Faculty of Engineering
School of Photovoltaic and Renewable Energy Engineering

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

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UNSW SYDNEY Australia's Global University

ARENA Australian Government Australian Renewable Energy Agency

ACAP

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

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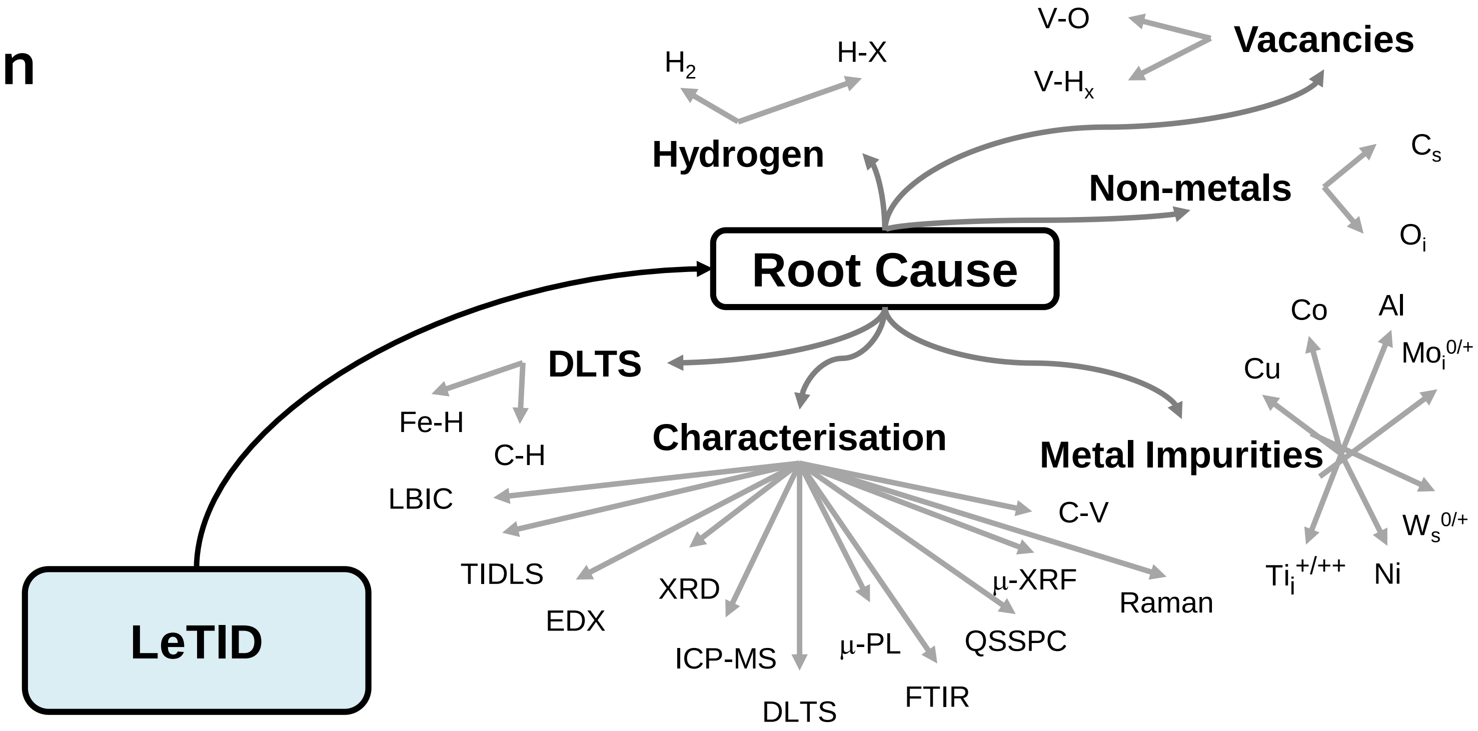
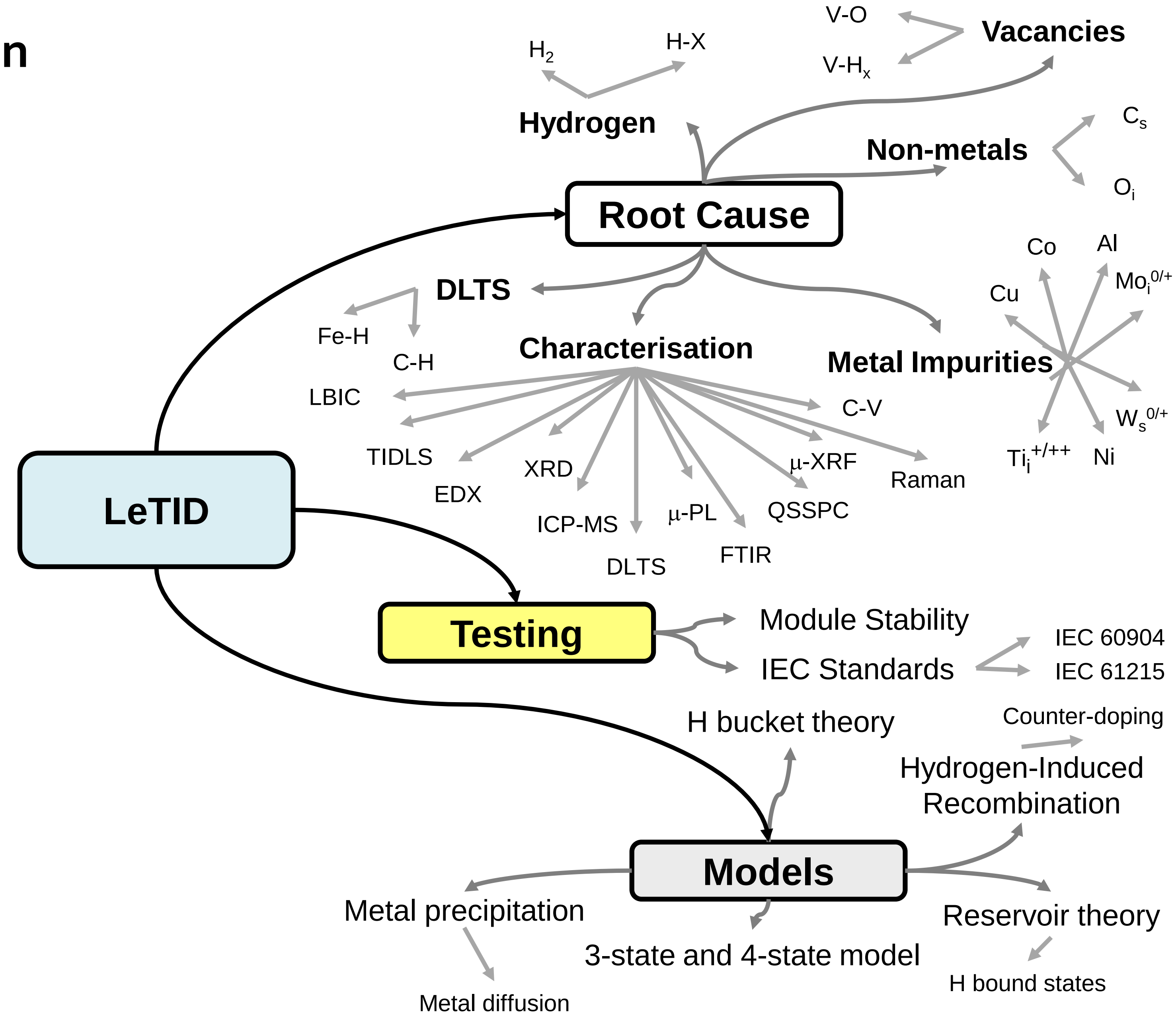


LeTID – Key Areas of Investigation



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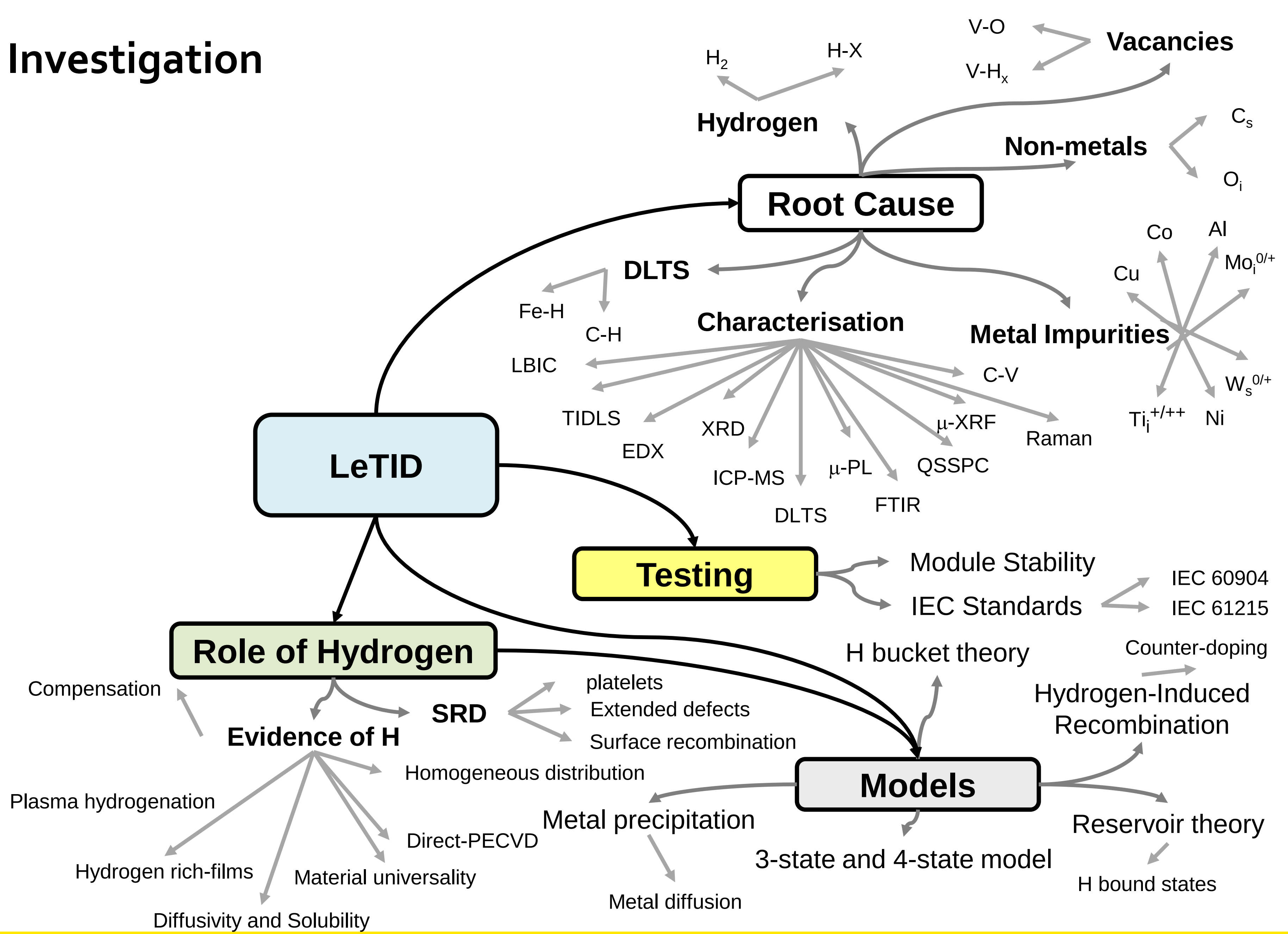

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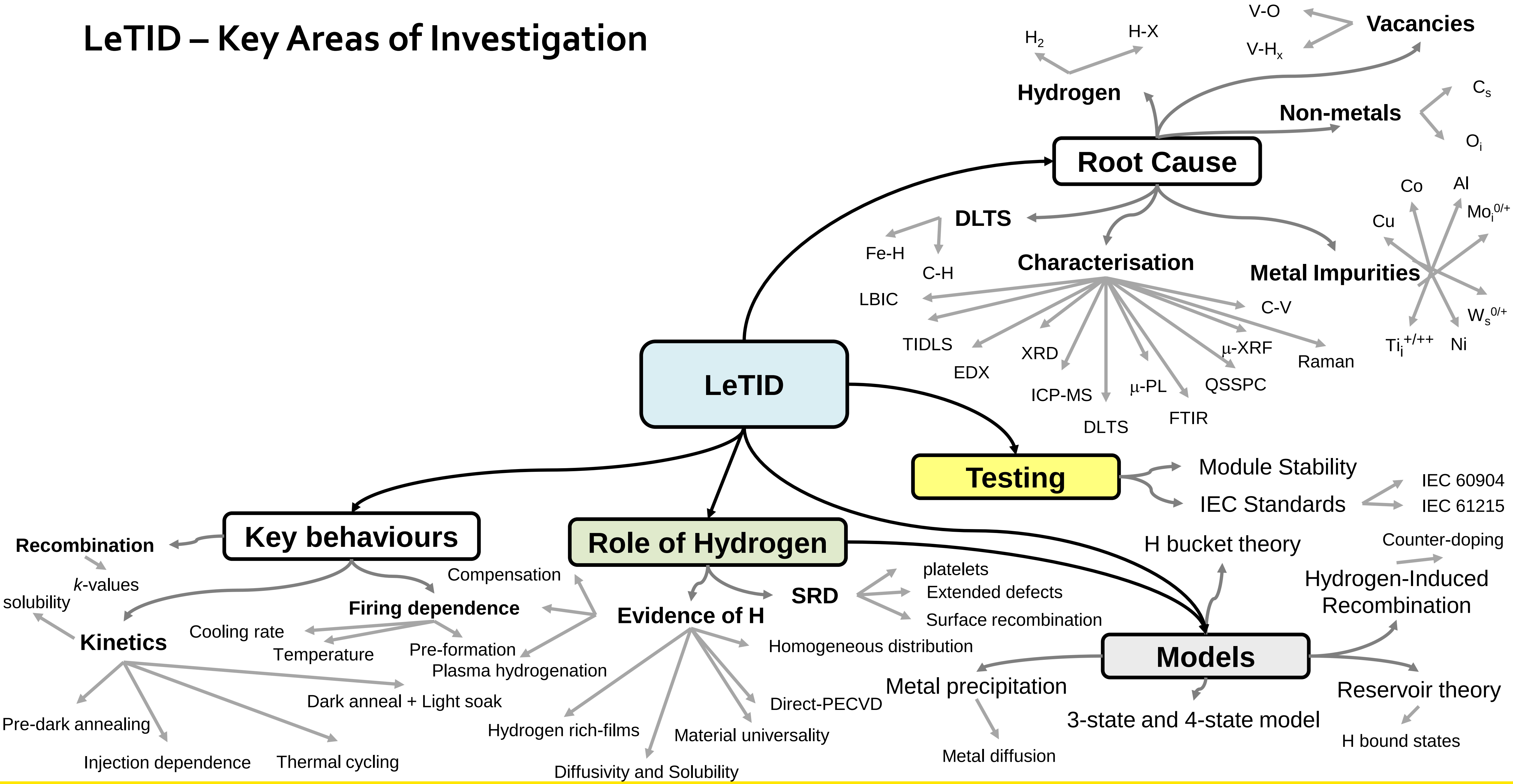

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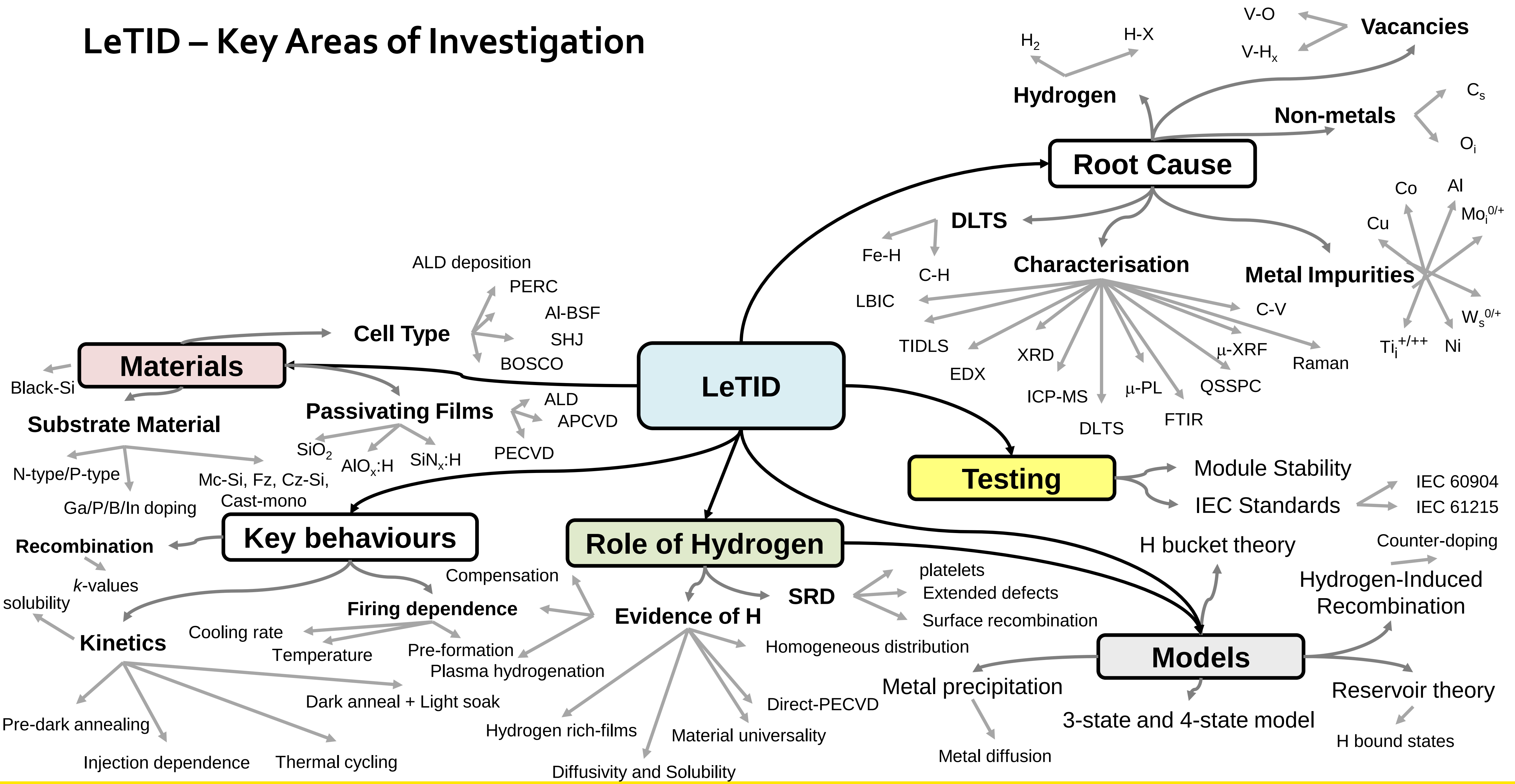
LeTID – Key Areas of Investigation



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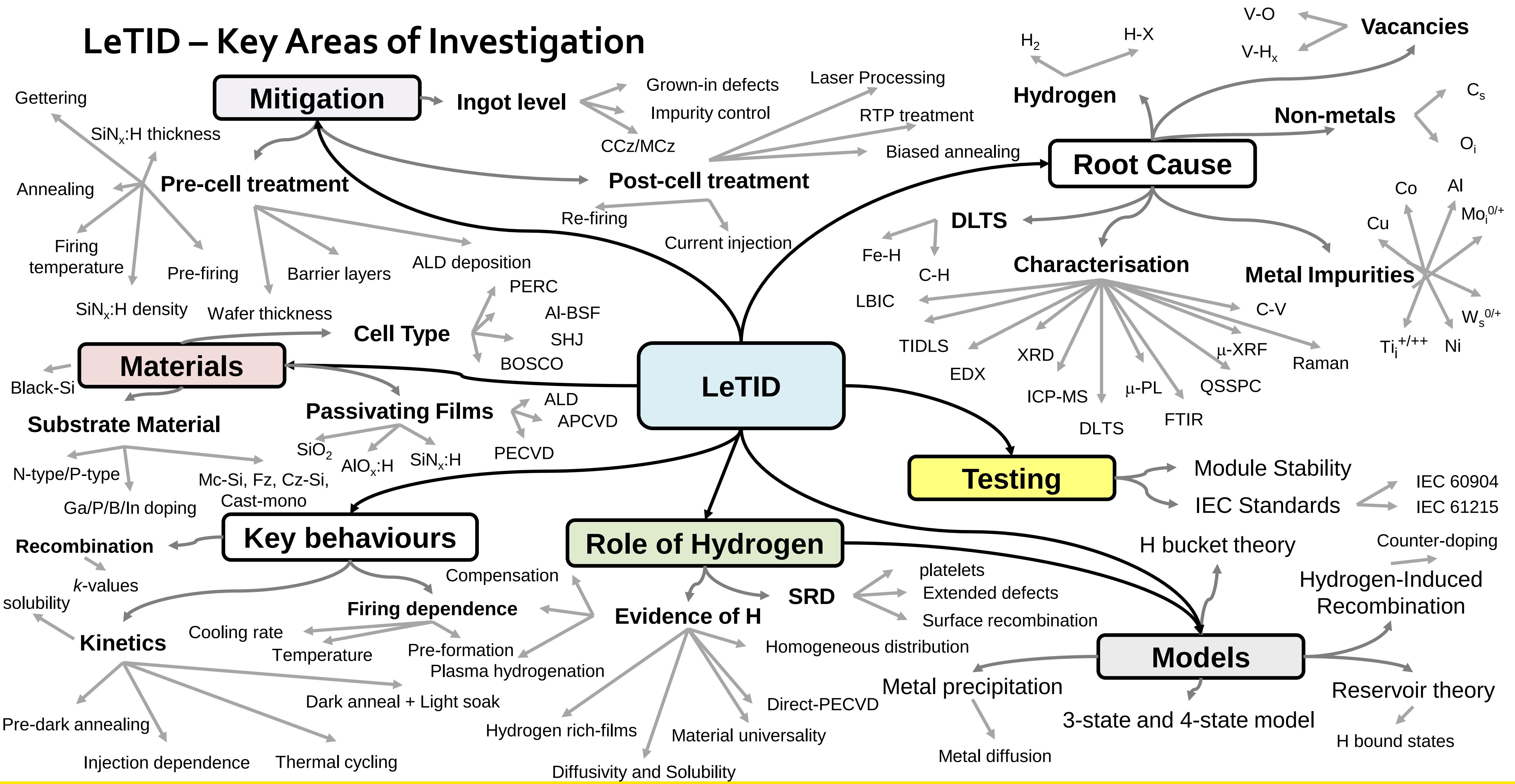
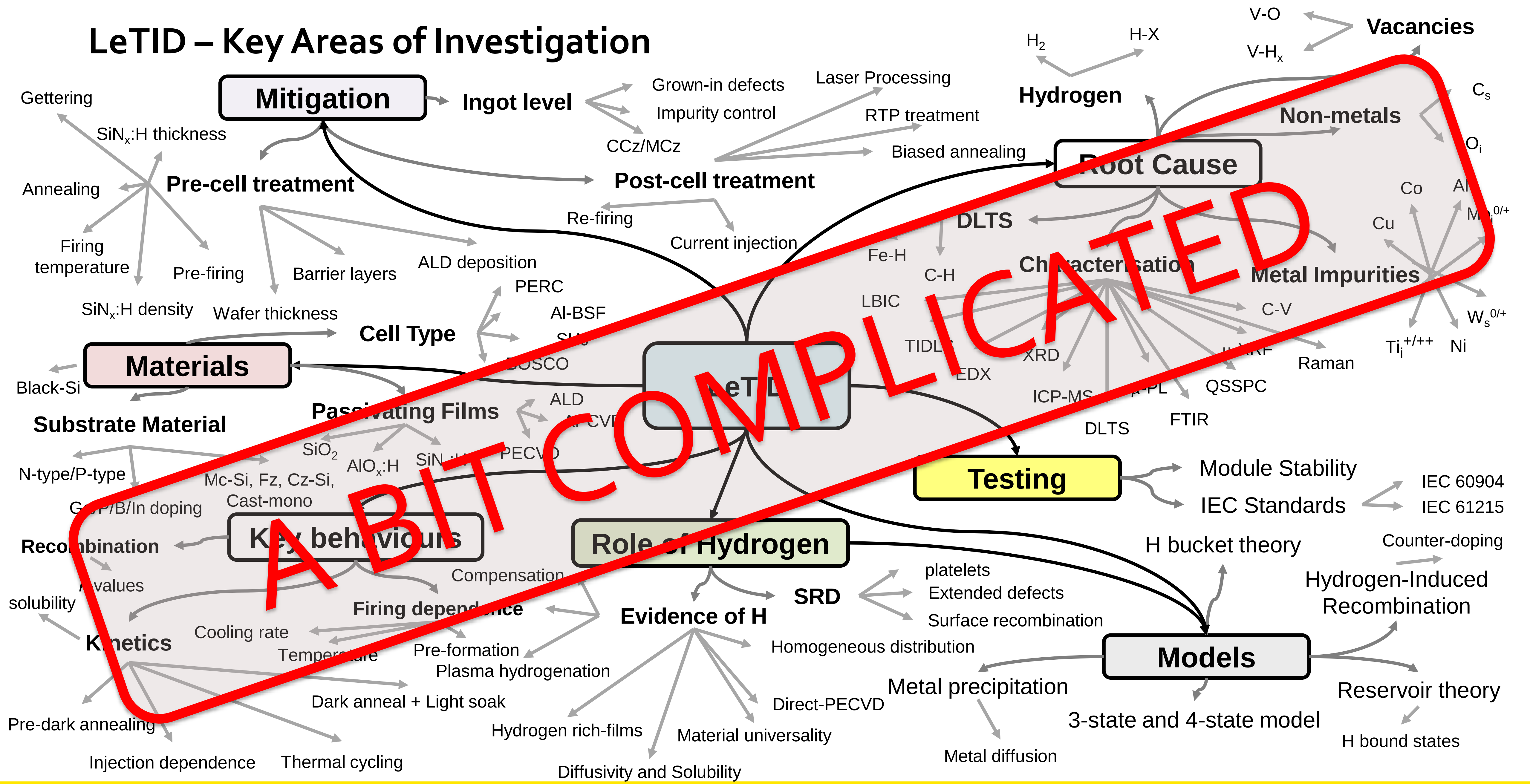


LeTID – Key Areas of Investigation



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Presentation Outline

1. A brief history of LeTID

2. Evaluating the Root Cause of LeTID

3. Our proposed LeTID model

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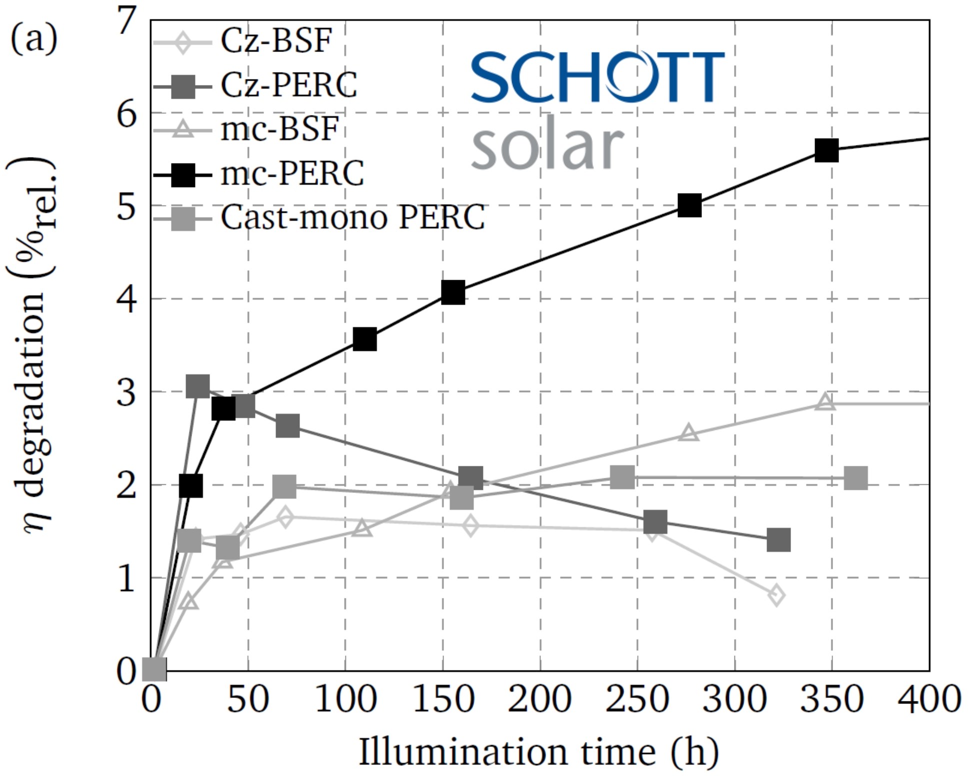
The Past – Beginnings of LeTID



Ramspeck *et al.*, 27th EUPVSEC, (2012), 861-865.

Reference	Type	Rel. Deg	Condition
Sio *et al.*	Cell	4.3%	65 °C, 1sun
Chan *et al.*	Cell	12.7%	70 °C, 0.46 kW/m^2
Luka *et al.*	Cell	10%	75 °C, 1sun
Ramspeck *et al.*	Cell	6%	75 °C, 0.4 kW/m^2
Petter *et al.*	Cell	**16%**	75 °C, 1sun
Deniz *et al.*	Cell	4.4%	75 °C, J_{SC}
Krauss *et al.*	Cell	11.2%	80 °C, 0.8 kW/m^2
Fertig *et al.*	Module	11%	85 °C, MPP, 1 kW/m^2
Kersten *et al.*	Module	11%	85 °C, MPP
Nakayashiki *et al.*	Module	7.5%	Outdoor
Kersten *et al.*	Module	10%	Outdoor

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

[1] Ramspeck et al., 27th EUPVSEC, (2012), 861-865.

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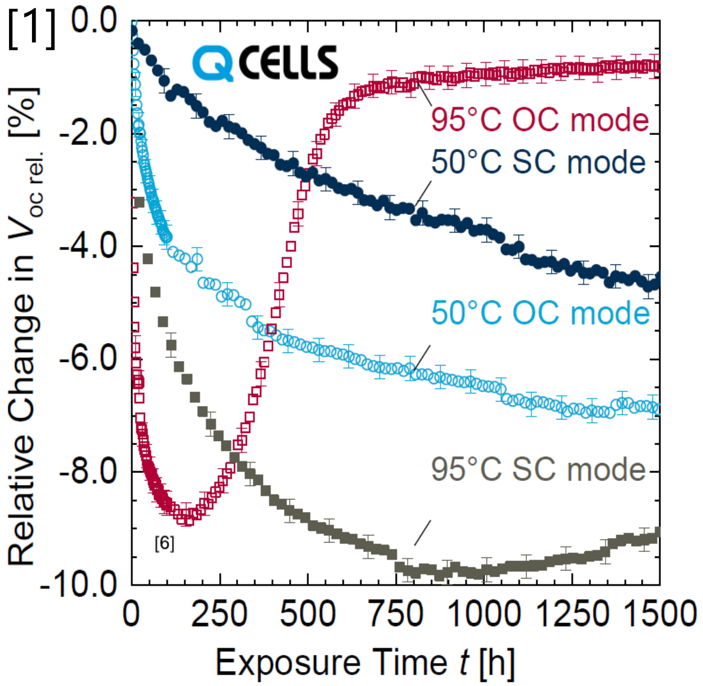
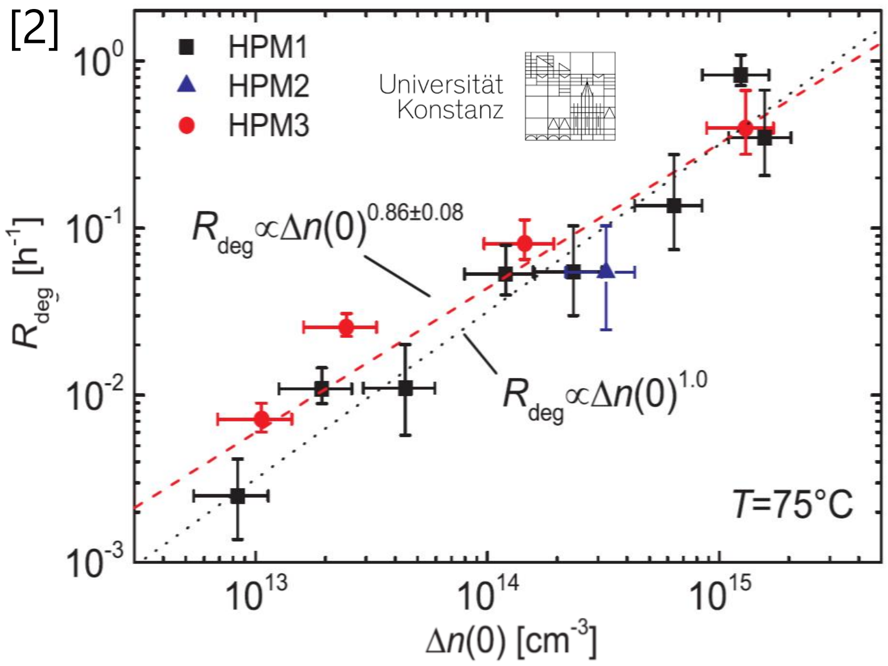
The Past – Early Observations

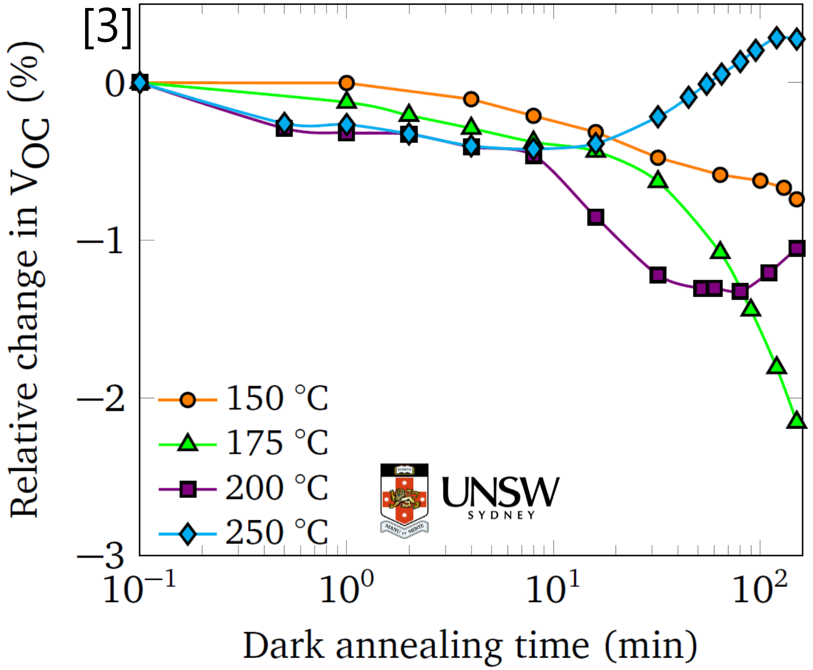
- In 2015, Kersten *et al.* showed that the degradation was accelerated at higher T, thus calling it LeTID



Kersten *et al.*, Sol. Energy Mater. Sol. Cells. 142 (2015) 83–86



Kwapil *et al.*, Sol. Energy Mater. Sol. Cells, 173 (2017), 80–84

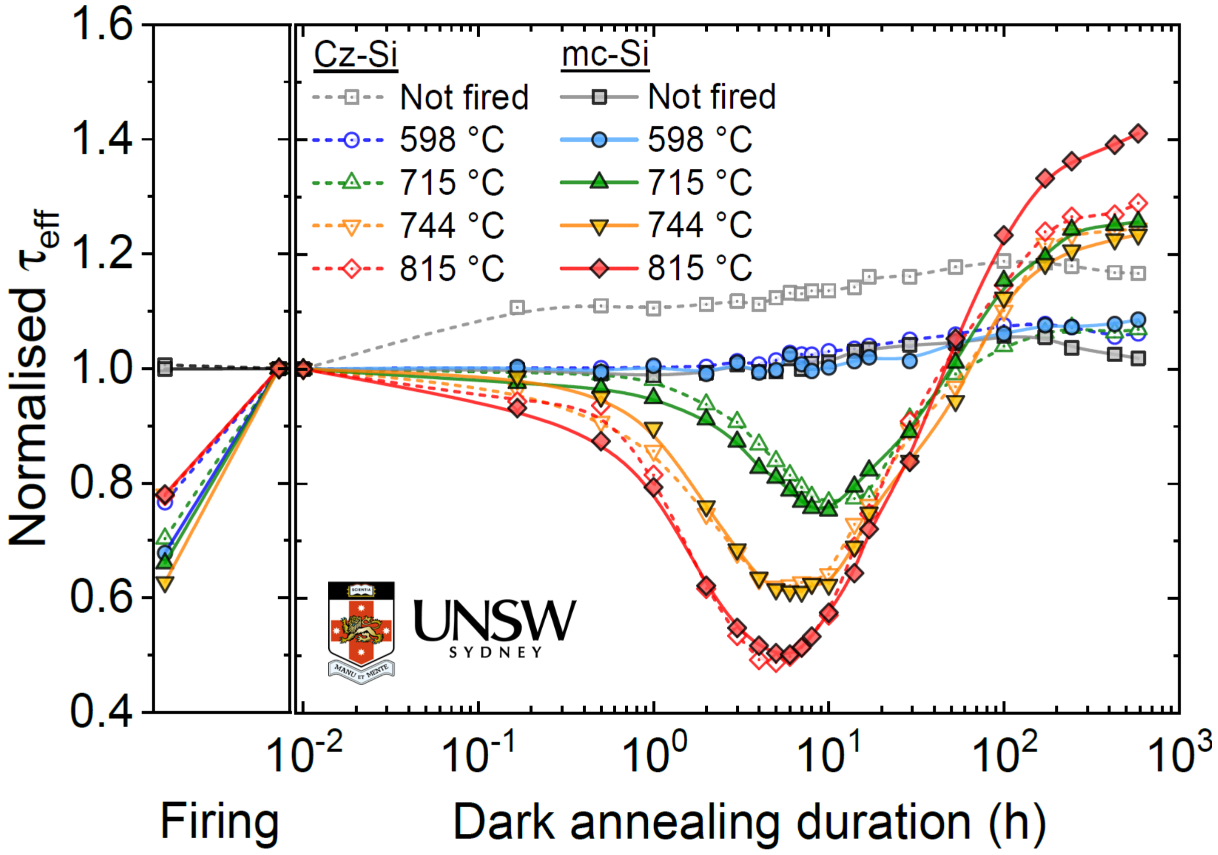


Chan *et al.*, Sol. RRL. 1 (2017) 1600028.

- Later in 2017, Kwapil *et al.* demonstrated a dependence of the degradation reaction on Δn. 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

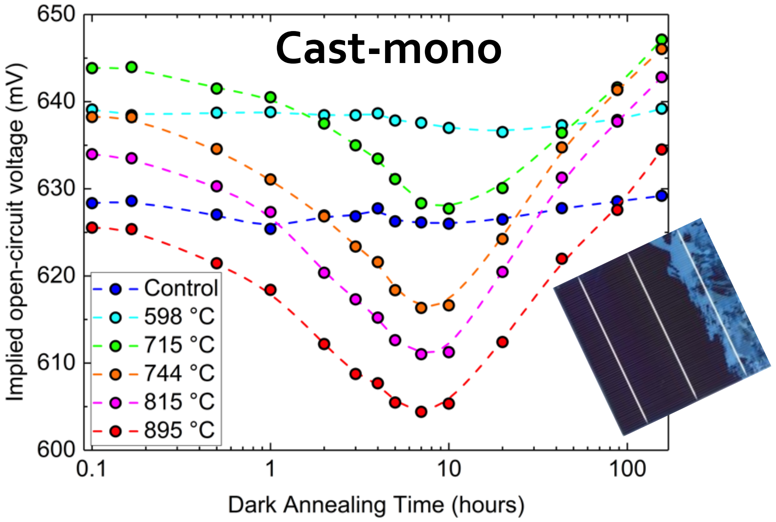
- This provided a method of testing p-type Cz wafers without activating B-O defects

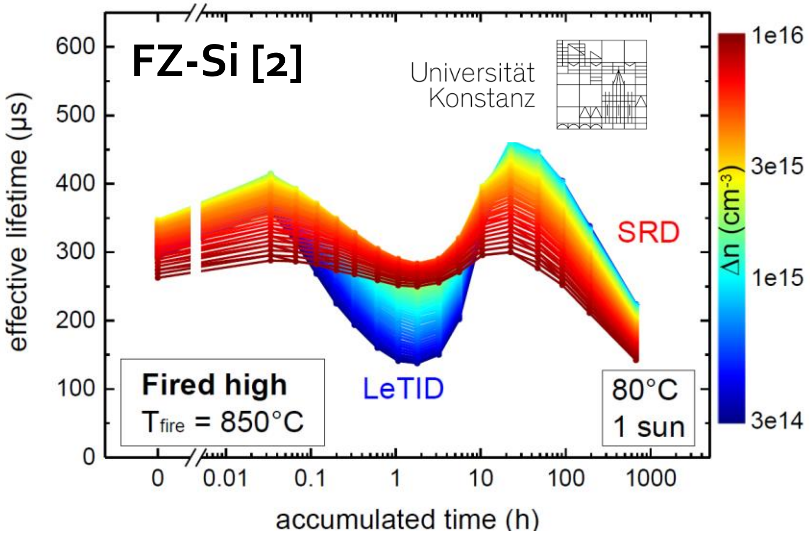


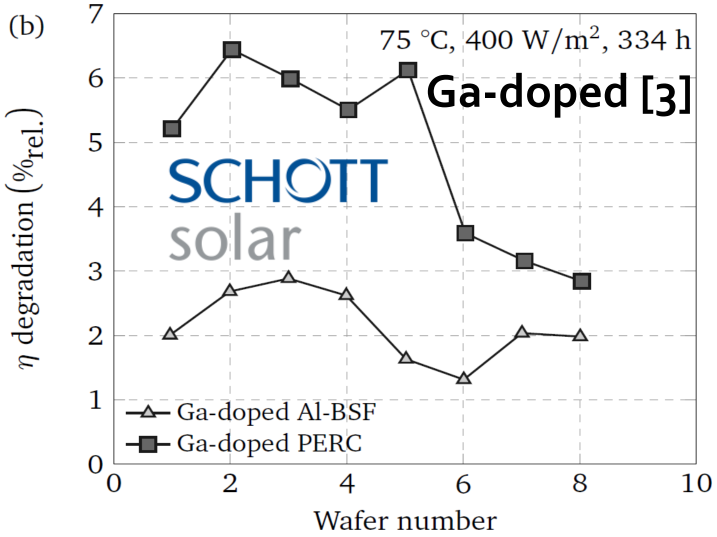
Chen *et al.*, Sol. Energy Mater. Sol. Cells. 172 (2017) 293–300.

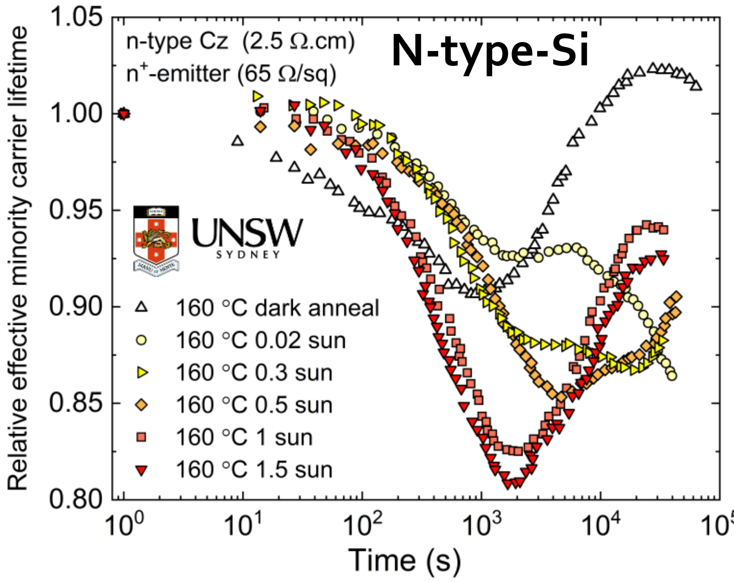
- As part of my PhD, we showed that LeTID also manifests itself in Cz materials

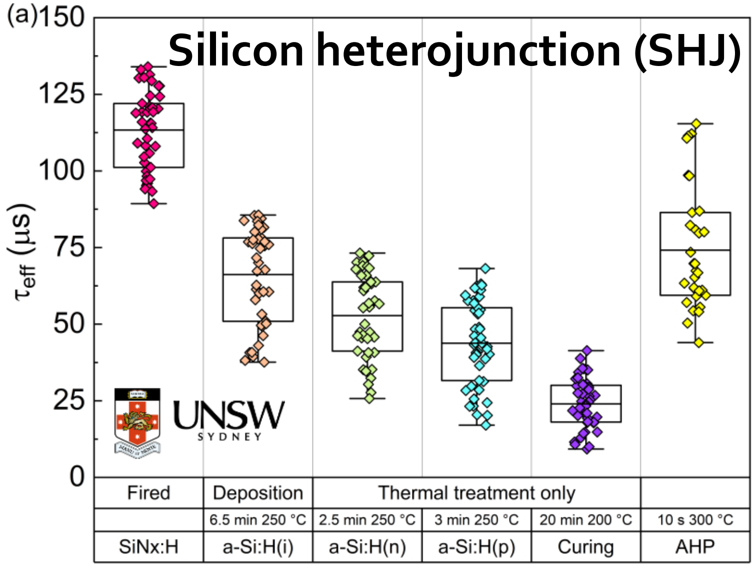
The Past – A Universal Defect in Silicon

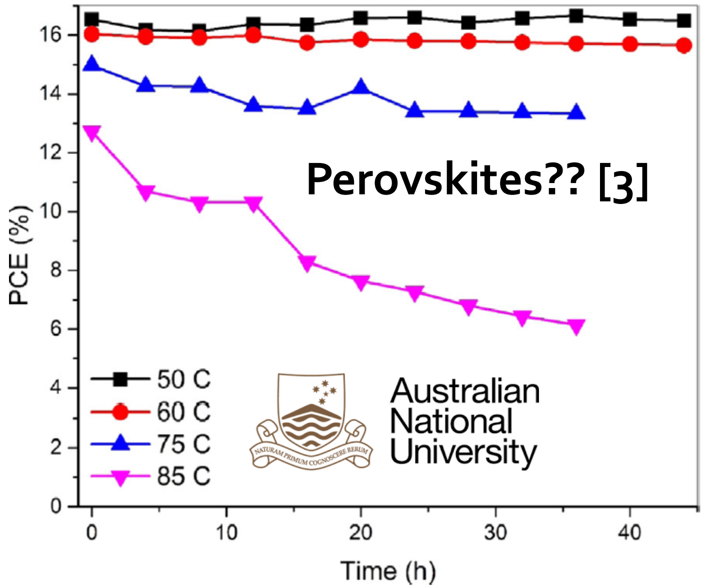












[1] Sperber *et al.*, AIP Conf. Proc., 2019: p. 140011.
[2] Ramspeck et al., 27th EUPVSEC, (2012), 861-865.
[3] Duong *et al.*, Sol. Energy Mater. Sol. Cells. 188 (2018) 27–36.

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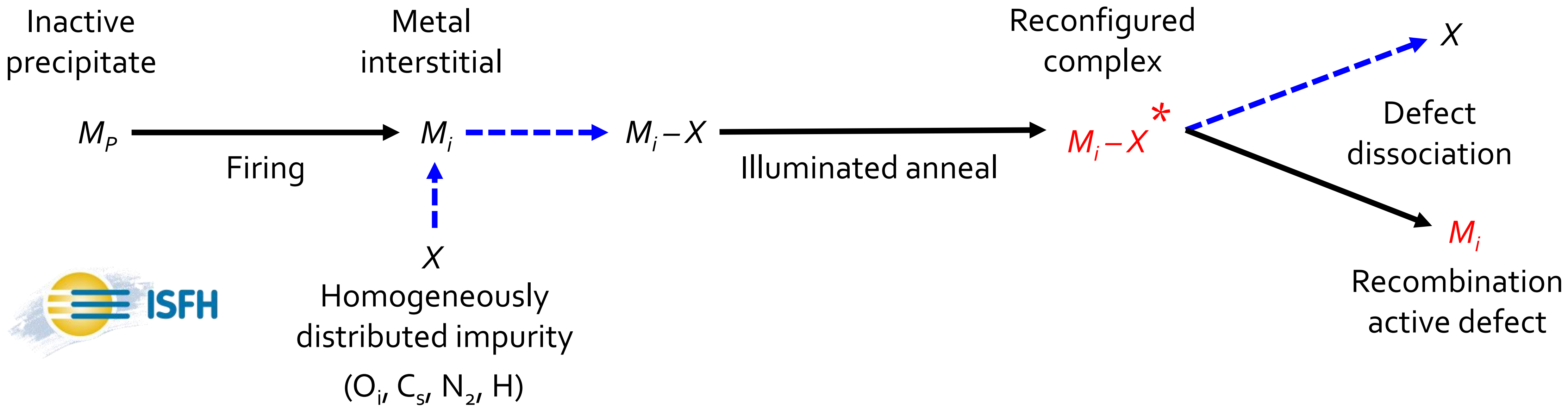
The Past – Evaluating the Root Cause – Metal Impurities

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



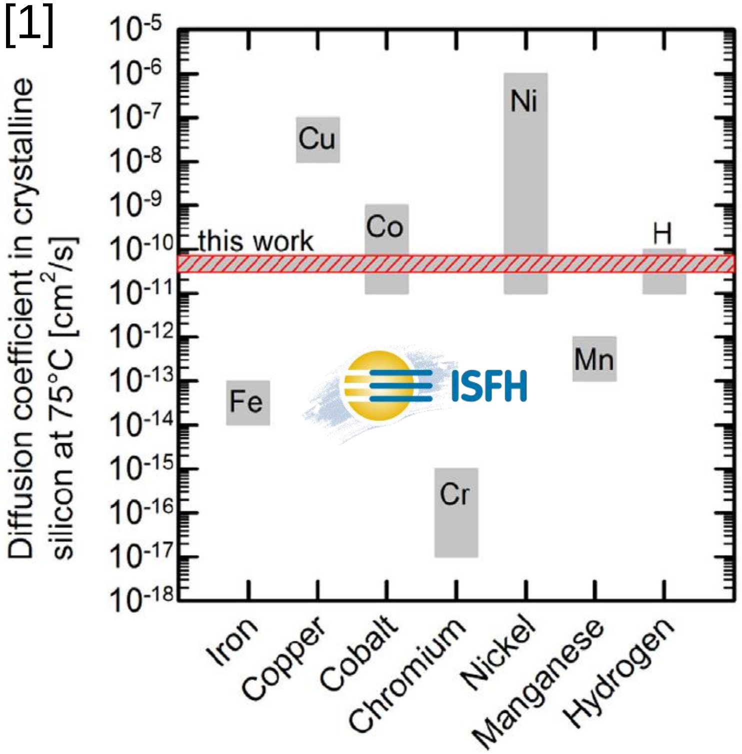
1. **Before firing:** metallic impurities reside in a recombination inactive precipitated state (M_P).
2. **Firing (T > 600 °C):** precipitates dissolve into interstitials (M_i).
3. **Cooldown:** M_i bond with a homogeneously distributed impurity to form a $M_i - X$ complex.
4. **Illuminated annealing:**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

[1] Bredemeier *et al.*, Energy Procedia. 92 (2016) 773–778.

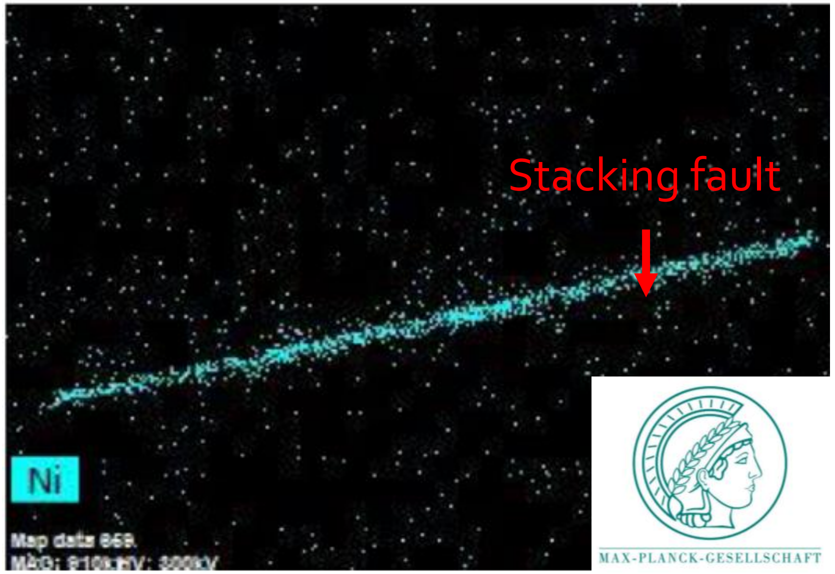
The Past – Evaluating the Root Cause – Metal Impurities

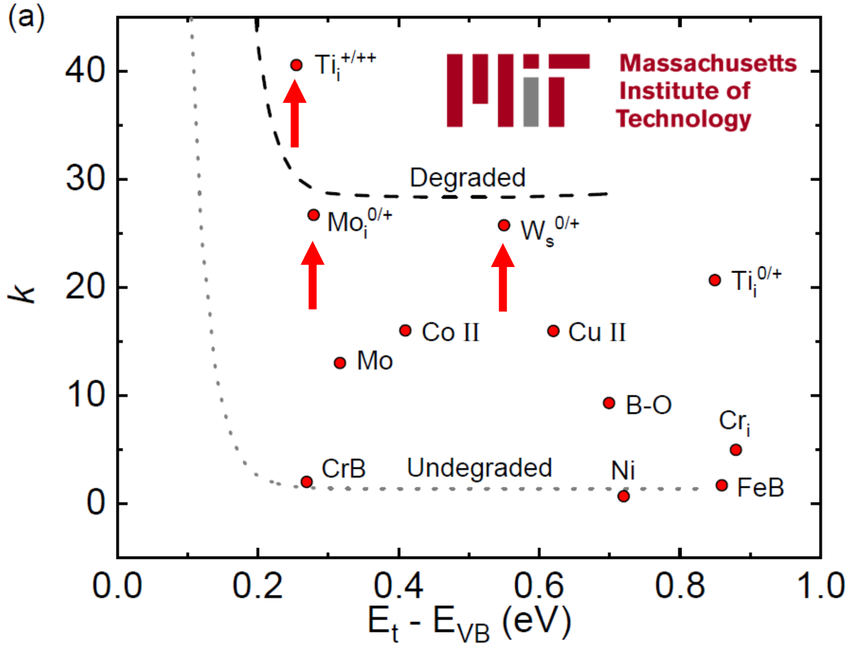
- In 2017, Bredemeier et al. suggested Co and Ni as a possible metal impurity
- It was suggested that diffusion of the metals towards the surface could explain regeneration.

[1]



d [2]



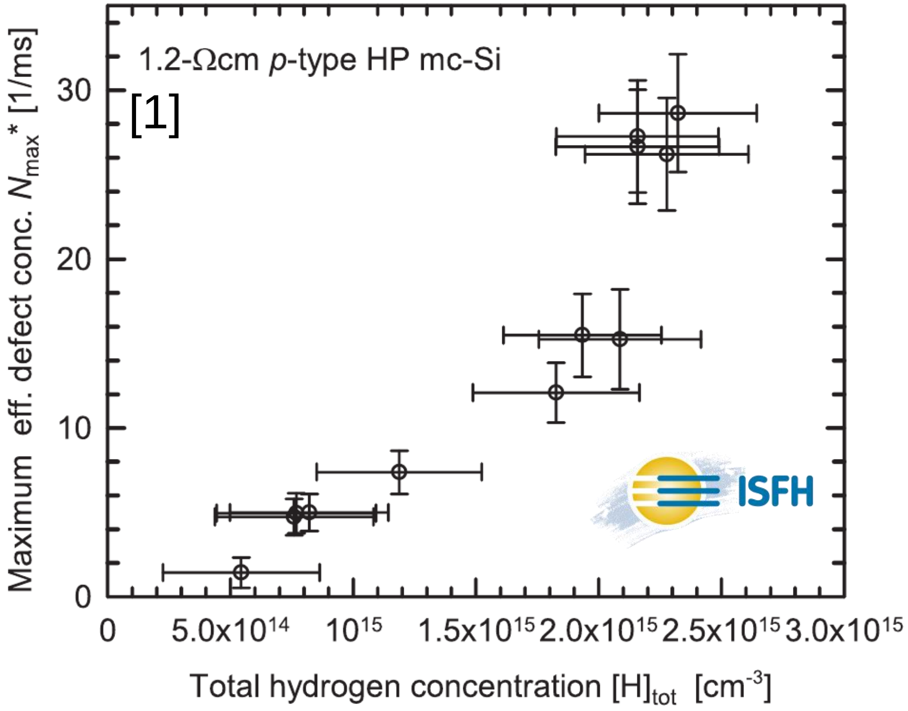


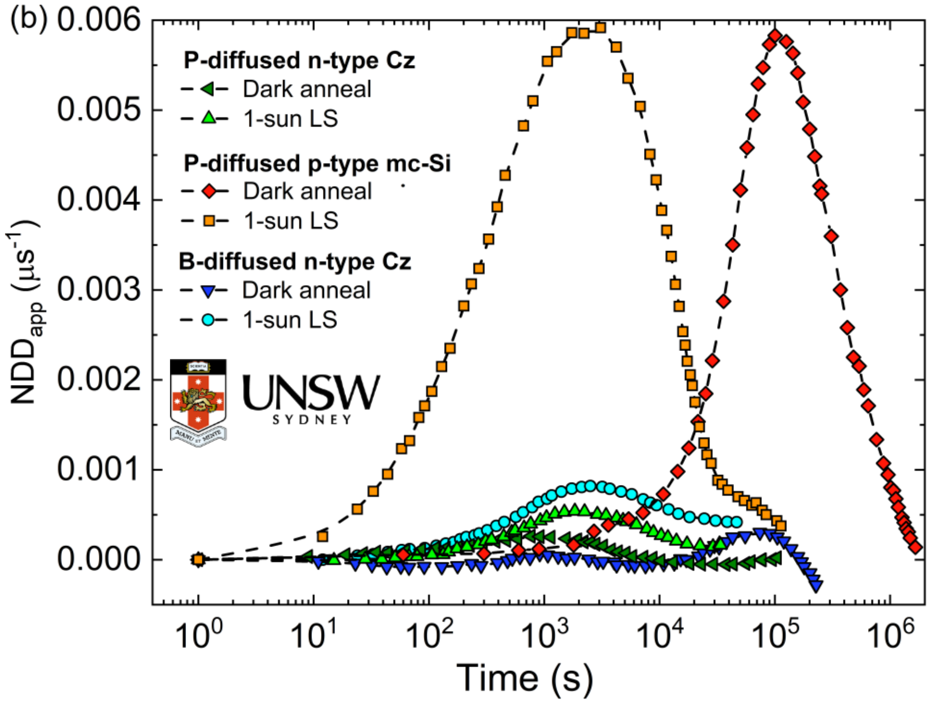
- Deniz *et al.* (2018), found Ni precipitation using TEM and energy dispersive x-ray (EDX) measurements.
- TIDLS by UNSW, MIT – defect recombination properties (k-value) close to $Ti_i^{++/+}$, $Mo_i^{o/+}$ or $W_s^{o/+}$.

[1] Bredemeier *et al.*, Sol. RRL. 2 (2018) 1700159.
[2] Deniz *et al.*, Sol. RRL. 2 (2018) 1800170.
[3] Jensen *et al.*, 44th IEEE PVSC, 2017: pp. 3300–3303.

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?

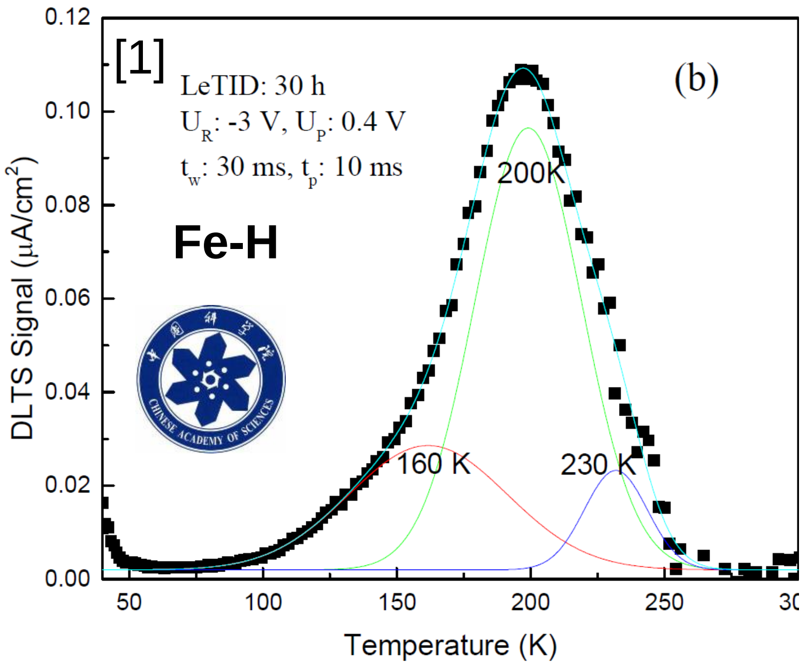
[1] Schmidt *et al.*, IEEE J. Photovoltaics. 9 (2019) 1497–1503.

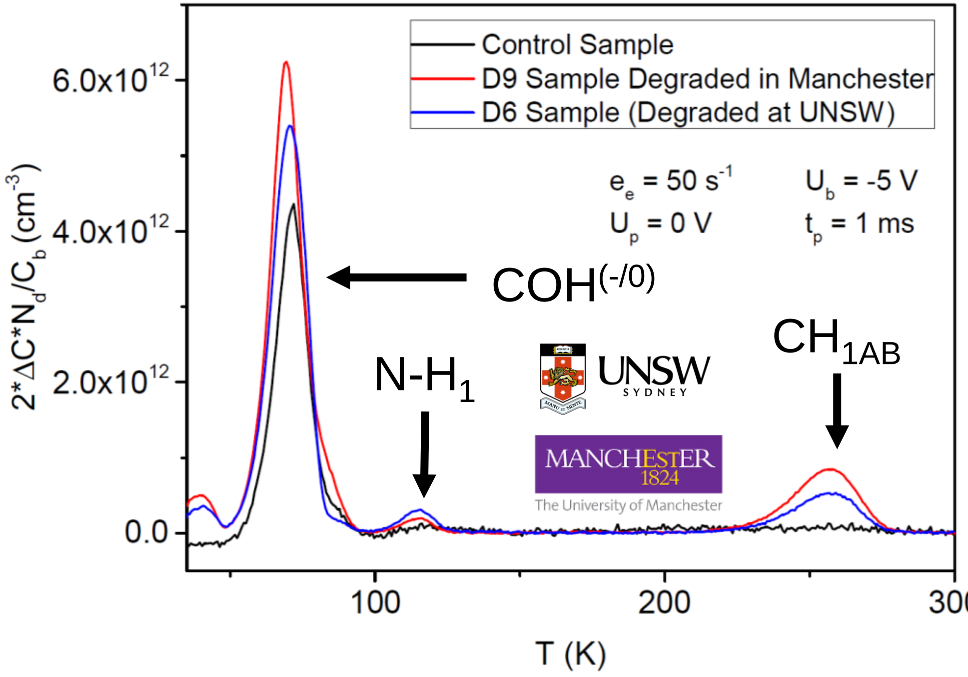
The Present – H-X Complexes and Deep Level Transient Spectroscopy

- Hydrogen can form complexes with almost everything

- **Ag-H$_X$** (Graff 2000…)
- **Au-H** (Deixier 1998…)
- **B-H** (Sah 1983…)
- **C-H** (Anderson 2002…)
- **C-O-H** (Vaqueiro-Contreras 2017)
- **Co-H$_X$** (Scheffler 2013…)
- **Cr-H** (Sadoh 1994…)
- **Cu-H** (Yarykin 2013…)
- **Fe-H** (Szwacki 2007…)
- **Ni-H$_X$** (Shiraishi 1999…)
- **P-H** (Seager 1990…)
- **Pd-H** (Jones 1999…)
- **Pt-H$_X$** (Hohne 1994…)
- **Si-V-H$_X$** & **Si-V-O-H$_X$** (Bonde 1999)
- **Ti-H$_X$** (Scheffler 2015…)
- **V$_X$-H$_Y$** (Graff 2000…)
- **Va-H$_X$** (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.

[1] Chunlan *et al.*, *GADEST Conference 2019.*

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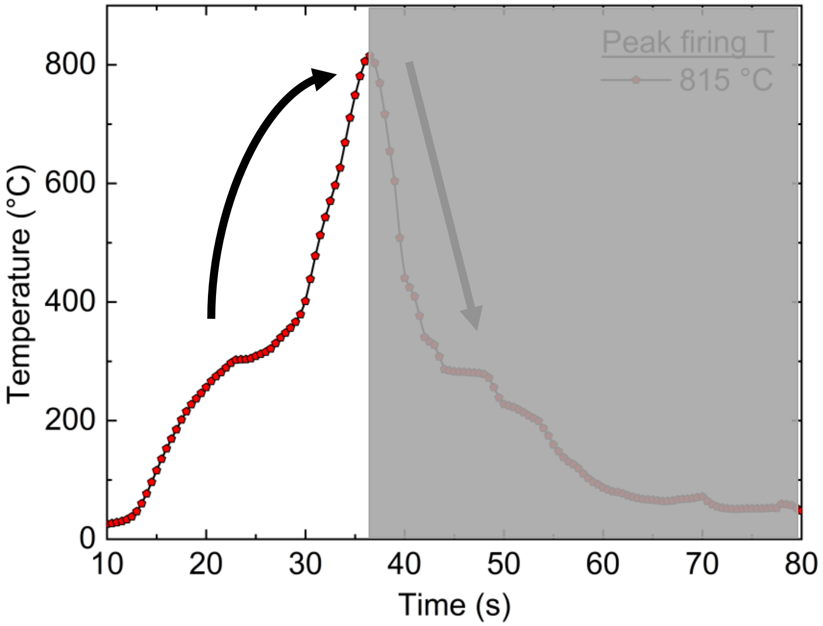
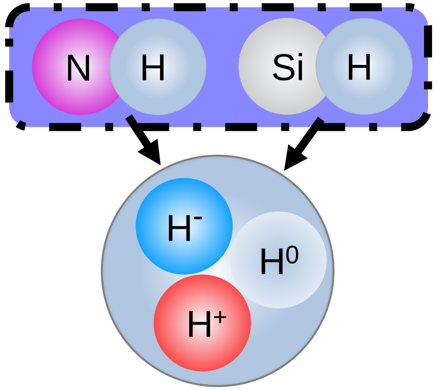
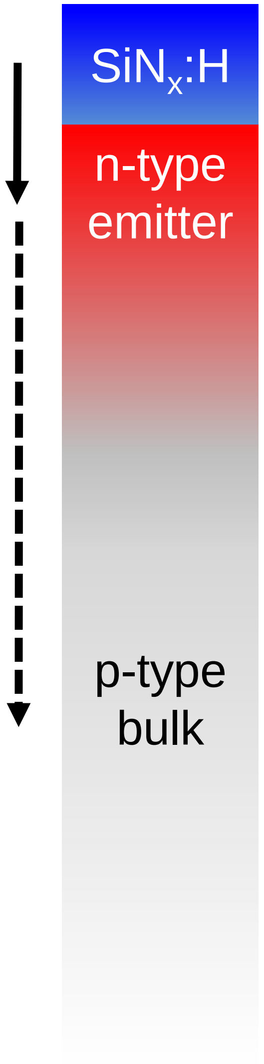
The Present – A Hydrogen-X Defect Model

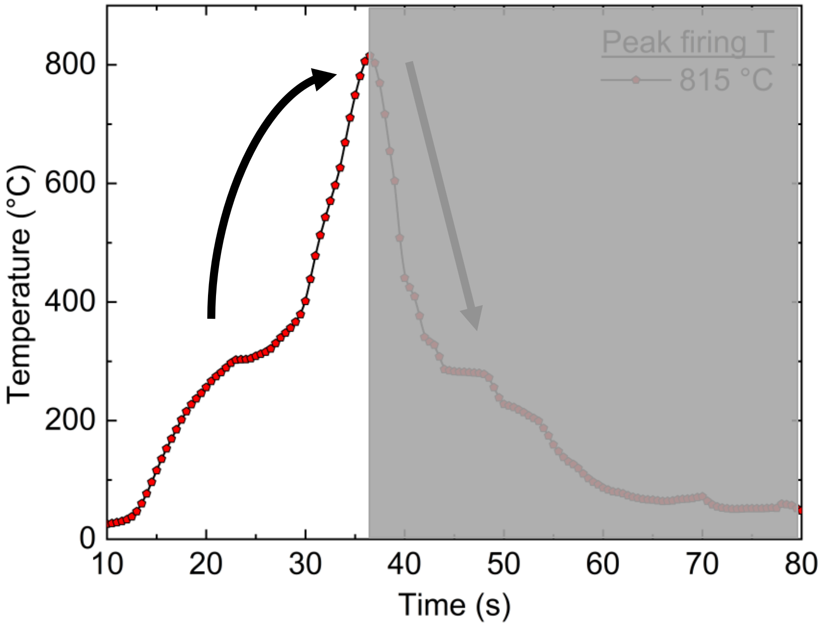


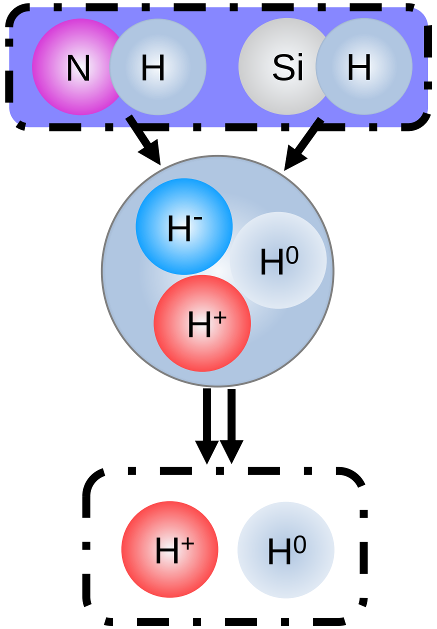


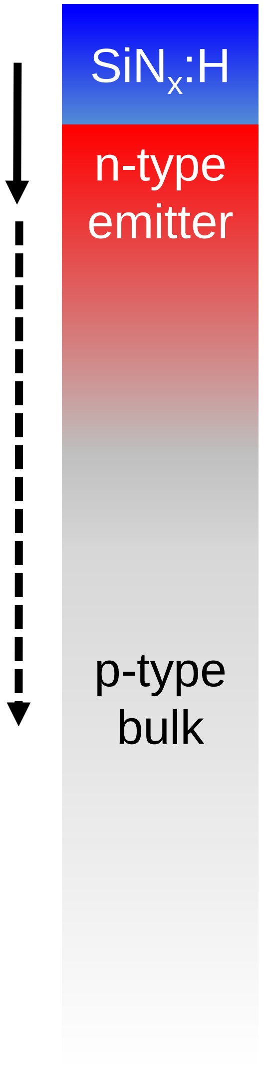


- **During firing (peak)** – H diffuses into Si as interstitials

The Present – A Hydrogen-X Defect Model







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

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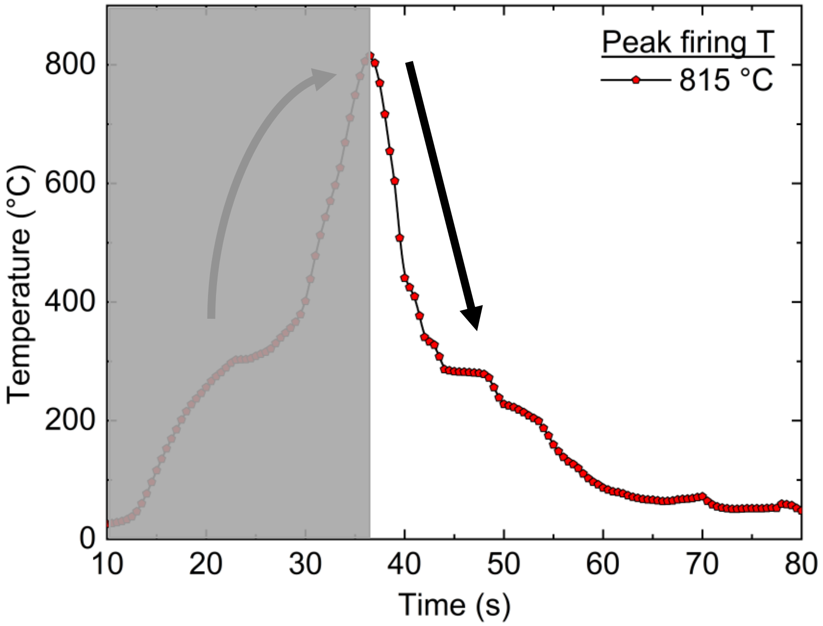
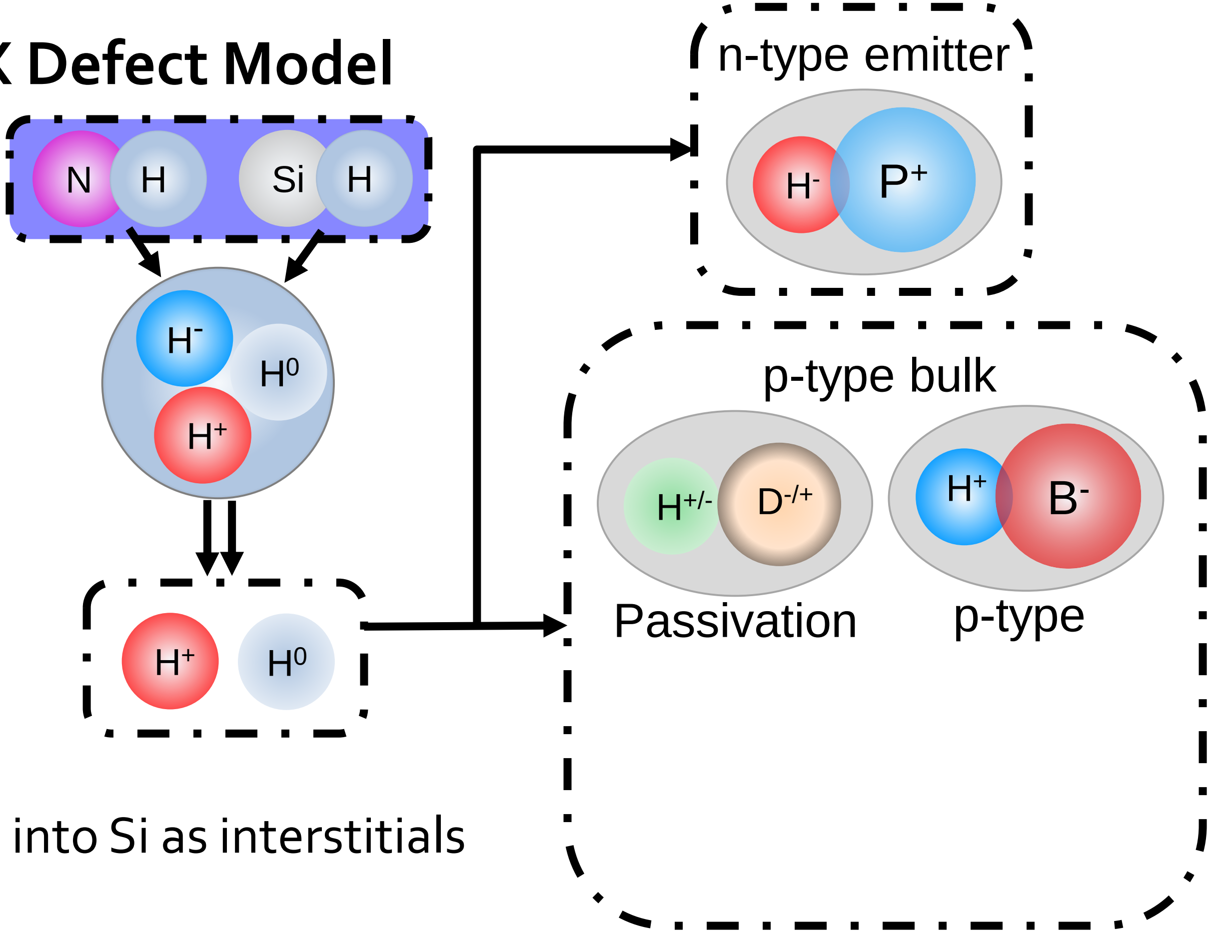
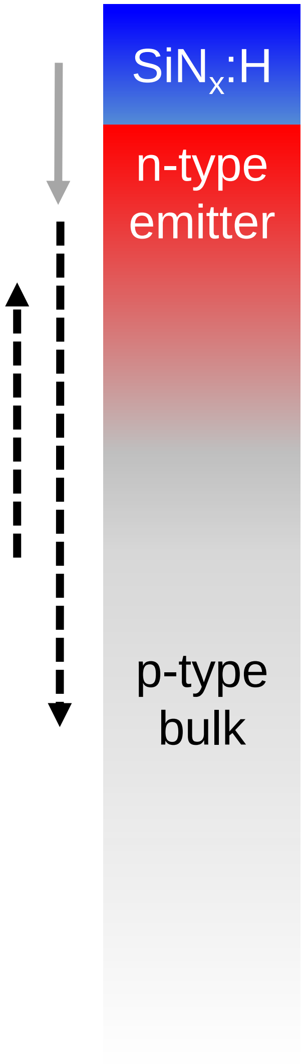
The Present – A Hydrogen-X Defect Model



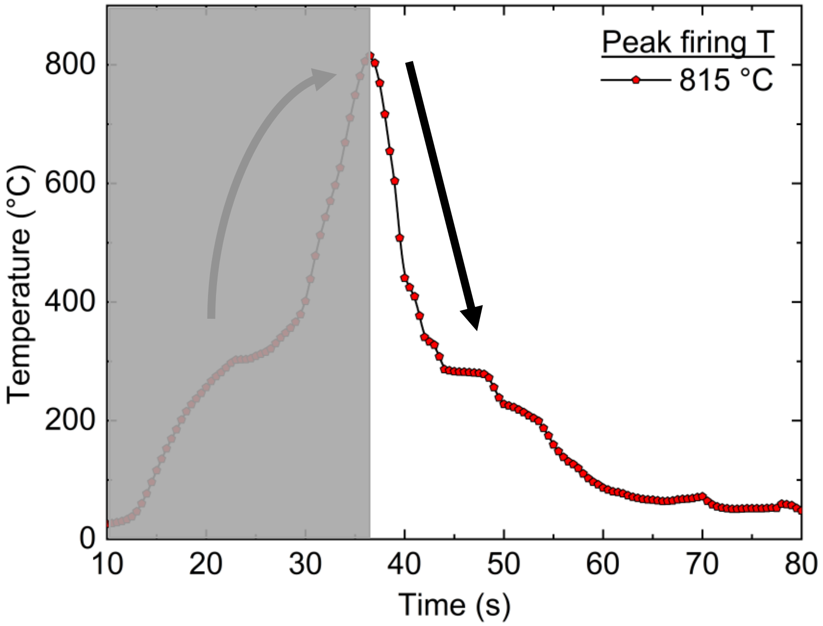


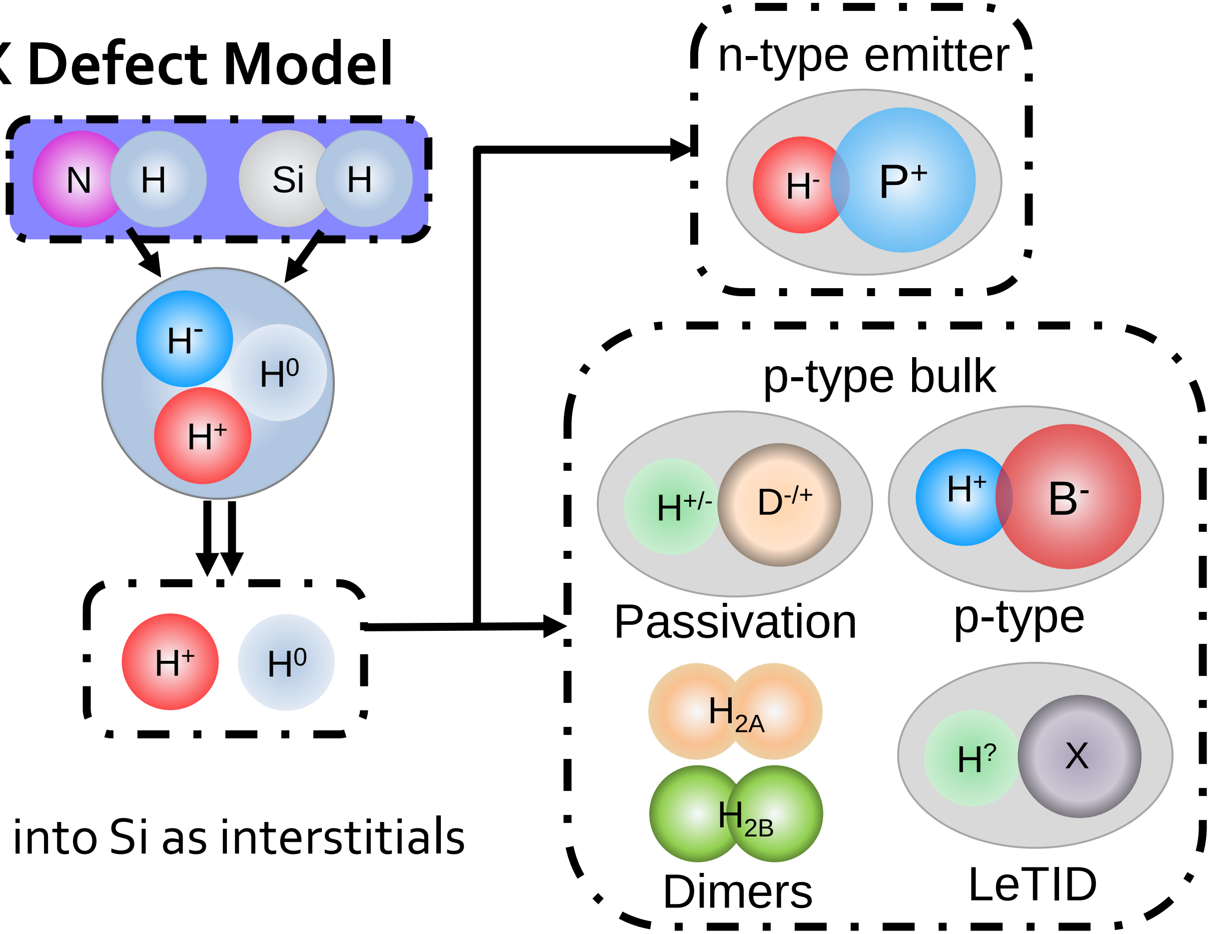


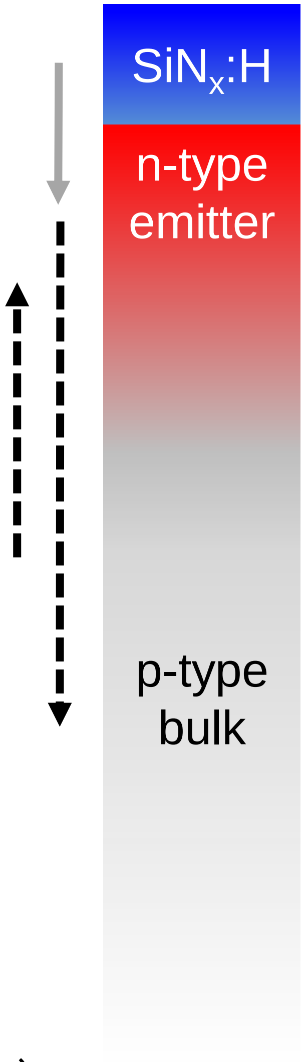
- **During firing (peak)** – H diffuses into Si as interstitials

- 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.

The Present – A Hydrogen-X Defect Model

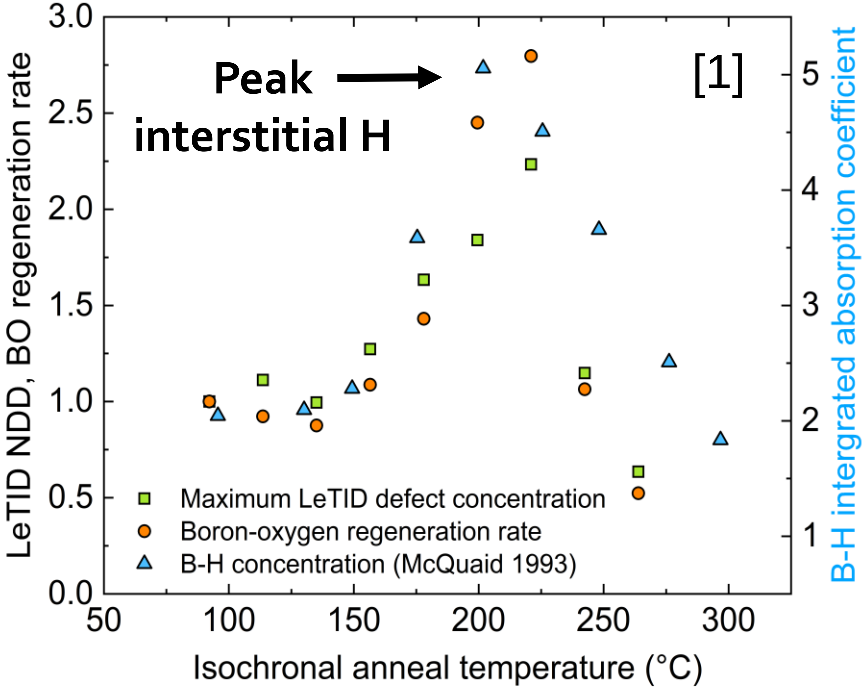


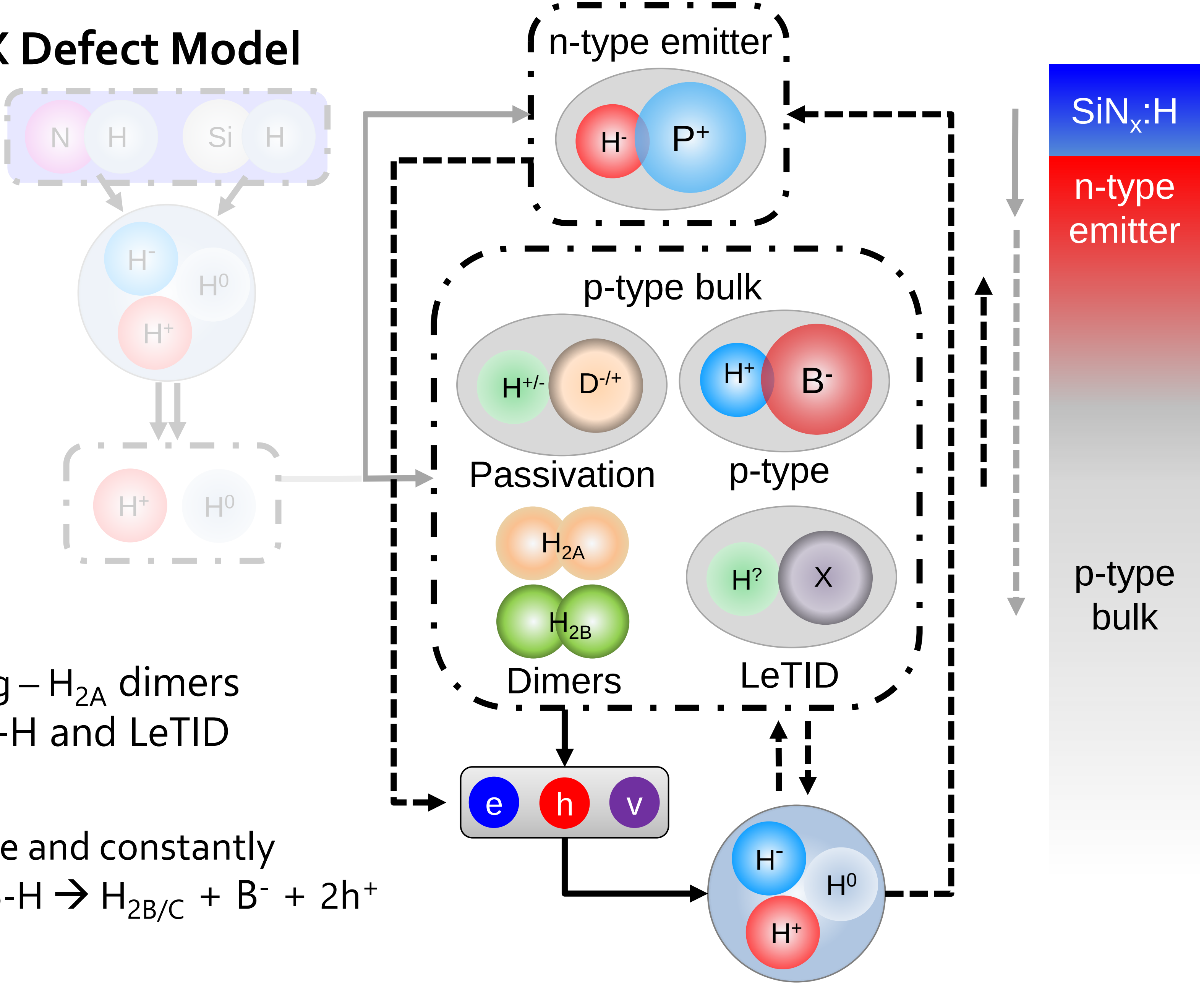




- **During firing (peak)** – H diffuses into Si as interstitials
- At high temperatures, the Si conductivity is intrinsic → H is largely in the H^+ state
- **During cooling (quenching)** – H forms B-H pairs in the bulk and passivates defects.
- It also pre-forms LeTID, however, a majority of H is frozen in metastable dimer states ($H_{2A/B}$)

The Present – A Hydrogen-X Defect Model

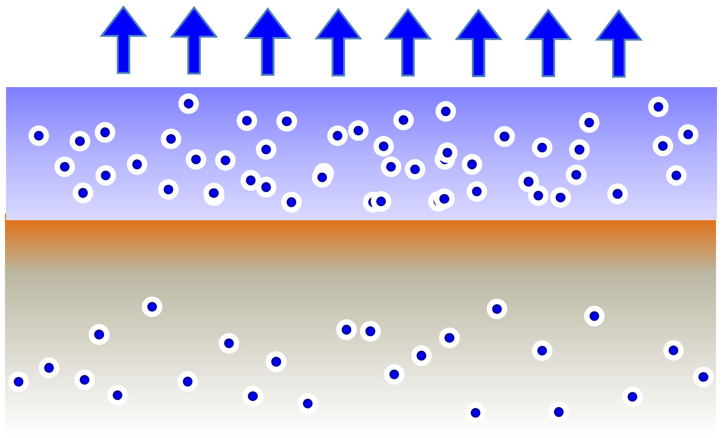


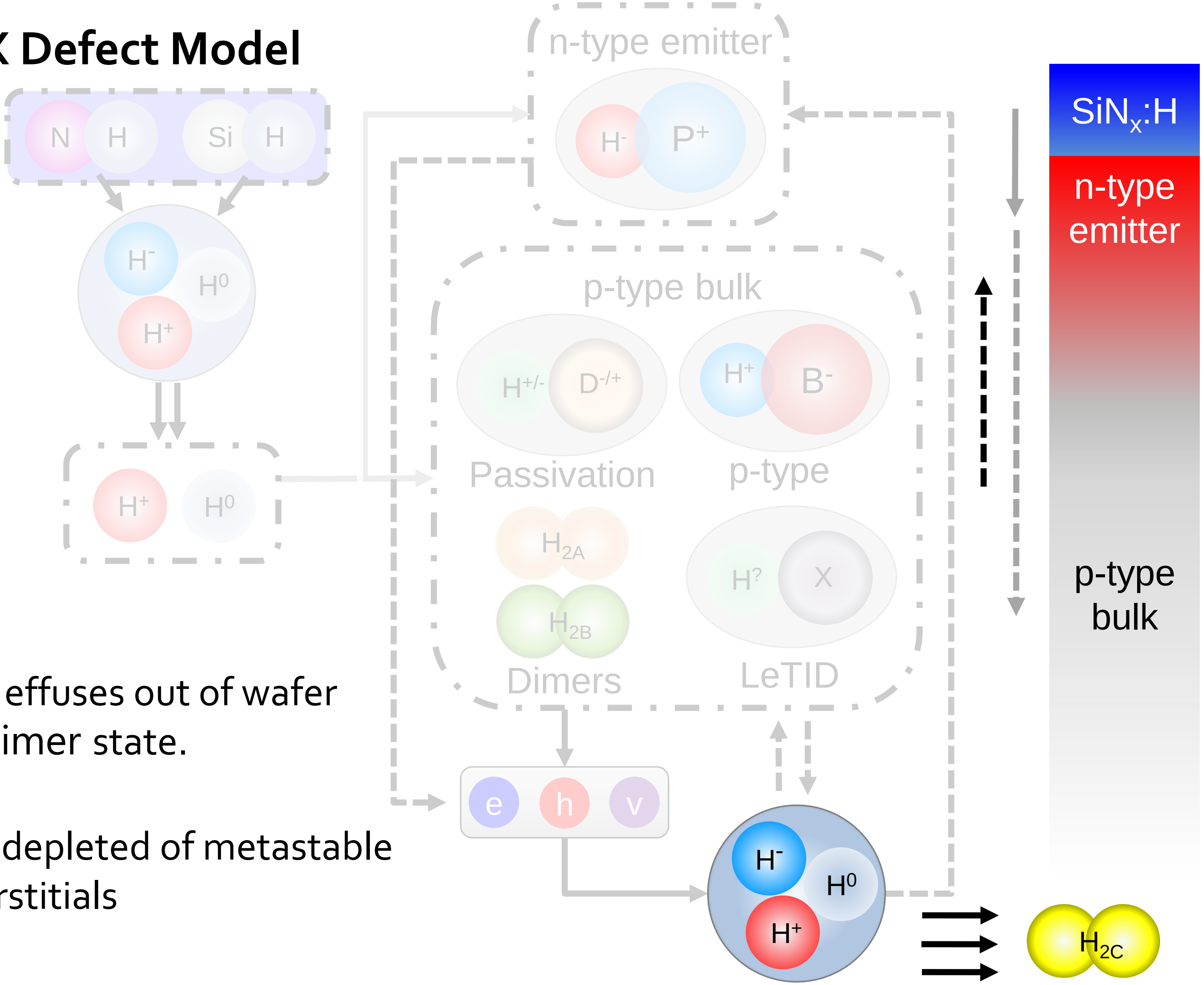


- During annealing or light soaking – H_{2A} dimers dissociate and contribute to B-H and LeTID
- All of these bonds are metastable and constantly breaking and forming e.g. $H^+ + B\text{-}H \rightarrow H_{2B/C} + B^- + 2h^+$

[1] Fung *et al.*, AIP Conf. Proc., 2018: p. 130004.

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

[1] Fung *et al.*, AIP Conf. Proc., 2018: p. 130004.

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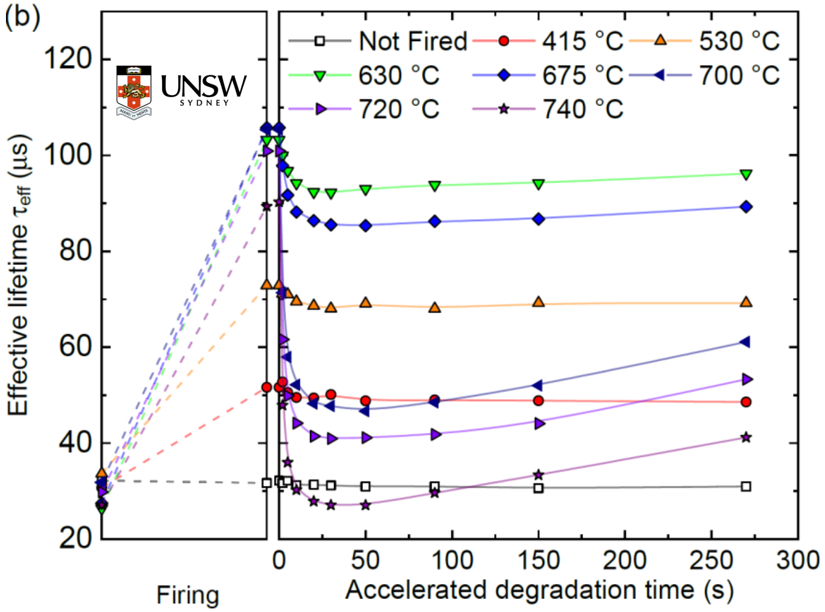
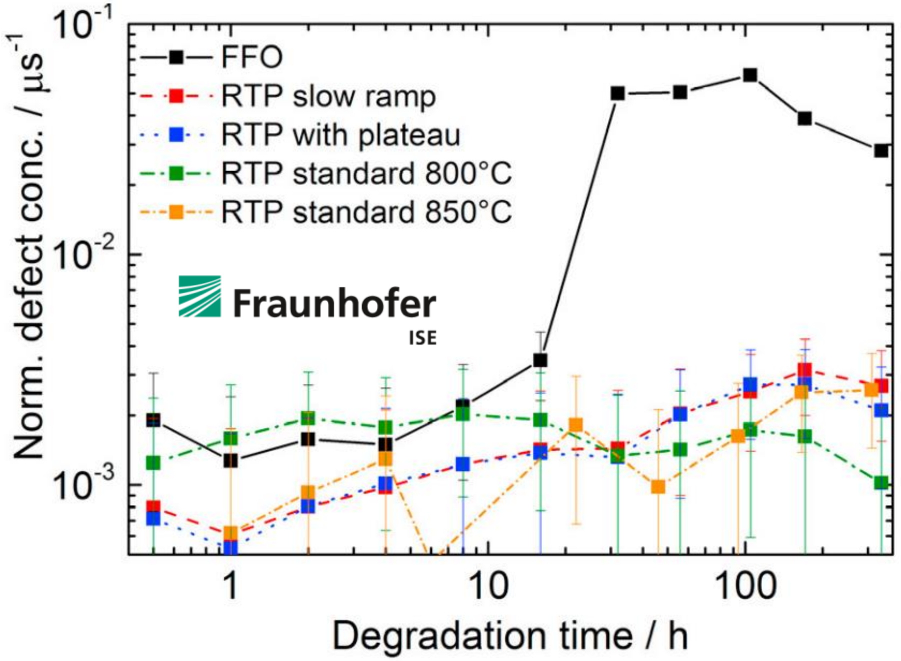
The Present – Mitigation of LeTID – Process Modification

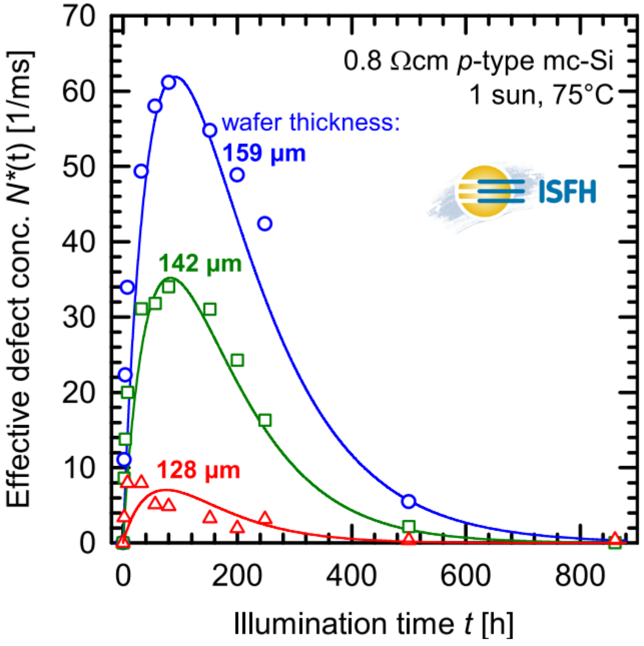
- There are many ways of reducing the hydrogen content within the silicon wafers to reduce LeTID



Chan *et al.*, IEEE J. Photovoltaics. 6 (2016) 1473–1479.



R. Eberle *et al.*, Energy Procedia, (2017) pp. 712–717.

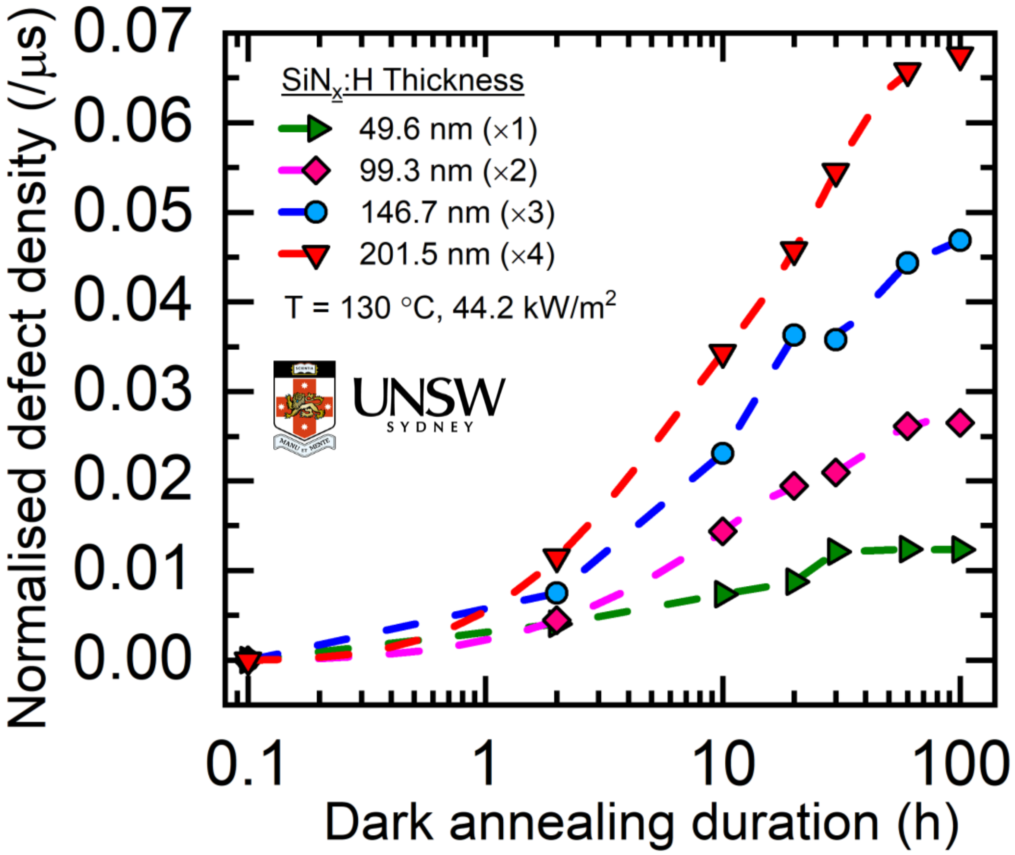


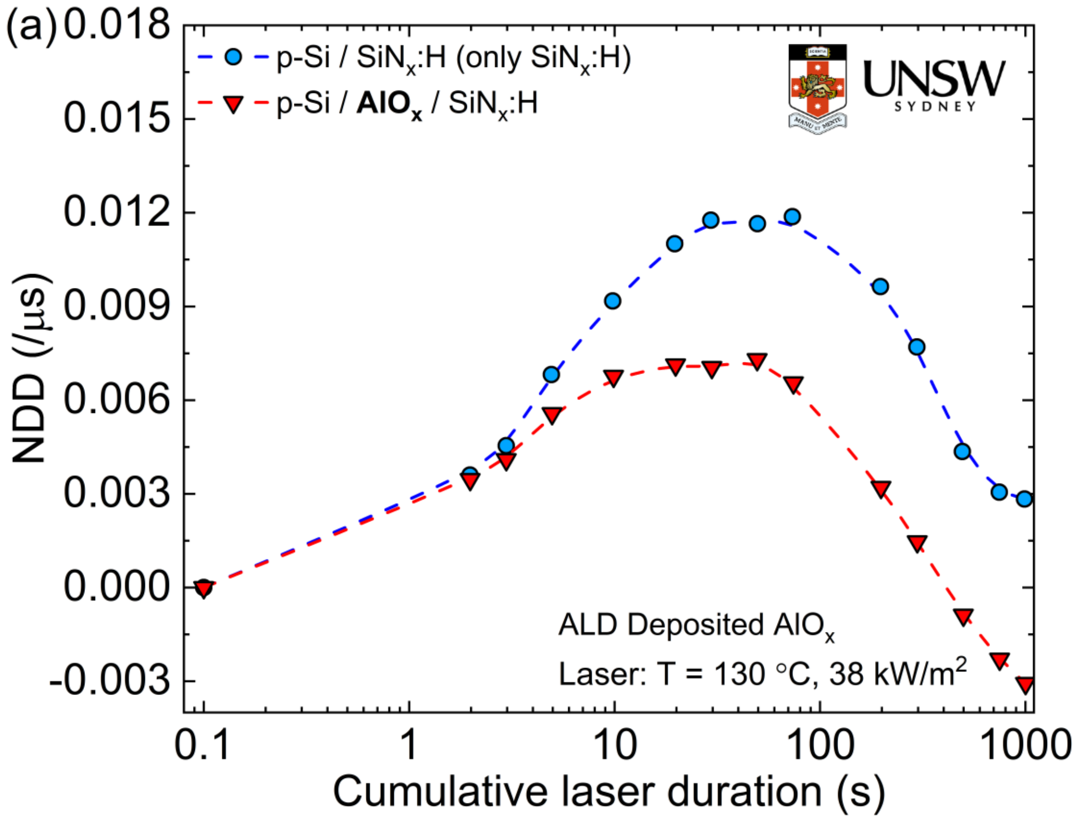
Schmidt *et al.*, IEEE J. Photovoltaics. 9 (2019) 1497–1503

- Reducing peak firing → Less H in-diffusion or Slower-cooling → More H effusion
- Thinner wafers have demonstrated lower LeTID → Faster defect effusion

The Present – Mitigation of LeTID – Process Modification

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

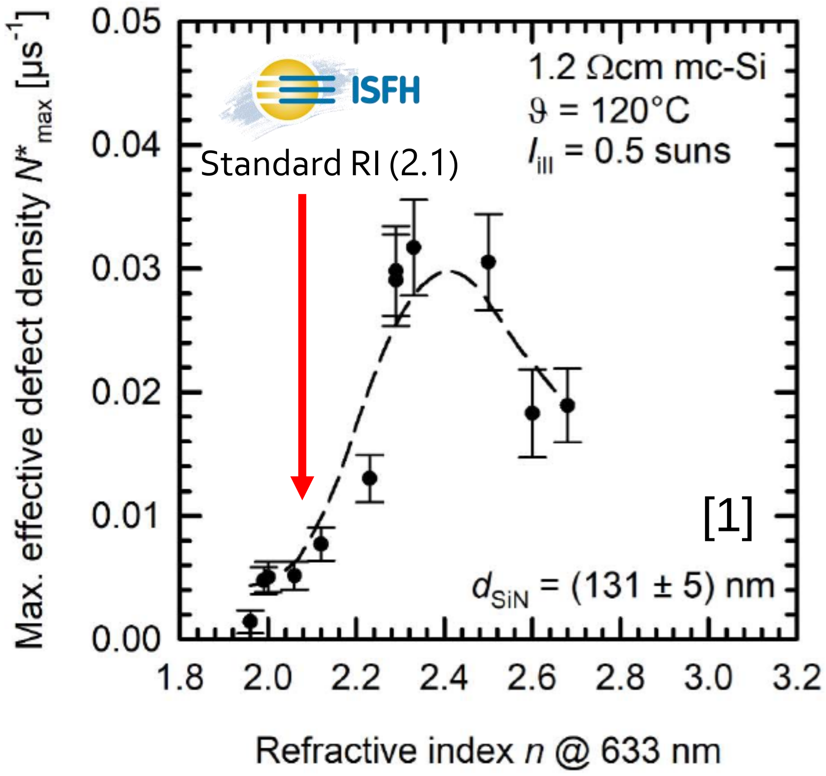


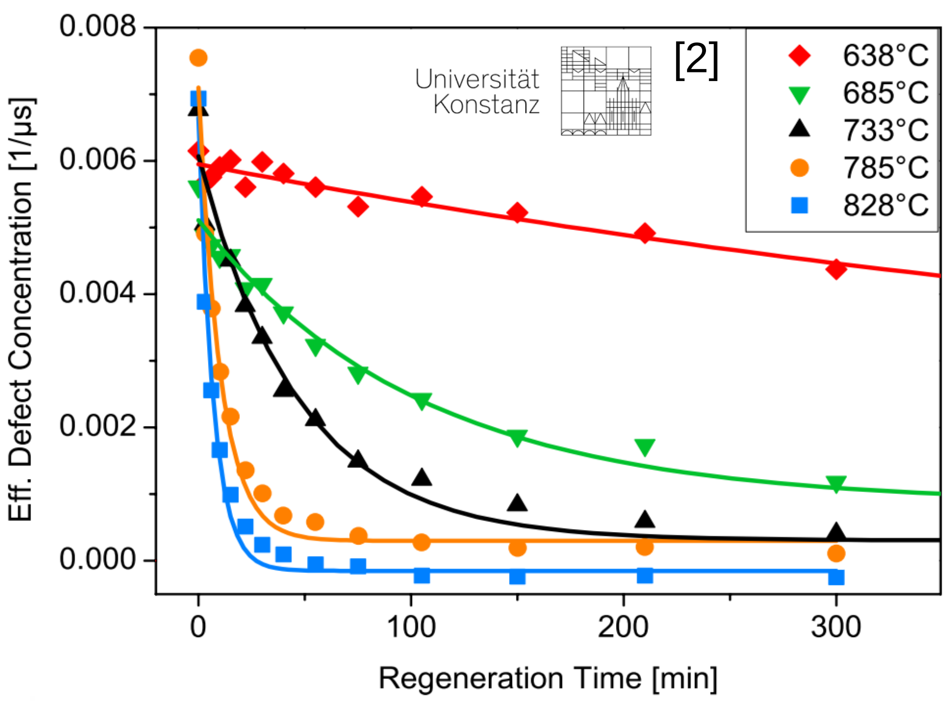


[1] Varshney *et al.*, IEEE J. Photovoltaics. 9 (2019) 601–607.
[2] Varshney *et al.*, *IEEE J. Photovoltaics*, 2019 (in press)

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.



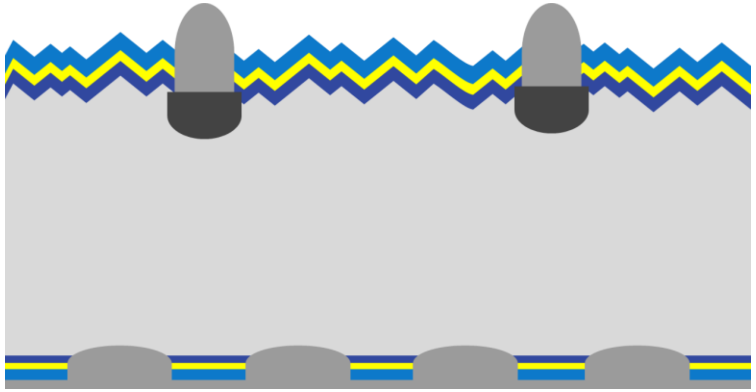


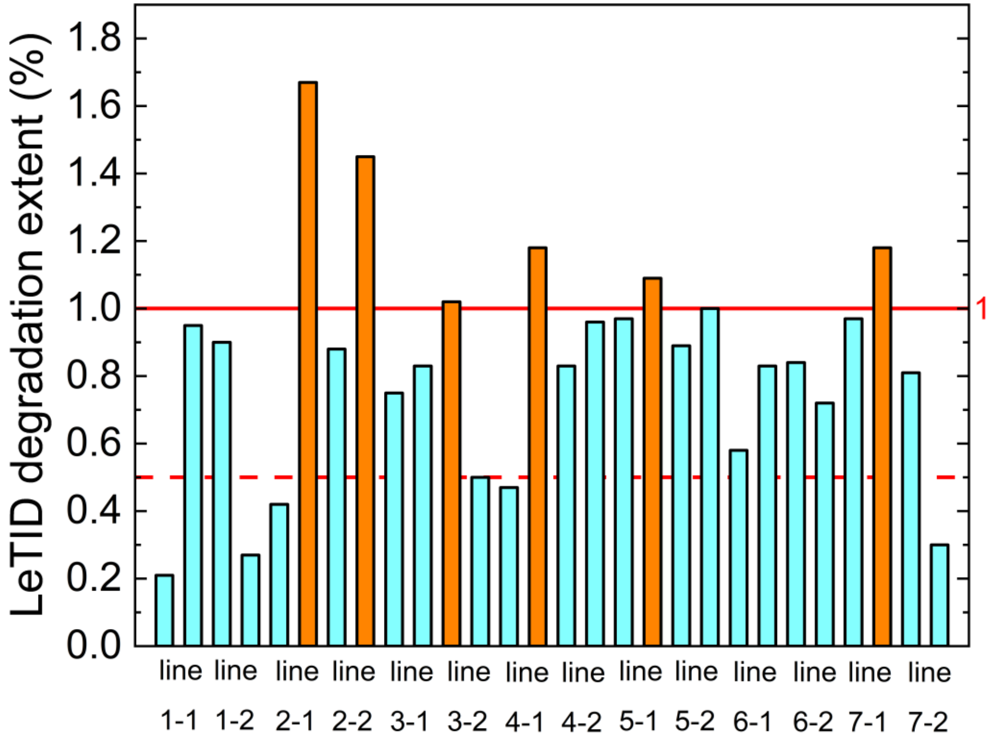
- Commercial LeTID mitigation usually involves post-cell treatments

1. Light based treatments
2. Current Injection
3. Biased annealing

[1] Bredemeier *et al.*, Phys. Status Solidi – Rapid Res. Lett. 13 (2019) 1900201.
[2] Wilking et al., J. Appl. Phys. 114 (2013) 194512

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 AlO_x:H passivation on both sides – hydrogen lean blocking layer
4. SiO_2 layer on both sides – hydrogen blocking layer

Risen solar technology

Risen Solar, Jager series Technical White Paper, 2018.

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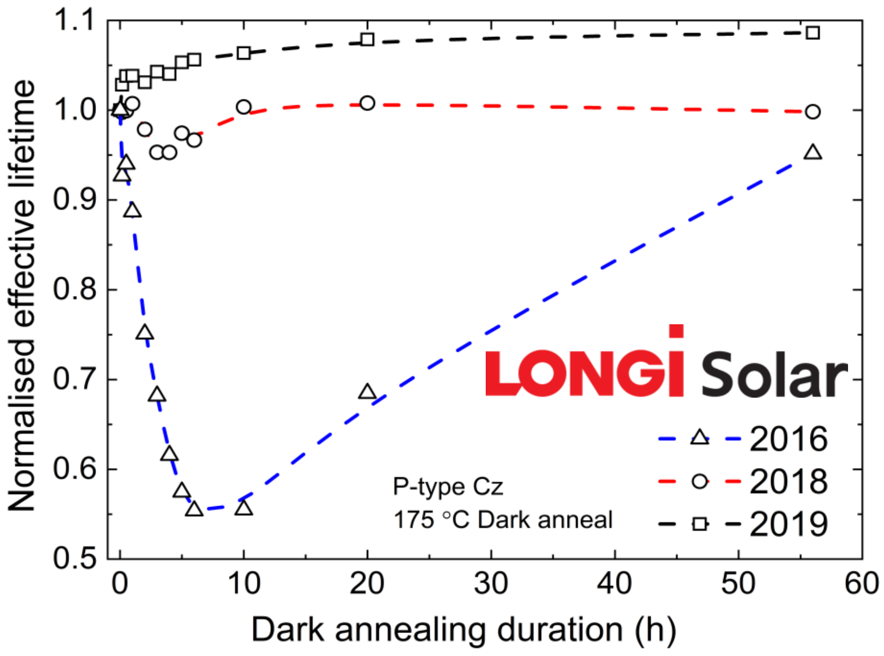
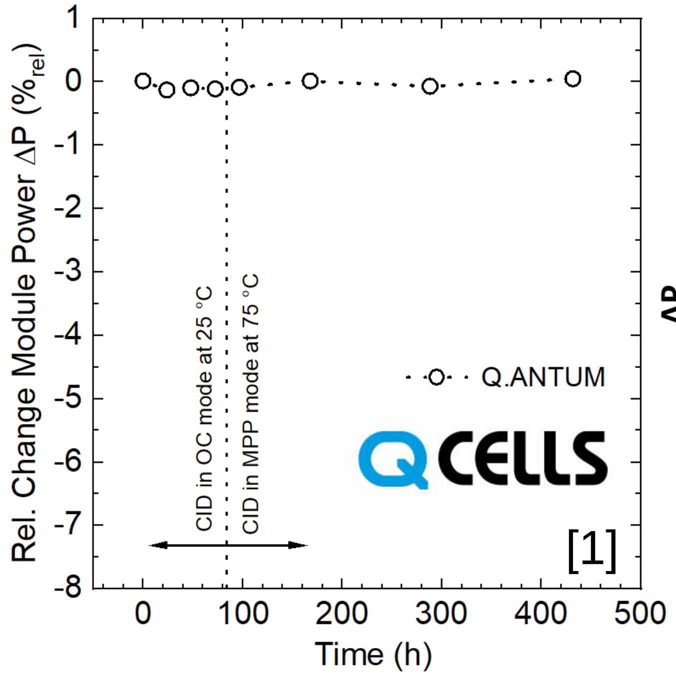
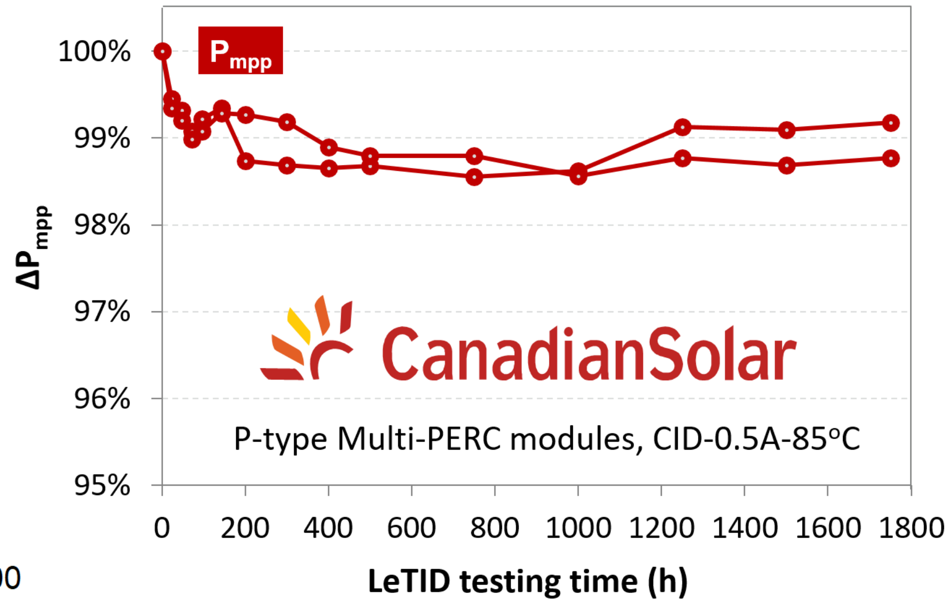
What Lies Ahead – Will LeTID Remain a Problem for Commercial PV?

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







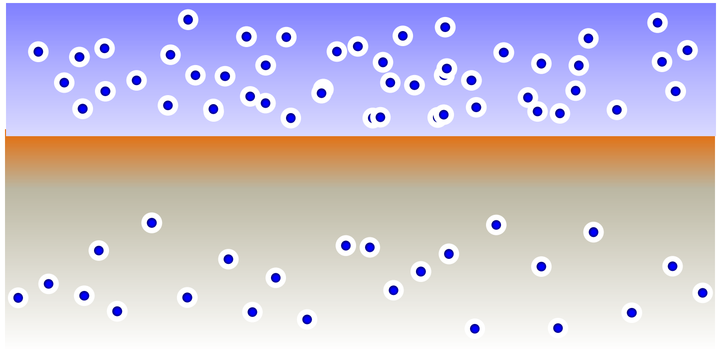
- Wafer quality is constantly improving with some wafers that are already LeTID free.
- Choosing better wafer sources + applying mitigation treatments will solve LeTID in both mc-Si and Cz-Si

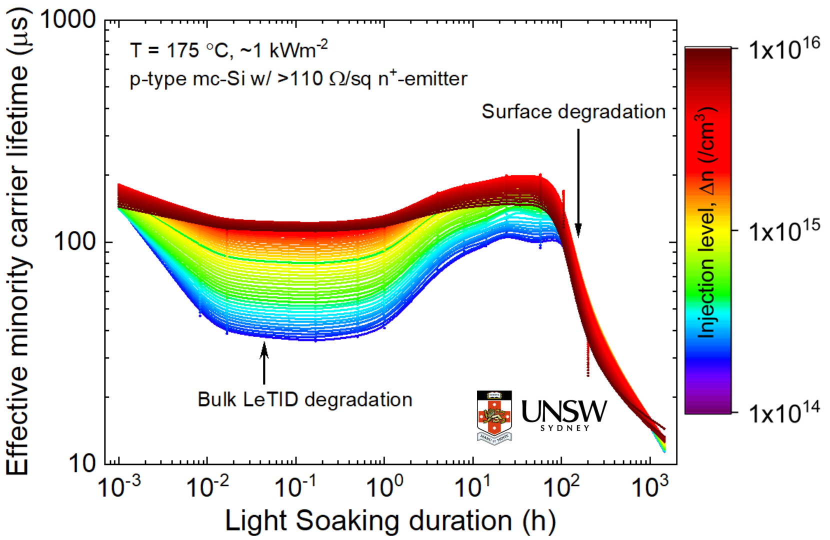
[1] Fertig *et al.*, Sol. Energy Mater. Sol. Cells. 200 (2019) 109968.

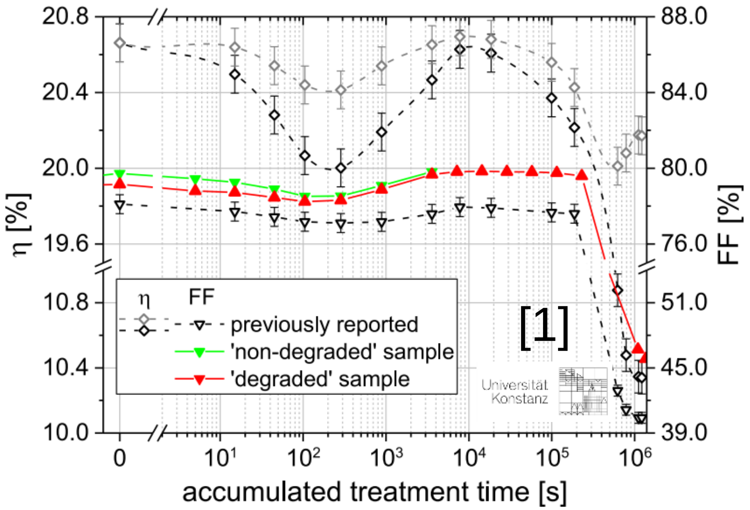
What Lies Ahead – Hydrogen-Induced Surface Degradation

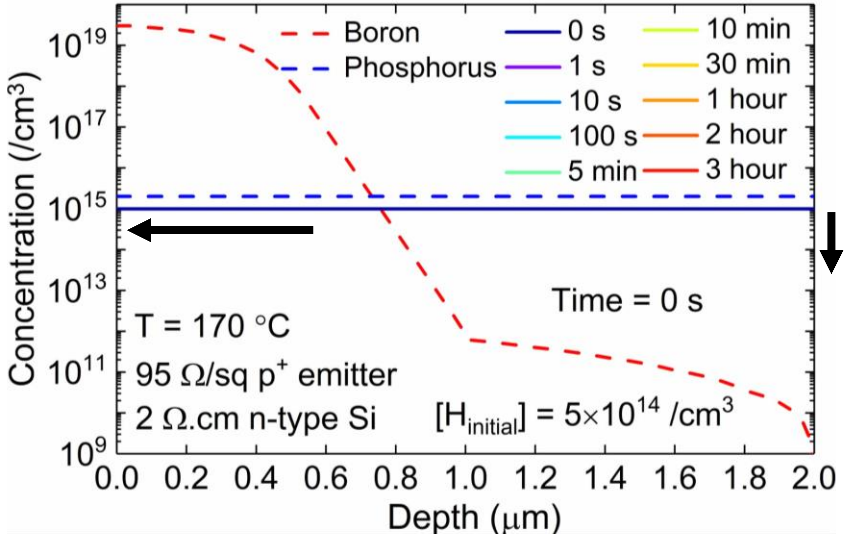
- As LeTID recovers, hydrogen diffuses out towards the surfaces.

- Too much H at the interface can lead to the formation of hydrogen-induced defects → 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].





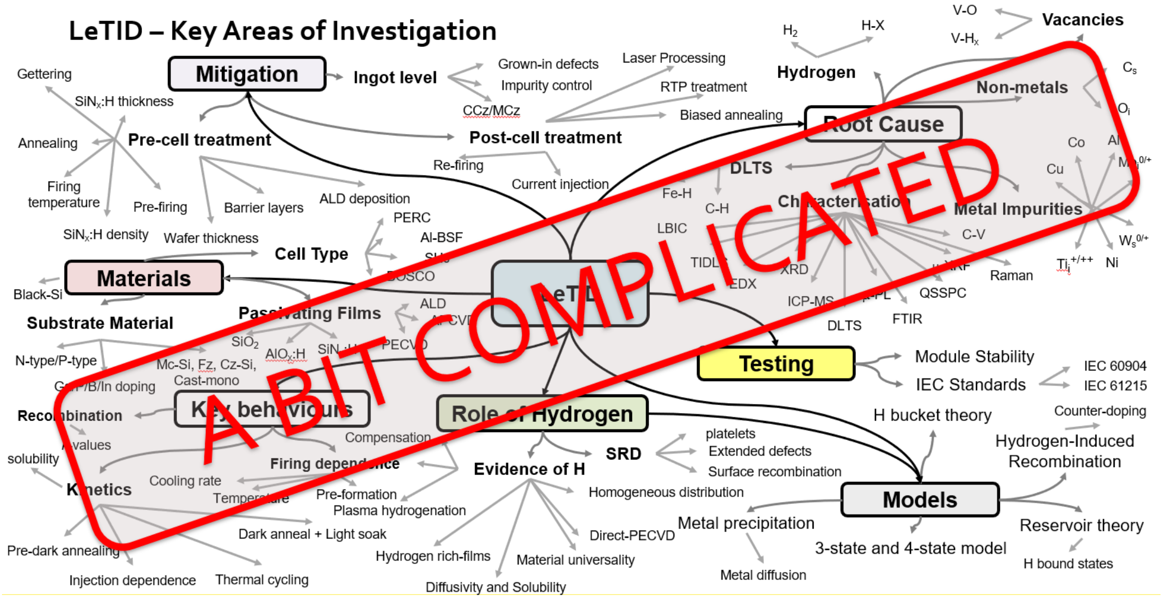


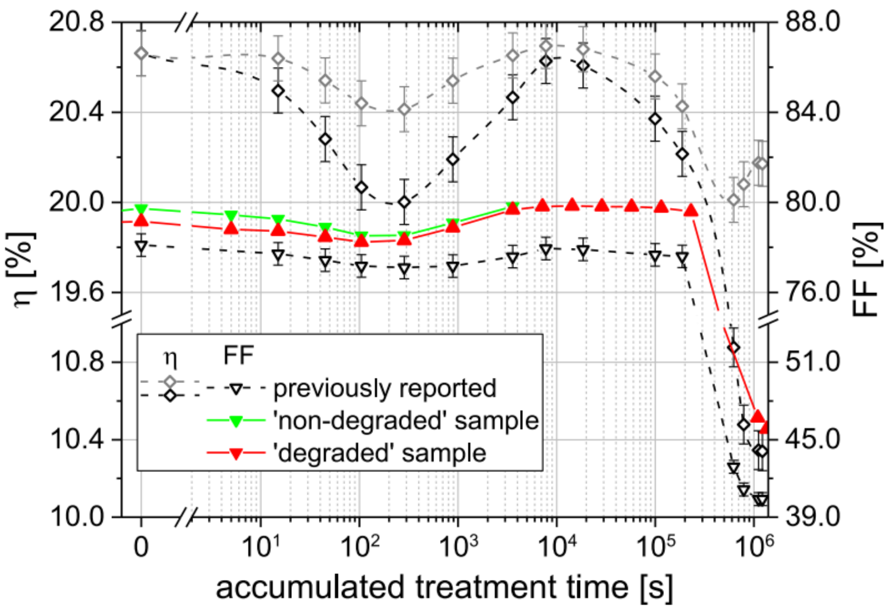


[1] Herguth *et al.*, IEEE J. Photovoltaics. (2018) 1–12.

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!





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Thank you for your attention. Daniel.chen@unsw.edu.au