Light- and Elevated Temperature-Induced Degradation (LeTID): the Past, the Present and What Lies Ahead

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Light- and Elevated Temperature Induced Degradation (LeTID)

- LeTID is now a very well known in both academia and industry

- There have been over 200 conference and journal publications worldwide
LeTID – Key Areas of Investigation

LeTID
LeTID – Key Areas of Investigation

Root Cause

- Hydrogen
- Vacancies
- Non-metals
- Metal Impurities

Characterisation

- DLTS
- EDX
- TIDLS
- XRD
- ICP-MS
- μ-PL
- μ-XRF
- QSSPC
- FTIR

LeTID

Key Areas of Investigation

- Fe-H
- C-H
- LBIC
- C-V
- H₂
- H-X
- V-O
- V-H₂
- H₂O
- C₆
- O₂
- Ti⁰⁺⁺
- Al
- Mo⁰⁺⁺
- W⁰⁺⁺
- Cu
- Co
- Ni
- Al
- C-V
LeTID – Key Areas of Investigation

Root Cause

Characterisation

Metal Impurities

Module Stability

IEC Standards

H bucket theory

Hydrogen-Induced Recombination

Reservoir theory

Metal precipitation

3-state and 4-state model

Metal diffusion

Models

Testing

LeTID

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C6

O2

Co

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Mo0/+1

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Ni

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IEC 61215

H bound states

Reservoir theory

H bound states

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H2
LeTID – Key Areas of Investigation

Role of Hydrogen
- Evidence of H
  - Compensation
  - Plasma hydrogenation
  - Hydrogen rich-films

Models
- Metal precipitation
- Diffusivity and Solubility
- Material universality
- Direct-PECVD
- 3-state and 4-state model

Testing
- Platelets
- Extended defects
- Surface recombination
- SRD
- Homogeneous distribution
- IEC Standards
- Reservoir theory
- H bucket theory
- Counter-doping
- Hydrogen-Induced Recombination

Root Cause
- Metal Impurities
  - Non-metals
  - C
  - O
  - Al
  - Ti
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LeTID
- H₂
- H-X
- V-O
- V-H₂
- Vacancies

Factors
- IEC 60904
- IEC 61215
- Material universality
- Homogeneous distribution
- Direct-PECVD
- SRD
- Reservoir theory
- H bound states
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Key Areas of Investigation

Compensation
Diffusivity and Solubility
Homogeneous distribution
Material universality
Metal precipitation
Metal diffusion
Reservoir theory
H bound states
LeTID – Key Areas of Investigation

Materials
- Black-Si, Si
- Substrate Material
  - N-type/P-type
  - Ga/P/B/In doping
Passivating Films
- SiO₂, Al₂O₃:H, Si₃N₄:H
- ALD deposition
- ALD, APCVD
- PERC, BSF, SHJ, BOSCO
- Cell Type
- Key behaviours
  - Firing dependence
    - Temperature
    - Cooling rate
      - Pre-dark annealing
      - Injection dependence
      - Thermal cycling
    - Dark anneal + Light soak
- Compensation
  - Pre-formation
  - Plasma hydrogenation
  - Diffusivity and Solubility
  - Material universality
  - Metal precipitation
    - Metal diffusion
    - Metal precipitation
    - 3-state and 4-state model
    - Reservoir theory
    - H bound states
  - Material stability
    - SRD
    - Extended defects
    - Surface recombination
    - Homogeneous distribution
    - Direct-PECVD
    - Material universality
    - Metal precipitation
    - Metal diffusion
    - Metal precipitation
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Root Cause
- Hydrogen
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Presentation Outline

1. A brief history of LeTID

2. Evaluating the Root Cause of LeTID

3. Our proposed LeTID model

4. Mitigation Strategies for LeTID
   - Is LeTID going to be a problem for the industry?
   - What happens after LeTID?
The Past – Beginnings of LeTID

- First identified in 2012 on mc-PERC solar cells by Ramspeck et al.
- Average degradation in efficiency of up to 10%\(_{\text{rel}}\) on untreated cells and as much as 16%\(_{\text{rel}}\) in some studies

<table>
<thead>
<tr>
<th>Reference</th>
<th>Type</th>
<th>Rel. Deg</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sio et al.</td>
<td>Cell</td>
<td>4.3%</td>
<td>65 °C, 1sun</td>
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<tr>
<td>Chan et al.</td>
<td>Cell</td>
<td>12.7%</td>
<td>70 °C, 0.46 kW/m²</td>
</tr>
<tr>
<td>Luka et al.</td>
<td>Cell</td>
<td>10%</td>
<td>75 °C, 1sun</td>
</tr>
<tr>
<td>Ramspeck et al.</td>
<td>Cell</td>
<td>6%</td>
<td>75 °C, 0.4 kW/m²</td>
</tr>
<tr>
<td>Petter et al.</td>
<td>Cell</td>
<td>16%</td>
<td>75 °C, 1sun</td>
</tr>
<tr>
<td>Deniz et al.</td>
<td>Cell</td>
<td>4.4%</td>
<td>75 °C, (J_{\text{SC}})</td>
</tr>
<tr>
<td>Krauss et al.</td>
<td>Cell</td>
<td>11.2%</td>
<td>80 °C, 0.8 kW/m²</td>
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<td>Fertig et al.</td>
<td>Module</td>
<td>11%</td>
<td>85 °C, MPP, 1 kW/m²</td>
</tr>
<tr>
<td>Kersten et al.</td>
<td>Module</td>
<td>11%</td>
<td>85 °C, MPP</td>
</tr>
<tr>
<td>Nakayashiki et al.</td>
<td>Module</td>
<td>7.5%</td>
<td>Outdoor</td>
</tr>
<tr>
<td>Kersten et al.</td>
<td>Module</td>
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</table>

The Past – Early Observations

- In 2015, Kersten et al. showed that the degradation was accelerated at higher T, thus calling it LeTID.

- Later in 2017, Kwapil et al. demonstrated a dependence of the degradation reaction on $\Delta n$. Adding illumination increases the reaction rate.

- In 2017, Chan et al. observed that degradation also occurs during dark annealing.
The Past – A Discovery of LeTID in Czochralski

• This provided a method of testing p-type Cz wafers without activating B-O defects

• As part of my PhD, we showed that LeTID also manifests itself in Cz materials

The Past – A Universal Defect in Silicon

Cast-mono

FZ-Si [2]

Ga-doped [3]

Silicon heterojunction (SHJ)

Perovskites?? [3]

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The Past – Evaluating the Root Cause – Metal Impurities

- In 2016, Bredemeier et al. proposed that metallic impurities (M) are the root cause of LeTID.

1. **Before firing**: metallic impurities reside in a recombination inactive precipitated state ($M_P$).
2. **Firing** ($T > 600 \, ^\circ C$): precipitates dissolve into interstitials ($M_i$).
3. **Cooldown**: $M_i$ bond with a homogeneously distributed impurity to form a $M_i – X$ complex.
4. **Illuminated annealing**: The complex reconfigures itself into a $M_i – X^*$ complex then dissociates into $M_i$.

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The Past – Evaluating the Root Cause – Metal Impurities

- In 2017, Bredemeier et al. suggested Co and Ni as a possible metal impurity.
- It was suggested that diffusion of the metals towards the surface could explain regeneration.

- Deniz et al. (2018), found Ni precipitation using TEM and energy dispersive x-ray (EDX) measurements.
- TIDLS by UNSW, MIT – defect recombination properties (k-value) close to $\text{Ti}^{+3/2+}$, $\text{Mo}^{0/+}$ or $\text{W}^{0/+}$.

The Present – Hydrogen-Induced Degradation

- There are now many studies suggesting that hydrogen is responsible for LeTID.

- Recently, Schmidt et al. demonstrated for the first time, a direct correlation between [H] and LeTID.
- In experiments, we observe different amounts of LeTID in different materials.
  - Is something inherent to the wafer also involved – Could it be a H-X complex?

The Present – H-X Complexes and Deep Level Transient Spectroscopy

- Hydrogen can form complexes with almost everything
  - Ag-H\textsubscript{X} (Graff 2000...)
  - Au-H (Deixier 1998...)
  - B-H (Sah 1983...)
  - C-H (Anderson 2002...)
  - C-O-H (Vaqueiro-Contreras 2017)
  - Co-H\textsubscript{X} (Scheffler 2013...)
  - Cr-H (Sadoh 1994...)
  - Cu-H (Yarykin 2013...)
  - Fe-H (Szwacki 2007...)
  - Ni-H\textsubscript{X} (Shiraishi 1999...)
  - P-H (Seager 1990...)
  - Pd-H (Jones 1999...)
  - Pt-H\textsubscript{X} (Hohne 1994...)
  - Si-V-H\textsubscript{X} & Si-V-O-H\textsubscript{X} (Bonde 1999)
  - Ti-H\textsubscript{X} (Scheffler 2015...)
  - V\textsubscript{X}-H\textsubscript{Y} (Graff 2000...)
  - Va-H\textsubscript{X} (Sadoh 1992...)
  - And many more....

- DLTS is a good method for identifying recombination active traps

- Recent DLTS studies have hypothesised that Fe-H or C-H complexes may be defect behind LeTID. Further measurements are needed to confirm this.

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During firing (peak) – H diffuses into Si as interstitials
The Present – A Hydrogen-X Defect Model

- **During firing (peak)** – H diffuses into Si as interstitials

- At high temperatures, the Si conductivity is intrinsic $\rightarrow$ H is largely in the $H^+$ state
During firing (peak) – H diffuses into Si as interstitials

At high temperatures, the Si conductivity is intrinsic → H is largely in the H⁺ state

During cooling (quenching) – H forms B-H pairs in the bulk and passivates defects.
• **During firing (peak)** – H diffuses into Si as interstitials

• At high temperatures, the Si conductivity is intrinsic → H is largely in the $H^+$ state

• **During cooling (quenching)** – H forms B-H pairs in the bulk and passivates defects.

• It also pre-forms LeTID, however, a majority of H is frozen in metastable dimer states ($H_{2A/B}$)
The Present – A Hydrogen-X Defect Model

- During annealing or light soaking, $H_{2A}$ dimers dissociate and contribute to B-H and LeTID.

- All of these bonds are metastable and constantly breaking and forming, e.g., $H^+ + B\text{-H} \rightarrow H_{2B/C} + B^- + 2h^+.$

The Present – A Hydrogen-X Defect Model

- Net motion of H is towards the surface and out of silicon.
- With long-duration annealing, H effuses out of wafer or transforms into a stable $H_{2C}$ dimer state.
- LeTID recovers when the bulk is depleted of metastable dimers, bound states and H interstitials.

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The Present – Mitigation of LeTID – Process Modification

- There are many ways of reducing the hydrogen content within the silicon wafers to reduce LeTID

- Reducing peak firing → Less H in-diffusion or Slower-cooling → More H effusion

- Thinner wafers have demonstrated lower LeTID → Faster defect effusion

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**Graphs and References**

- Schmidt et al., IEEE J. Photovoltaics. 9 (2019) 1497–1503
The Present – Mitigation of LeTID – Process Modification

• We can also reduce the hydrogen content within the SiNₓ:H films.
• Reducing the thickness of SiNₓ:H → lower Si-H and N-H bond density → lower [H] released during firing
• Deposition of ALD AlOₓ under the SiNₓ:H as barrier for hydrogen in-diffusion

The Present – Mitigation of LeTID – Process Modification

- Tuning the SiN$_x$:H refractive index to release less hydrogen during firing
- At low RI < 1.9, SiN$_x$:H films have high atomic density → reduces H diffusivity
- Hydrogen is important as it allows for the passivation of bulk defects (e.g. B-O in p-type)
- Lower [H] causes B-O regeneration to become slower → LID mitigation techniques become less effective.

- Commercial LeTID mitigation usually involves post-cell treatments
  1. Light based treatments
  2. Current Injection
  3. Biased annealing

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The Present – An Example of Commercial ANTI-LeTID Solar Cells and Modules

- Risen solar (Jäger Series) combine many techniques:
  1. Low temperature firing – reduces hydrogen in-diffusion
  2. Current-injection post-cell processing
  3. ALD $\text{AlO}_x:\text{H}$ passivation on both sides – hydrogen lean blocking layer
  4. $\text{SiO}_2$ layer on both sides – hydrogen blocking layer

What Lies Ahead – Will LeTID Remain a Problem for Commercial PV?

LeTID is both a material-inherent and process-induced defect

- Wafer quality is constantly improving with some wafers that are already LeTID free.
- Choosing better wafer sources + applying mitigation treatments will solve LeTID in both mc-Si and Cz-Si

What Lies Ahead – Hydrogen-Induced Surface Degradation

• As LeTID recovers, hydrogen diffuses out towards the surfaces.

• Too much H at the interface can lead to the formation of hydrogen-induced defects $\rightarrow$ surface degradation (increased $J_{0s}$).

• On PERC cells, this long-term degradation can cause up to a **10% absolute** drop in efficiency due to an decrease in FF [1].

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Summary

• LeTID is a complicated but well understood problem.

• There are many mitigation techniques for commercial PERC solar cell

• Beyond LeTID, we need to start assessing the impact of hydrogen-induced surface degradation and finding solutions.

• I hope that you have learnt something from my talk!
Thank you for your attention. Daniel.chen@unsw.edu.au