CHARACTERIZATION OF OXYGEN-RELATED DEFECTS IN CZOCHRALSKI SILICON WAFERS

CHEETAH Characterization Workshop 14-01-2015
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SUMMARY

• Context – moving towards more stringent material requirements

• Oxygen-related defects in silicon - a reservoir of lifetime killers

• Introduction to OxyMap

• Examples of applications

• Conclusion and outlook
SUMMARY

- Context – moving towards more stringent material requirements
- Oxygen-related defects in silicon - a reservoir of lifetime killers
- Introduction to OxyMap
- Examples of applications
- Conclusion and outlook
Higher efficiency cell technologies are entering the market
- Mostly on monocrystalline Czochralski wafers

ITRPV expected mass production efficiency by 2025
• Require very high carrier lifetimes ($\tau$) + less tolerance to medium/low quality wafers

Large oxygen (O) incorporation from crucible in Cz-Si (1-15×10^{17} cm^{-3})

Interstitial oxygen (O_{i}) precursor of critical species for the industry

**Oxygene-related defects in silicon**

- **Lifetime killers (black core)**
- **Lifetime killers (LID)**
- **Resistivity shifters + lifetime killers**

Other defects also concerned (Vacancy-O complexes, Nitrogen-O complexes)

- Need to monitor [O_{i}] and O-related defects!

“**Only two third** of the Cz-Si wafers are defect-free. 29% exhibit oxygen thermal donors and 4% severe oxygen precipitation”

Fraunhofer ISE (PV Mag. 2012)

Estimated **10-20% of shipped wafers affected by oxygen cluster rings** with cells below efficiency specs.

- rings 1-2% abs. efficiency drops
- discs 4-6% abs. efficiency drops

ECN/Yingli (PVSEC 2015)
SUMMARY

• Context – moving towards more stringent material requirements

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**OXYMAP OVERVIEW**

- **OxyMap** relies on the change in resistivity ($\rho$) during an intentional formation of Thermal Donors
  - Small O-related clusters formed at around 450°C
  - Double donors $\Rightarrow$ $\rho$ shift
  - Unwanted $\Rightarrow$ Can be annihilated above 600°C

- **TD generation rate at 450°C highly dependent on $[O_i]$**

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**Graph:**

- Kinetics x50
- High sensitivity of the $\rho$ shift on $[O_i]$ $\Rightarrow$ ground principle of OxyMap
OXYMAP OVERVIEW

All resistivity ($\rho$) measurements performed using non-contact Eddy currents

→ OxyMap is **non-destructive** and **independent of wafer morphology** (thickness or surface state)

$\rho_1$ 450° C anneal $\rho_2$ High T anneal $\rho_3$

$[TD]_{\text{as-grown}}$ $[O_i]$ Intentional Dopant concentration ([B], [P]…)

OXYMAP OVERVIEW
[O\textsubscript{i}] VARIATIONS MEASUREMENTS

- Linescans performed on the diagonal of the solar wafer
  - Due to the radial symmetry of the O-related defects distribution, linescans along the wafer diagonal are enough to thoroughly characterize a wafer
FULL INGOT CHARACTERIZATION

- Example: Reconstruction from 25 wafers scanned through an ingot
  - Process control for routine products
  - Optimized feedback for R&D purposes

[Graph showing [Oi] (cm⁻³) vs. Solidified fraction (%) and Distance to center (%)]
COMPARISON WITH EXISTING TECHNIQUES

- Fourier Transform InfraRed spectroscopy (FTIR) routinely applied on thick polished slices (application to solar wafers tricky)

Various samples used for the comparison

- 2 mm thick p and n type samples
- Resistivity 0.5 - 10 Ω.cm
- Top, middle and bottom ingots (different thermal histories)
- Different Cz pulling parameters (seed and crucible rotation speeds, pulling speed)
- [O_i] covering the whole Cz range

Very good agreement between OxyMap and FTIR measurements Confirmed by tests made for industrial partners
OXYMAP OVERVIEW

- $\rho_1$ with $[TD]_{\text{as-grown}}$
- $450^\circ \text{C}$ anneal
- $\rho_2$ with High T anneal
- $\rho_3$

- $[O_i]$ (Thermal History Index (linked to wafer position))
- Intentional Dopant concentration ([B], [P]…)

Flowchart:

1. $\rho_1$ to $[TD]_{\text{as-grown}}$
2. $450^\circ \text{C}$ anneal
3. $\rho_2$ with High T anneal
4. $\rho_3$

Connections:

- $[TD]_{\text{as-grown}}$ to $[O_i]$
- $[O_i]$ to Intentional Dopant concentration ([B], [P]…)
- Thermal History Index (linked to wafer position)
THERMAL HISTORY : DEFINITION

- \([O_i] = \) driving force for O-defects formation
- Thermal history : \(T=f(t)\), governs the amplitude of formation
  - Larger thermal histories = larger [defects]

**Thermal history strong function of height**

![Graph showing temperature and time after crystallization](image)

**Thermal History Index (THI)**

\[
THI \approx \frac{1}{60} \left( \frac{[TD]_{as\text{-}grown}}{k_t \times [O_i]^{3.44}} \right)^{1.02}
\]

Measured with OxyMap

RECONSTRUCTION OF THE INGOT THERMAL HISTORY

- Pulling process issues can be quickly identified
  - valuable feedback for R&D purposes (hotzone optimizations)

Extended cooling time requiring crystallisation process optimizations

Reconstruction from measurements on 25 wafers

Courtesy from E. Letty
OXYMAP OVERVIEW

$\rho_1$  

$[TD]_{as\text{-}grown}$

$450° \text{ C anneal}$

$\rho_2$  

[O$_i$]

High T anneal

$\rho_3$

Intentional Dopant concentration ([B], [P]…)

Thermal History Index (linked to wafer position)

Cell LID predictions

For boron-doped Cz
PREDICTION OF LIGHT-INDUCED DEGRADATION AT CELL LEVEL DUE TO THE BORON-OXYGEN COMPLEXES

- Degradation amplitude = strong function of [B] and [O_i] [1]
- Induced cell LID losses ($\Delta V_{oc}$, $\Delta J_{sc}$, $\Delta FF$, $\Delta$Efficiency) modeled with PC1D and adjusted to CEA experimental results obtained on BSF and PERC cells

Models for Al-BSF and PERC architectures

Representative results obtained

LID tests were made in accordance with EN50380 and IEC61215

LID PREDICTION – COMPARISON TO INDUSTRIAL DATA

- OxyMap predictions validated within uncertainty by comparison with industrial LID losses measurements.

- Potential interest from:
  - wafer and cell manufacturers to identify high-LID wafers
  - module manufacturers to improve the cell matching (after cell LID)

<table>
<thead>
<tr>
<th>Al-BSF cells</th>
<th>PERC cells</th>
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<tbody>
<tr>
<td>Measured relative efficiency losses (%)</td>
<td>Predicted relative efficiency losses (%)</td>
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<tr>
<td>Predicted relative efficiency losses (%)</td>
<td>Measured relative efficiency losses (%)</td>
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More industrial data to be collected
OXYMAP OVERVIEW

\[ \rho_1 \rightarrow 450^\circ C \text{ anneal} \rightarrow \rho_2 \rightarrow \text{High T anneal} \rightarrow \rho_3 \]

- \([TD]_{\text{as-grown}}\)
- \([O_i]\)
- Intentional Dopant concentration ([B], [P]...)
- \(\text{Cell LID predictions}\)

**Concerns low-T cell processes**

- Lifetime limited by as-grown TD (\(\tau_{TD}\))
- Thermal History Index (linked to wafer position)

For boron-doped Cz
CARRIER LIFETIME LIMITED BY AS-GROWN TD

- High $[\text{TD}_{\text{as-grown}}]$ is incompatible with high bulk carrier lifetime
  - Critical for low-T cell processes for which TD are not suppressed

2D reconstruction of the carrier lifetime limited by TD$_{\text{as-grown}}$ from a diagonal OxyMap linescan

Models to be published in 2016

Confirmation from 2D carrier lifetime mapping ($\mu$W-PCD)
The R&D version now available from AET Solar Tech, France

http://aetsolartech.com/oxymap/

- Non destructive
- No restriction on wafer thickness
- No restriction on wafer surface roughness

Characterization of O-related defects / Detection of defective wafers / Feedback for ingot and cell R&D dvpts
Thanks for your attention!
ANALYSING THE SORTING STRATEGIES OF WAFFERS

- Better quality check of incoming wafers that reveals the sorting strategy of wafer providers

Measurements of the $[TD]_{as-grown}$ shows that the Cz wafer provider A mixes wafers.
Applicable on thin wafers

- Poor FTIR performance on thin wafers (random scattering of IR beam at surfaces and chaotic internal multireflexions)
- OxyMap performs equally good for whatever the thickness
Can measured wafers be transformed into efficient cells?

No detectable impact of the measurement on the final cells efficiencies noticed for AlBSF process.
EFFICIENCY VARIATIONS VS INGOT HEIGHT TODAY

- Large variations of stabilized $\eta$ observed along the ingot height (both p and n-type Si)

"Only two third of the Cz-Si wafers are defect-free. 29% exhibit oxygen thermal donors and 4% severe oxygen precipitation"

Fraunhofer ISE (???)

"Estimated 10-20% of shipped wafers affected by rings -> cells below efficiency specs. “rings” 1-2%, “discs” 4-6% abs. eff”

“Recombination active defects in ring shape related to oxygen cluster formation during ingot growth”

ECN/Yingli (PVSEC 2015)

Already today, O-related defects do not allow to leverage efficiency improvements permitted by high efficiency cell processes  ➔ Monitoring is required
HOW TO LEVERAGE LINESCANS

Unusual $[TD]_{\text{ini}}$ profile explained by huge lateral variations in thermal history across the wafer.

Linescans bring valuable new insight on pulling process issues in this case very bended isothermals during ingot cooling suggesting high residual stress within the wafer.
SmartER SELECTION OF WAFERS TO BE USED FOR PROCESS OPTIMIZATION

Very large and unexpected resistivity changes after high T steps can occur due to high [TD]_{ini}

x2 resistivity change (much larger can occur)

Quick and accurate access to the resistivity before and after high T step (>600°C) is essential for cell process developments

Can strongly complicate interpretation of process development results!
CONCLUSIONS

- A large set of accurate data can be obtained to help material qualification along the value chain

Data over the diagonal of the wafer
- $[O_i]$ and spatial homogeneity
- Initial resistivity and resistivity after high T process steps
- $[TD_{as-grown}]$ and spatial homogeneity

Additional features:
- Position of the wafer in the original ingot
- Detection of low-efficiency wafers
- Predictions of the cell LID losses
- Estimation of the carrier lifetime limited by TD
- Feedback on crystallization issues for crystal growers

Non destructive ✔
No restriction on wafer thickness ✔
No restriction on wafer surface roughness ✔
CARRIER LIFETIME LIMITED BY AS-GROWN TD

- High concentrations of as-grown TD is incompatible with high bulk carrier lifetime
  - From the measured $[TD_{ini}]$, OxyMap predicts the carrier lifetime limited by TD

\[ \tau_{TD} \sim [TD_{ini}]^{-2.5} \text{ over the 0.2-3 ms range!} \]

$[TD]_{ini, limit} = 6 \times 10^{14}$ cm$^{-3}$

$[TD]_{ini}$ range in Cz-Si: $10^{13} - 2 \times 10^{15}$ cm$^{-3}$