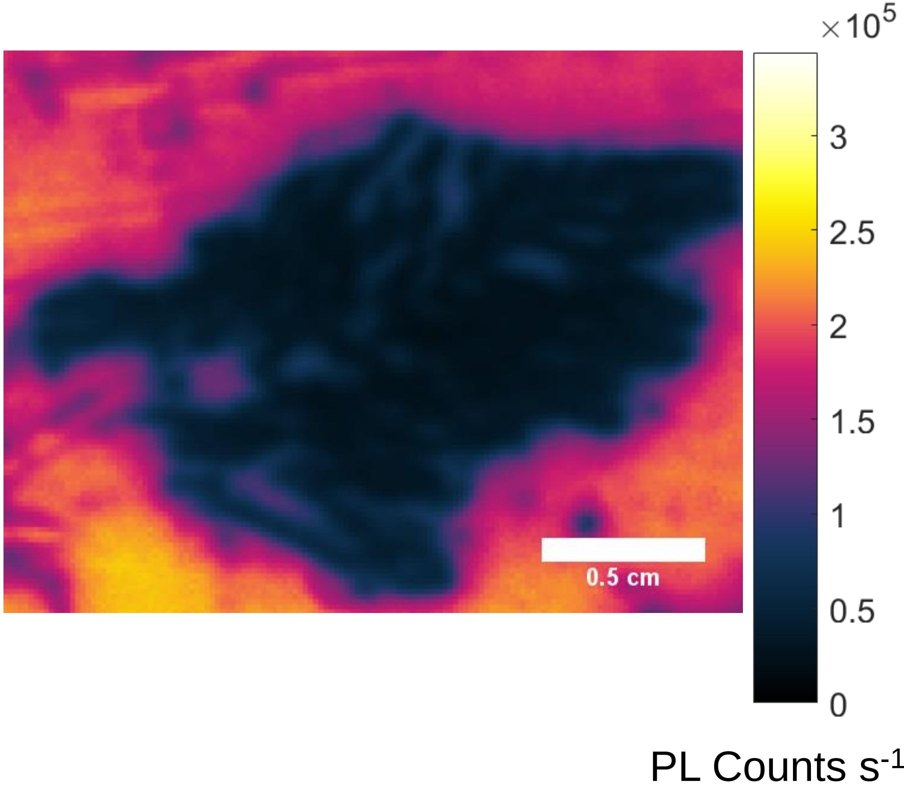
PL Counts s^{-1}

Photoluminescence

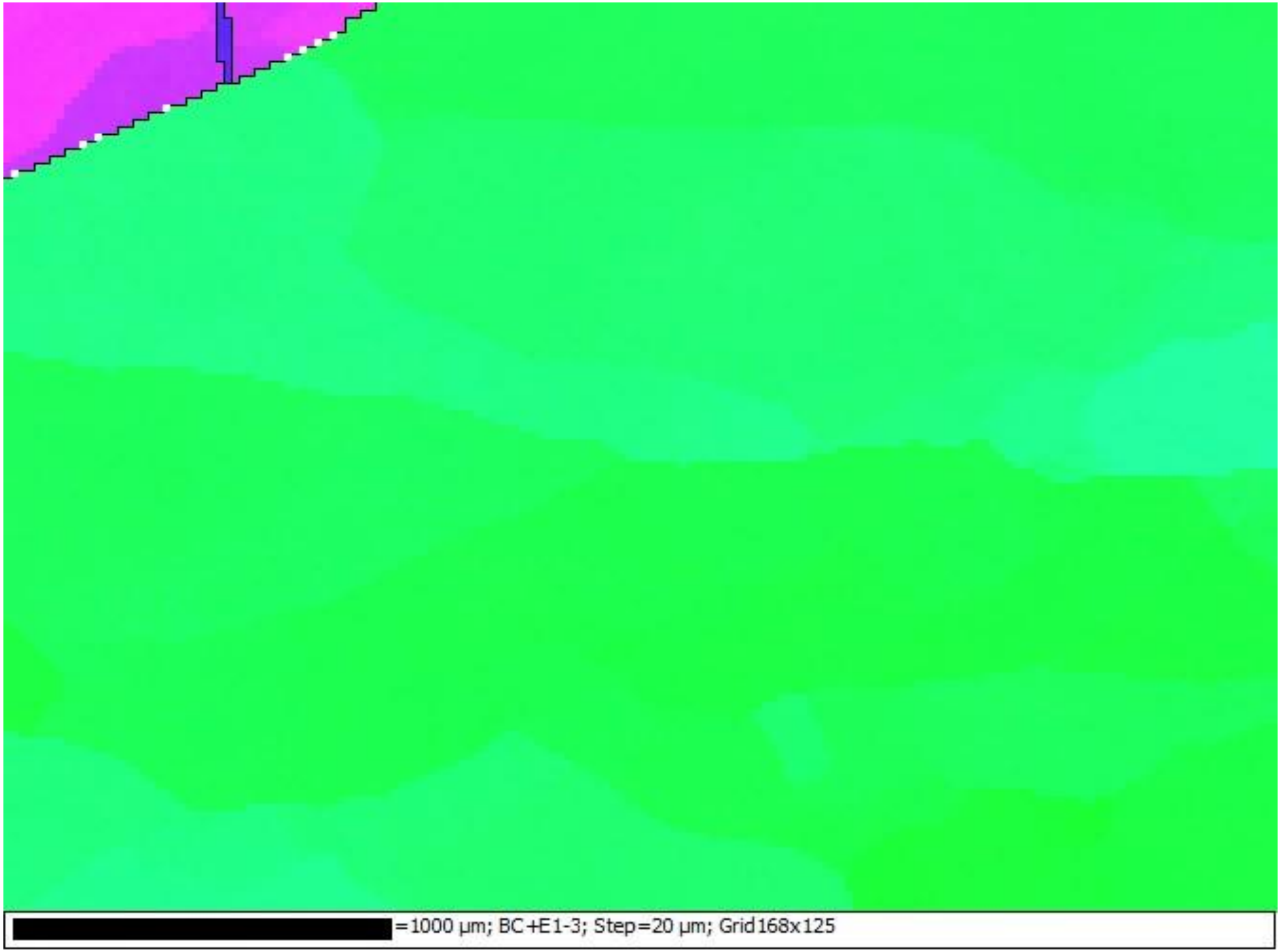
H passivated

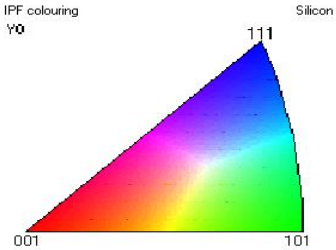


Gettered + H



Electron Back Scatter Diffraction (EBSD)

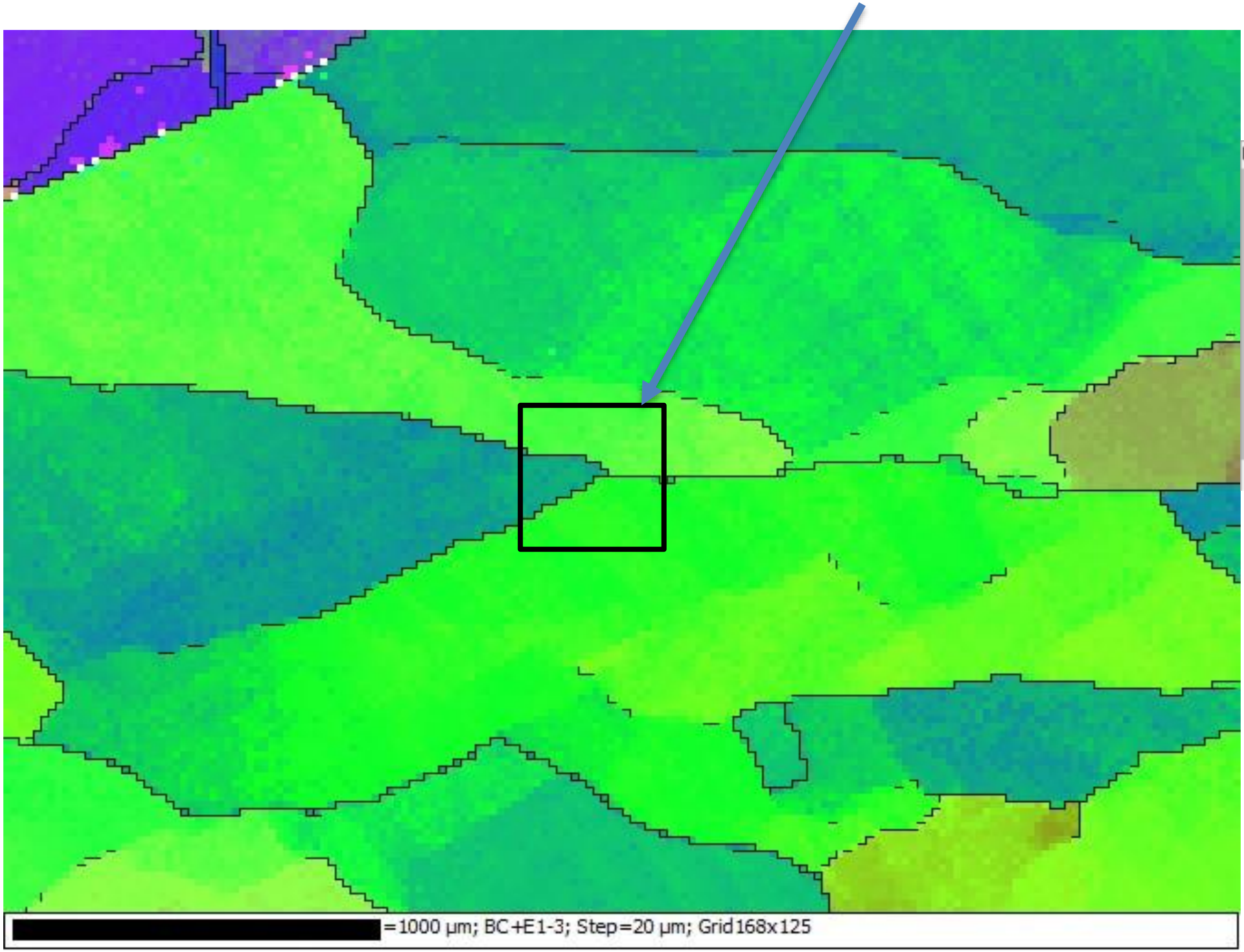


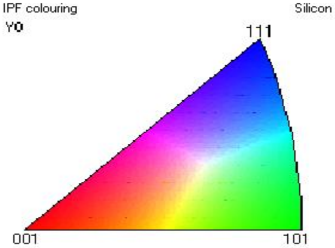


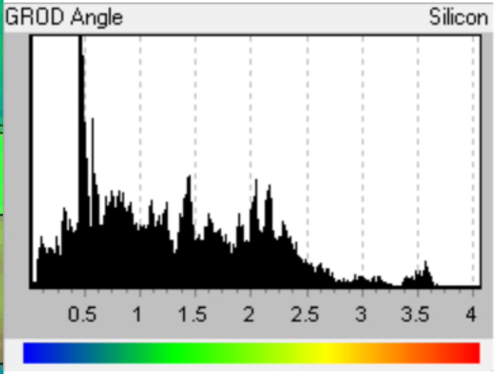
Extremely low grain misorientation

Require the use of grain reference orientation deviation mapping to observe the low angle grain boundaries

Electron Back Scatter Diffraction (EBSD)


Area of Interest





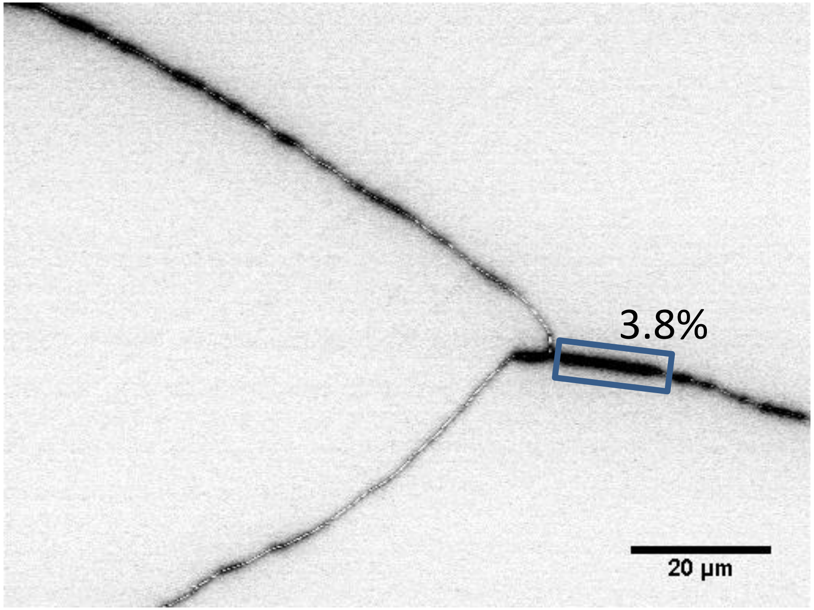
Area of a large concentration of small angle grain boundaries

misorientation < 5°

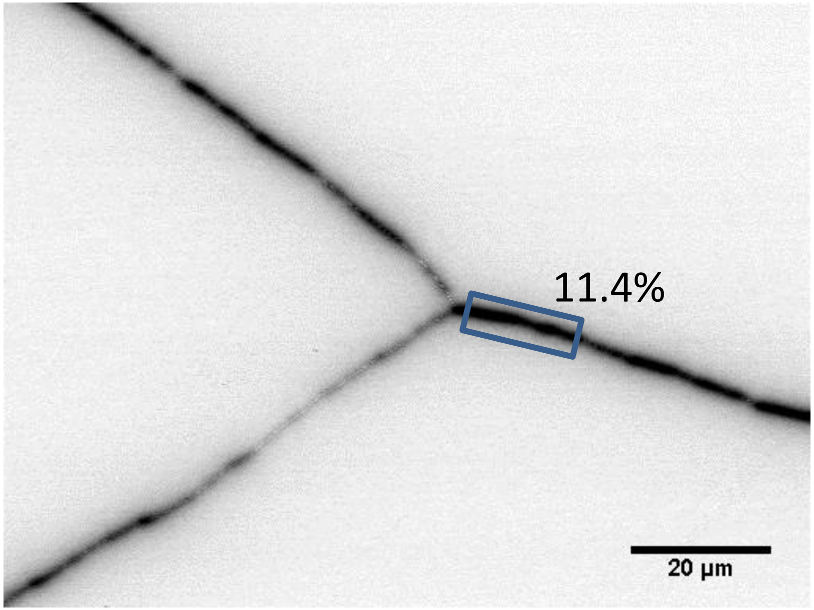
Electron Beam Induced Current (EBIC)

- Significant increase in EBIC contrast after gettering
- Low angle grain boundaries (3.8°) – array of edge dislocations

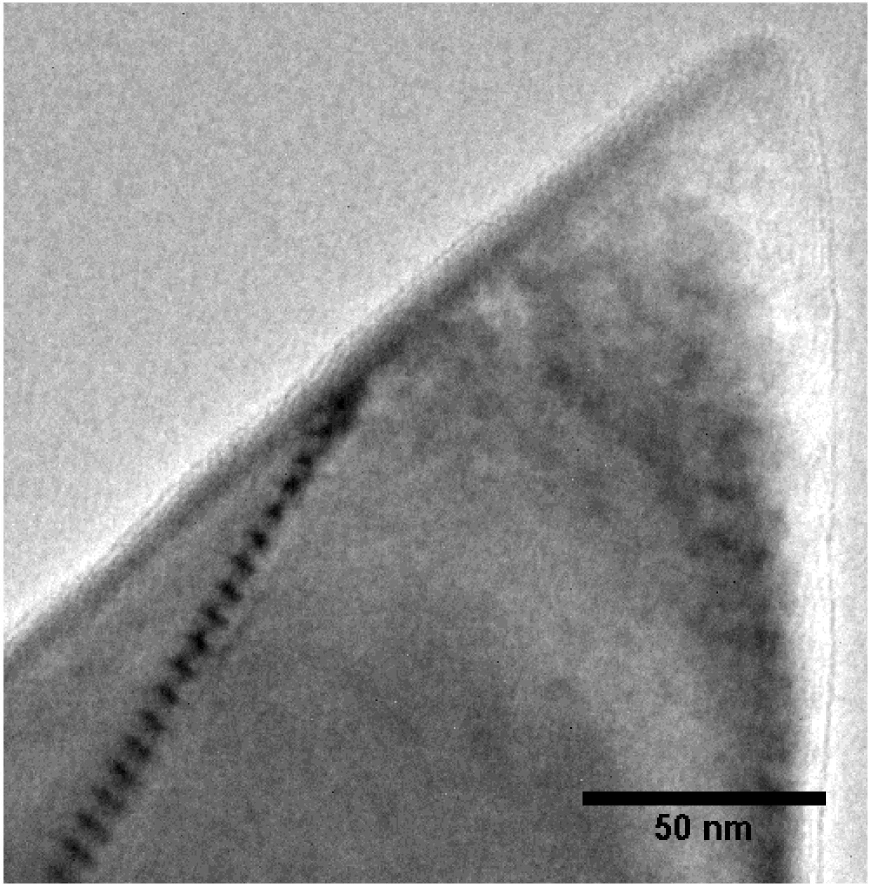
As - Cast

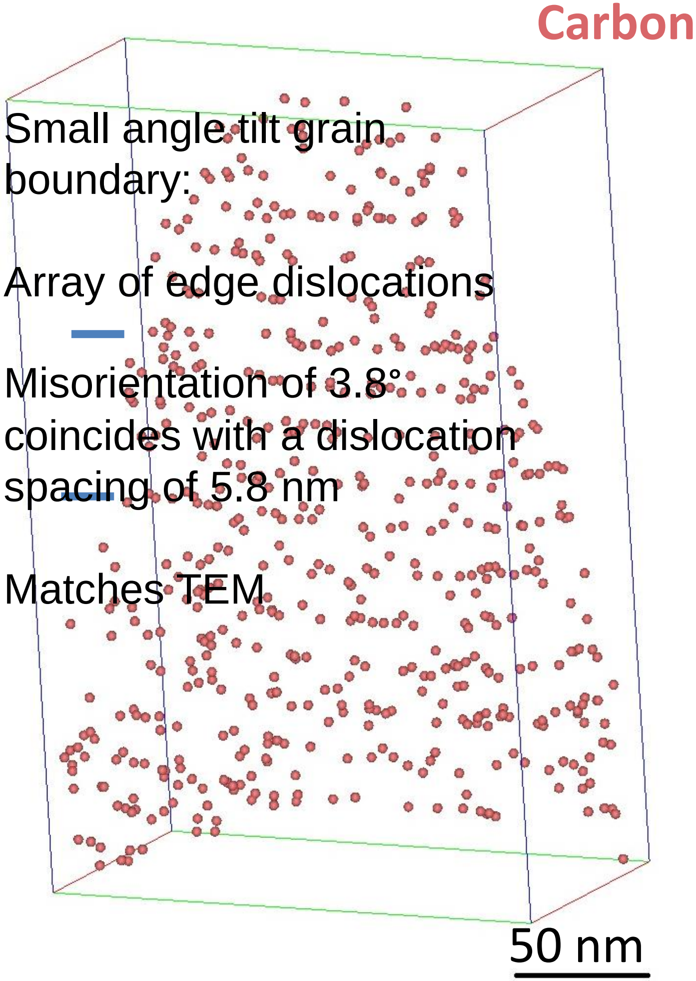


Gettered



TEM + APT – As Cast





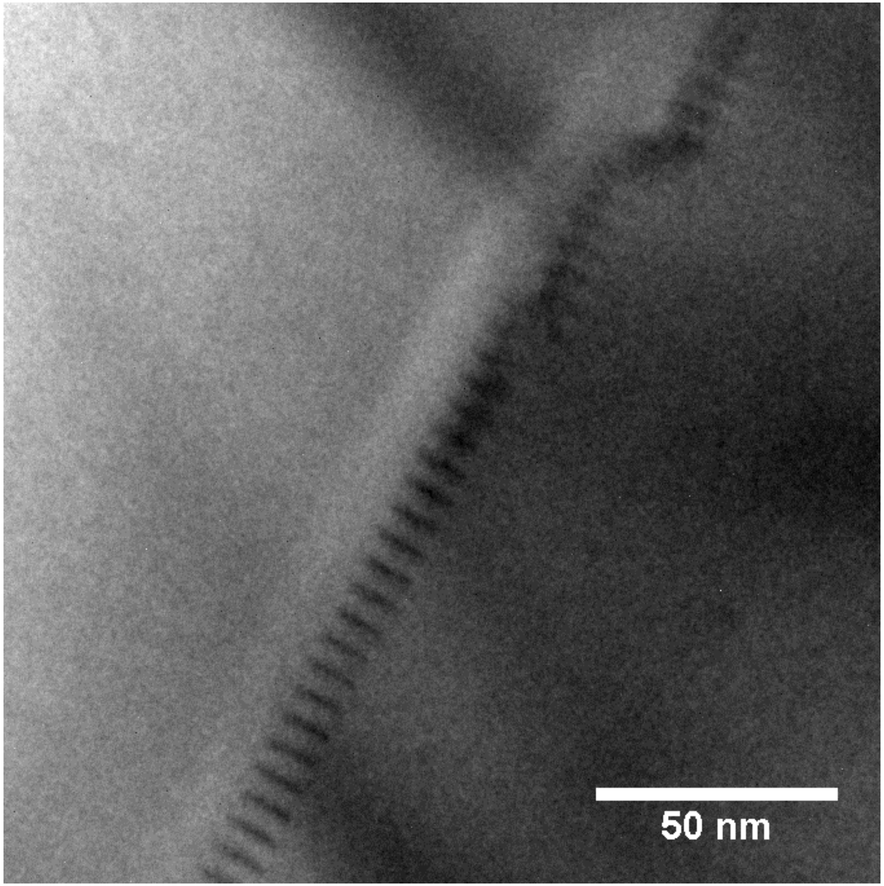
Small angle tilt grain boundary:

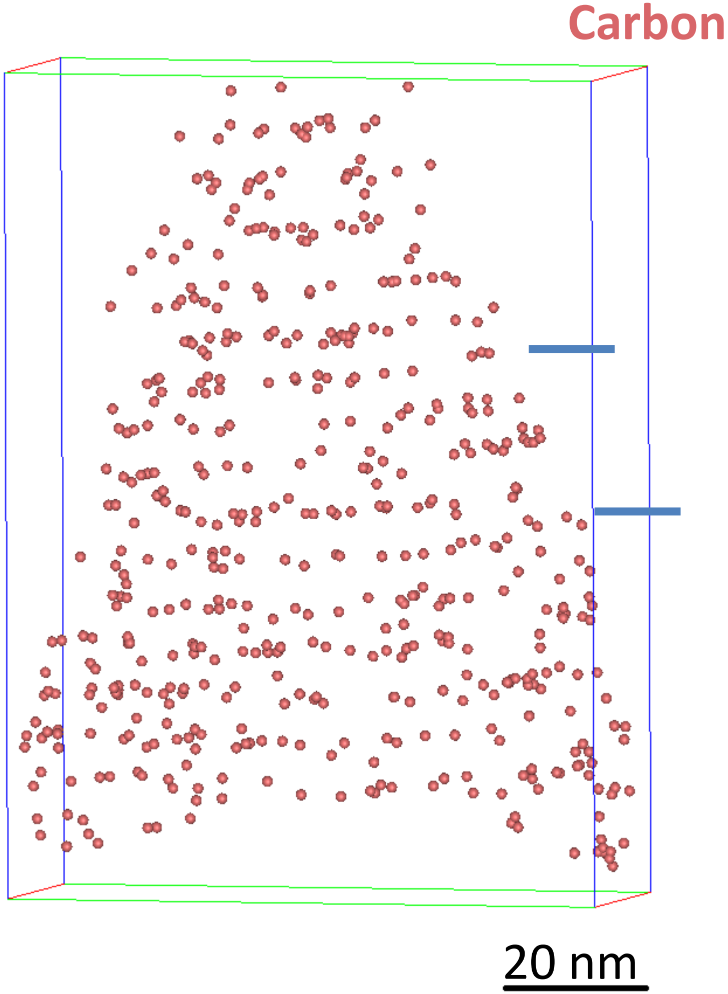
Array of edge dislocations

Misorientation of 3.8° coincides with a dislocation spacing of 5.8 nm

Matches TEM

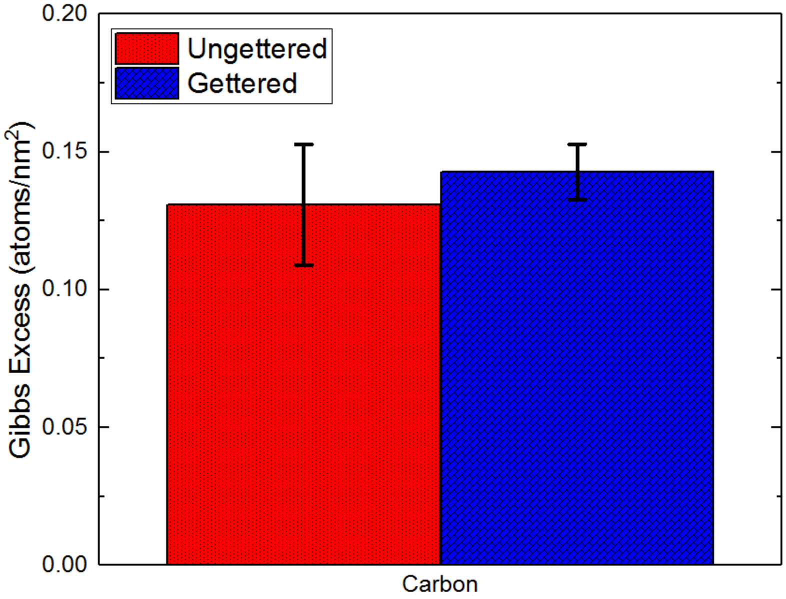
TEM + APT – Post Gettering





Small Angle GB- Conclusions

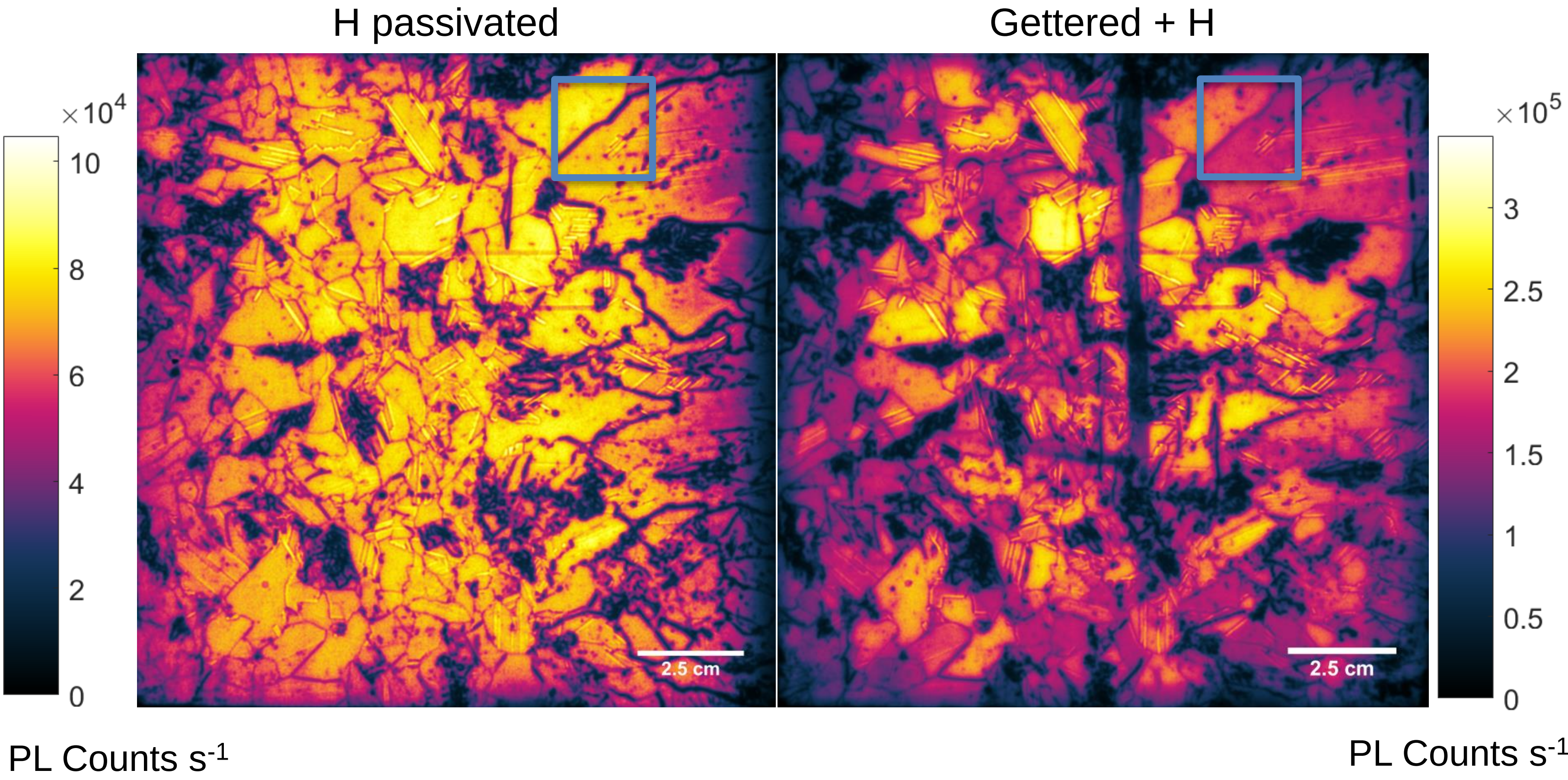
- No transition metals observed at a small angle recombination active GB both before and after gettering
- Spacing of dislocations matches expected in both TEM and APT
- Similar levels of C detected at GBs



Possible Explanations:

- Transition metal impurity levels below detection limit for APT (2-10 ppm)

Photoluminescence



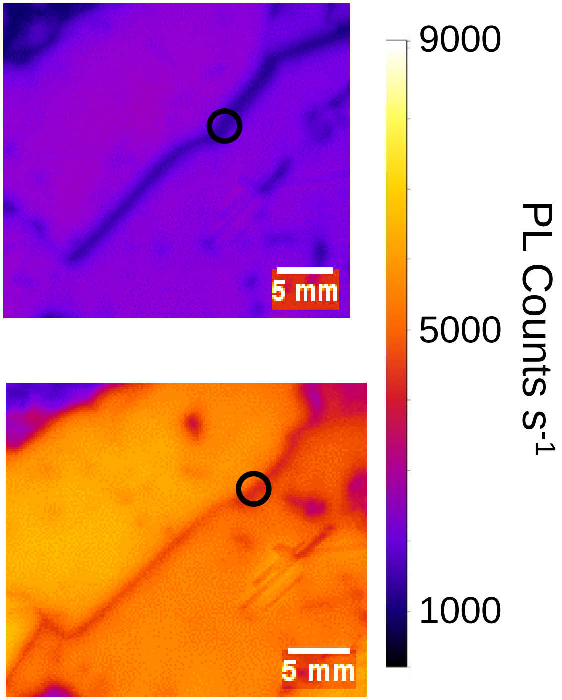
H passivated

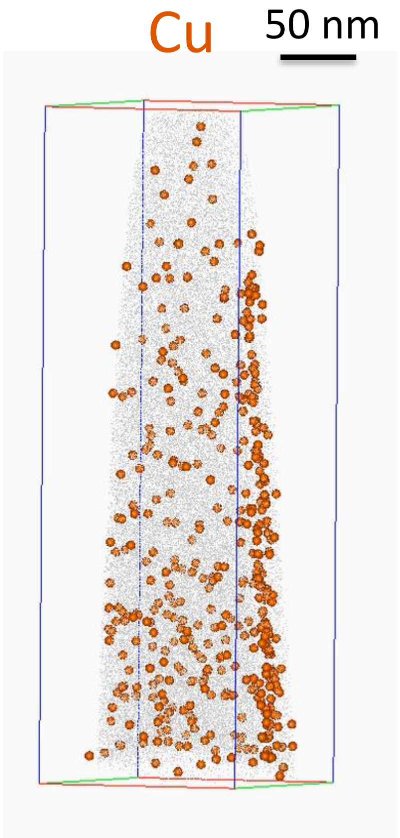
Gettered + H

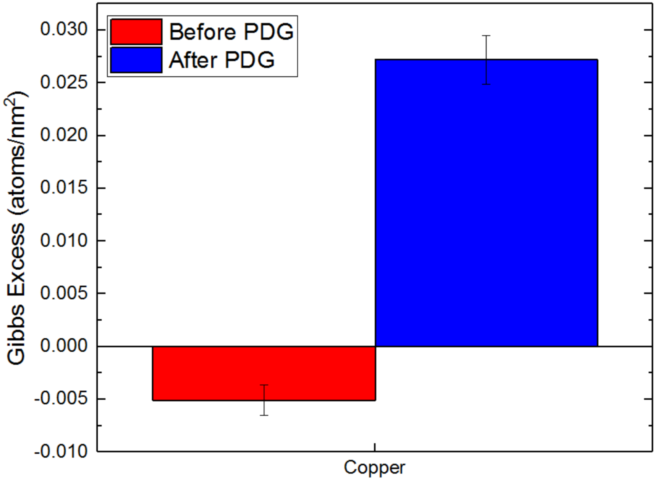
Atom Probe Tomography- Post PDG

Preliminary Study

- Random angle grain boundary (misorientation 49.62°)
- Grain boundary analysed still electrically active after PDG
- Large increase in copper at the GB after PDG – fast cool (internal gettering?)
- Again- no Fe or Ni detected at the boundary
- Lack of other grain boundaries around- concentration of impurities large enough to see Cu





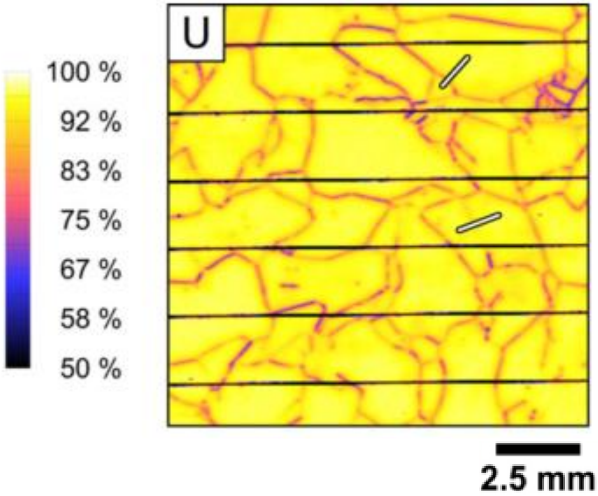


What about samples which have been Gettered and H passivated?

Effect of Gettering and Passivation

- Laser Beam Induced Current map of recombination in an unprocessed multicrystalline silicon wafer

LBIC map for ungettered HP mc-Si wafer

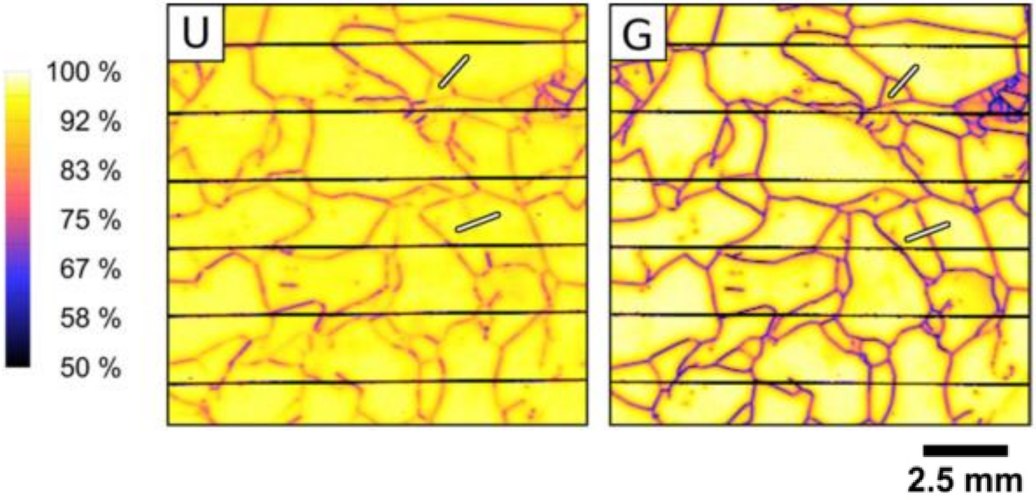


Adamczyk et al., 2018, J Appl Phys 12(5)

Effect of Gettering and Passivation

- After phosphorus diffusion gettering, intragranular regions are seen to improve
- However grain boundaries become more recombination active – indicates internal gettering to GBs

LBIC map for ungettered and gettered mc-Si wafers



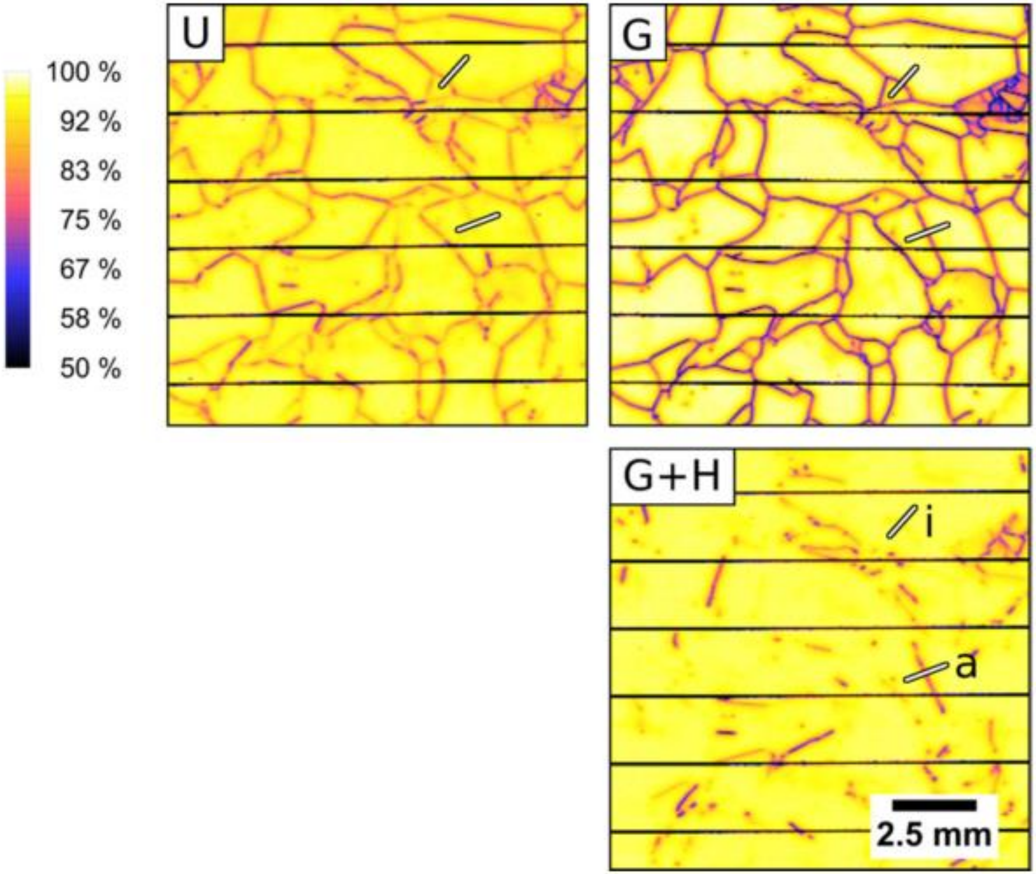
Adamczyk et al., 2018, J Appl Phys 12(5)

Effect of Gettering and Passivation

- With the use of hydrogen passivation grain boundaries become generally inactive, however performance is still limited by regions that remain electrically active

- Some specific grain boundaries (gbs) are still electrically active

LBIC map for ungettered, gettered and gettered + H passivation mc-Si wafers



Adamczyk et al., 2018, J Appl Phys 12(5)

Effect of Gettering and Passivation

- Some specific grain boundaries (GBs) which are still electrically active can be correlated to grain boundary type

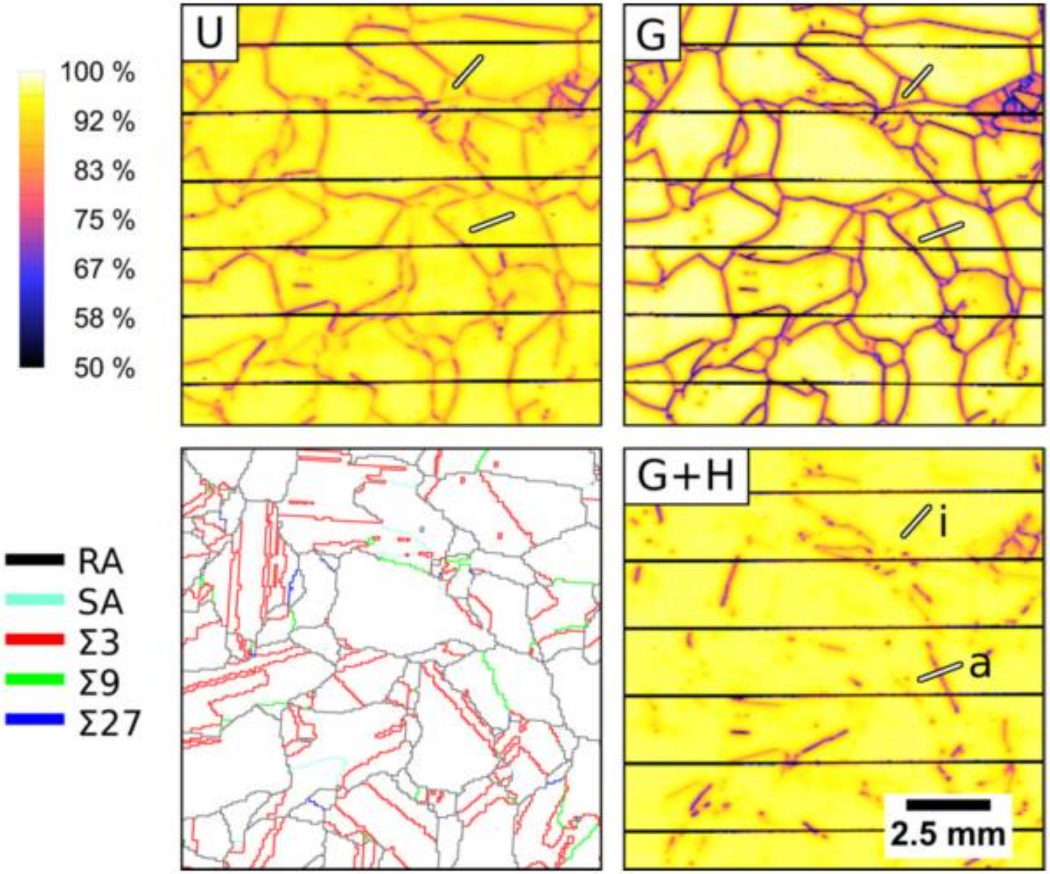
➡ Σ3 {111} gbs are electrically inactive

➡ RA grain boundaries tend to respond to H passivation and become inactive

➡ Σ9, Σ27 and SA GBs are generally electrically active

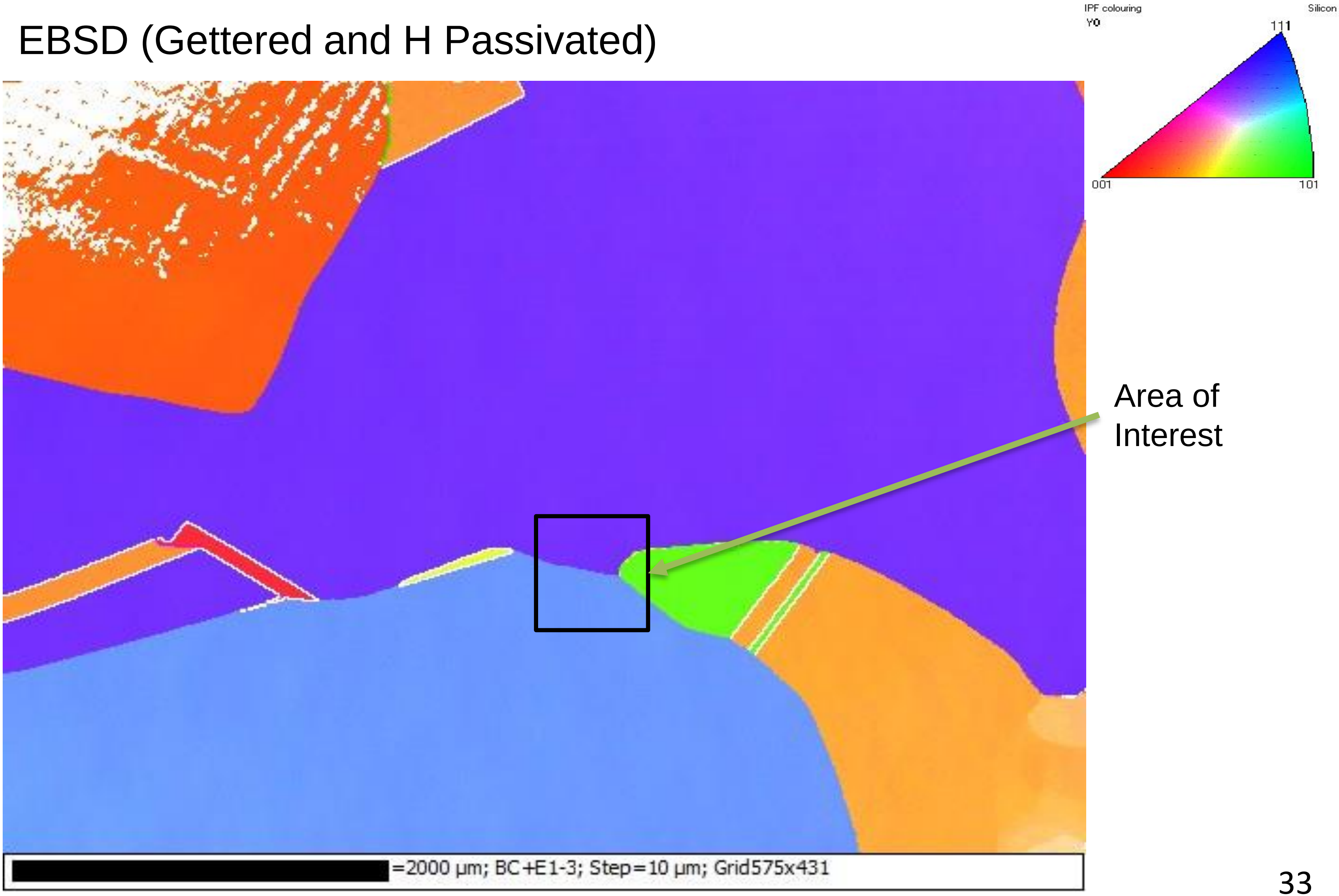
Why?

LBIC map for ungettered, gettered and gettered + H passivation and EBSD map for mc-Si wafers



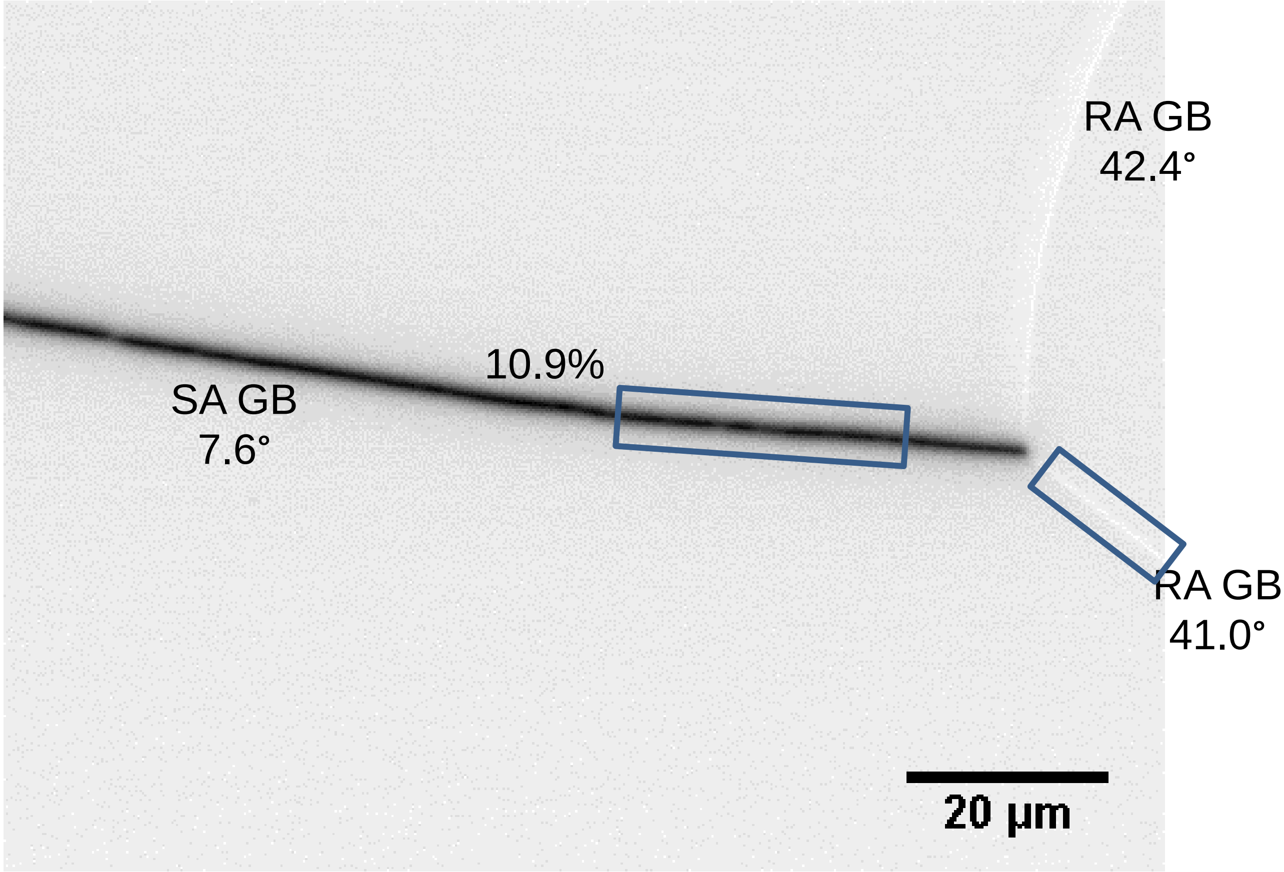
Adamczyk et al., 2018, J Appl Phys 12(5)

EBSD (Gettered and H Passivated)



Area of Interest

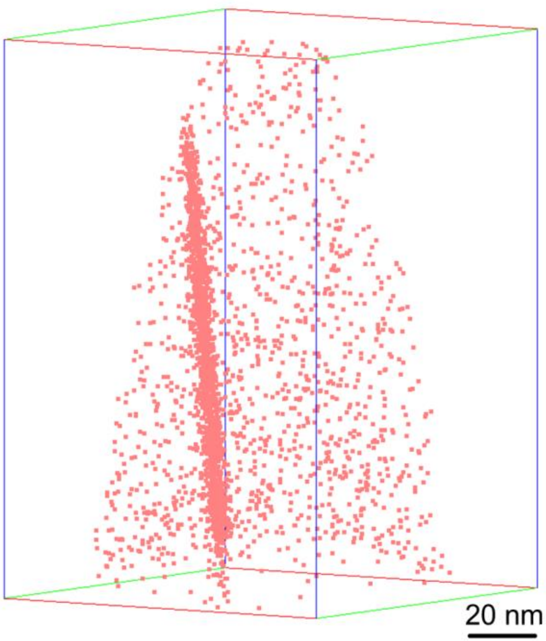
EBIC (Gettered and H Passivated)

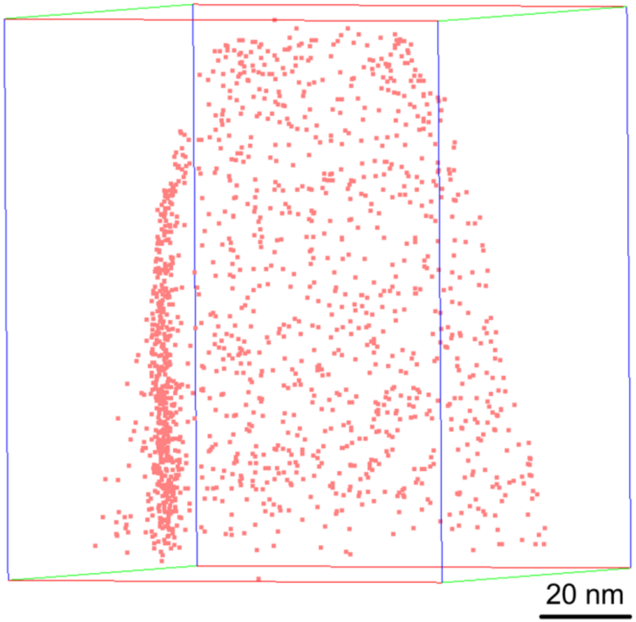


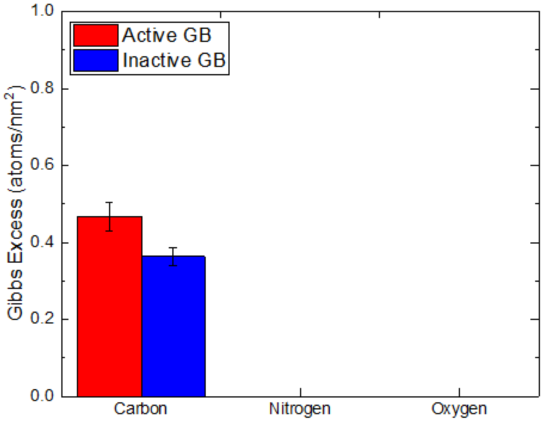
Active Grain Boundary

Inactive Grain Boundary

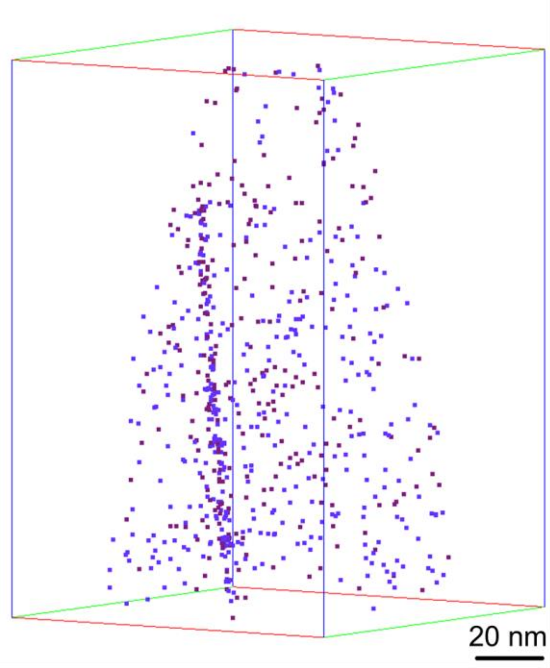
CARBON





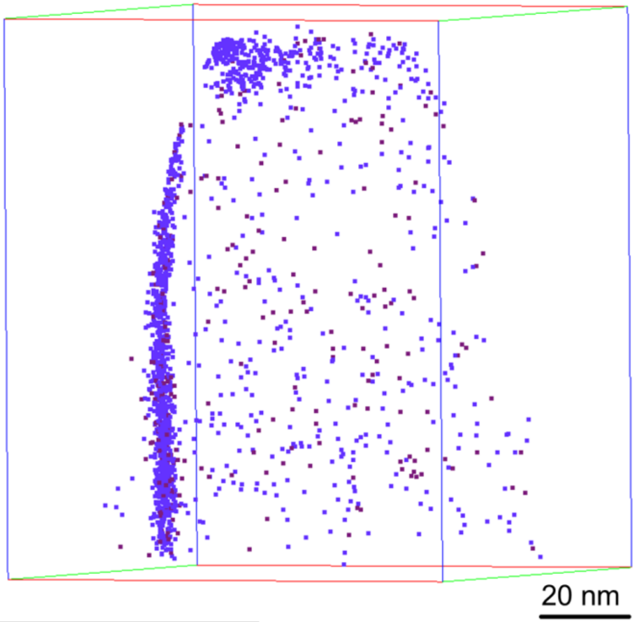


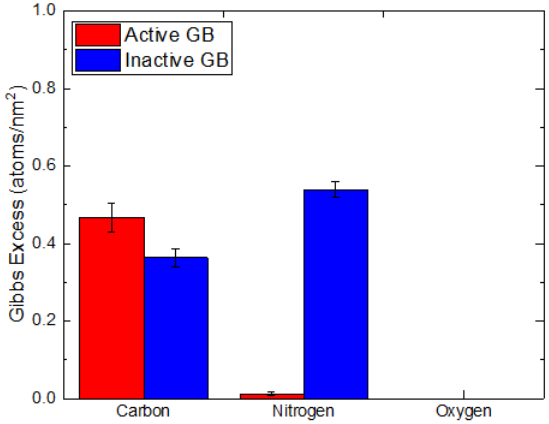
Active Grain Boundary



NITROGEN

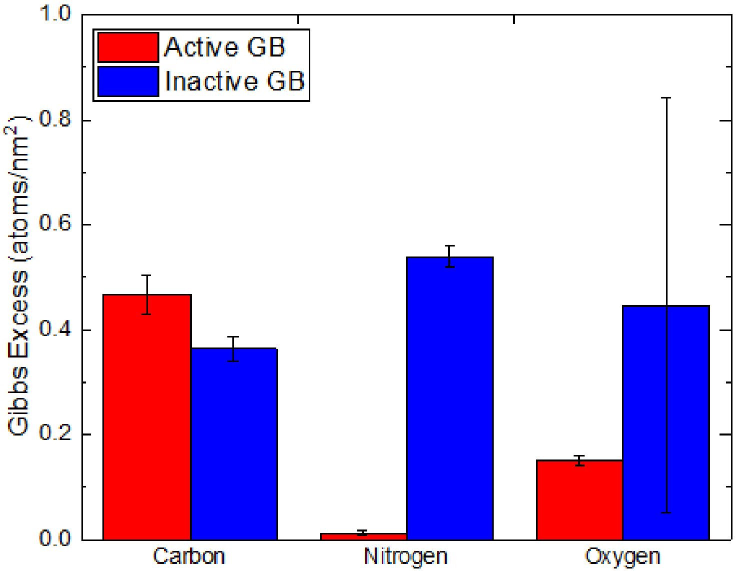
Inactive Grain Boundary





Summary

- No transition metals observed at either grain boundary
- Levels of nitrogen are much greater in the inactive grain boundary



Possible Explanations:

- Nitrogen passivation of grain boundary
- Transition metal impurity levels in active grain boundary below detection limit for APT (2-10 ppm)

➡ We are not evaluating the whole picture

Key Questions

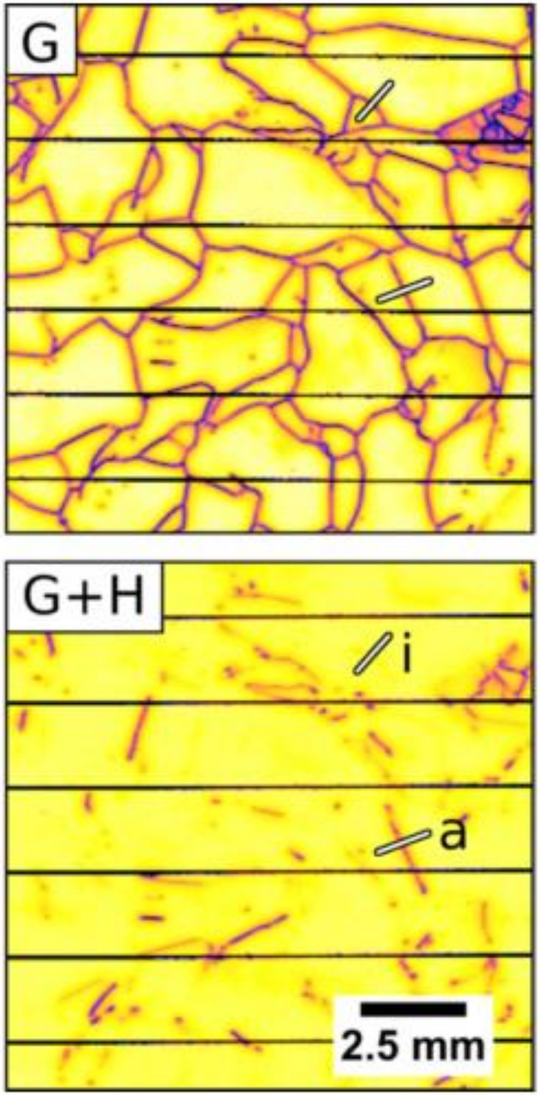
- What is the difference between **i** and **a**?
- Solar community does not know

➡ Hydrogen repelled by the local field at the boundary?

➡ Does hydrogen stay there? (lack of traps or the formation of molecular hydrogen)

➡ Role of grain boundary type – not all boundaries of the same type respond equally

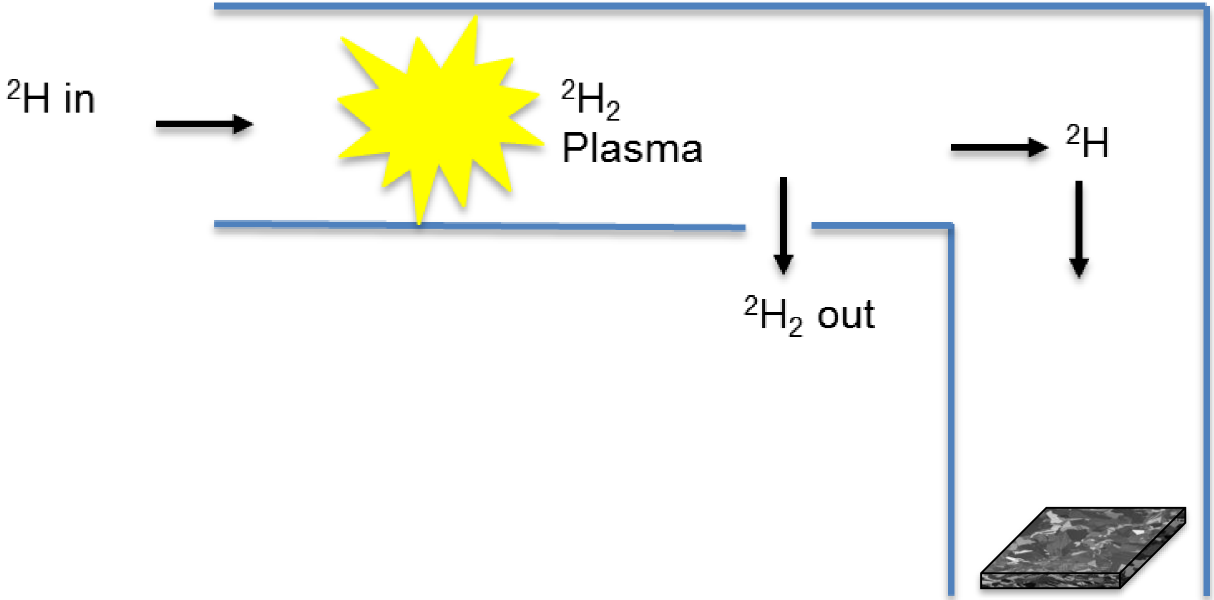
NEED: ➡ A method that allows for the unambiguous detection of hydrogen at specific defects



Adamczyk et al., 2018, J Appl Phys 12(5)

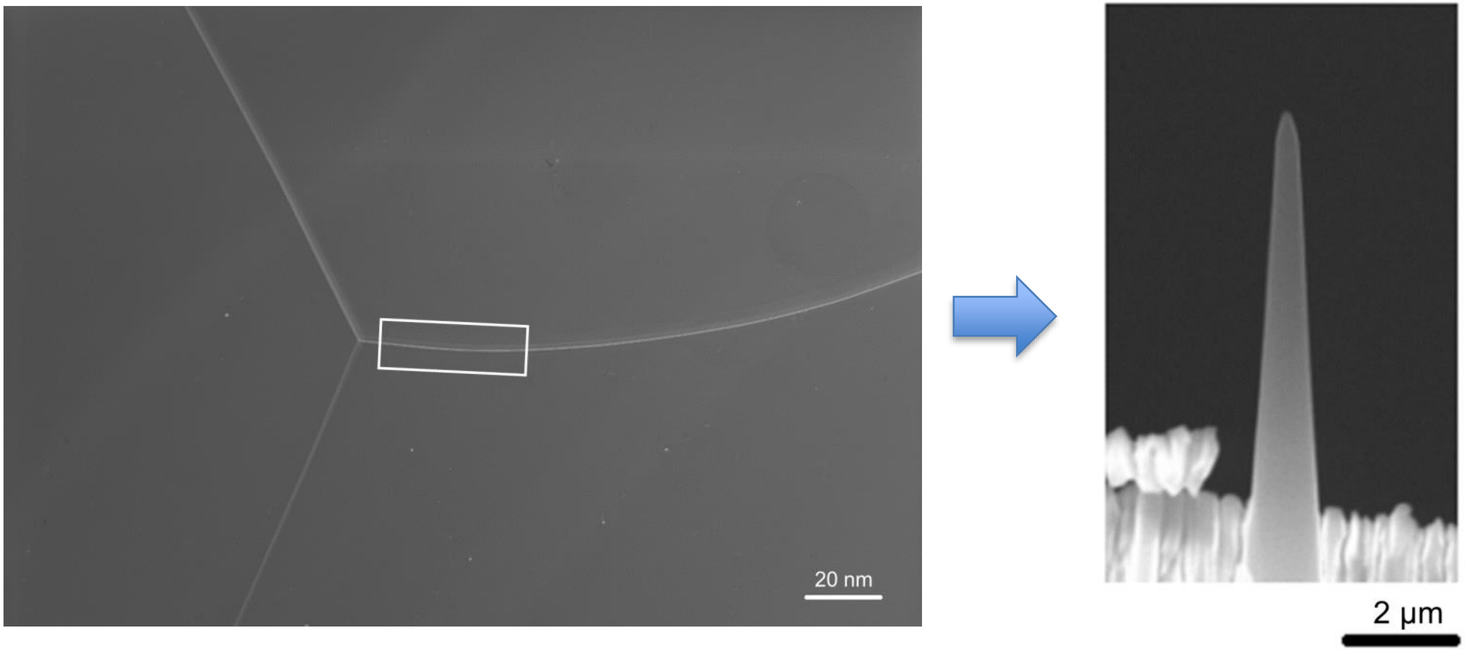
^{2}H Passivation – Using Atomic Hydrogen

- Samples were remote plasma charged using ^{2}H (Deuterium)
- Conditions: ^{2}H- plasma, 200 °C, 60 minutes, 30 W
- Sample does not contact the plasma- low surface damage (also sample not exposed to harmful UV radiation)
- Deuterium enters the sample as atomic ^{2}H – more closely replicates how hydrogen is introduced industrially



Random Angle Grain Boundary

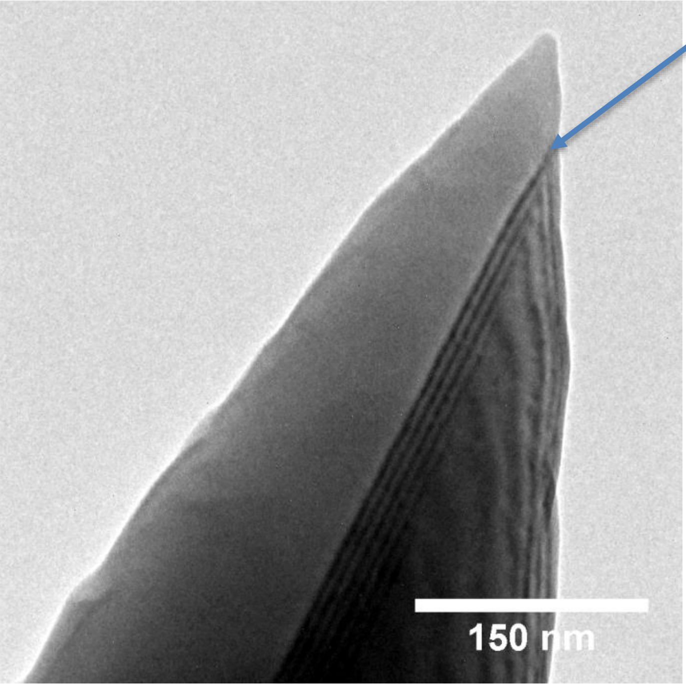
- Recombination active GB selected, which are known to respond to hydrogen passivation [Chen 2005]
- APT needle taken after ^{2}H plasma exposure, via focused ion beam techniques – grain boundary running along the length of the needle
- Needle geometry required for APT analysis

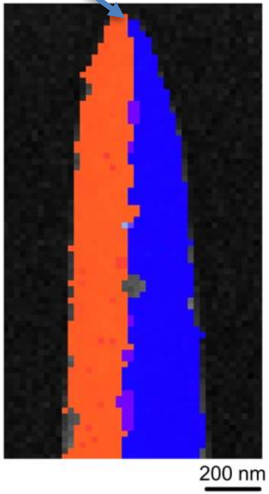


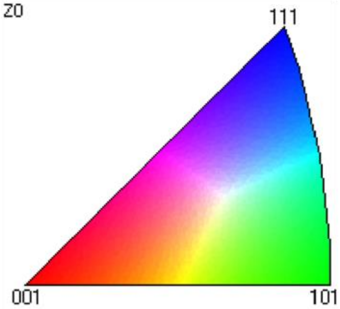
Random Angle Grain Boundary

- Prior to APT, TEM was performed on the needle to confirm the presence of the GB in the needle and following APT, transmission Kikuchi diffraction was used determine its misorientation and rotation axis

Grain Boundary



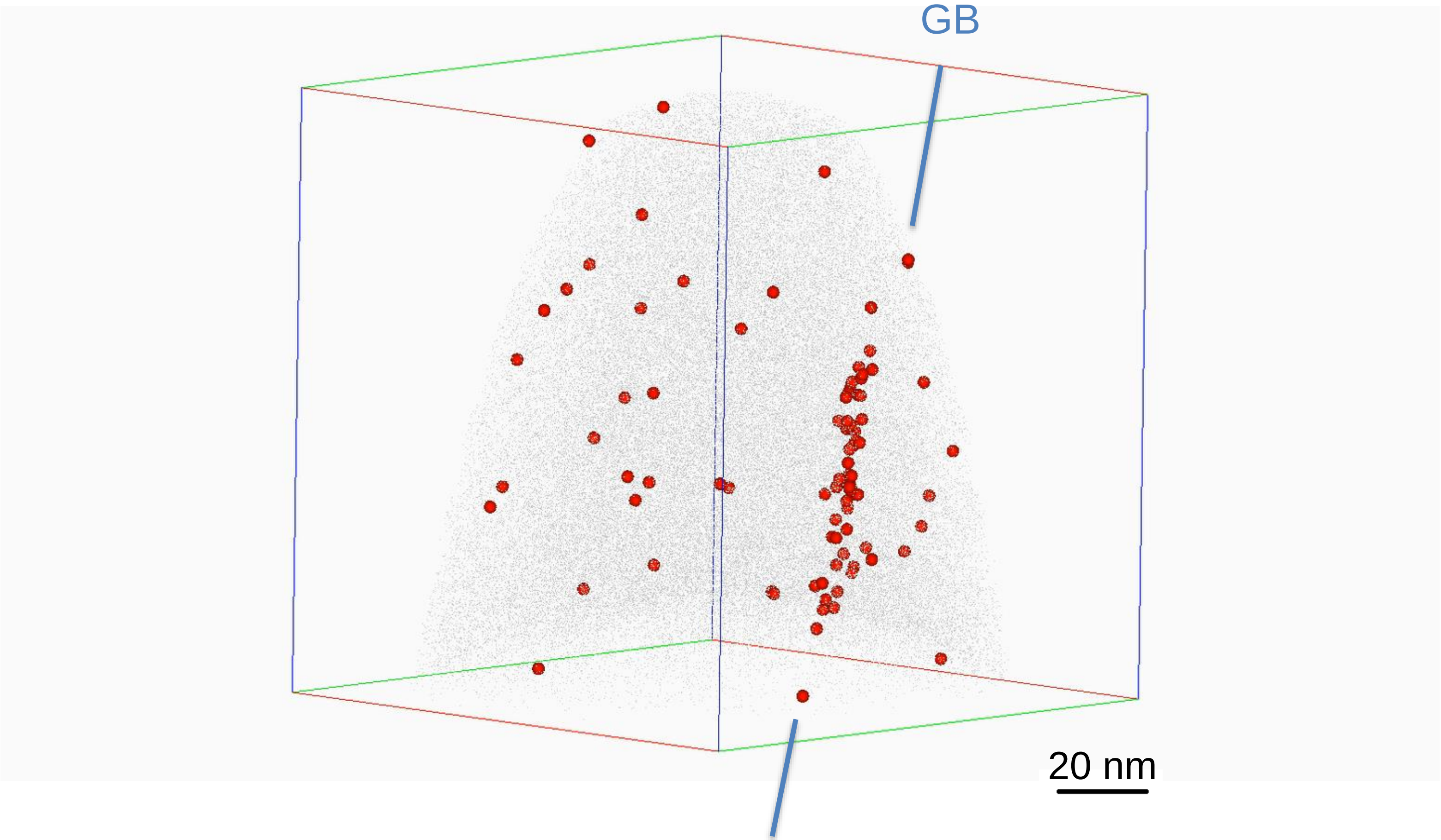




	Type	Misorientation	Rotation axis
GB	Random Angle	50°	$[\bar{4}3\bar{4}]$

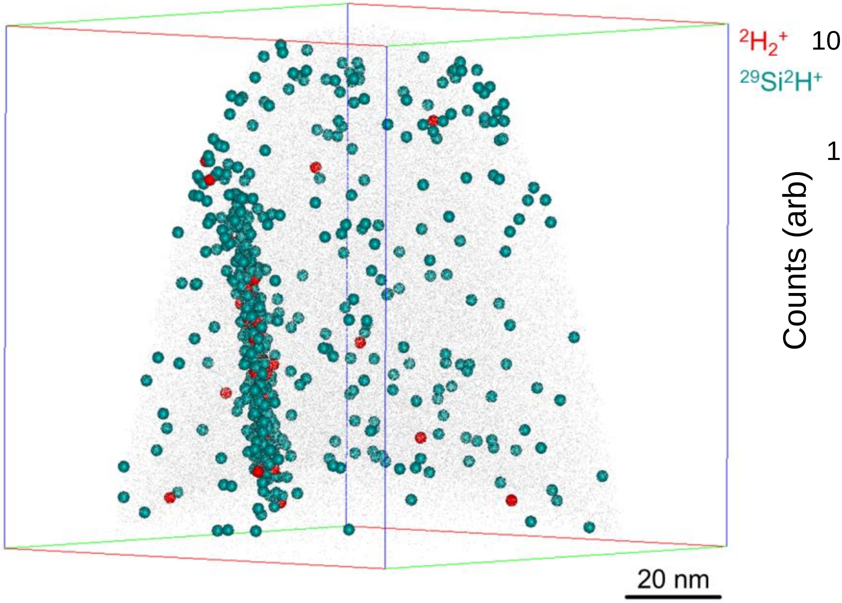
Random Angle Grain Boundary

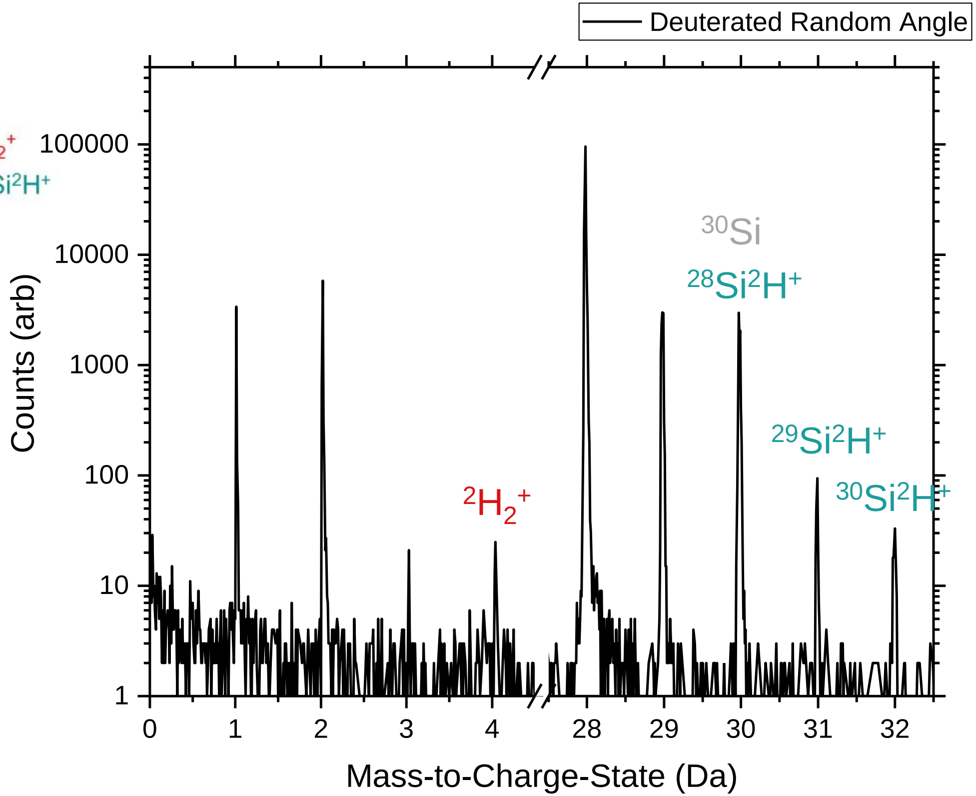
- Deuterium observed unambiguously (no overlaps) at 4 Da, in the form $^{2}H_2^+$



Random Angle Grain Boundary

- Vast majority of ^2H observed as Si^2H^+ at 30, 31 and 32 Da.
- Overlap between $^{28}Si^2H^+$ and ^{30}Si ⇨ Deconvolution required using relative peak heights and Si natural abundance

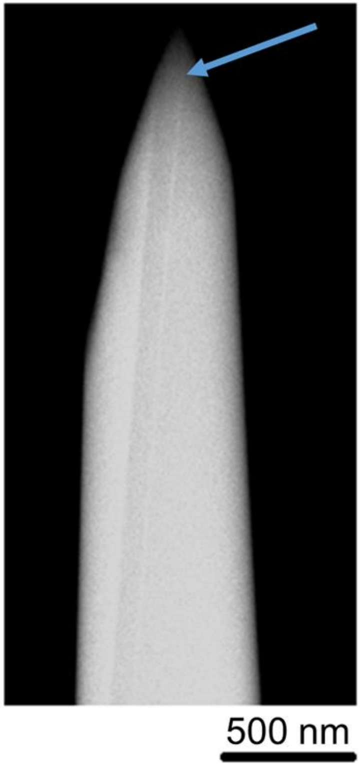


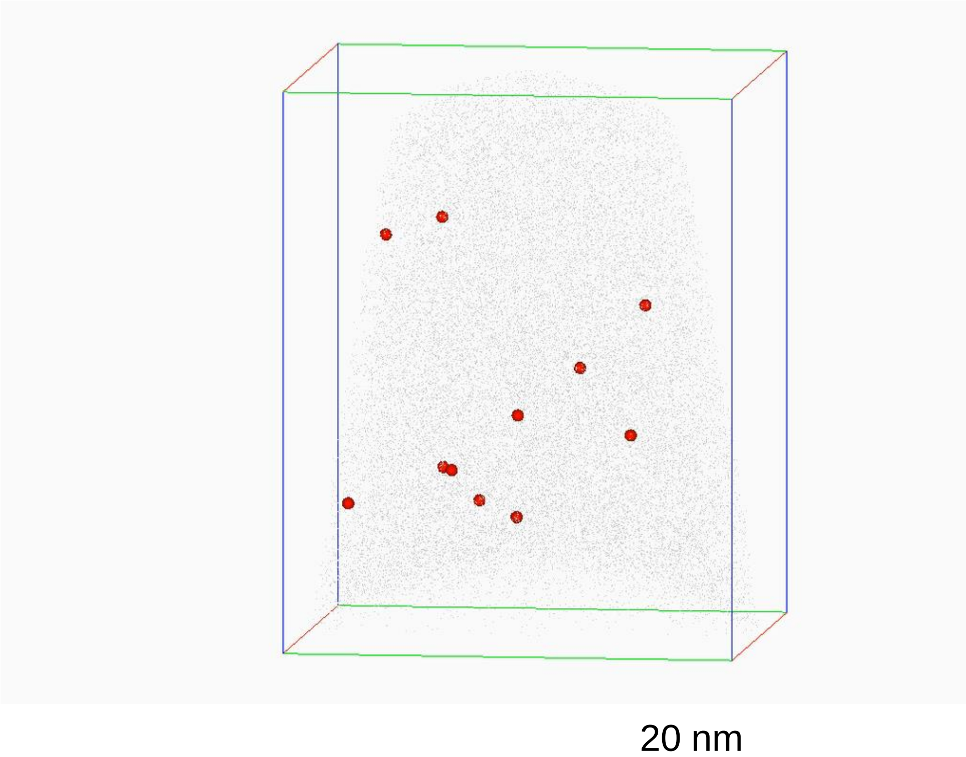


Σ3 Grain Boundary

- Σ3 {111} grain boundaries are known to be electrically inactive due to their low GB energy and lack of introduction of new deep levels in the band gap
- APT dataset containing a Σ3 {111} GB not only detects no impurities present, but also we have confirmed that no enrichment of ^{2}H is observed

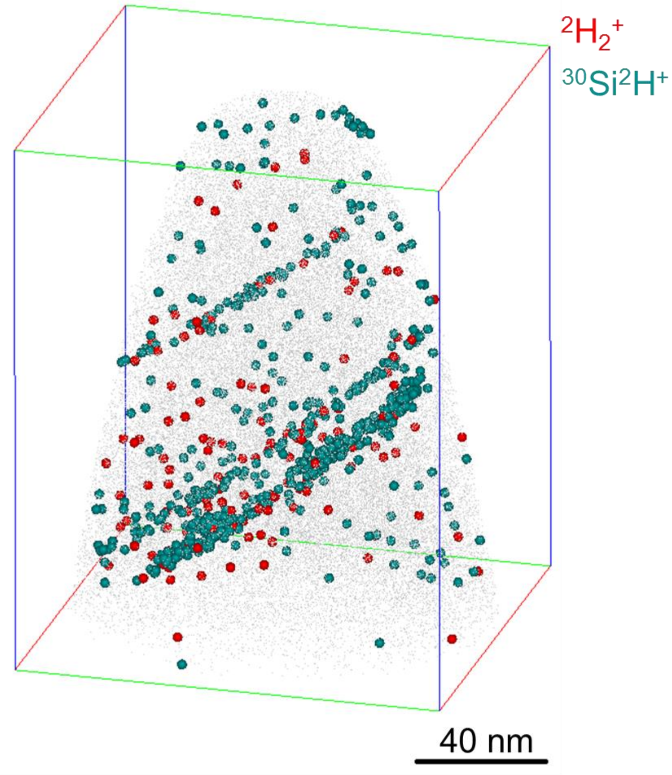
(Forward scattered image prior to APT confirming GB in the tip)

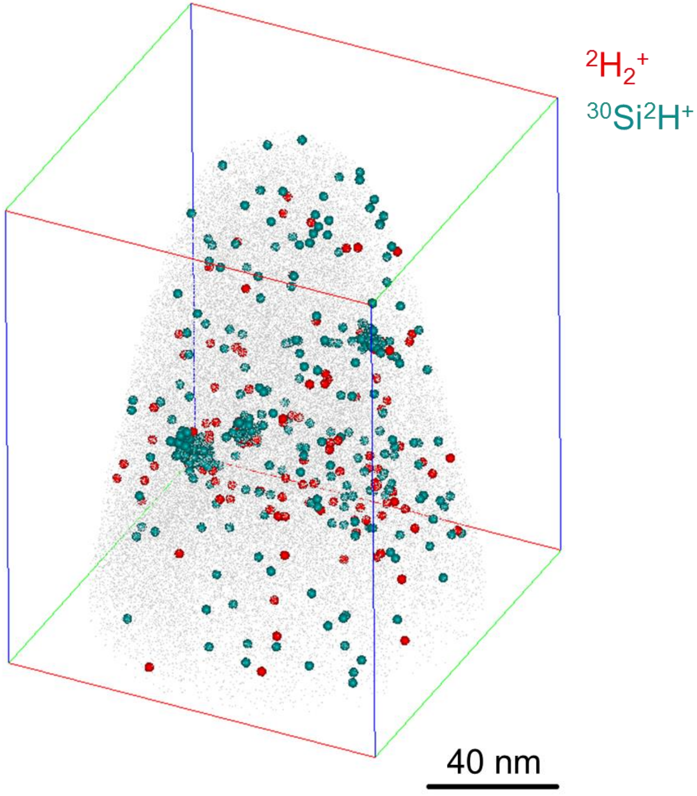




Dislocations

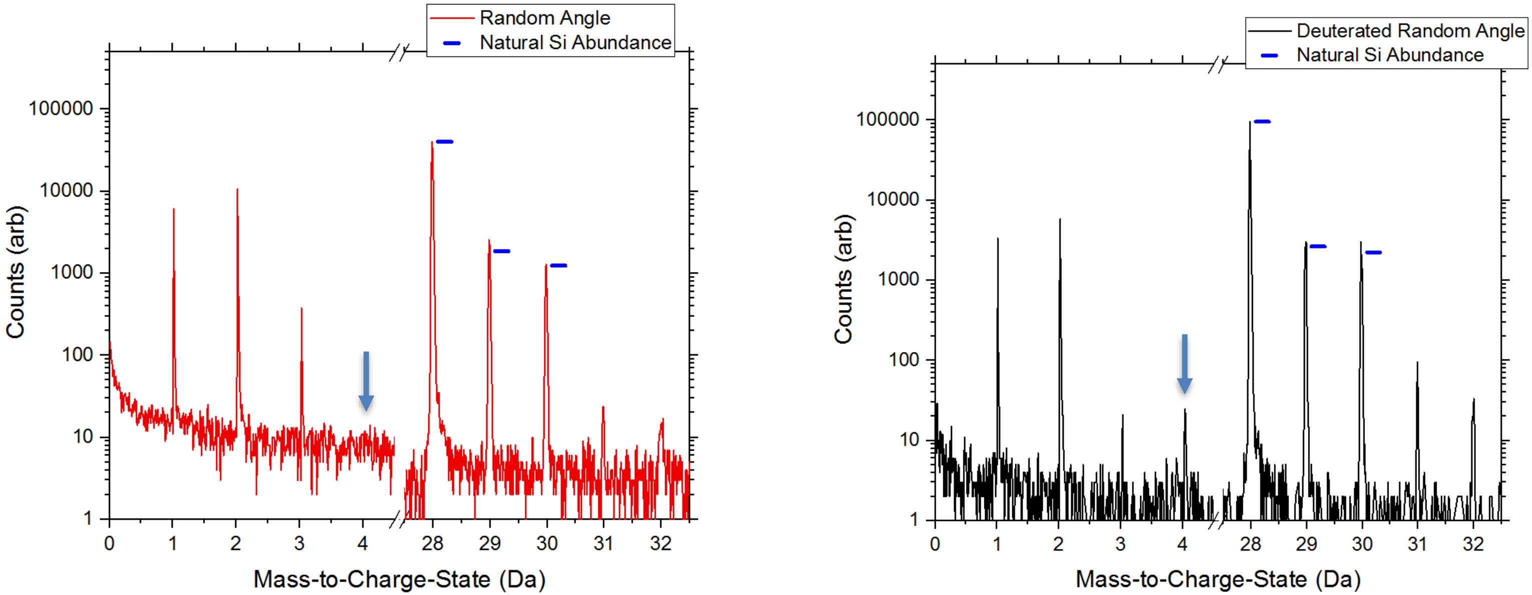
- Dislocations are of concern to solar cell manufacturers regarding passivation. In this study, ^{2}H was observed, at individual dislocations
- Dislocations observed both along the dislocation and end on in $^{2}H^{+}$ and $Si^{2}H^{+}$





Quantification of ^{2}H at defects

- An important feature of our method, is the ability to quantify the amount of ^{2}H present
- However, deconvolution is required to determine the quantity of Si^{2}H
- Uses the maximum likelihood method to estimate the quantity of ^{2}H from the peaks 30-32 Da- adjacent peaks and Si natural abundancy



Comparison of mass spectra from a non-passivated and ^{2}H passivated GB

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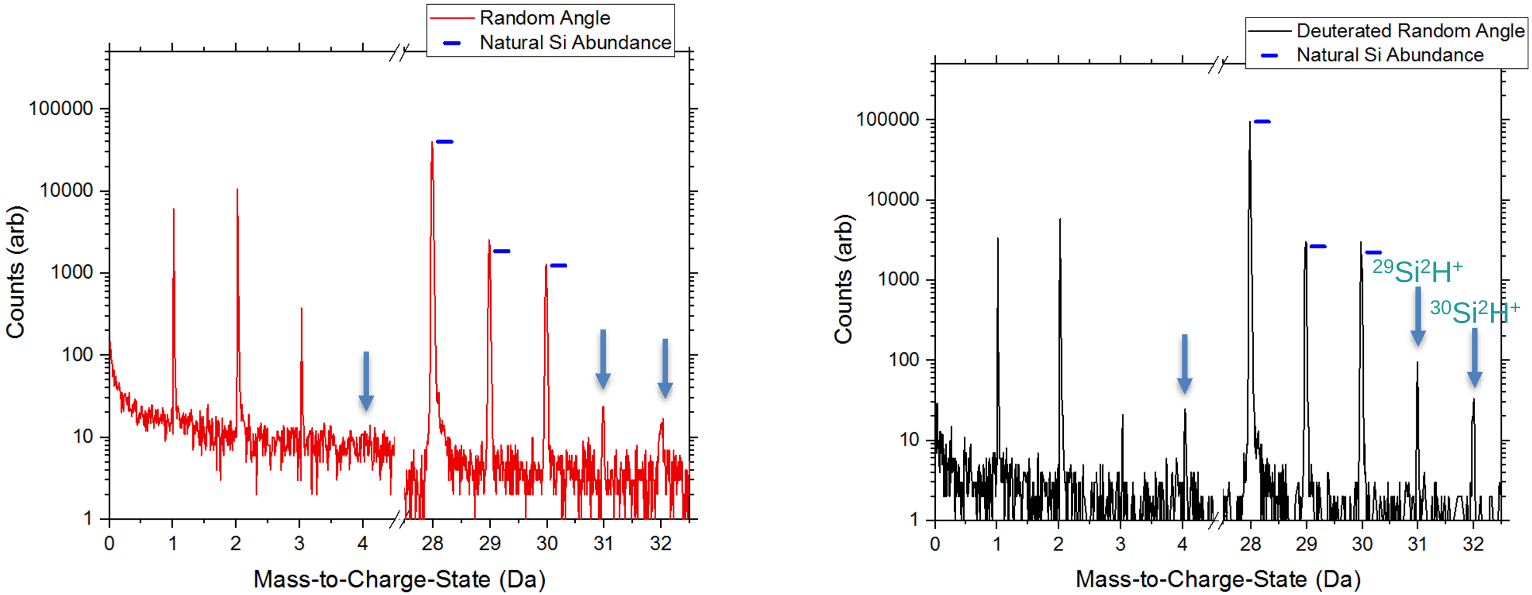

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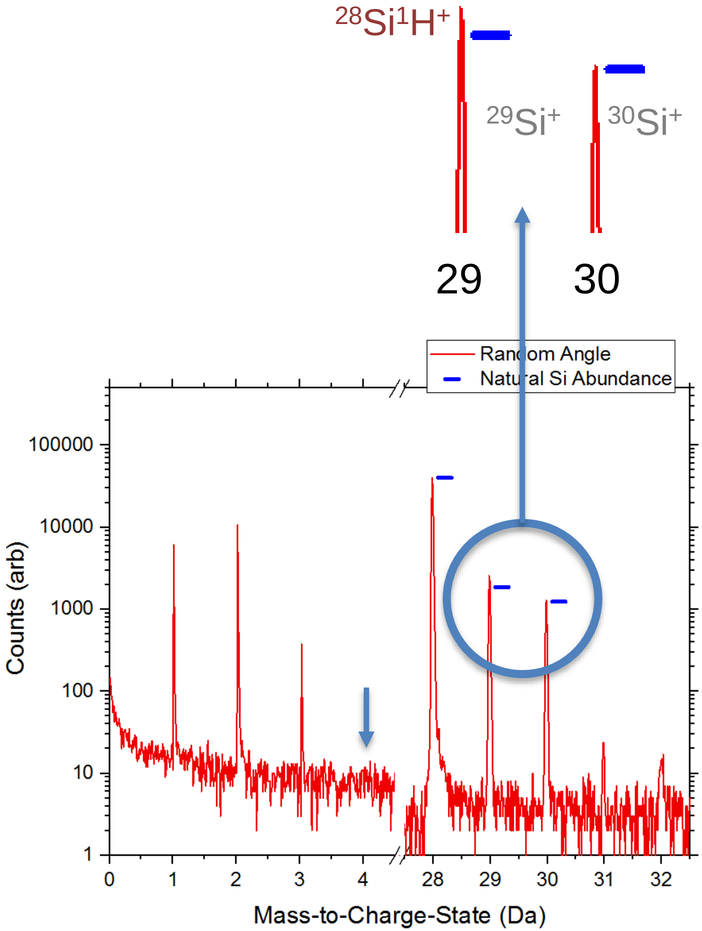
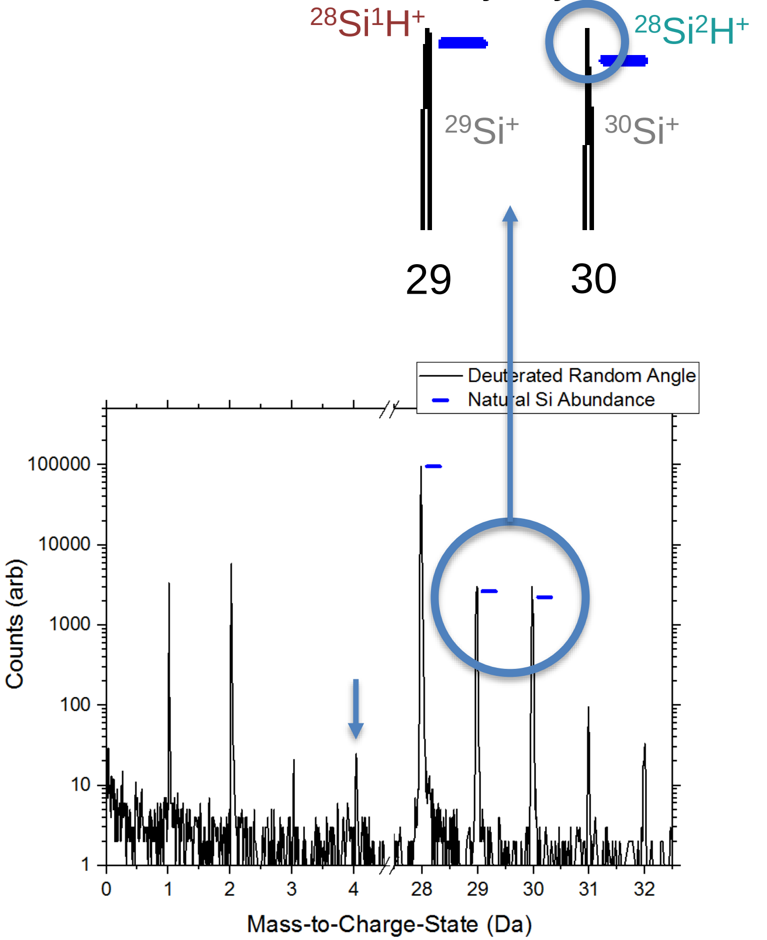


Majority of ^{2}H detected

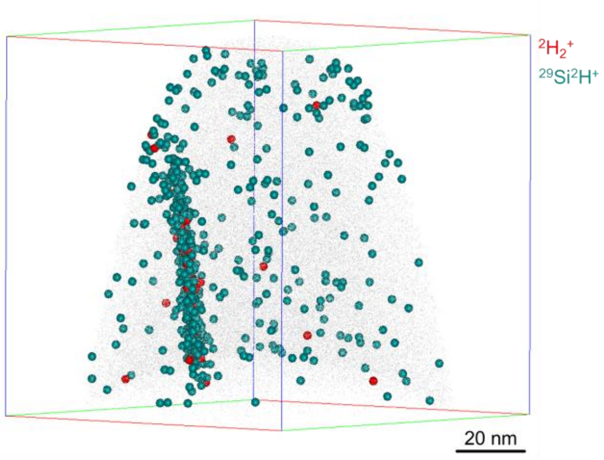


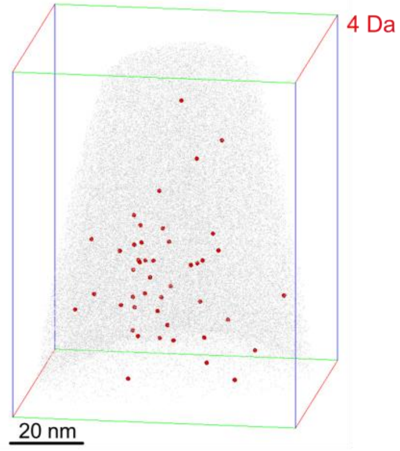
Comparison of mass spectra from a non-passivated and ^{2}H passivated GB

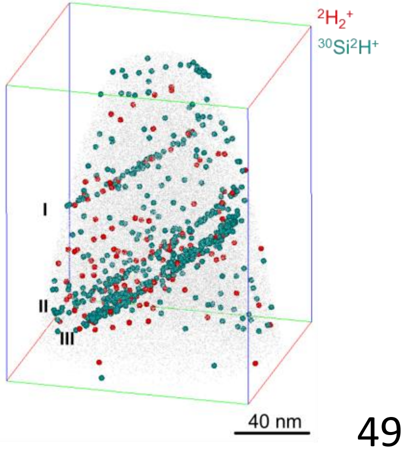
Quantification of ^{2}H at defects

- By extracting region of interest containing the grain boundary or dislocation, the ^{2}H quantity per defect can be determined
- Dislocation III can be seen to have significantly more ^{2}H than the other dislocations

	RA	**Σ3**	**I**	**II**	**III**
^{2}H Quantified	$1.4 \pm 0.15 \times 10^{14}$ counts cm^{-2}	0.0 counts cm^{-2}	14 ± 1.5 counts nm^{-1}	13 ± 2 counts nm^{-1}	22 ± 1.5 counts nm^{-1}







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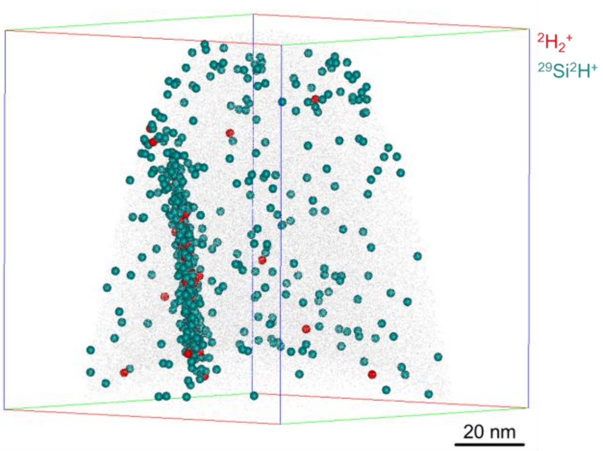
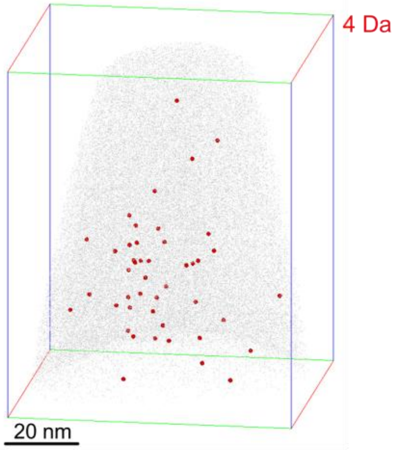
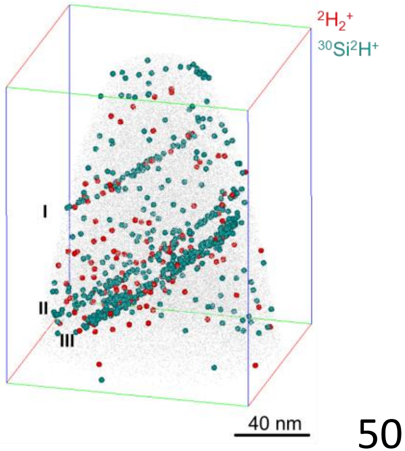
^{2}H atoms per atomic site in defect	≈0.2	Lower detection limit ≈2 x 10^{12} counts cm^{-2}	≈5	≈5	≈8







Summary

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- ^{2}H is introduced atomically in a method analogous to that used in industry
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→ Next Steps:

- Using EBIC, correlation of electrically activity with ^{2}H distribution
- Finally investigate why some boundaries respond and some don't

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WARWICK
THE UNIVERSITY OF WARWICK

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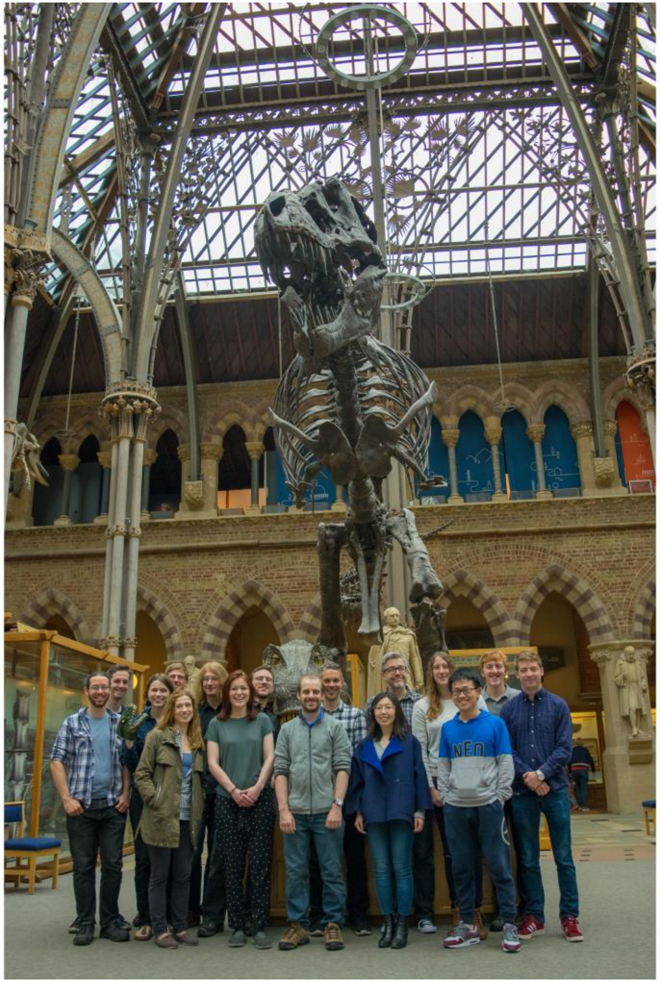
SYDNEY

Thanks for listening



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Diffusion of Deuterium

Deuterium only introduced effectively atomically

7 orders of magnitude difference in diffusivity