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]

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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.
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.

  ![EBIC image of mc-Si wafer](image)

  - Large quantities of recombination active grain boundaries and intragrain dislocations.

- Small amounts of impurities (e.g. transition metals) decorate these defects and cause recombination.
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\textsubscript{x}) during high temperature firing
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

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

c) 1.5%  2.3%  1.7%  1.8%  6.7%

d) 12.9%  13.5%  12.6%  16.0%  13.3%
Atom Probe Tomography

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

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

Oxygen

Carbon

50 nm

50 nm
Colloidal Silica Contamination - APT

Before Polishing

Oxygen

Carbon

After Polishing

Oxygen

Carbon

50 nm

50 nm

50 nm

50 nm
Colloidal Silica Contamination - APT

Before Polishing

After Polishing

Ni

Cu

Ni

Cu
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$^{-1}$
Photoluminescence

H passivated

Gettered + H

PL Counts s⁻¹

PL Counts s⁻¹
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 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
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

Carbon

50 nm

20 nm
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

PL Counts s\(^{-1}\)

PL Counts s\(^{-1}\)
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

  - $\Sigma 3 \{111\}$ gbs are electrically inactive
  - RA grain boundaries tend to respond to H passivation and become inactive
  - $\Sigma 9$, $\Sigma 27$ and SA GBs are generally electrically active

Why?

Adamczyk et al., 2018, J Appl Phys 12(5)
EBSD (Gettered and H Passivated)

Area of Interest
EBIC (Gettered and H Passivated)

SA GB 7.6°

RA GB 42.4°

RA GB 41.0°

10.9%
Active Grain Boundary

Inactive Grain Boundary

CARBON

Gibbs Excess (atoms/nm²)

Carbon
Nitrogen
Oxygen

20 nm

20 nm
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
2H 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

<table>
<thead>
<tr>
<th>Type</th>
<th>Misorientation</th>
<th>Rotation axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB Random Angle</td>
<td>50°</td>
<td>[434]</td>
</tr>
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Random Angle Grain Boundary

- Deuterium observed unambiguously (no overlaps) at 4 Da, in the form $^2\text{H}_2^+$
Random Angle Grain Boundary

- Vast majority of $^2$H observed as Si$^2$H$^+$ at 30, 31 and 32 Da.

- Overlap between $^{28}$Si$^2$H$^+$ 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 $^2\text{H}$ 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, $^2\text{H}$ was observed, at individual dislocations

- Dislocations observed both along the dislocation and end on in $^2\text{H}^+$ and Si$^2\text{H}^+$
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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Quantification of $^2$H at defects

Comparison of mass spectra from a non-passivated and $^2$H passivated GB
Quantification of $^2\text{H}$ at defects

- By extracting region of interest containing the grain boundary or dislocation, the $^2\text{H}$ quantity per defect can be determined.

- Dislocation III can be seen to have significantly more $^2\text{H}$ than the other dislocations.

<table>
<thead>
<tr>
<th></th>
<th>RA</th>
<th>$\Sigma 3$</th>
<th>I</th>
<th>II</th>
<th>III</th>
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<tr>
<td>$^2\text{H}$</td>
<td>$1.4 \pm 0.15 \times 10^{14}$ counts cm$^{-2}$</td>
<td>0.0 counts cm$^{-2}$</td>
<td>$14 \pm 1.5$ counts nm$^{-1}$</td>
<td>$13 \pm 2$ counts nm$^{-1}$</td>
<td>$22 \pm 1.5$ counts nm$^{-1}$</td>
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<th>$\Sigma 3$</th>
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<tr>
<td>2$^2$H atoms per atomic site in defect</td>
<td>$1.4 \pm 0.15 \times 10^{14}$ counts cm$^{-2}$</td>
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</tr>
<tr>
<td>$^2$H Quantified</td>
<td>$\approx 0.2$</td>
<td>Lower detection limit $\approx 2 \times 10^{12}$ counts cm$^{-2}$</td>
<td>$\approx 5$</td>
<td>$\approx 5$</td>
<td>$\approx 8$</td>
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Summary

• Method presented that allows for mapping of hydrogen at defects in multicrystalline silicon that has the potential to underpin future development of hydrogen passivation

• \(^2\)H is introduced atomically in a method analogous to that used in industry

• Quantification of \(^2\)H at individual defects is possible, using deconvolution of Si\(^2\)H\(^+\) peaks

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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**Next Steps:**

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Diffusion of Deuterium

Deuterium only introduced effectively atomically

7 orders of magnitude difference in diffusivity