Faculty of Engineering
School of Photovoltaic and Renewable Energy Engineering

Hydrogen Redistribution and Surface Effects in Silicon Solar Cells

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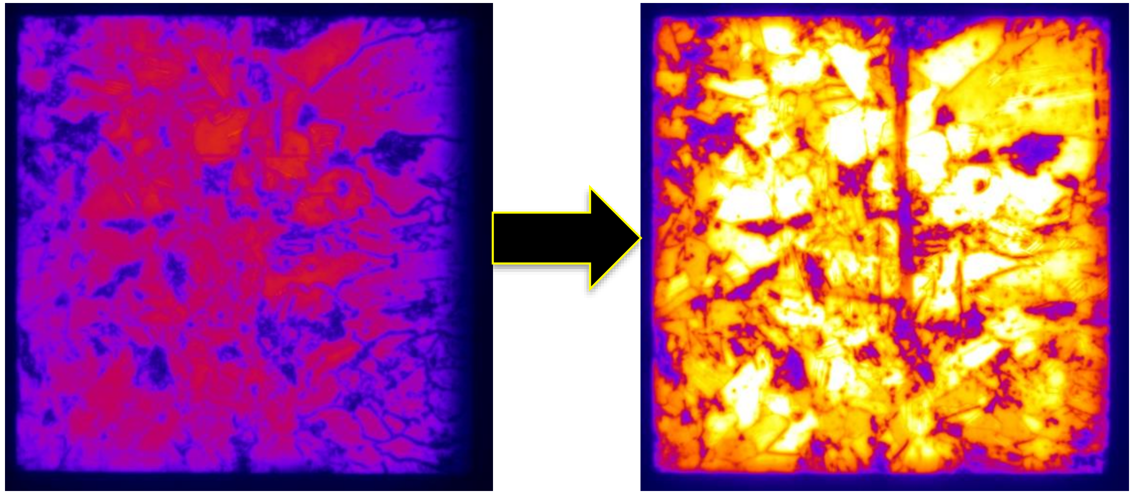
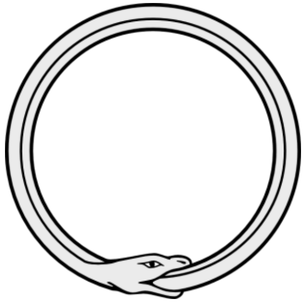
Outline

- ~~Shameless Self Indulgence~~ Hydrogen in Silicon
- Transport of Hydrogen in Silicon
- A number of surface effects important for solar cell structures reported recently
  - Contact Resistance
  - Surface Degradation
- Nature and location of surface defects

Hydrogen – an unrequited love

- Necessary for highest efficiencies in nearly every commercial cell architecture
  - Surface Passivation
  - Mitigation of B-O defect
  - Passivation of other impurities and crystallographic defects
- Can’t get rid of it
- Enormous impact on device performance while remaining below detection limit
- Interacts with vacancies, interstitials, dangling bonds, dopants, dislocations, grain boundaries and other impurities
- Even the most basic properties are not well established
- Has been identified as playing a role in LeTID





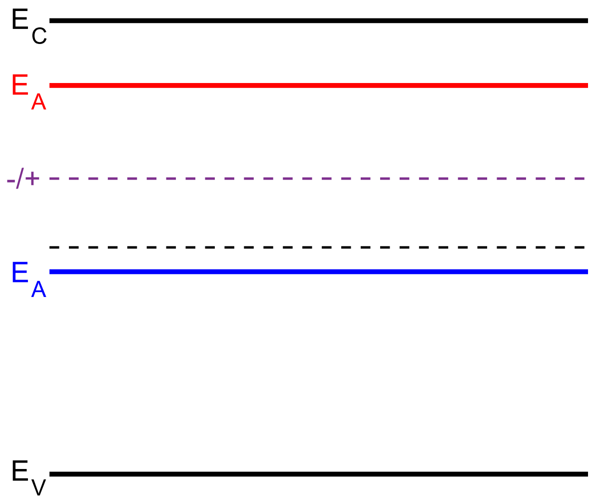
SPECULATION

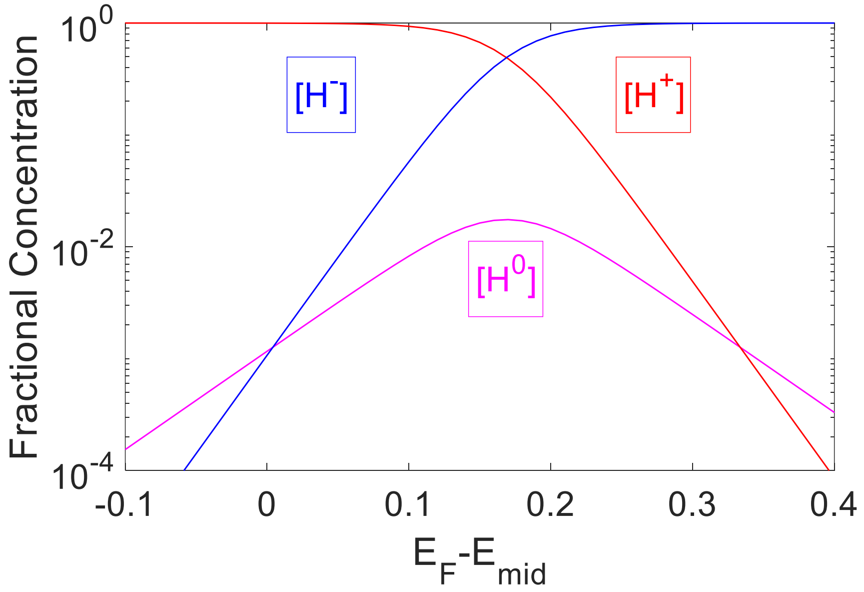
WARNING:
GRAPHIC CONTENT

This gallery contains graphic images that some viewers may find disturbing

Simulation of Hydrogen Transport

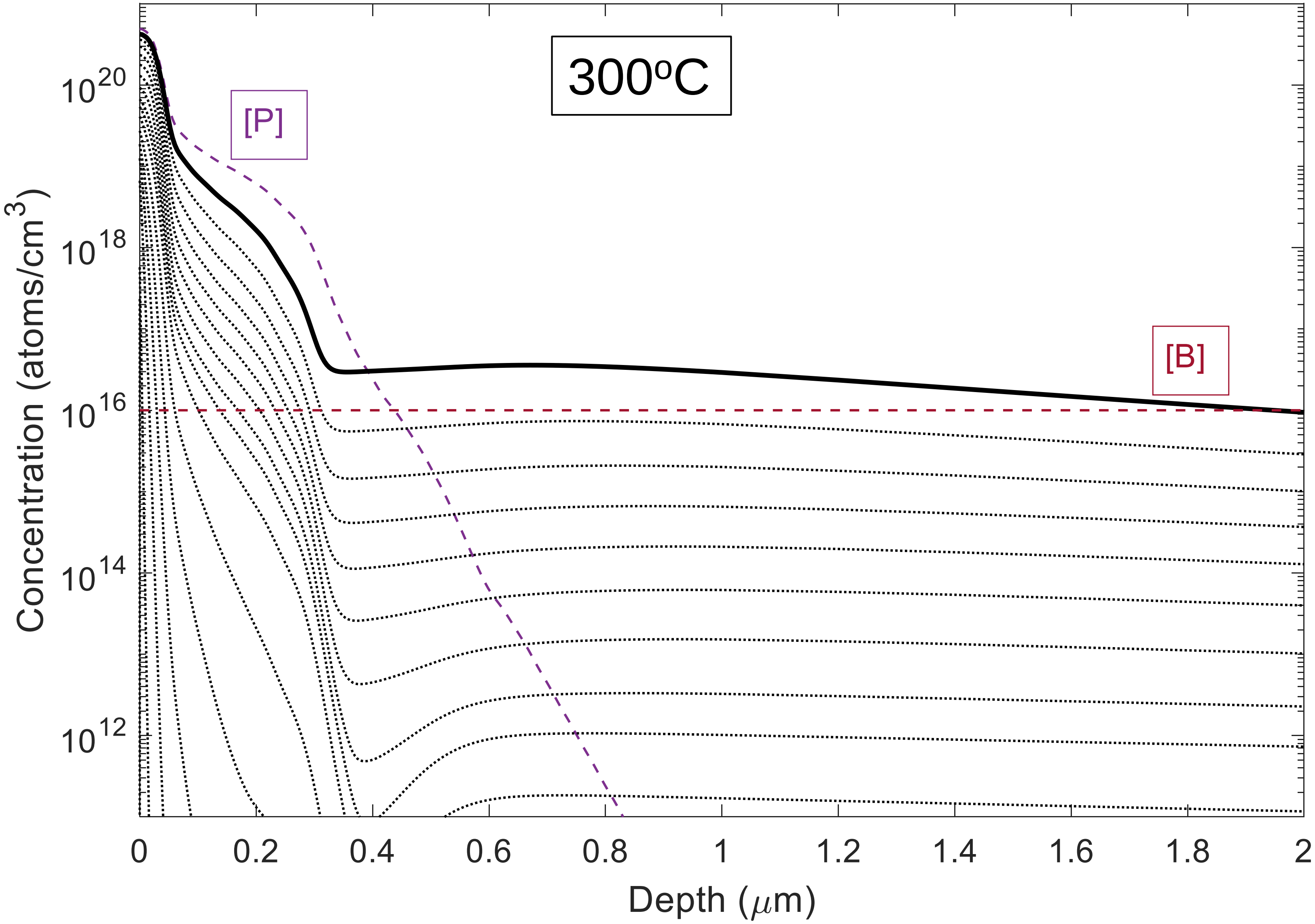
- Simulate general behaviour of hydrogen in solar cell structures during thermal processing
- Immobile
  - Hydrogen-boron (HB) and hydrogen-phosphorous (HP) pairs [1]
- Largely Immobile
  - Hydrogen dimers (H_2A and H_2C) [2]
- Mobile
  - Interstitial hydrogen (H^+,H^0,H^-)
  - Concentrations dependent upon fermi/quasi-fermi levels[3,4]
- Interaction with electric fields critical
- Model will be updated throughout ACAP fellowship



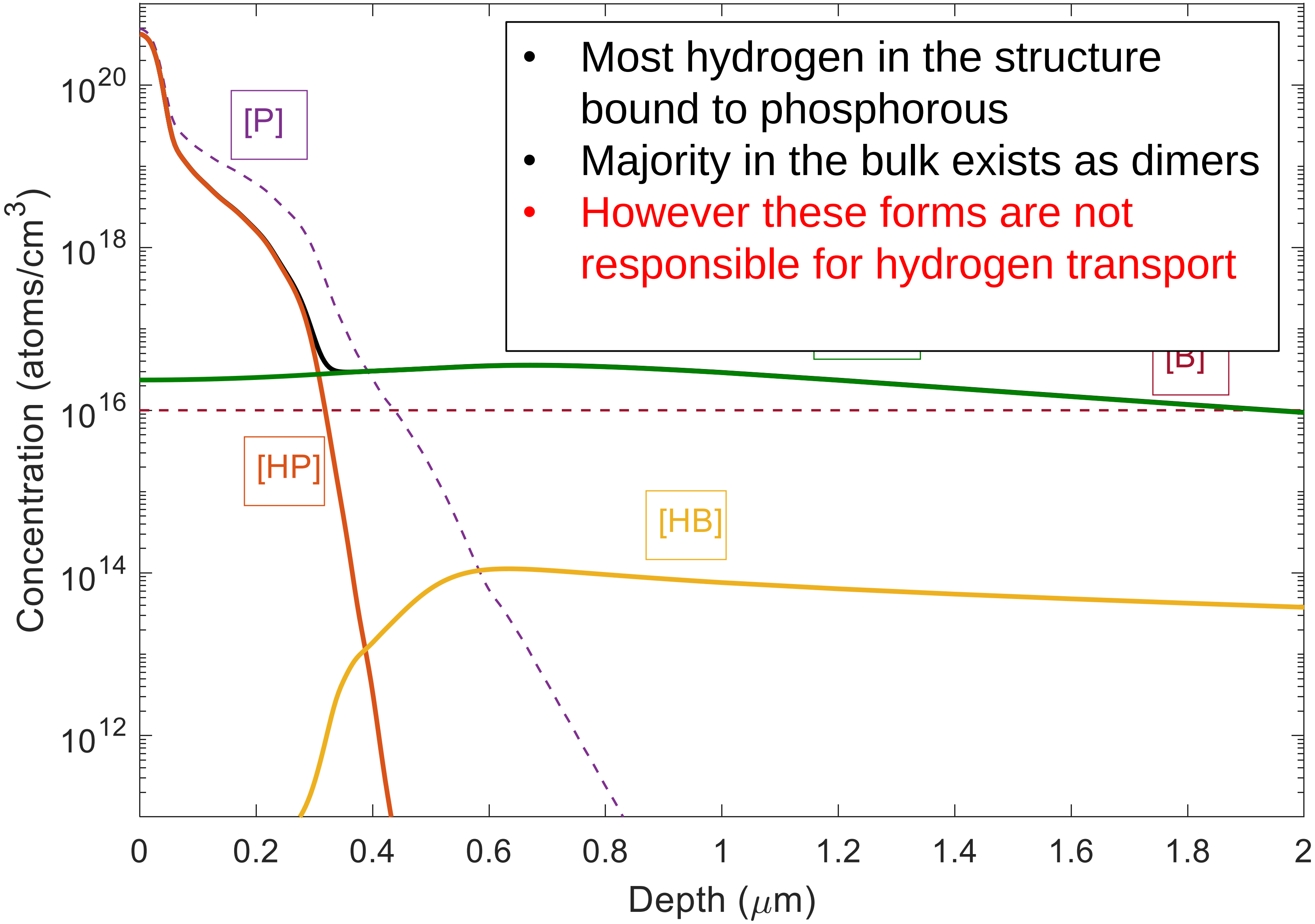


[1] Zundel, T. and Weber, J. (1989) Phys. Rev. B, 39(8), 13549, [2] Voronkov, V.V. and Falster, R. (2017) Phys. Stat. Sol. (B), 254(6), 1600779

[3] Herring, C. *et al.* (2001) Phys. Rev. B, 64(12), 125209, [4] Sun, C. et al. (2015) J. Appl. Phys. 117(4), 45702

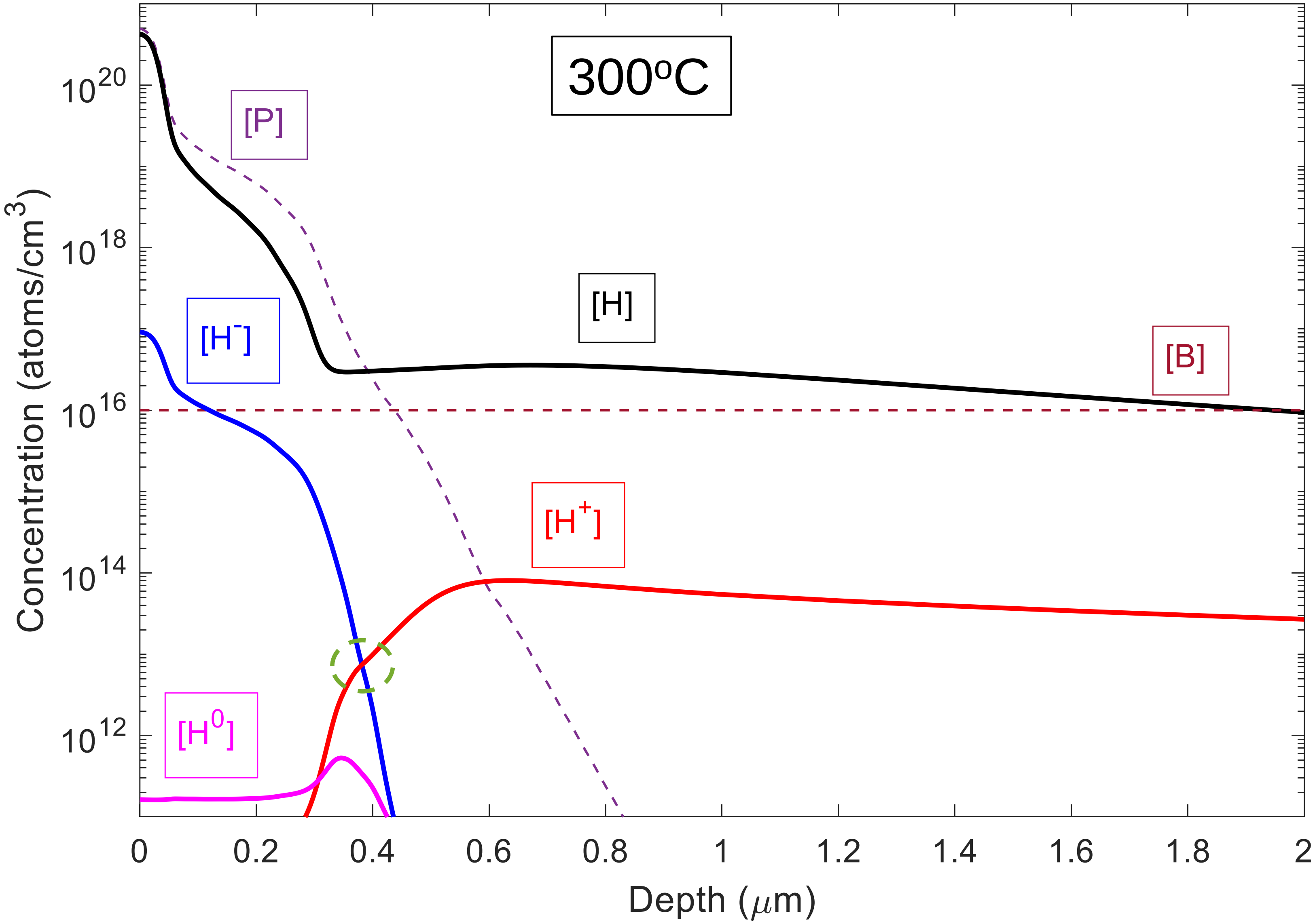


Hamer, P. *et al.* (2018) J. Appl. Phys., 123(4), 043108



- Most hydrogen in the structure bound to phosphorous
- Majority in the bulk exists as dimers
- However these forms are not responsible for hydrogen transport

Hamer, P. *et al.* (2018) J. Appl. Phys., 123(4), 043108



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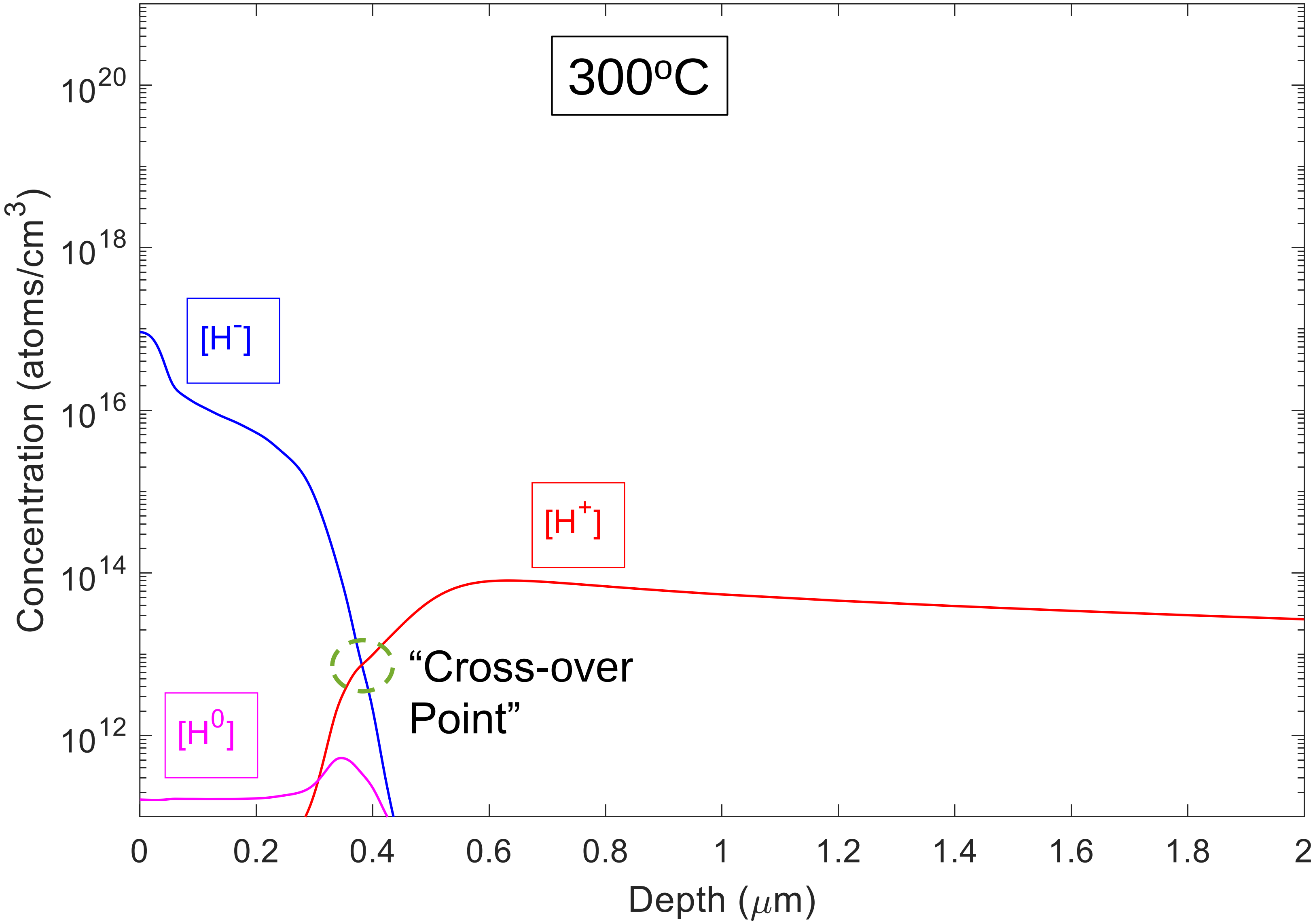
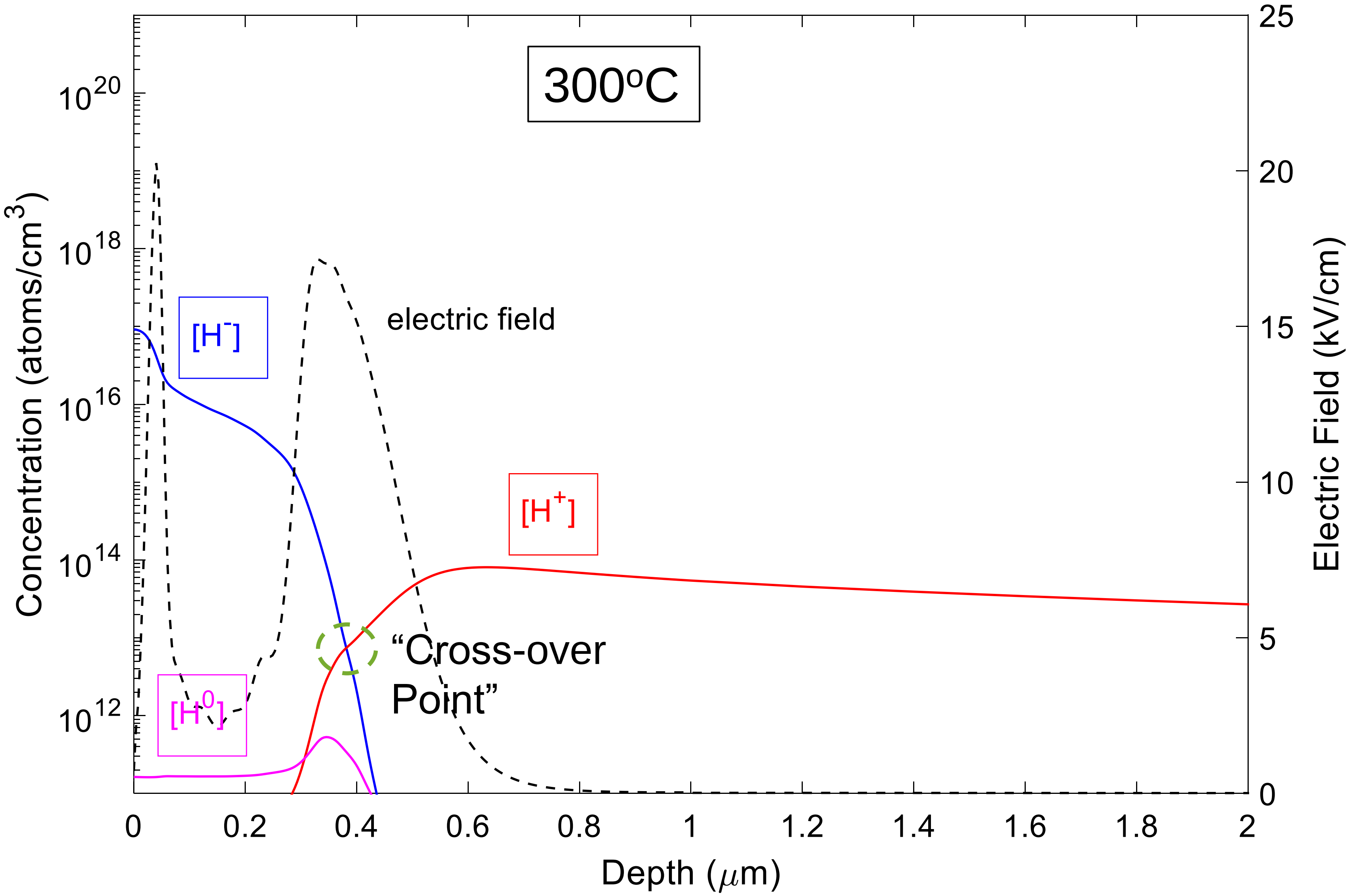


Hamer, P *et al.* (2018) J. Appl. Phys., 123(4), 043108



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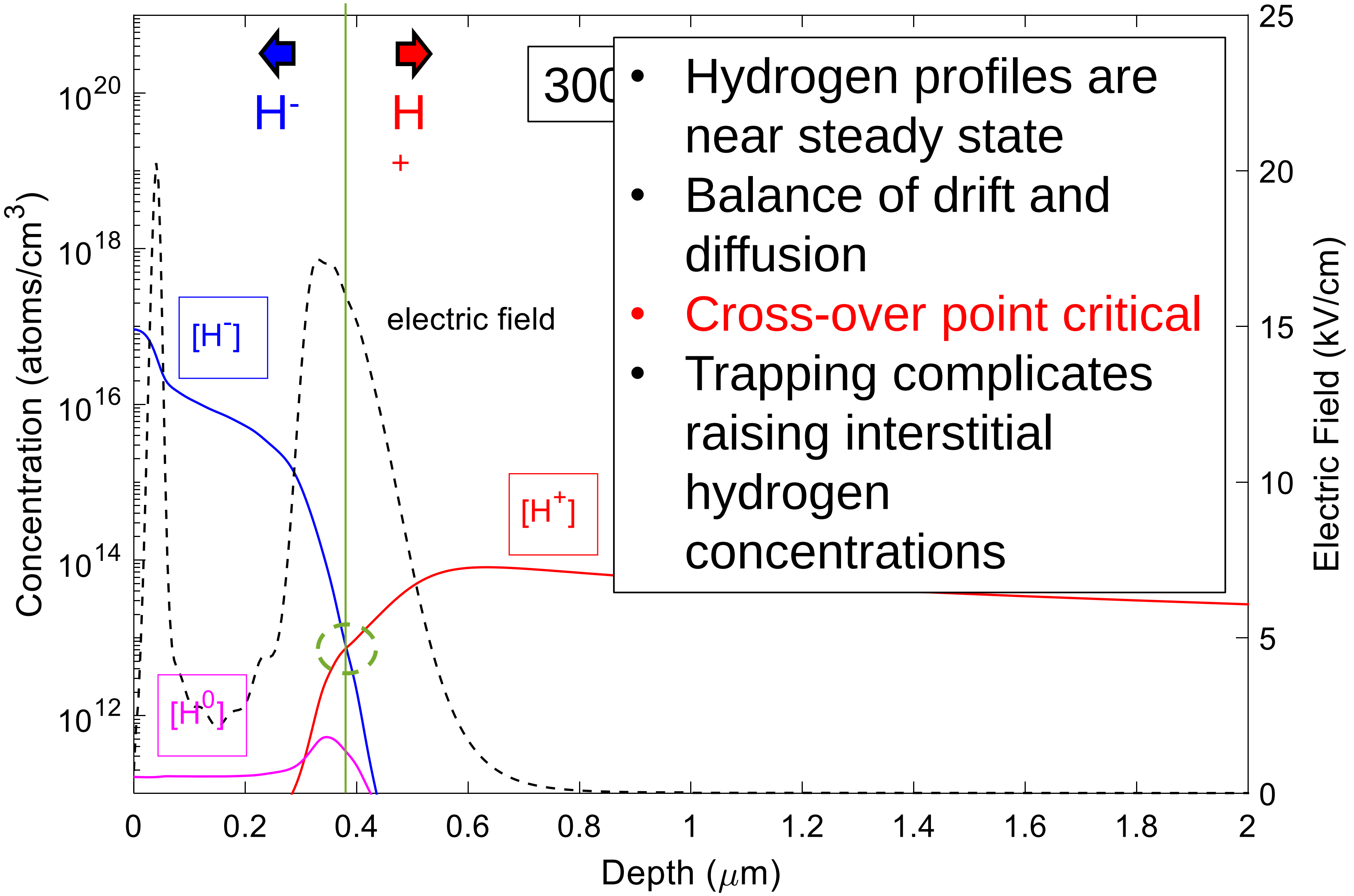
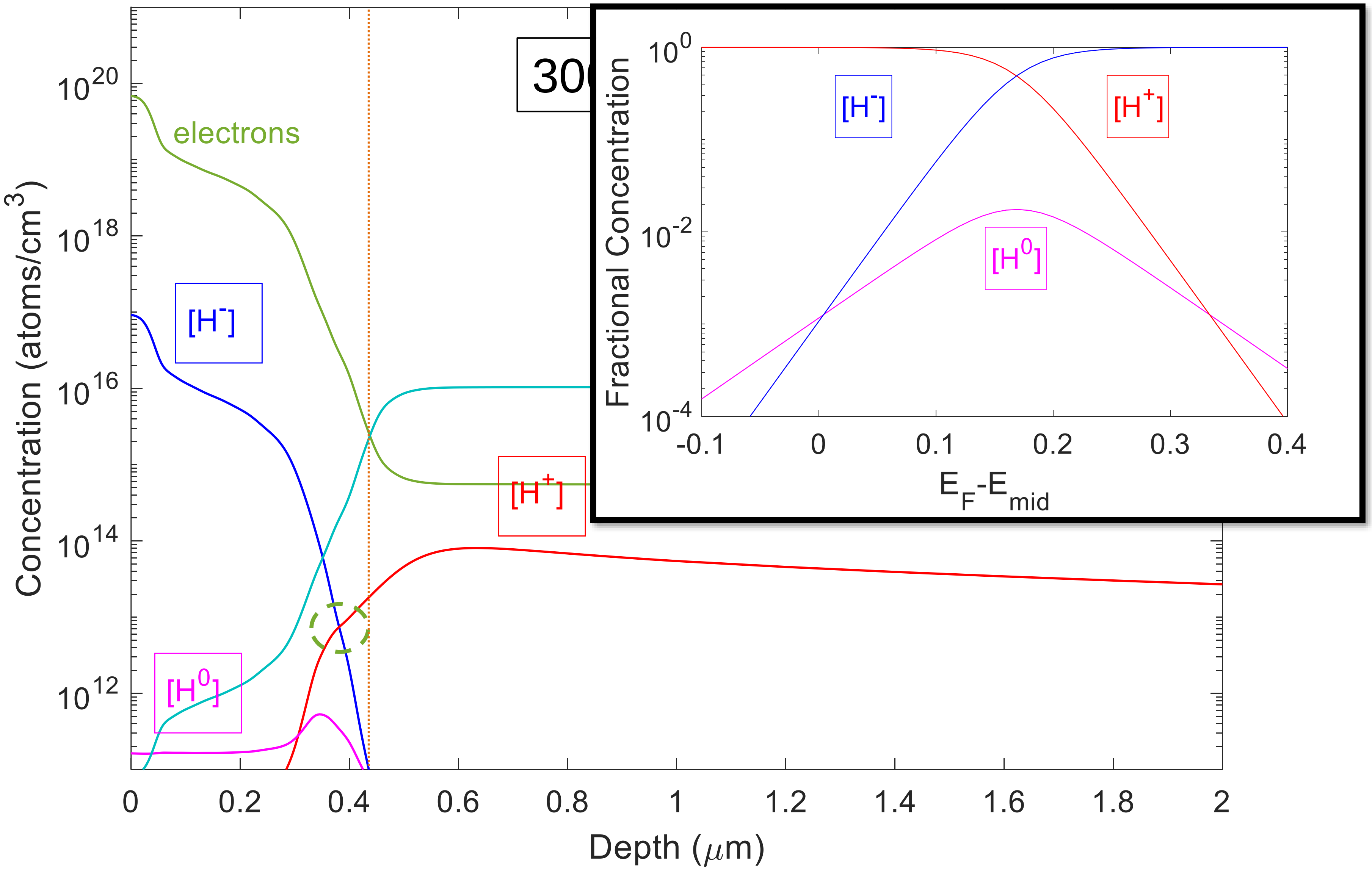


- Hydrogen profiles are near steady state
- Balance of drift and diffusion
- Cross-over point critical
- Trapping complicates raising interstitial hydrogen concentrations

Hamer, P. *et al.* (2018) J. Appl. Phys., 123(4), 043108



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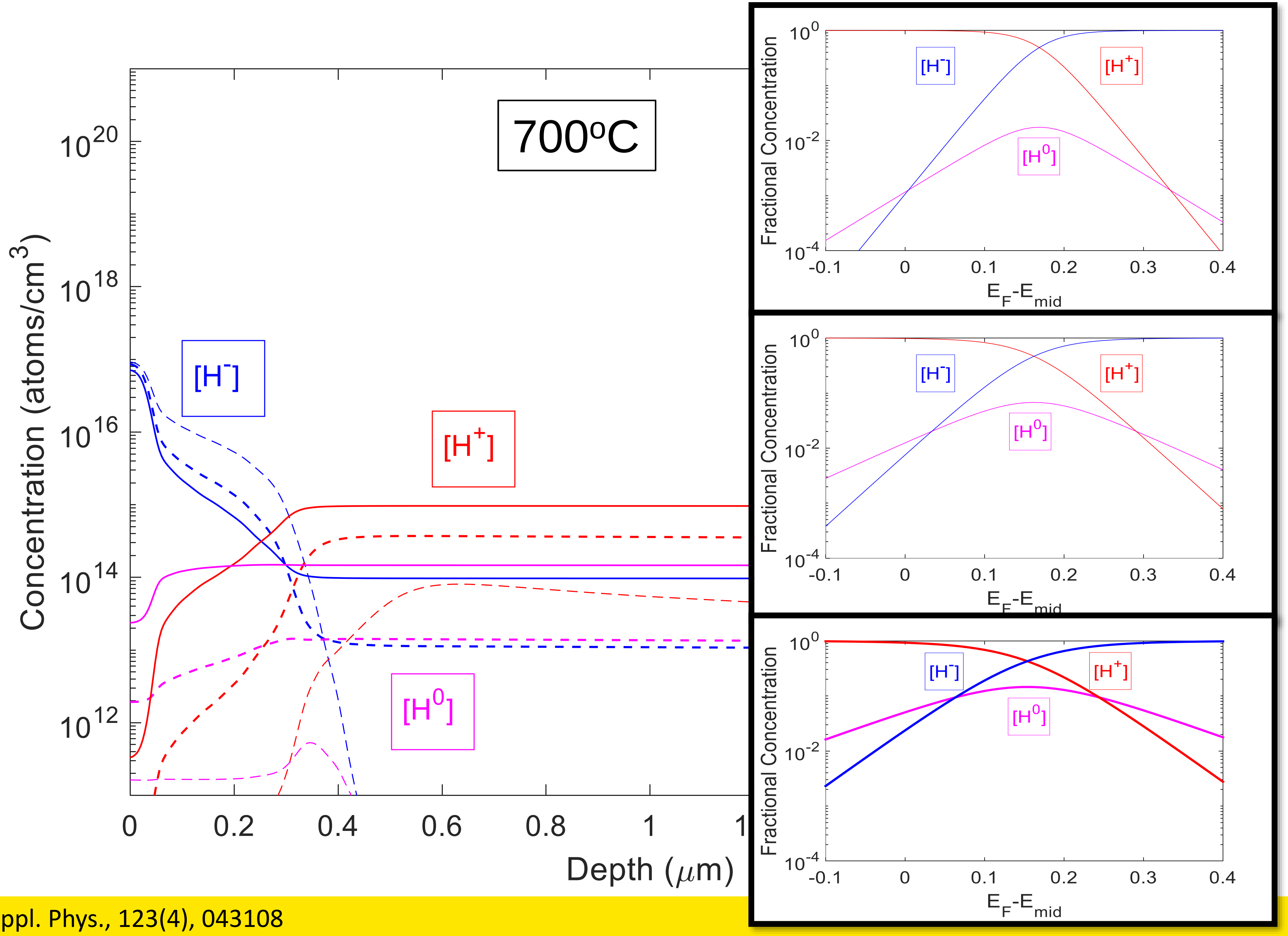

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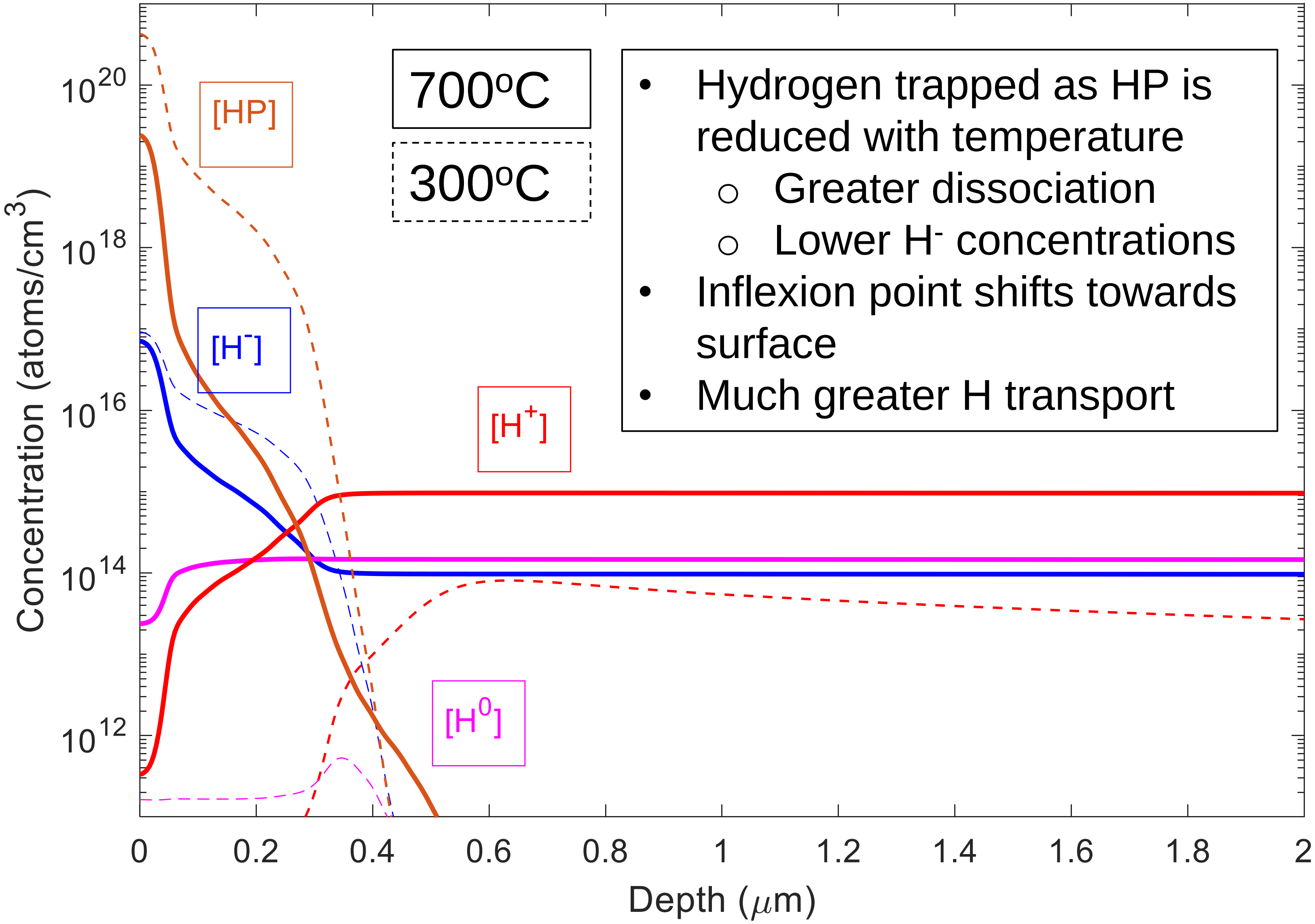
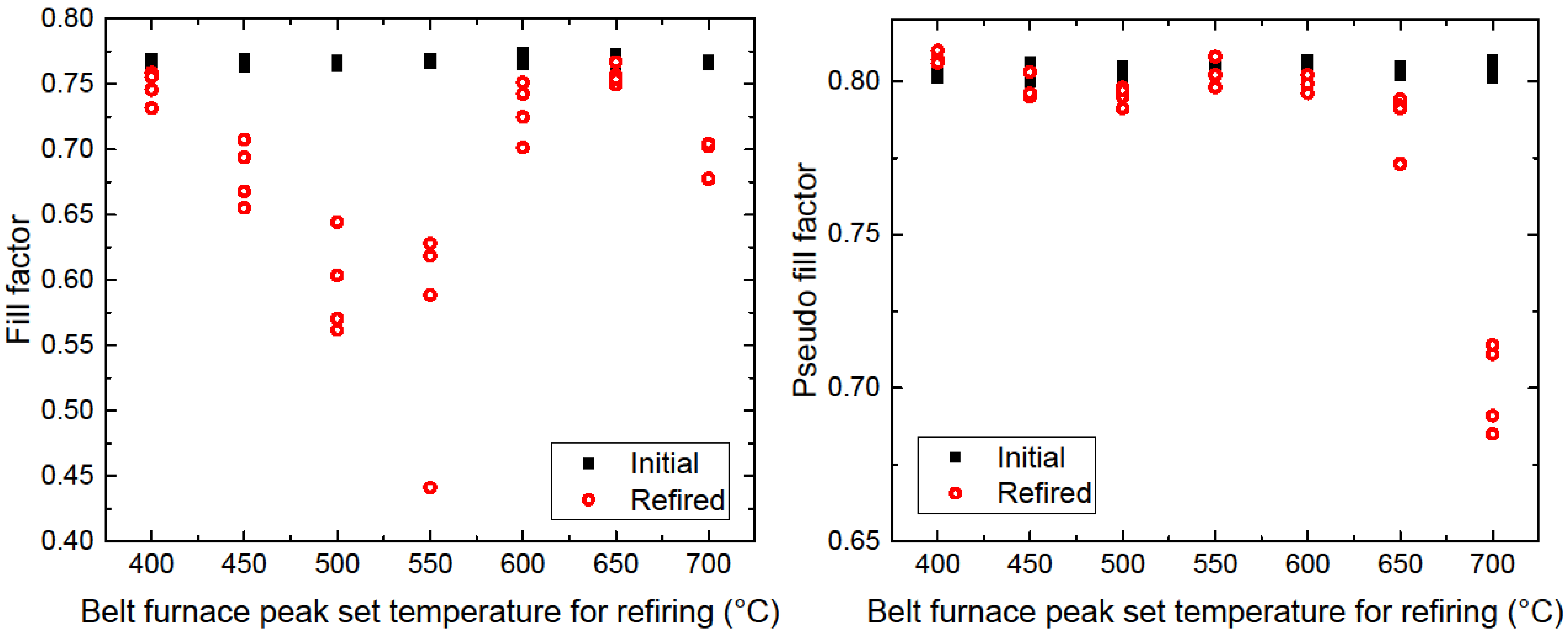


- Hydrogen trapped as HP is reduced with temperature
  - Greater dissociation
  - Lower H^- concentrations
- Inflexion point shifts towards surface
- Much greater H transport

Hamer, P *et al.* (2018) J. Appl. Phys., 123(4), 043108

Surface Effects - Contact Resistance



Fill factor (a) and pseudo fill factor (b) as a function of belt furnace annealing (BFA) set temperature before (black squares) and after (red circles) annealing for p-type mc-SI PERC cells [1].

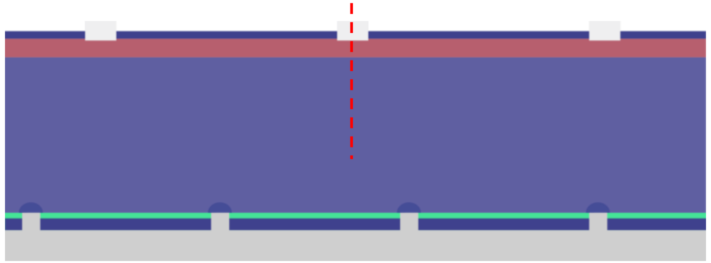
- Extended thermal processes *post-firing* lead to drop in fill-factors
- Investigation reveals this is due to an increase in front contact resistance

[1] Chan, C. *et al.* (2017) Solar RRL, 1(11), 1700129

In-Situ Monitoring of R_S

4 terminal I-V measurements @ 350^{o}C
Total time: 4 hours

- Series resistance completely overwhelms diode characteristics
- At lower temperature the time taken for R_S to increase goes up
- However maximum R_S achievable also increases
- Effect is unstable and reversible
- Re-distribution of Hydrogen



In-Situ Monitoring of R_S

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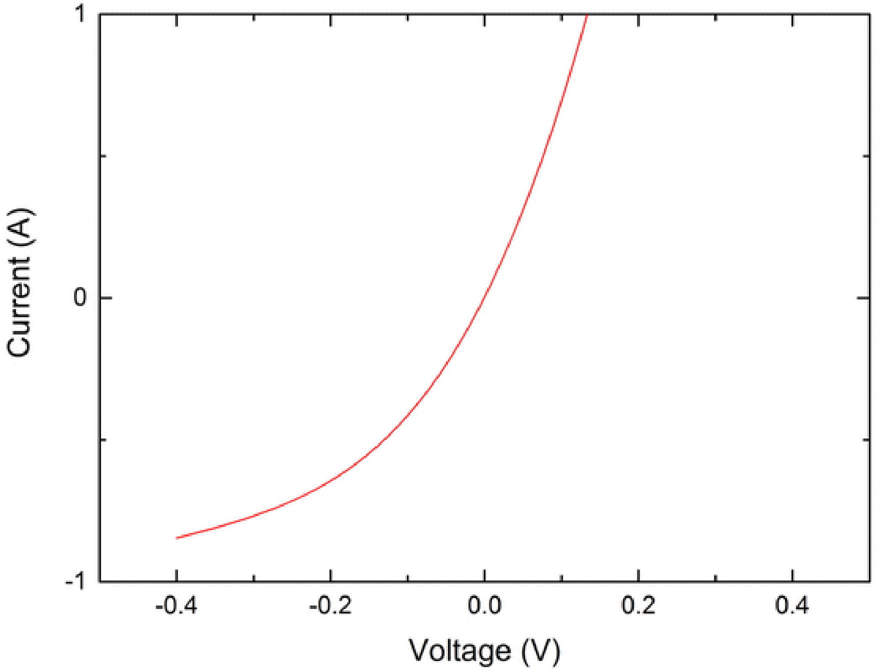

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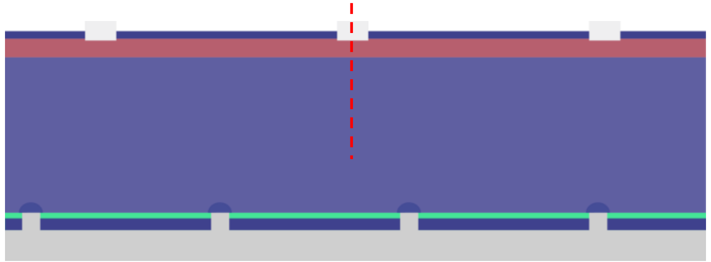
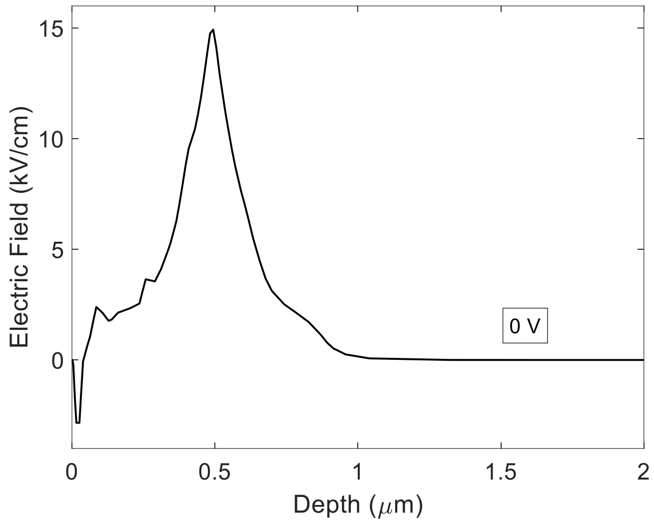
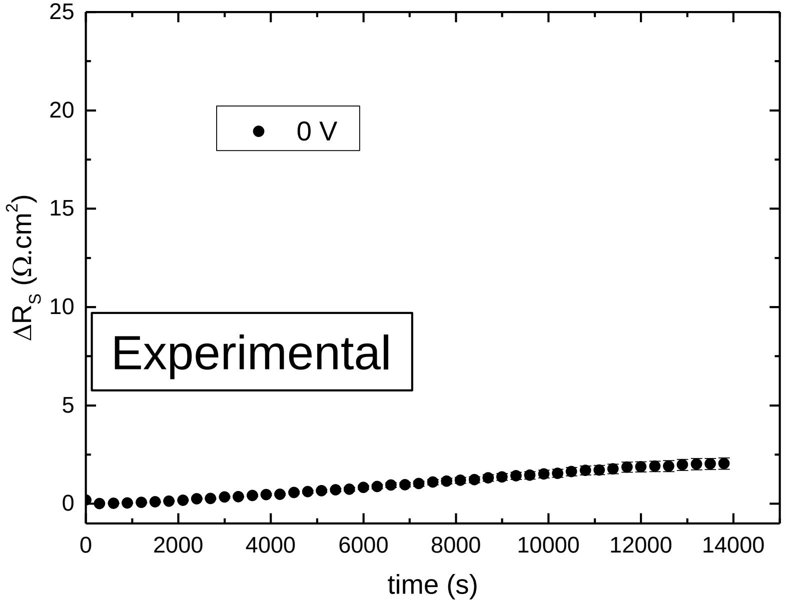
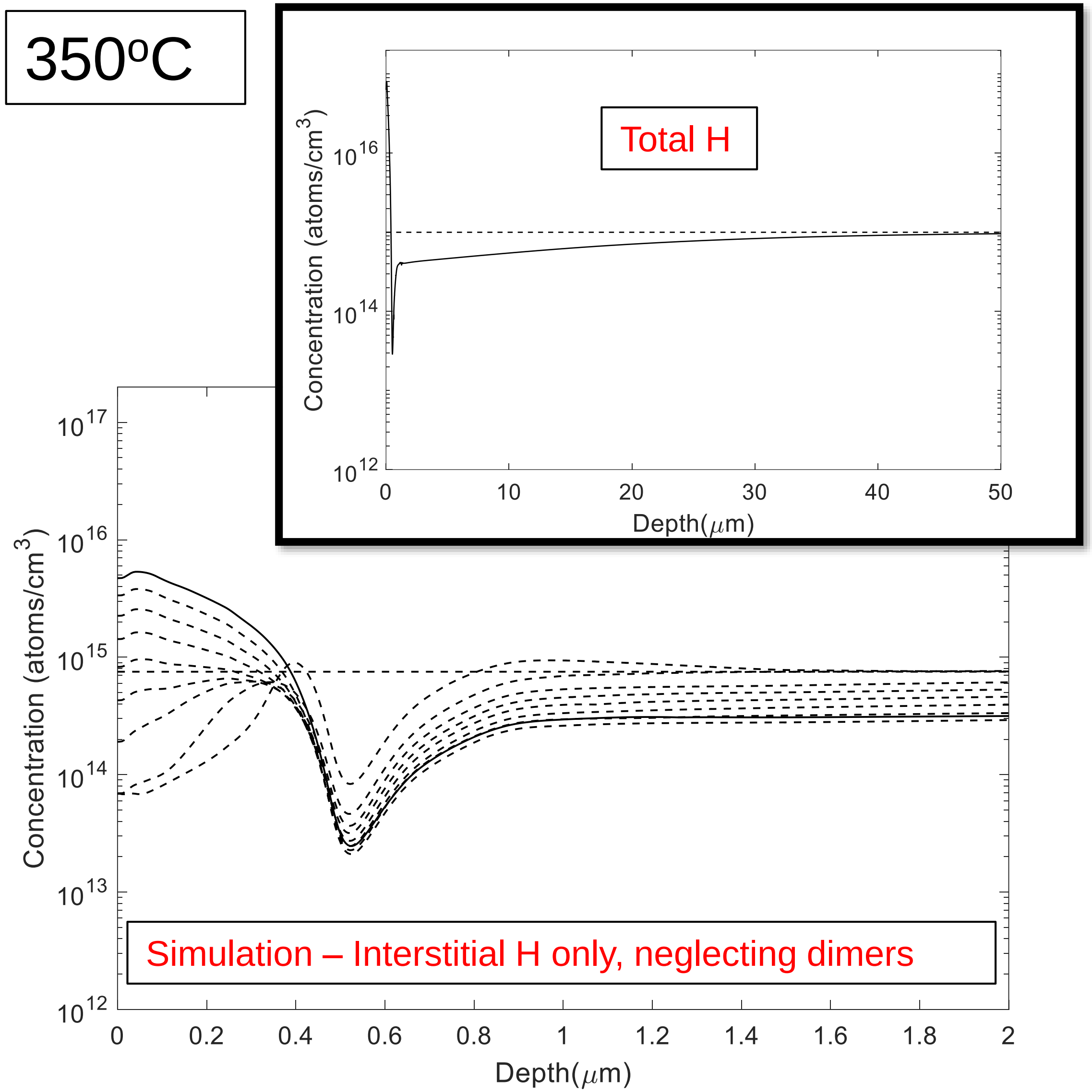


350^{o}C

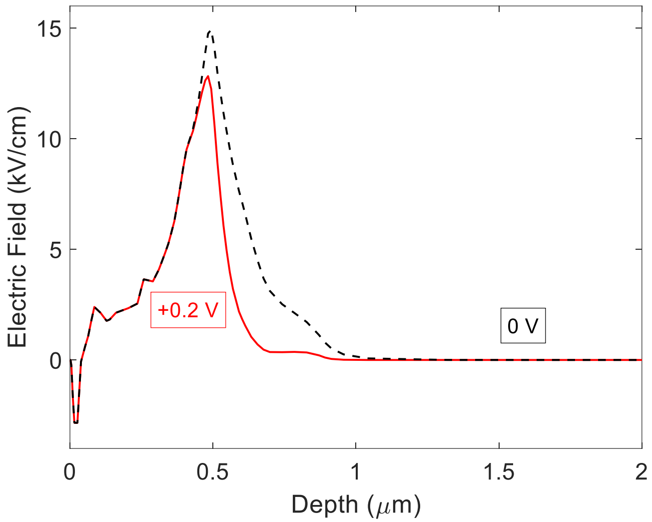



Experimental

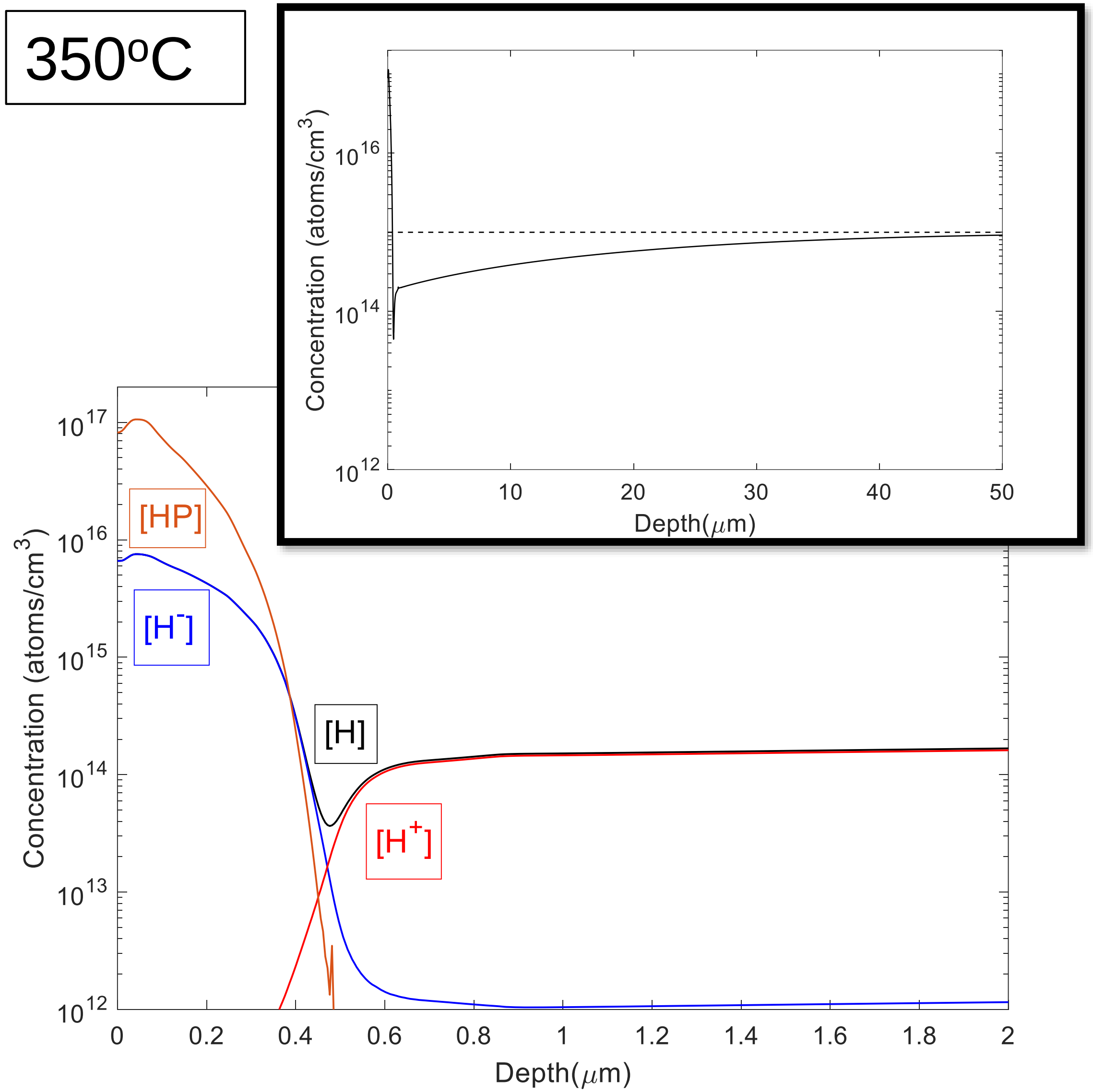

Total H

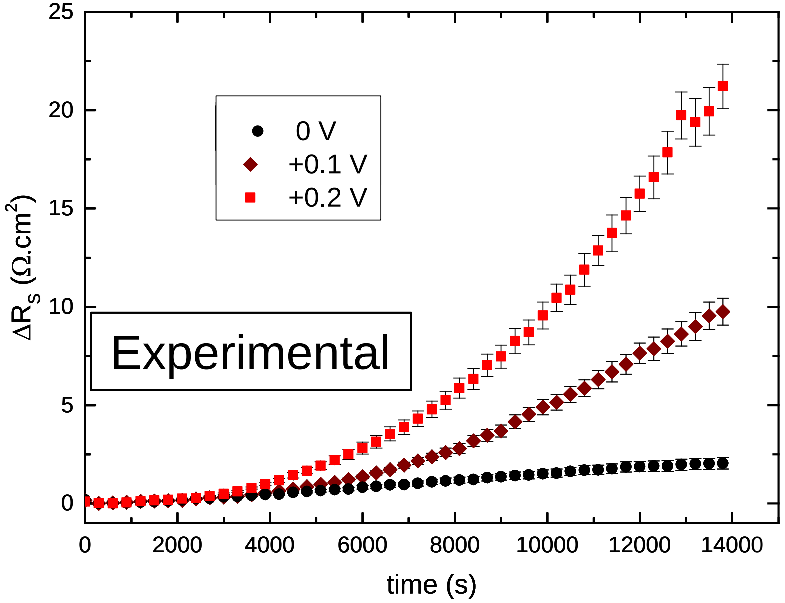
Simulation – Interstitial H only, neglecting dimers

Hamer, P. *et al.* (2018) Sol. Energy Mat. Sol. Cells, 184, pp. 91-97

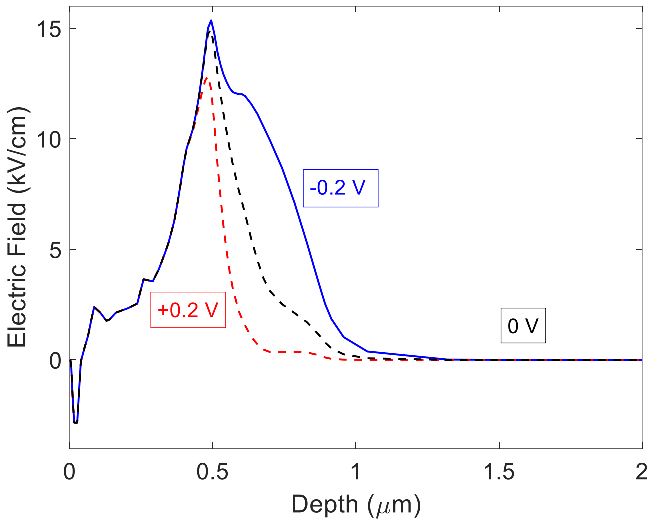


350°C

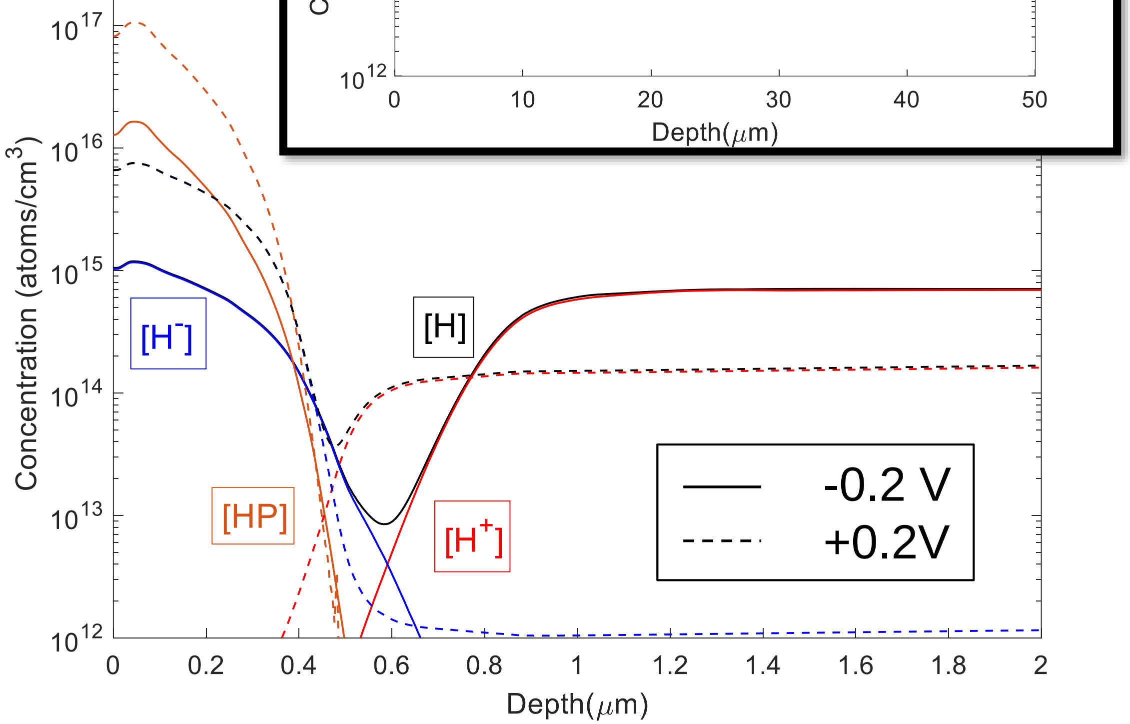


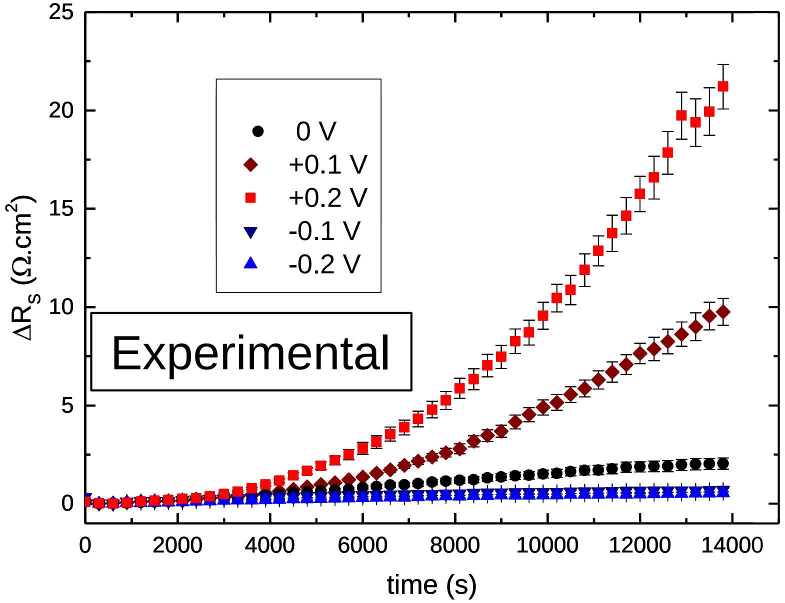


Hamer, P. *et al.* (2018) Sol. Energy Mat. Sol. Cells, 184, pp. 91-97



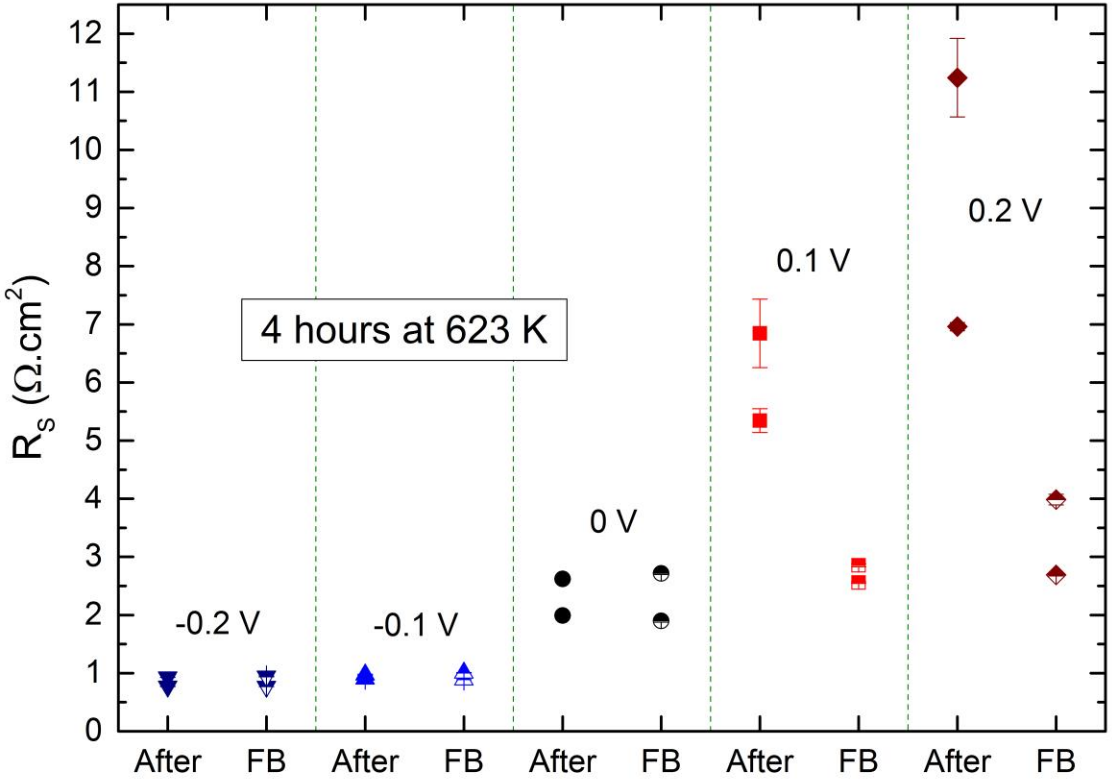
350ºC





Hamer, P. *et al.* (2018) Sol. Energy Mat. Sol. Cells, 184, pp. 91-97

After Process

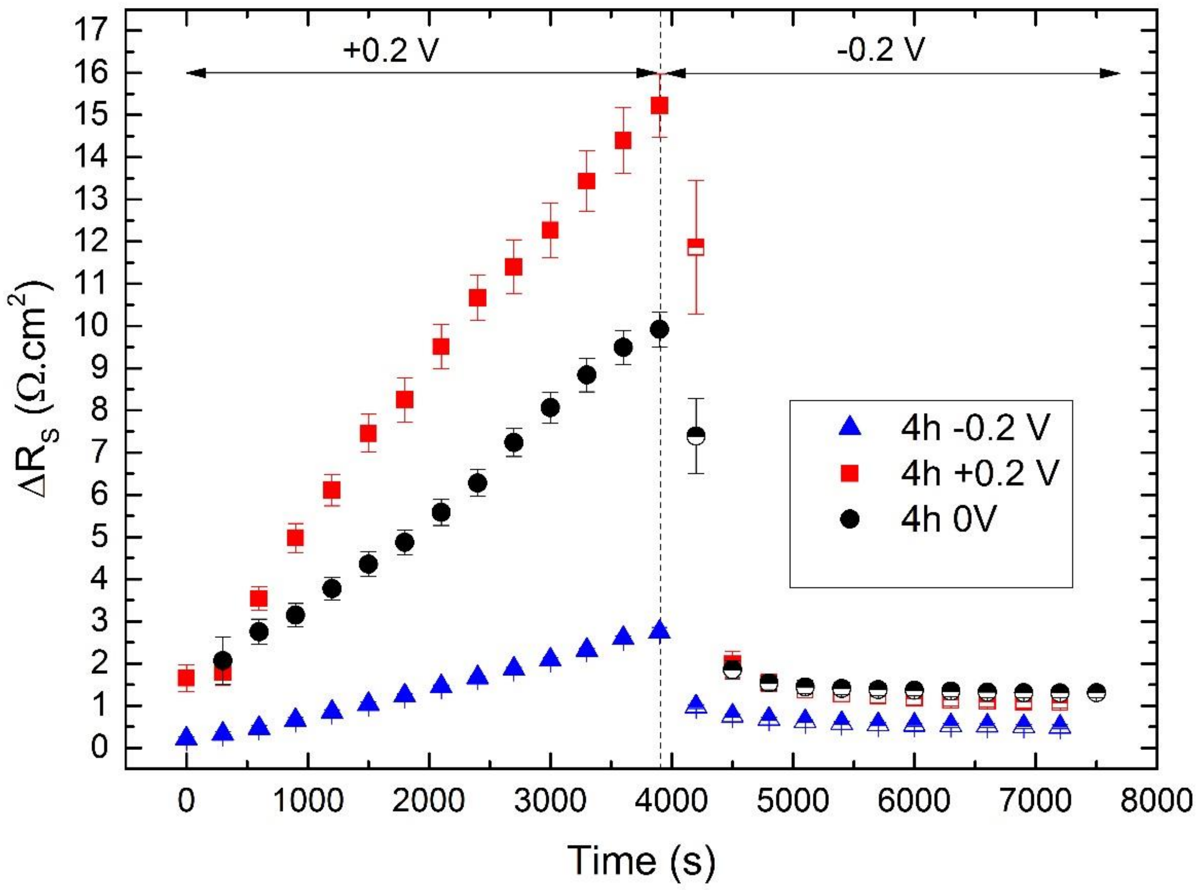


FB: 1A forward current passed at room temperature for 120 s to reduce contact res.

- Increase in R_S observed in-situ corresponds to increase at room temperature
- Reverse biased samples show negligible increase over original R_S
- The majority of the increase is unstable, and can be *temporarily* reversed by applying a large forward current at room temperature.

Hamer, P. *et al.* (2018) Sol. Energy Mat. Sol. Cells, 184, pp. 91-97

Reversibility



- Previous thermal treatment plays a role
- Possible to (almost) completely reverse change in R_S
- Then stable at room temperature
- Implies long range redistribution

Final R_S 1.06 Ω.cm^2

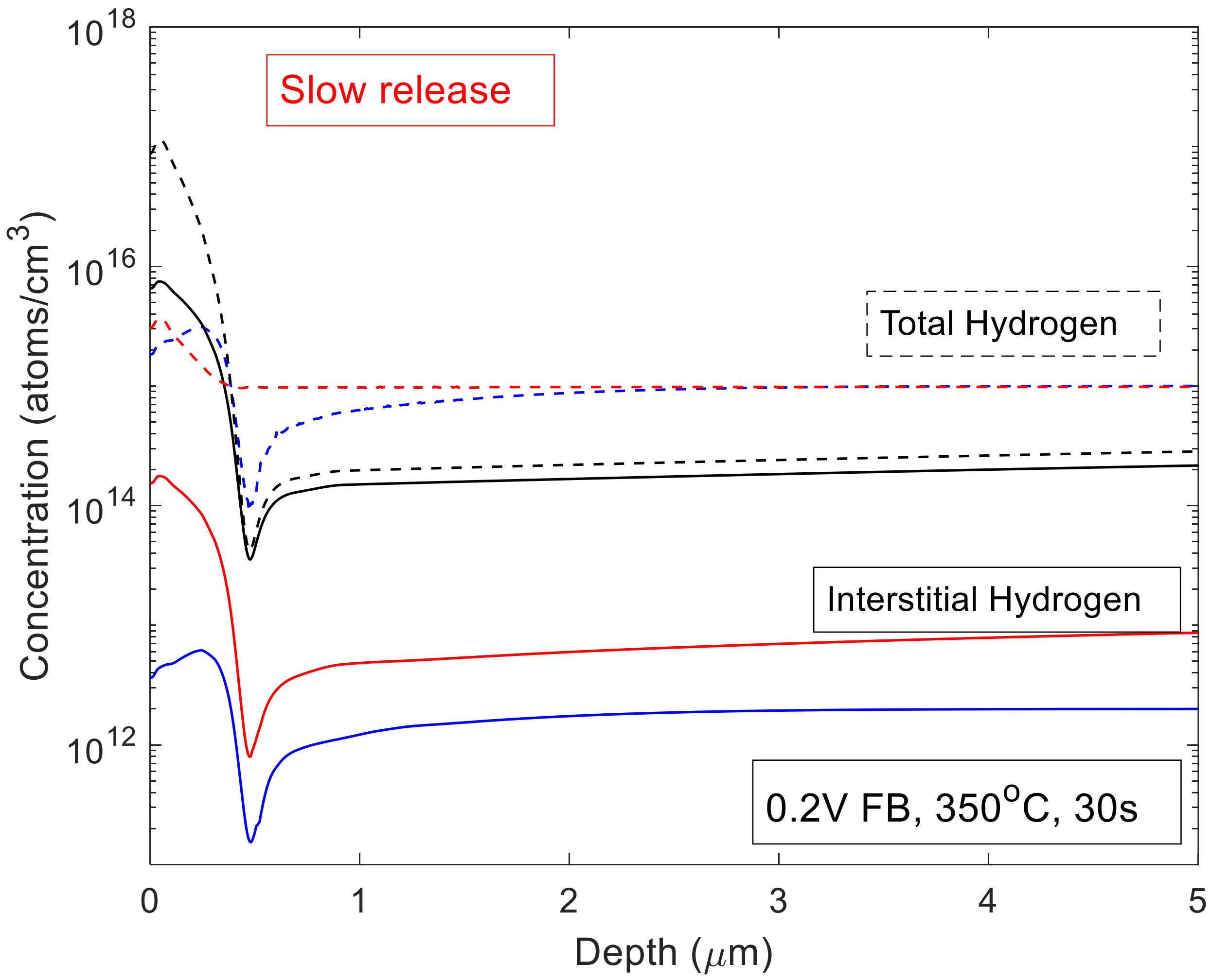
Final R_S 0.93 Ω.cm^2

Final R_S 0.75 Ω.cm^2

Hamer, P. *et al.* (2018) Sol. Energy Mat. Sol. Cells, 184, pp. 91-97

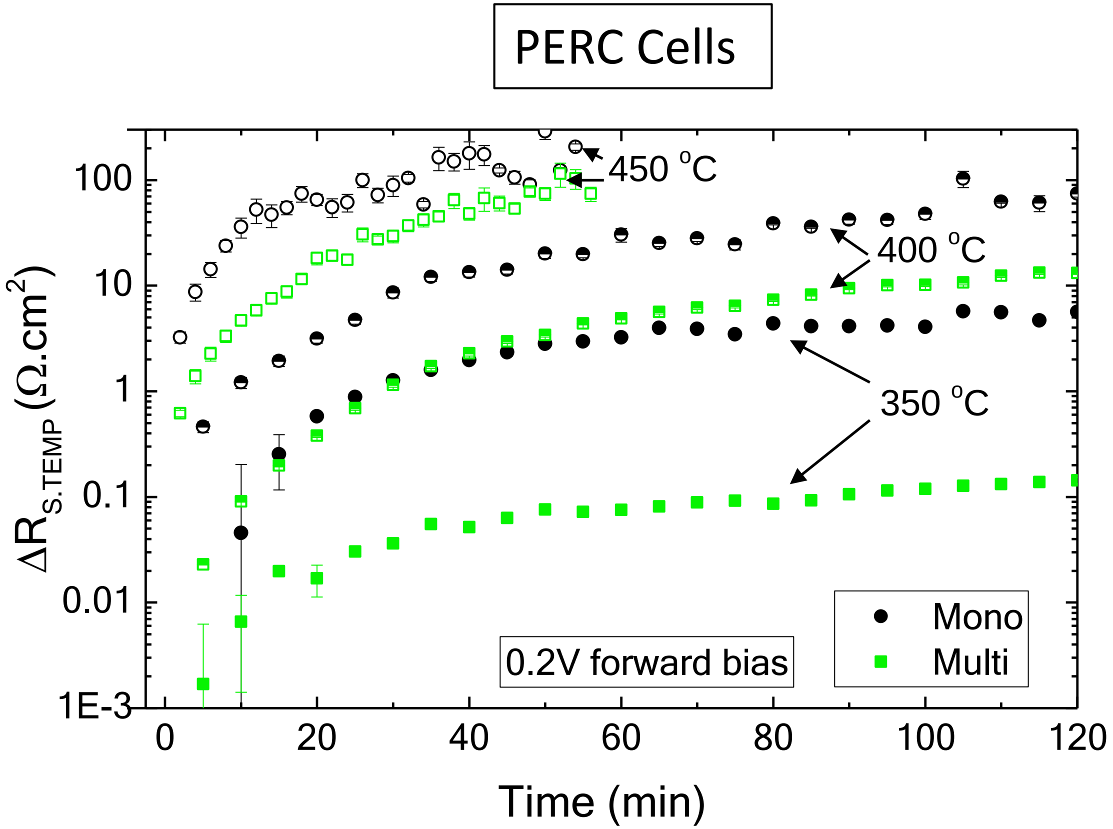
Kinetics of Hydrogen Redistribution

- Transport of hydrogen dominated by interstitial form
- Overall rate likely determined by release from bound forms
- Expect hydrogen dimers in monocrystalline silicon
- Multi?

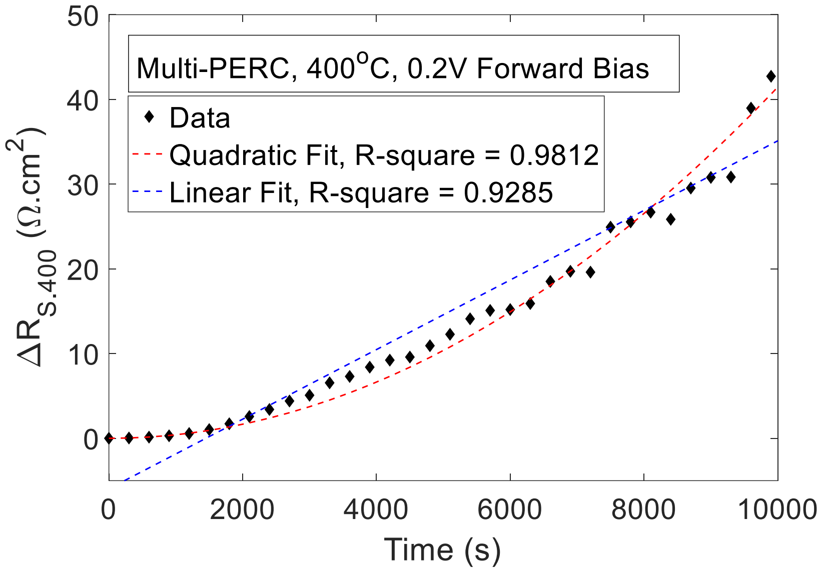


Hamer, P. *et al.* (2018) Proceedings of the 7th WCPEC, pp. 1682-1686

Dependence upon bulk material and cell structure



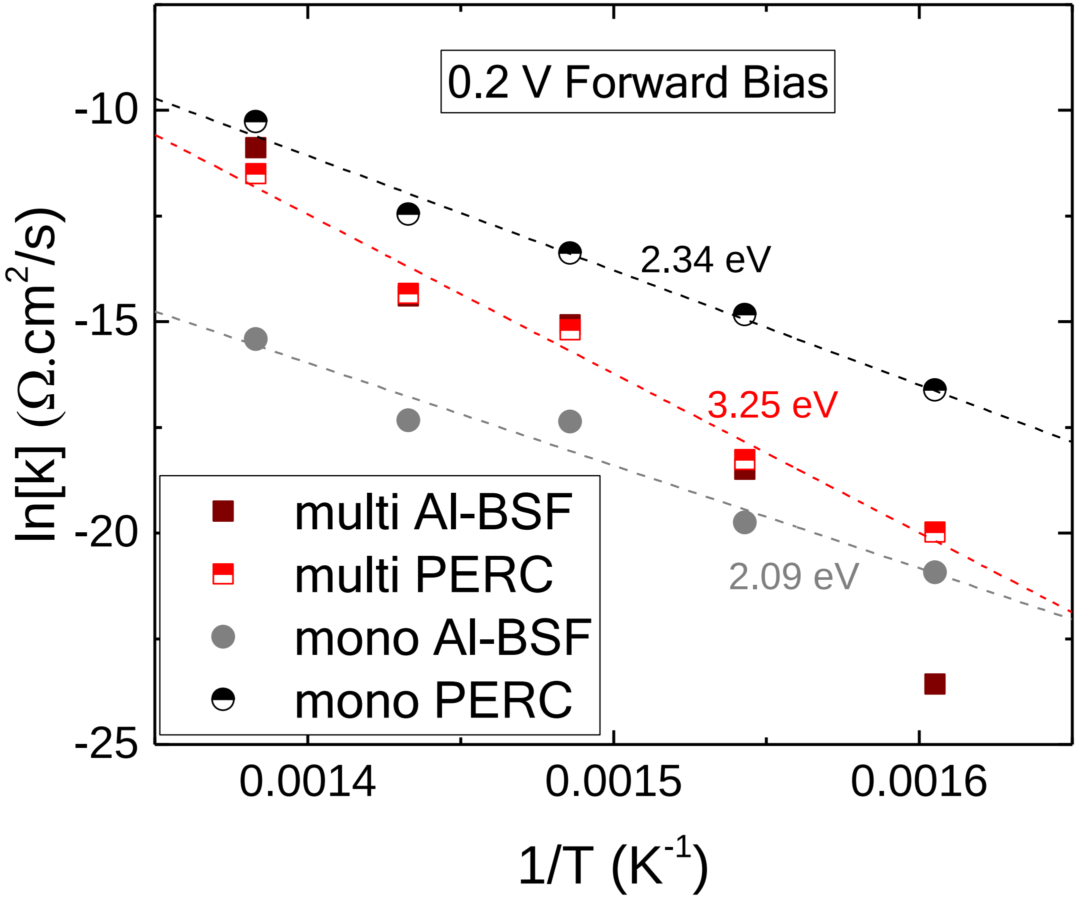
In Situ measurements of change in series resistance for Mono and Multi PERC cells annealed under forward bias at temperatures between 350-450^{o}C



- Best fit to data with quadratic relation
- Mono shows more rapid increase in series resistance, with reduced temperature dependence

Hamer, P. *et al.* (2018) Proceedings of the 7th WCPEC, pp. 1682-1686

Dependence upon bulk material and cell structure

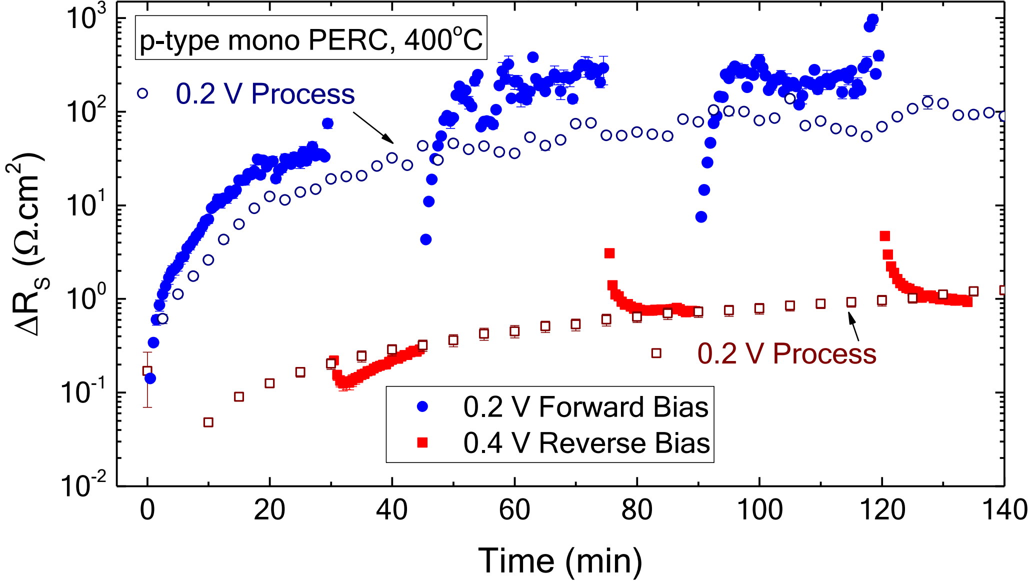


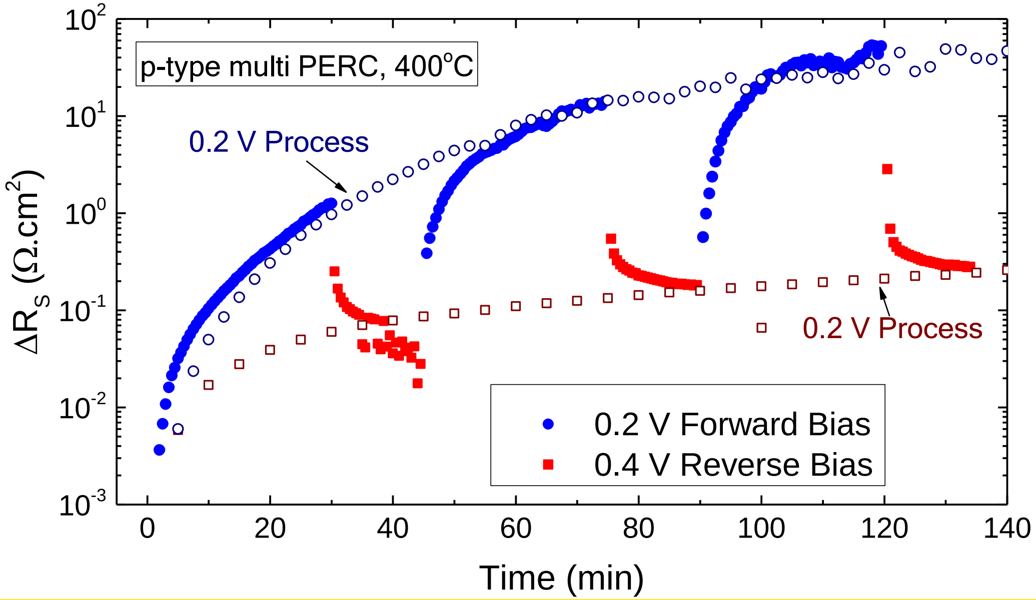
Arrhenius plot of fitted quadratic rate constant for Mono and Multi PERC and Al-BSF cells at temperatures between 350 and 450°C.

- No significant difference in activation energy observed between PERC and Al-BSF
- Mono Al-BSF approximately 2 orders of magnitude slower at all temps
  - Less Hydrogen
- Multi devices show a significantly higher activation energy
  - Different bound form

Hamer, P. *et al.* (2018) Proceedings of the 7th WCPEC, pp. 1682-1686

Reversibility





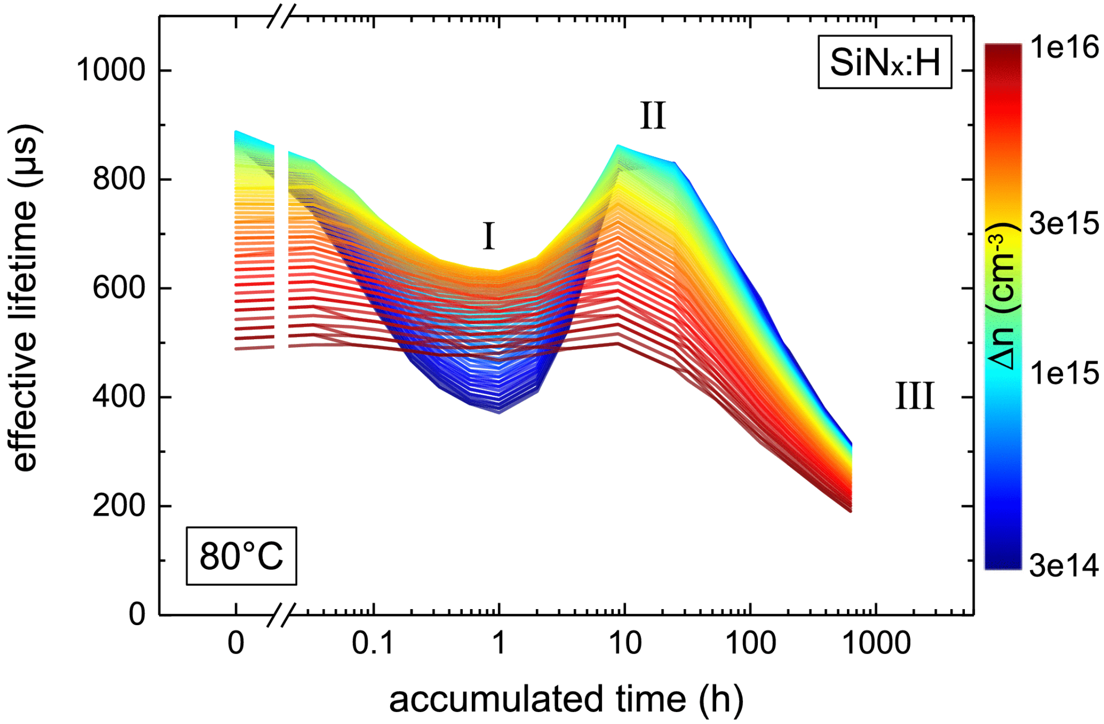
- Contact Resistance Increase has a reversible and non-reversible part
- Changes persist to room temperature measurements
- Still shows a strong dependence on material
- ΔR_S a somewhat questionable measure
- In order to extract physically meaningful information we require a more detailed model of the contact

In Situ measurement of change in series resistance for Mono and Multi PERC cells with fixed applied bias (open symbols) and with switched bias (closed symbols).

Hamer, P. *et al.* (2018) Proceedings of the 7th WCPEC, pp. 1682-1686

Surface Effects - Degradation

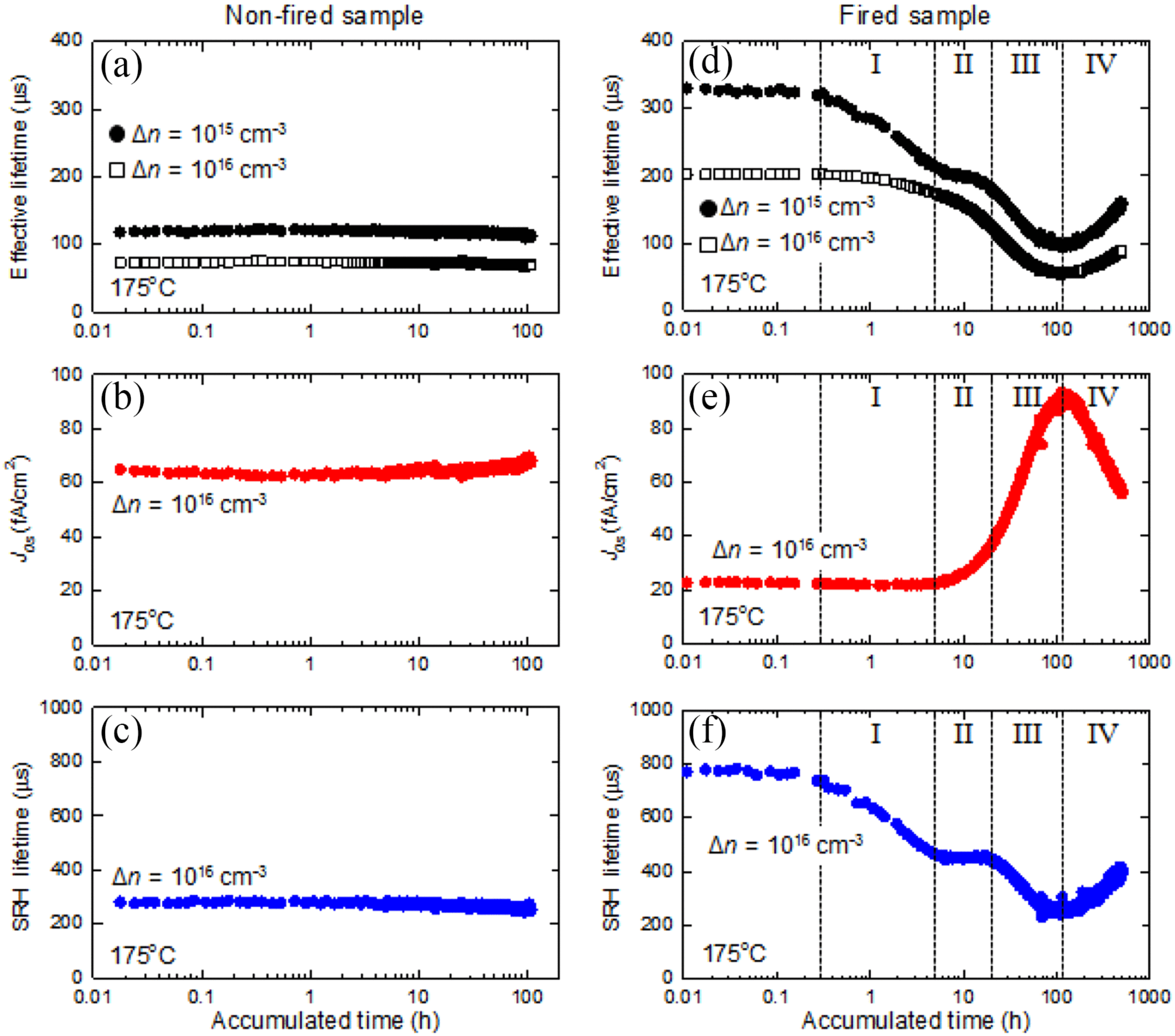
- Recently observed phenomenon where the surfaces of dielectric passivated samples appears to degrade [1-4]
- Long time-scale, usually observable after LeTID has begun to recover with an apparently linked timescale
- First observed on $SiN_X:H$ passivated samples but subsequently on $SiO_2/SiN_X:H$, $SiO_XN_Y:H/SiN_X:H$ and $AlO_X:H/SiN_X:H$ stacks
- Thermally activated and often accelerated by illumination
- Not necessarily well described by a simple increase in $J_{0.surface}$



Injection-resolved evolution of τeff during LID treatment at 80 °C and ~1 sun equivalent illumination of a B-doped FZ-Si. Injection levels are color-coded, ranging from Δn=$3x10^{14}$cm−3 (blue) to Δn=$1x10^{16}$cm−3 (red) [2].

[1] Sperber, D. *et al.* (2016) Energy Procedia, 92, 211-217, [2] Sperber, D. *et al.* (2017) IEE J. of Photov., 7(6), 1627-1634,
[3] Sperber, D. *et al.* (2018) Sol. Energy Mat. Sol. Cells, 188, 112-118, [4] Sperber, D. *et al.* (2018) Phys. Stat. Sol. (A), 215(24), 1800741

Dependence on firing time/temperature



- Surface degradation only really apparent in fired samples
- Difference in fired/unfired dielectrics or due to the introduction of hydrogen
- Often manifests as changes in extracted J_{0S} *and* τ_{bulk}

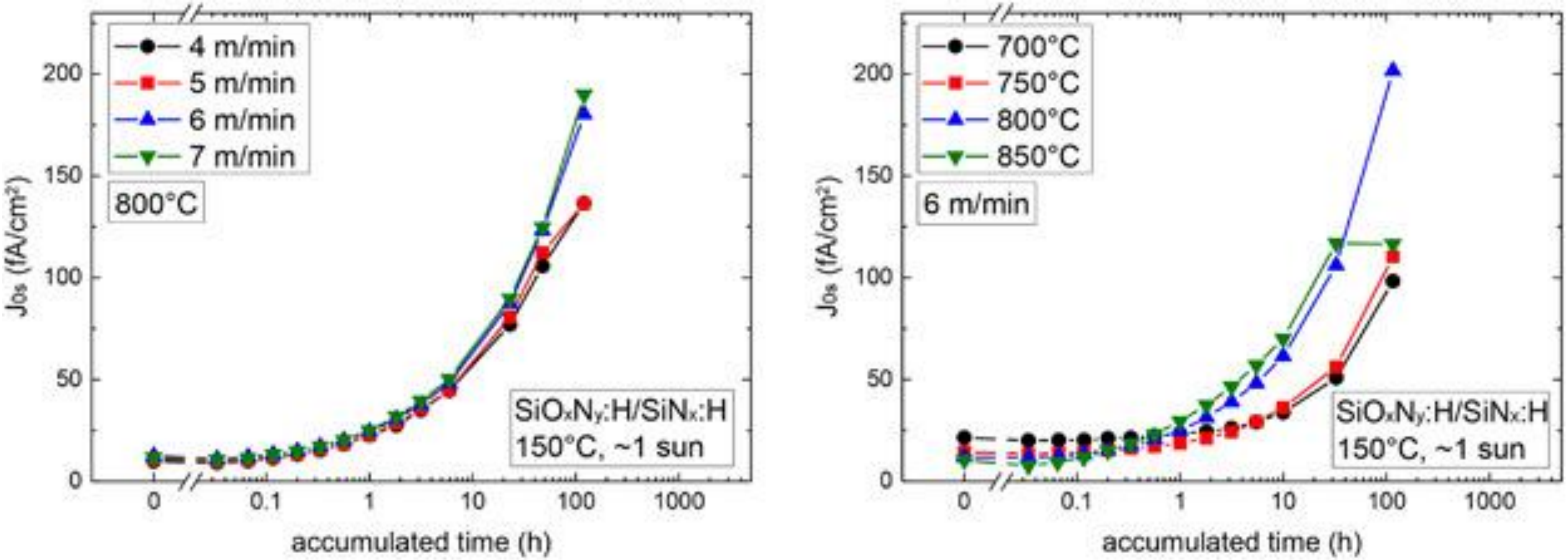
SPECULATION

a), d) Effective lifetime, b), e) extracted J_{0S} and c), f) extracted τ_{bulk} for a-c) Non-fired and d-f) Fired p-type ? Ω.cm wafers passivated with SiN_X:H under dark annealing at 175°C [1].

[1] Kim, K. *et al.* (2019) IEEE J. of Photov., 9(1), 97-105

Dependence on firing time/temperature

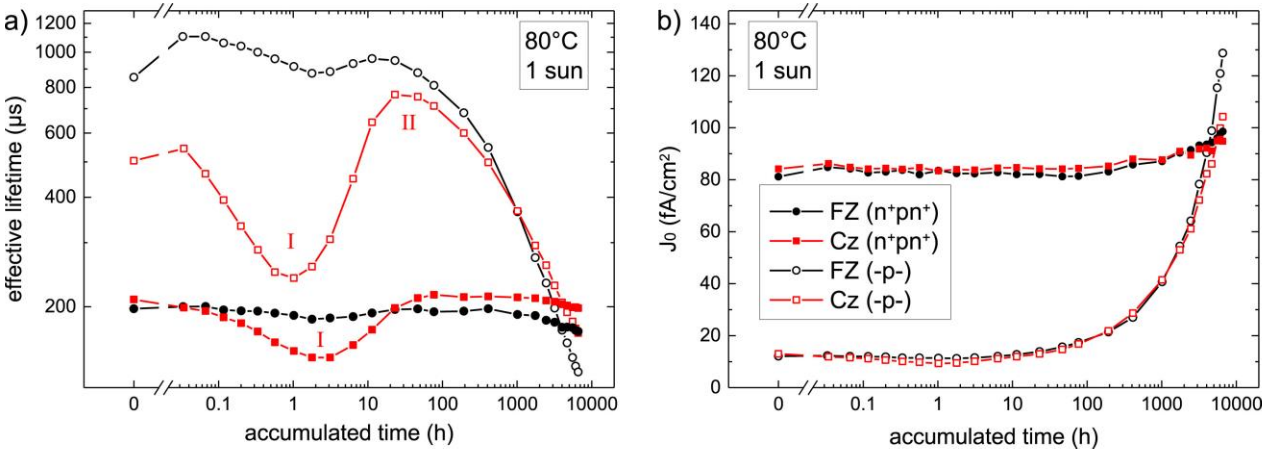
- Similar to LeTID, extent of degradation depends to some extent on firing conditions
- Increase in degradation with increased time/temperature
- Relatively weak dependence



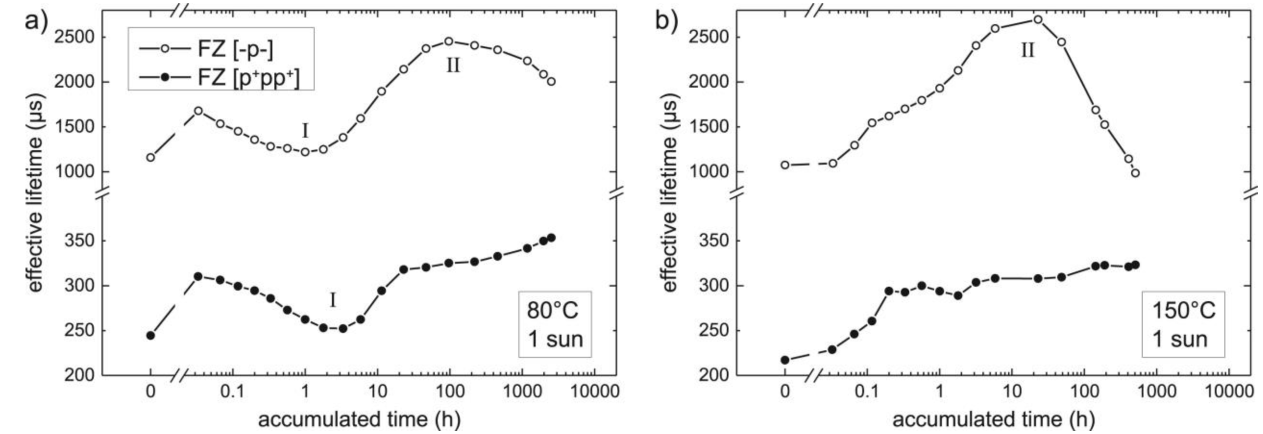
Measurement of J_{0s} of CZ-Si samples passivated with a SiOxNy:H/SiNx stack during treatment at ~1sun and 150^{o}C with variation of belt speed and peak temperature [1].

[1] Sperber, D. *et al.* (2018) Phys. Stat. Sol. (A), 215(24), 1800741

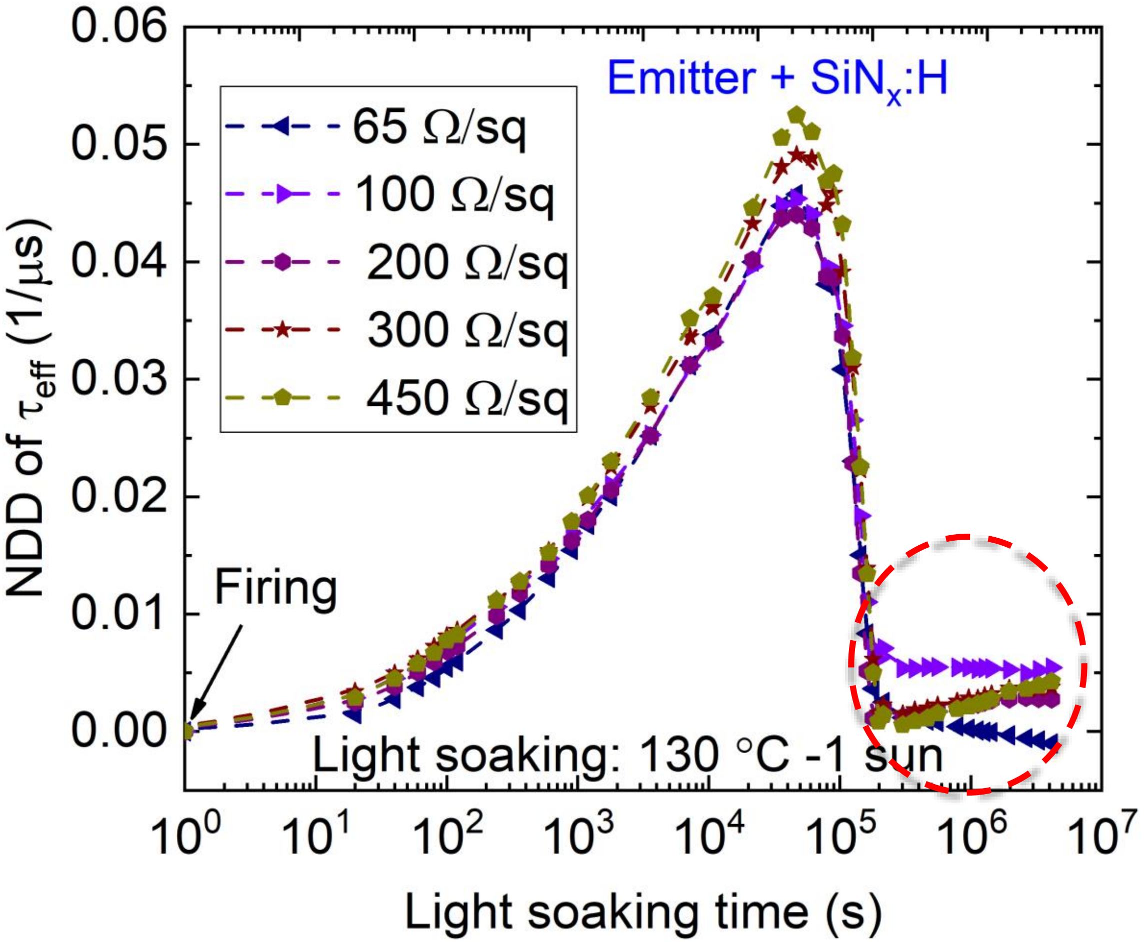
Emitter Diffusion -> Less degradation



(a) τ_{eff} of samples with and without P-emitter during treatment at 80 °C and ~1 sun illumination. (b) Calculated values of J_0 of the same samples [1].



(a) τ_{eff} of B-doped FZ-Si samples with and without B-diffused layer, fired at 800 °C, and treated at 80 °C and 1 sun. (b) Identically processed samples treated at 150 °C and 1 sun. All samples were made of B-doped FZ-Si ($N_d \approx 1.5 \cdot 10^{16}$ cm^{-3}, d ≈ 250 µm) [1].

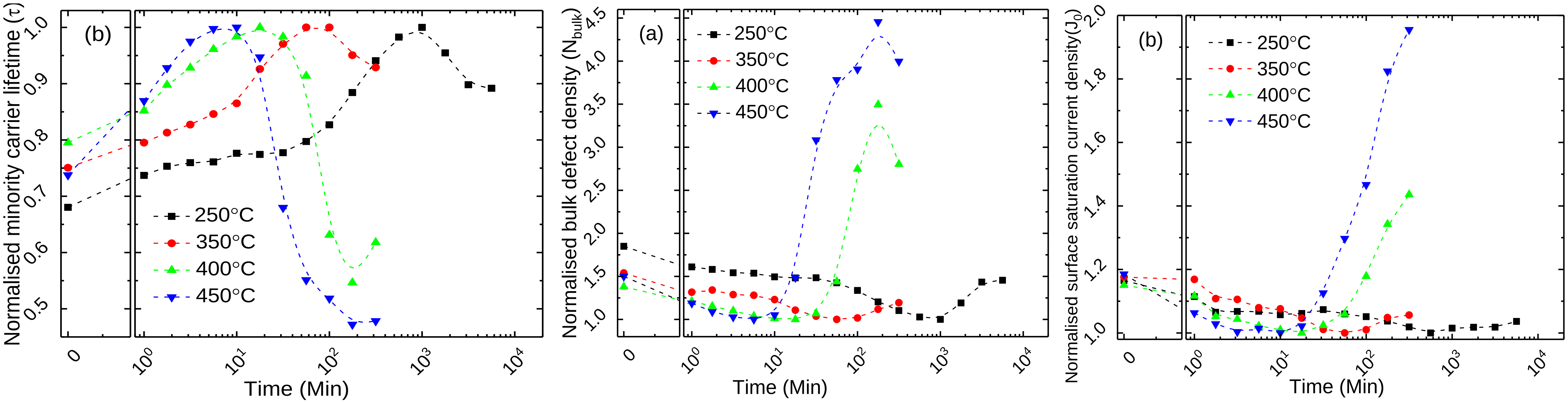


NDD for SiNX:H passivated p-type mc-SI samples with P-emitters of different resistivities during light soaking at 130°C [2].

[1] Sperber, D. *et al.* (2018) Sol. Energy Mat. Sol. Cells, 188, 112-118, [2] Sen, C. *et al.* Manuscript in preparation

Temperature dependence of degradation with emitters

- Annealing at higher temperatures (light or dark) leads to an increase in surface degradation observed with phosphorous emitters
- Degradation also observable on heavier emitters
- Observed at phosphorous doped rear surface of n-type bifacial cells

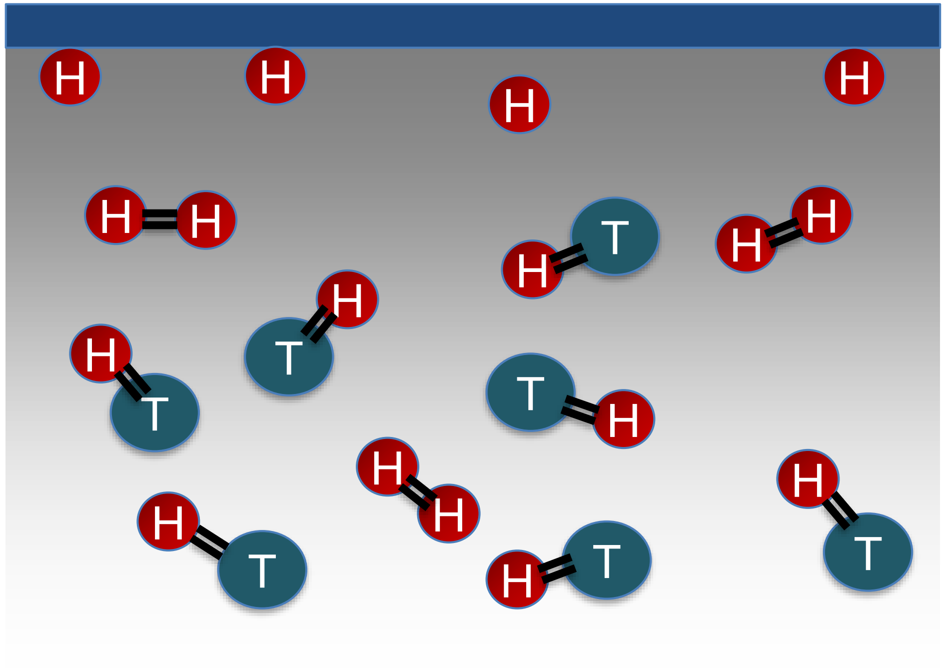


(a) Normalized carrier lifetime of *n*-type silicon bifacial cell structure vs, dark annealing during at 250 ℃, 350 ℃, 400 ℃, and 450 ℃. (b) The corresponding extracted normalized bulk defect density. (c) The extracted normalized surface J_0. Lines serve as a guide to the eye [1].

[1] X.Tan *et al.* manuscript in preparation

Surface Degradation and Hydrogen Redistribution

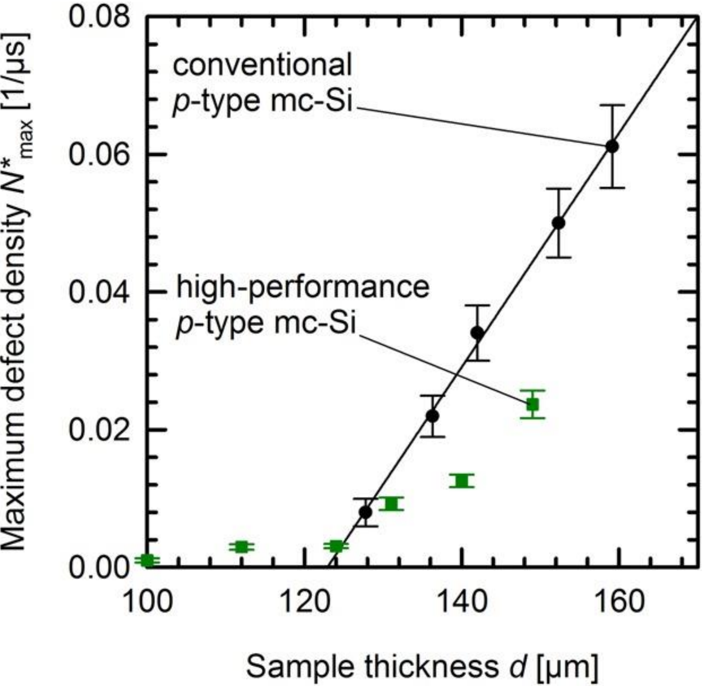
1. Hydrogen is released from unstable (largely recombination inactive) bound forms in the silicon bulk
2. The interstitial hydrogen is free to move about the silicon wafer, playing a role in LeTID (possibly through interaction with other impurities/defects)
3. Under the effect of the band bending at the silicon surface (and possibly the effect of defect formation) hydrogen redistributes towards the surface of the wafer
4. An excess of hydrogen near the silicon surface forms recombination active defects
5. ???? Hydrogen effuses from the wafer surface into the dielectric? Hydrogen throughout the wafer settles into a more stable, recombination inactive form?



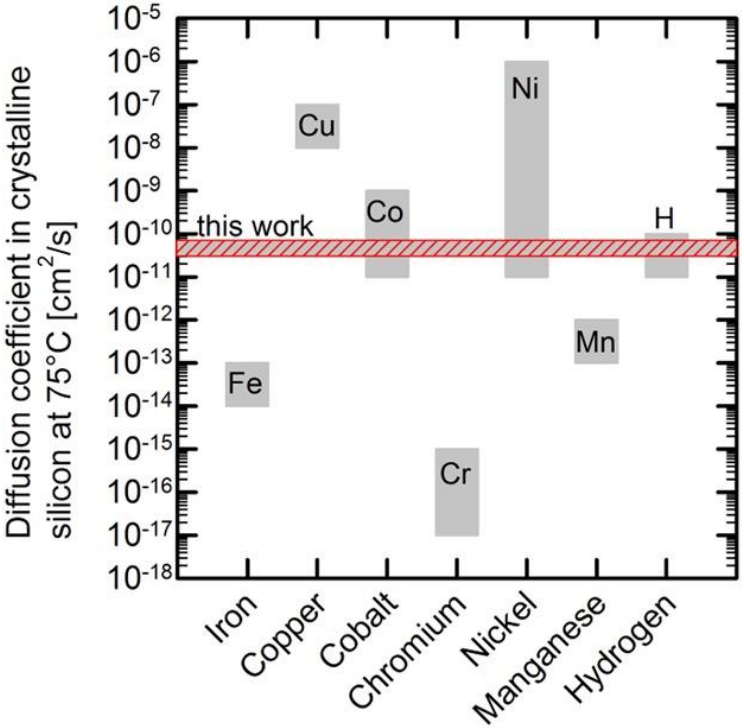
SPECULATION

Evidence in the Literature

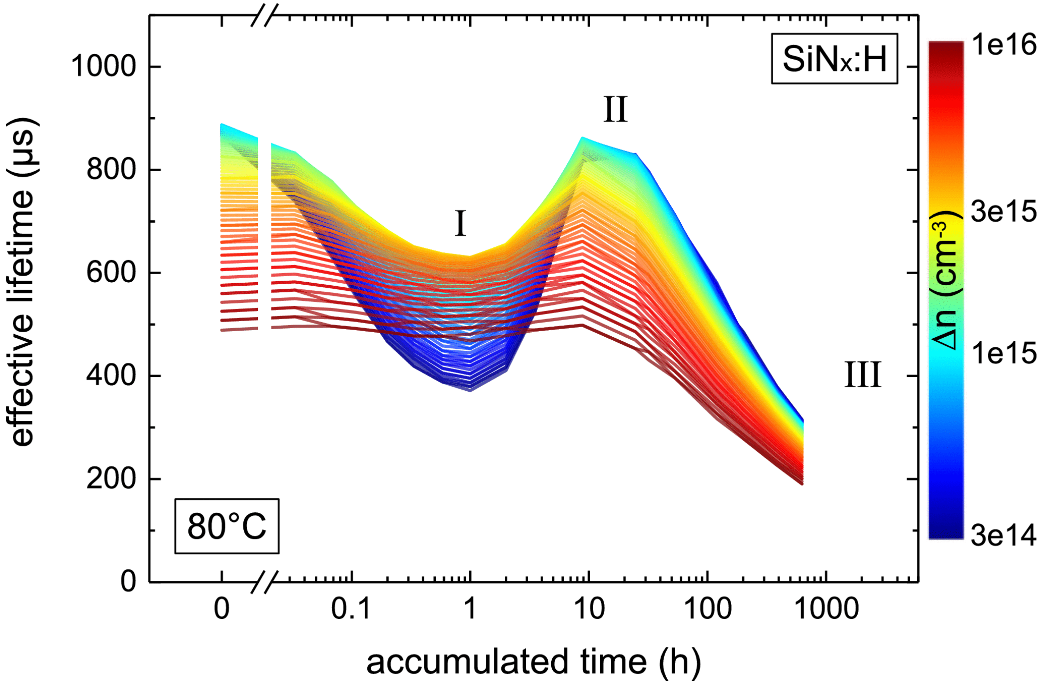
- Recovery rate of LeTID dependent on wafer thickness
- Surface degradation not visible until LeTID has begun to “regenerate”



Maximum defect concentration N_{max}* plotted versus the sample thickness d. The solid line is a linear fit to the measured data [1].



Comparison of the diffusion coefficient determined in this work (red shaded bar) with diffusion coefficients of various impurities in crystalline silicon extrapolated to a temperature of 75 °C [1].

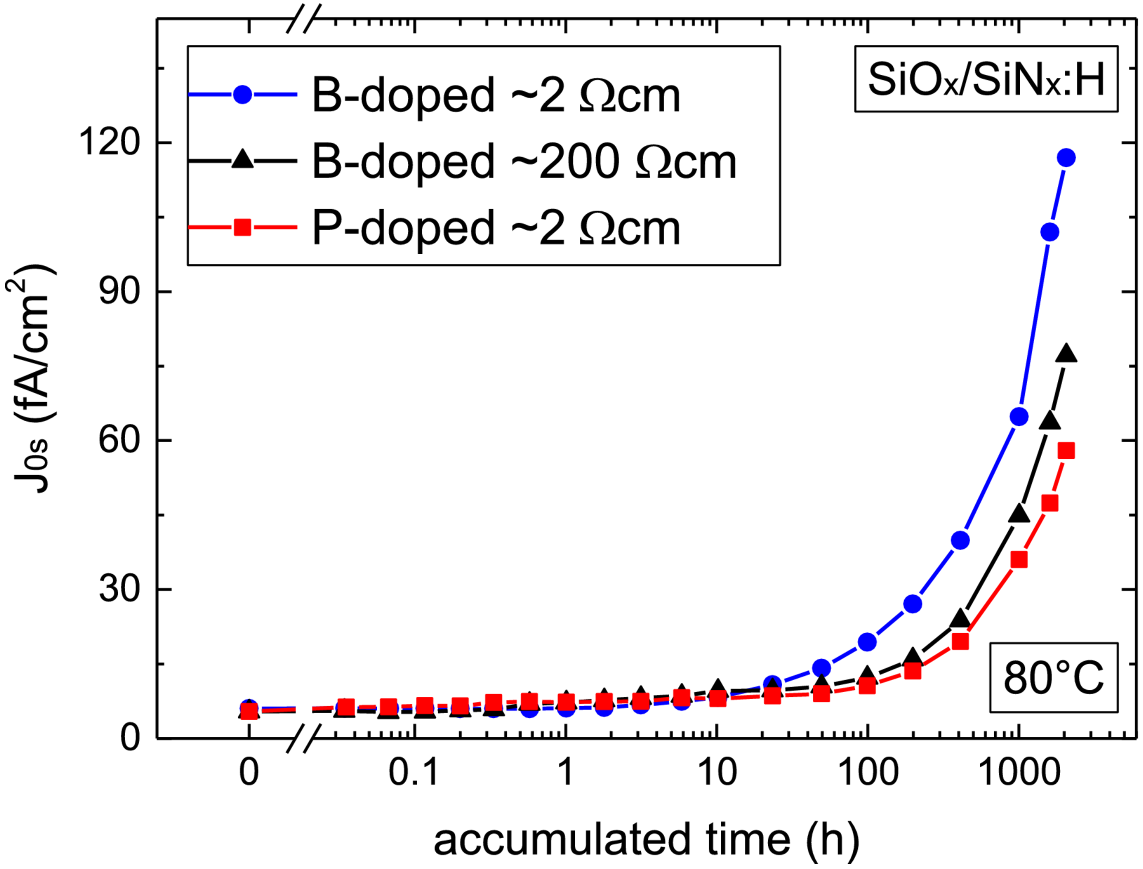


Injection-resolved evolution of τeff during LID treatment at 80 °C and ∼1 sun equivalent illumination of a B-doped FZ-Si. Injection levels are color-coded, ranging from Δn=3x10^{14}cm−3 (blue) to Δn=1x10^{16}cm−3 (red) [2].

[1] Bredemeier, D. *et al.* (2018) Solar RRL, 2(1), 1700159, [2] Sperber, D. *et al.* (2017) IEE J. of Photov., 7(6), 1627-1634

Key Questions

- Dependence on bulk material
- Dielectric layer present during firing vs. during degradation
- Effect of thermal annealing as used to mitigate LeTID/ cause contact resistance
- Some dependence on bulk material already reported [1]
  - Authors concluded that the differences could not be explained by different conditions at the surface
  - Internally at UNSW several examples of different rates depending on material (p- vs. n-type, mono- vs. multi-crystalline)

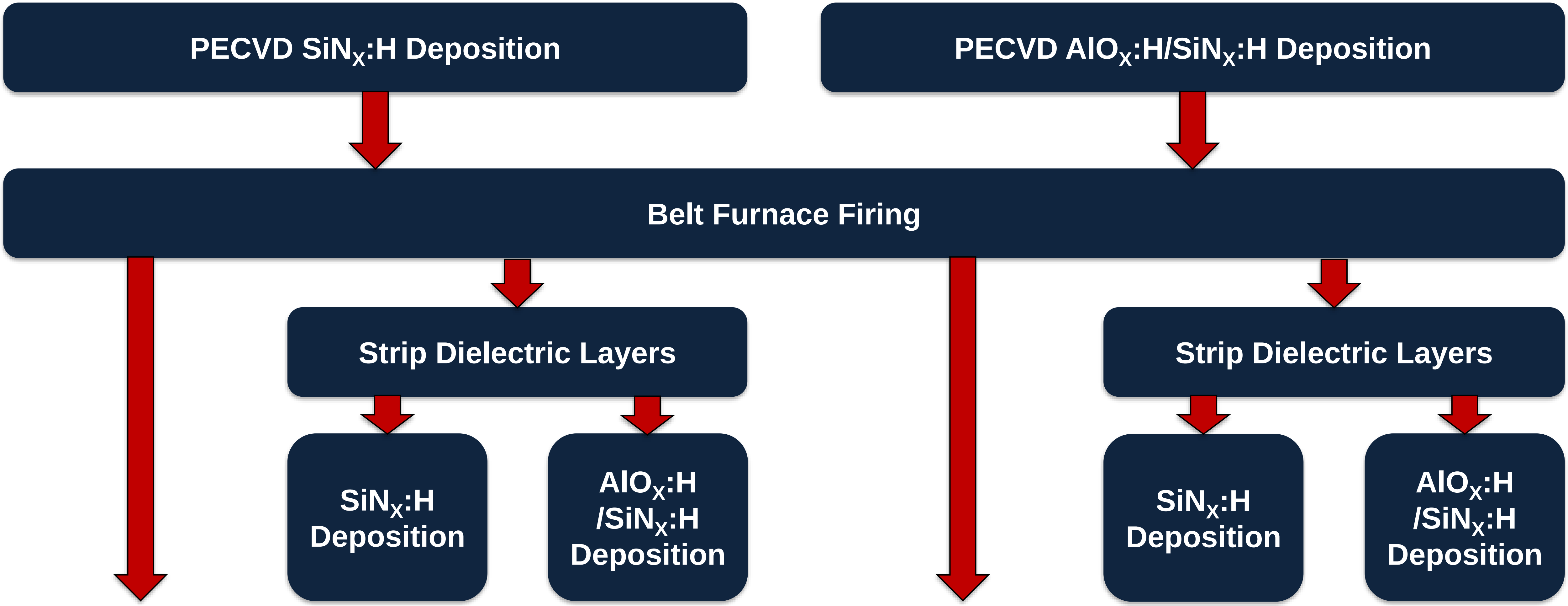


Evolution of J_{0s} of samples made of different FZ-Si base material and treated at 80 °C and ~1 sun equivalent illumination. All samples (thickness 250 μm) were processed identically and passivated with SiO_x /SiN_x:H. Instead of wet-chemical cleaning, the samples received only a dip in HF before thermal oxidation [1].

[1] Sperber, D. *et al.* (2017) IEE J. of Photov., 7(6), 1627-1634

Sample Preparation

CZ p-type 7 Ω.cm and n-type 1.1 Ω.cm



PECVD SiN_x:H Deposition

PECVD AlO_x:H/SiN_x:H Deposition

Belt Furnace Firing

Strip Dielectric Layers

SiN_x:H Deposition

AlO_x:H /SiN_x:H Deposition

Strip Dielectric Layers

SiN_x:H Deposition

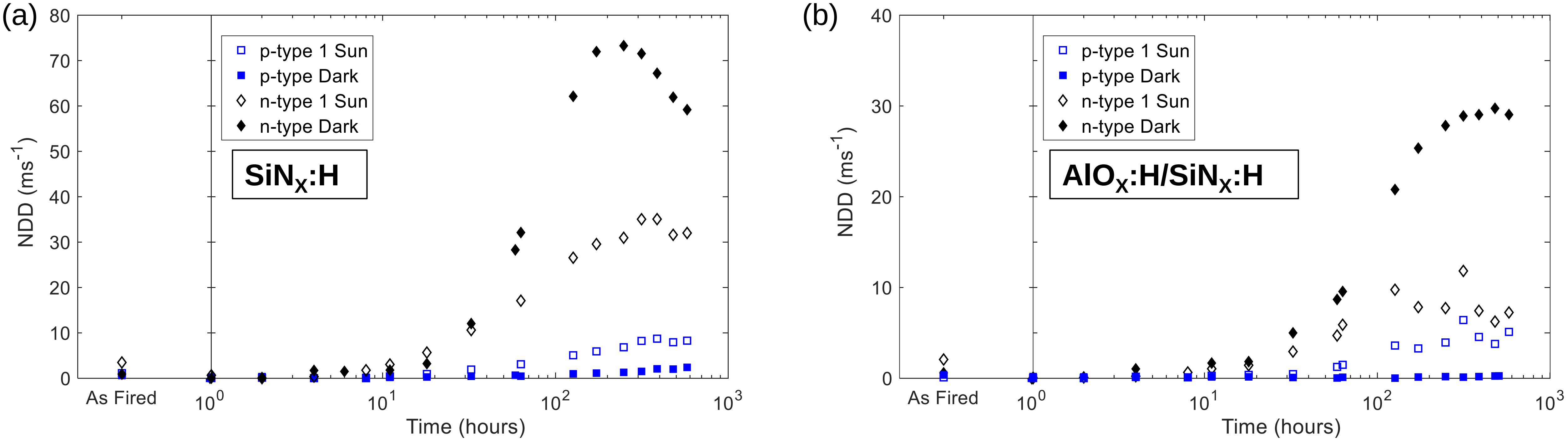
AlO_x:H /SiN_x:H Deposition

Degradation at 175°C in the dark or under 1 sun illumination

Dependence on Bulk Material

$$NDD = \frac{1}{\tau_{eff}} - \frac{1}{\tau_{initial}} \approx \frac{1}{\tau_{eff}} - \frac{1}{\tau_{max}}$$

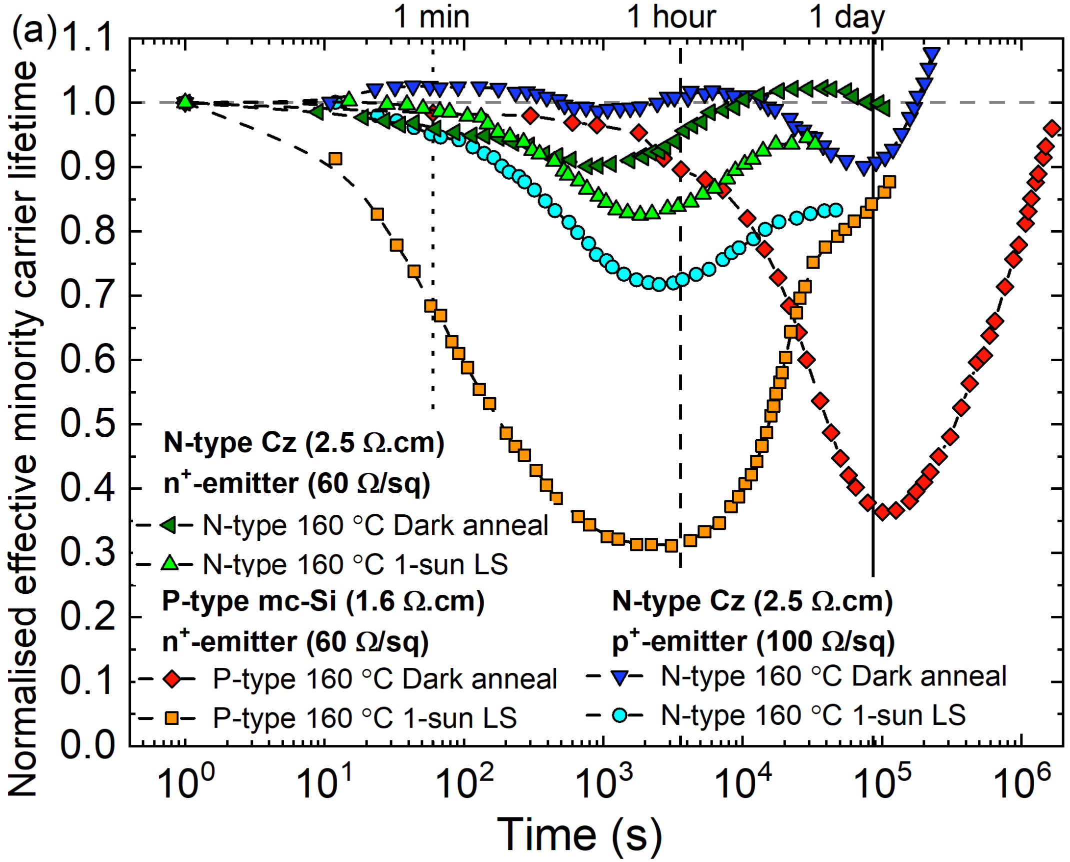
- Useful for comparing degradation on samples with very different lifetimes
- Only physically meaningful for a uniform bulk defect



Normalized defect density for 6 Ω.cm p-type (blue symbols) and 1.1 Ω.cm n-type CZ (black symbols) wafers as a function of time during annealing at 175°C under 1 sun equivalent illumination (open symbols) or in the dark (closed symbols) with (a) SiN$_X$:H passivation layers or (b) AlO$_X$:H/SiN$_X$:H passivation stacks

Correlation with LeTID behaviour

- Surface degradation in 1.1 Ω.cm n-type much more rapid and severe than in 7 Ω.cm p-type
- Different behaviour in the dark and under illumination
- General behaviour similar with both SiN_X:H and AlO_X:H/SiN_X:H layers
- Similar behaviours are observed for LeTID in n-type and p-type samples
- Both effects linked to the redistribution of hydrogen?
  - Requires greater effective diffusivity in n-type material (ie. $D_{H^-.eff} > D_{H^+.eff}$)
  - Effective diffusivity of hydrogen will be trap limited and dependent on charge state (e.g. trapping at Boron for H^+)
  - Under high injection hydrogen charge state distribution should be similar in both materials -> same effective diffusivity

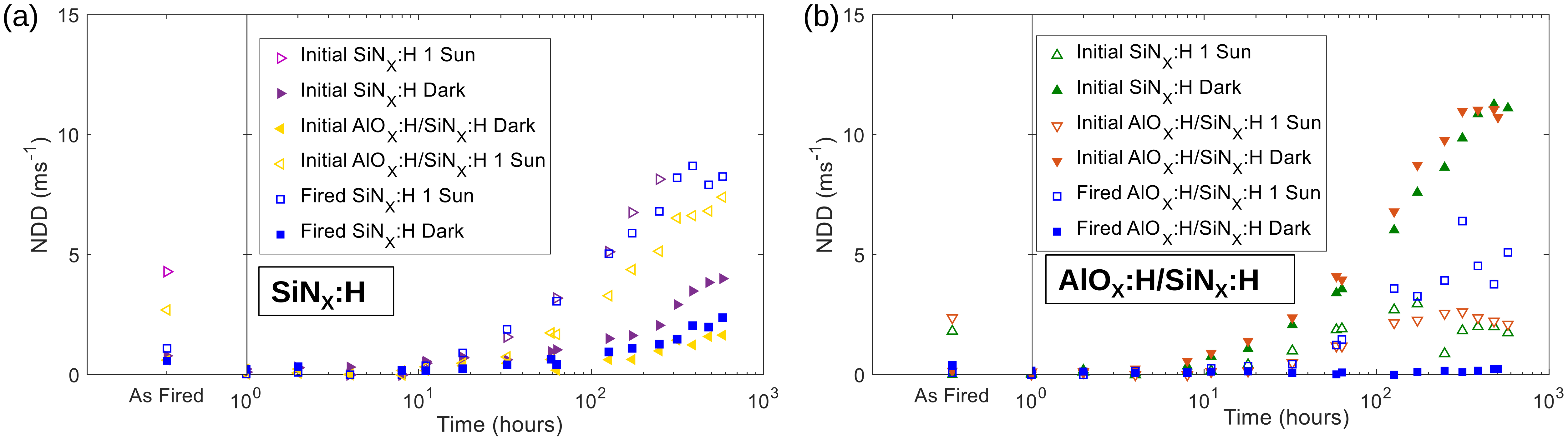


Normalized Defect Density as a function of time for n- and p-type samples with different emitters during light soaking and dark annealing at 160°C [1].

[1] Chen, D. *et al.* SiliconPV 2019

Importance of Dielectric During Firing

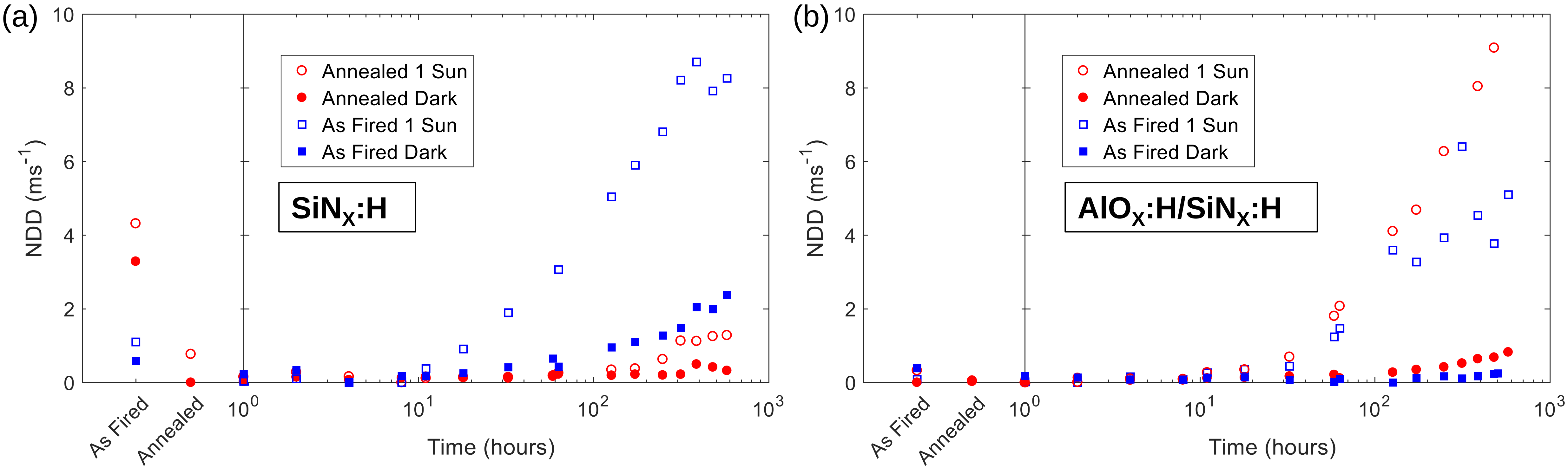
- No clear effect on which passivation layer was present during firing
- For SiN$_X$:H layers also no effect whether layer was fired or not
- For AlO$_X$:H/SiN$_X$:H stacks very different behaviour whether stack was fired or not



Normalized defect density for 6 Ω.cm p-type (blue symbols) and 1.1 Ω.cm n-type CZ (black symbols) wafers as a function of time during annealing at 175^{o}C under 1 sun equivalent illumination (open symbols) or in the dark (closed symbols) with (a) SiN$_X$:H passivation layers or (b) AlO$_X$:H/SiN$_X$:H passivation stacks

Effect of Annealing

- Annealing has very different effects depending on surface passivation
- This supports the idea of redistribution (whether hydrogen or something else) rather than changing states throughout the bulk
- Surface conditions are important during anneal



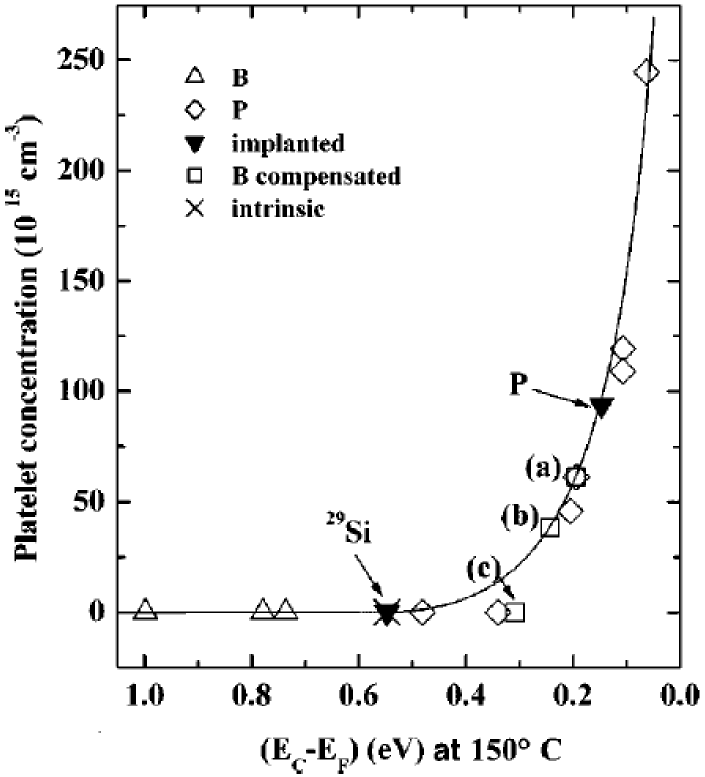
Normalized defect density for 6 Ω.cm p-type wafers as a function of time during annealing at 175^{o}C under 1 sun equivalent illumination (open symbols) or in the dark (closed symbols) with (a) SiN_X:H passivation layers or (b) AlO_X:H/SiN_X:H passivation stacks. Annealed samples were placed on a hotplate at 400oC for 30 minutes prior to degradation

Hydrogen Defect Formation

- Hydrogen related defects first reported in float-zone silicon exposed to hydrogen in 1987 [1]
- Best known defects are hydrogen platelets [1,2] which form along <111> planes and are used in the smart cut process
- Platelet formation requires [2]
  - >1e17 hydrogen atoms/cm^3
  - $E_F > \bar{\varepsilon}$ where $\bar{\varepsilon}$ is the mean value of the hydrogen donor and acceptor levels
- Hypothesised that a mix of charge states of hydrogen is required for forming the hydrogen dimers that lead to platelet formation

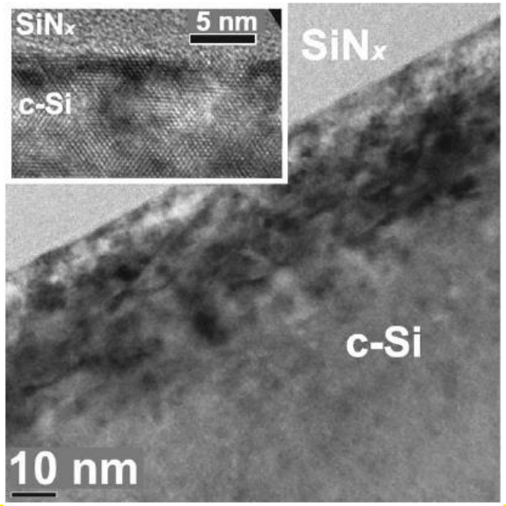
$$H^+ + H^0 \rightarrow H_{2x}$$
$$H^- + H^0 \rightarrow H_{2x}$$
$$H^+ + H^- \rightarrow H_{2x}$$
$$H^0 + H^0 \rightarrow H_{2x}$$

- Other hydrogen related defects appear to form under similar conditions and have been observed under nitride layers [3]



Platelet concentration in *c*-Si as a function of the Fermi energy at 150°C [2].

Cross-sectional TEM micrographs of single crystal silicon, viewed in a <110> projection.

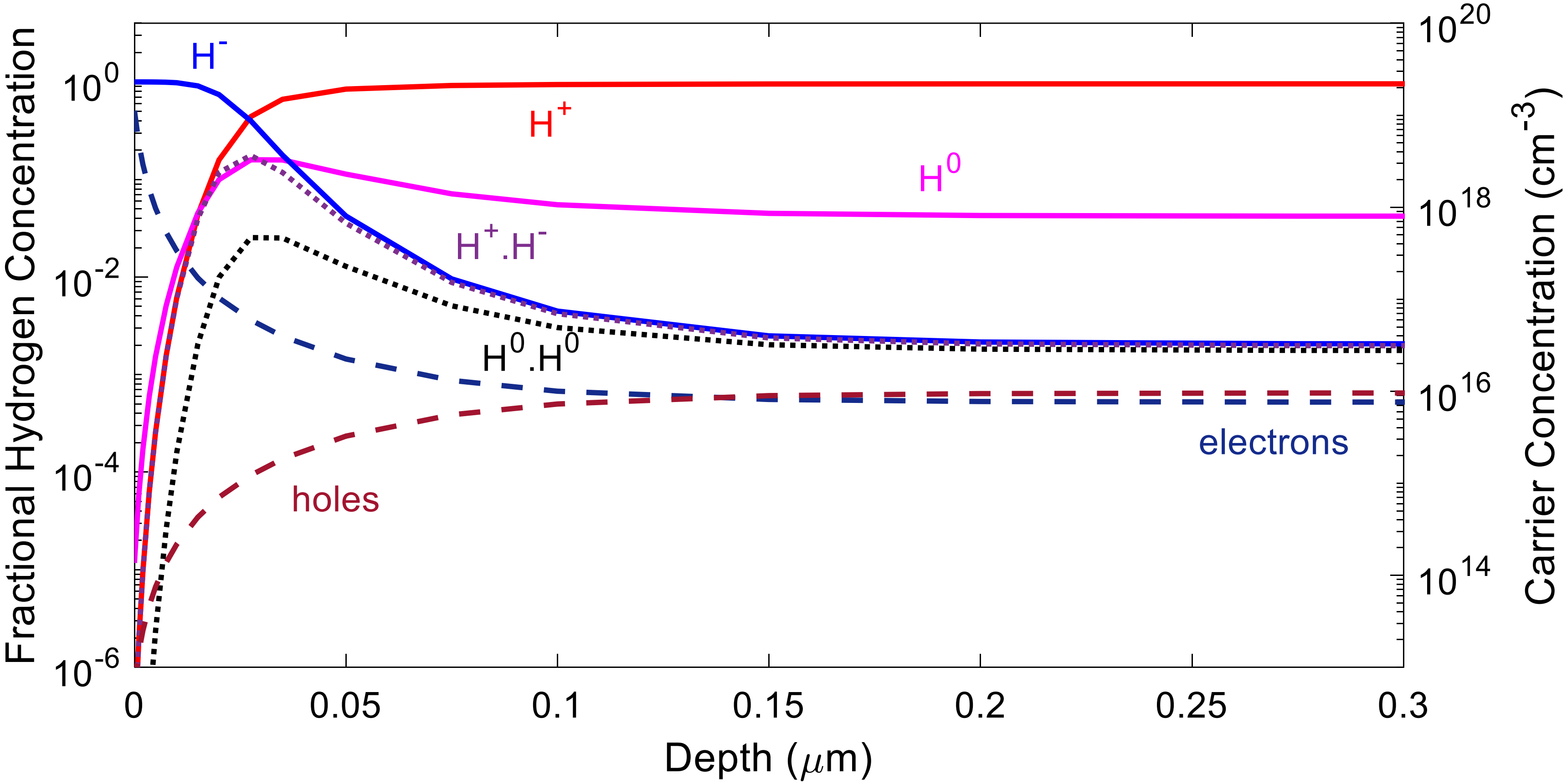


HRTEM images of a 30 nm thick defect-rich region in the Si substrate underneath a SiN*x* passivating layer. Short, non-connected defect-like contrasts are observed that are aligned almost parallel to the interface [3].

[1] Johnson, N.M. *et al.* (1987) Phys. Rev. B, 35(8), 4166-4169 [2] Nickel, N.H. *et al.* (2000) Phys. Rev. B, 62(12), 8012-8015

[3] Steingrube, S. *et al.* (2010) Proc. of the 25th EUPVSEC, 1748

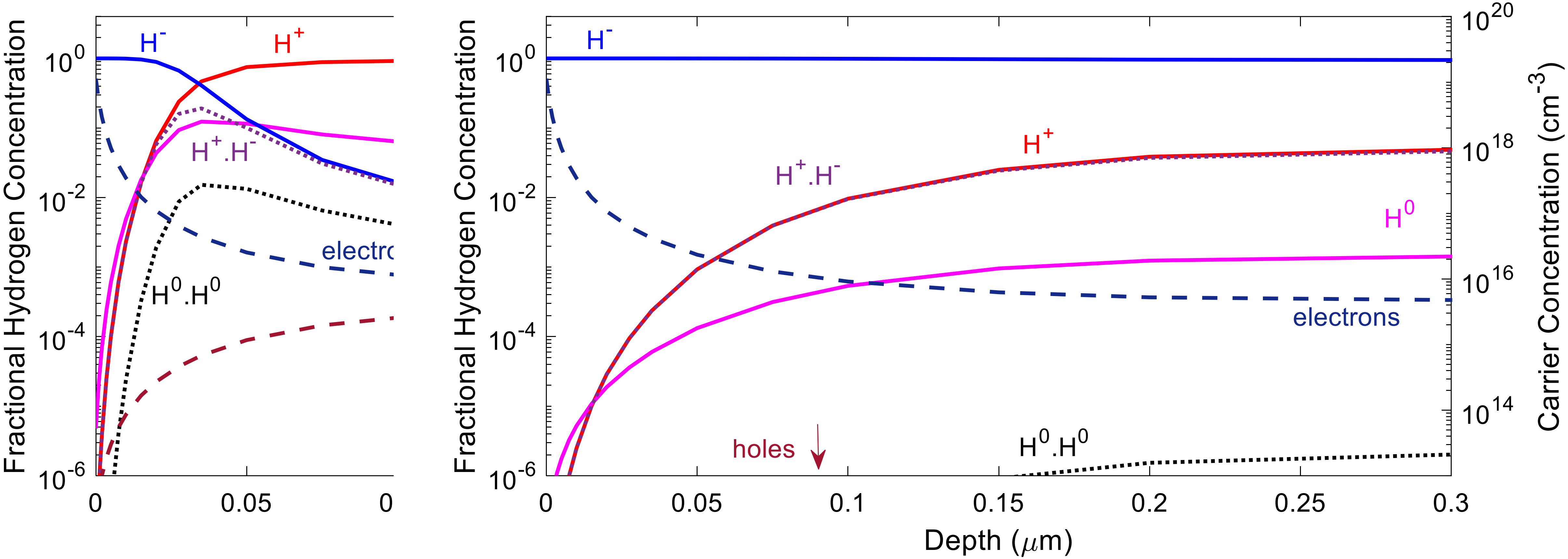
$SiN_X:H$ on p-type



Left Axis: Fractional concentrations of hydrogen in each charge state for $Q_f=2\times10^{12}$ on 2 Ω.cm p-type silicon under light soaking at 175°C. Right Axis: Carrier concentrations during the process.

- Formation of defects expected to be within the first 50 nm
- Fits well with defects observed by Steingrube et al. [ref]
- Injection dependence of lifetime expected to be “J_0 like”
- Important to also consider gradients in hydrogen concentration

SiN_X:H on n-type

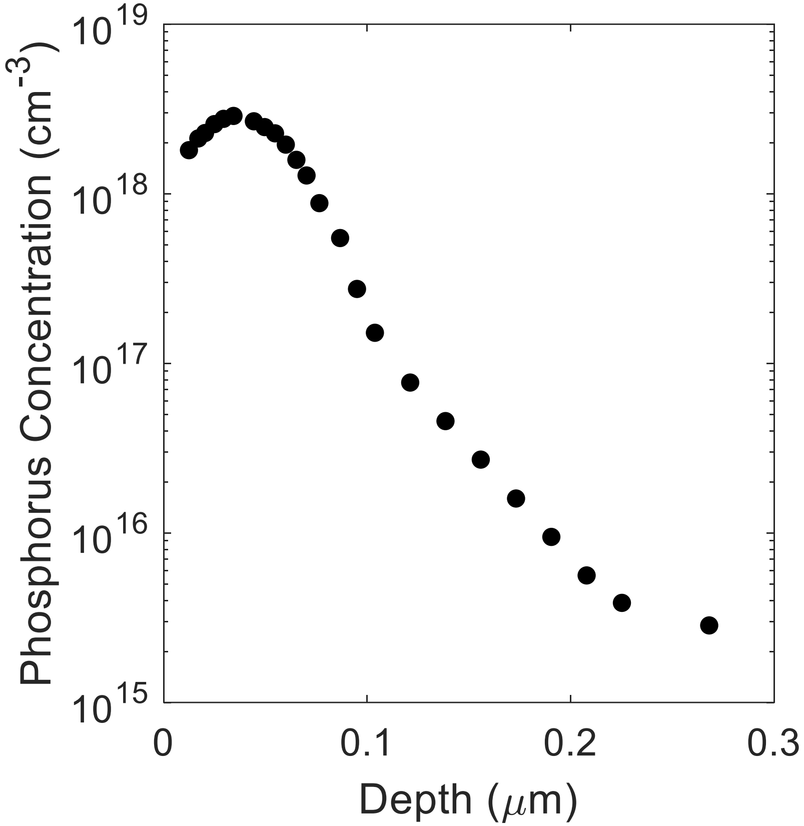


Left Axis: Fractional concentrations of hydrogen in each charge state for $Q_f=2\times10^{12}$ on 1 Ω.cm n-type silicon under light soaking at 175°C. Right Axis: Carrier concentrations during the process.

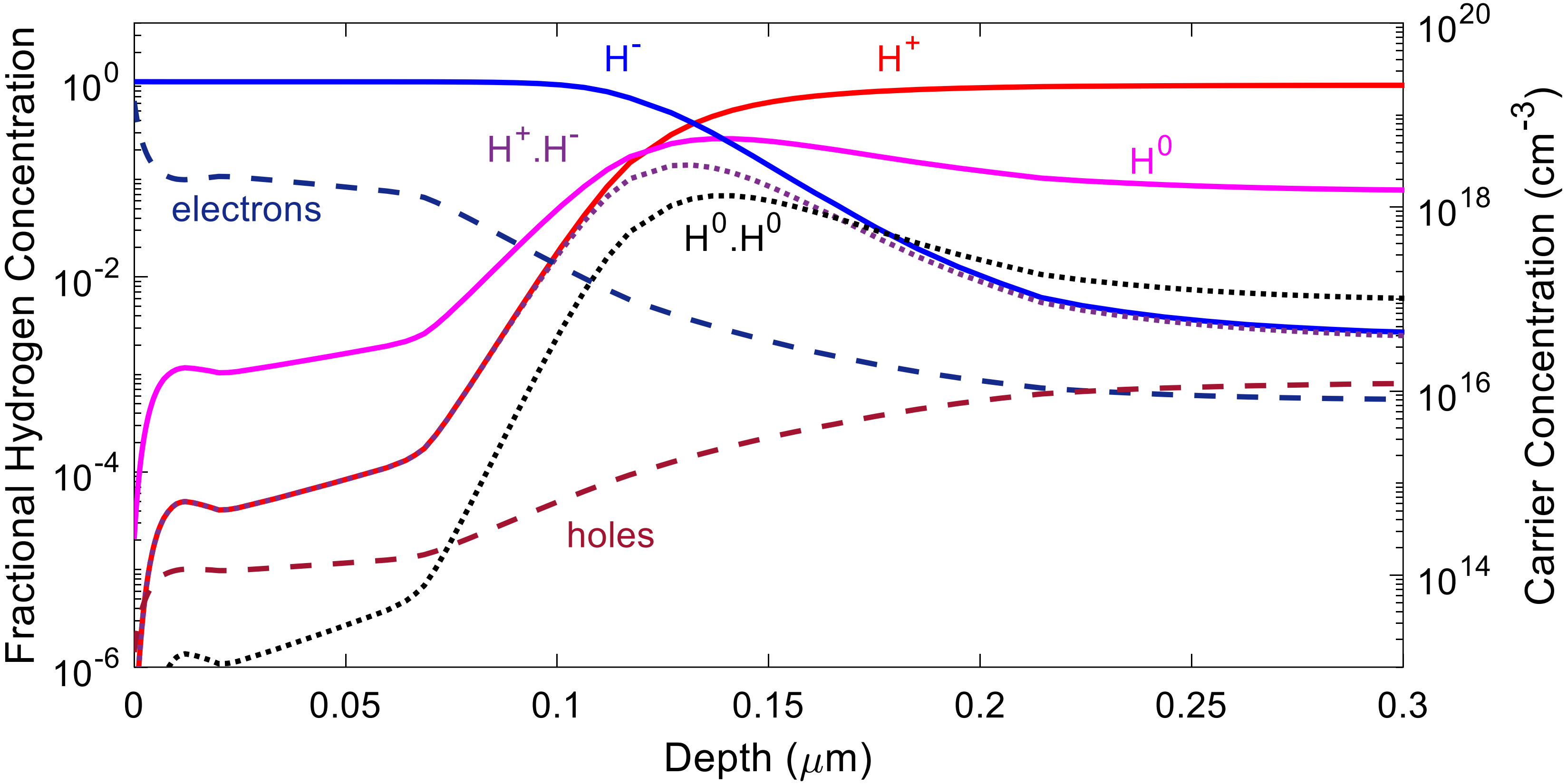
Left Axis: Fractional concentration of hydrogen in each charge state for $Q_f=2\times10^{12}$ on 1 Ω.cm n-type silicon under dark annealing at 175°C. Right Axis: Carrier concentrations during the process.

- Under illumination n-type not dissimilar to p-type
- In dark expect defects to form closer to the edge of the accumulation region

With light Emitter

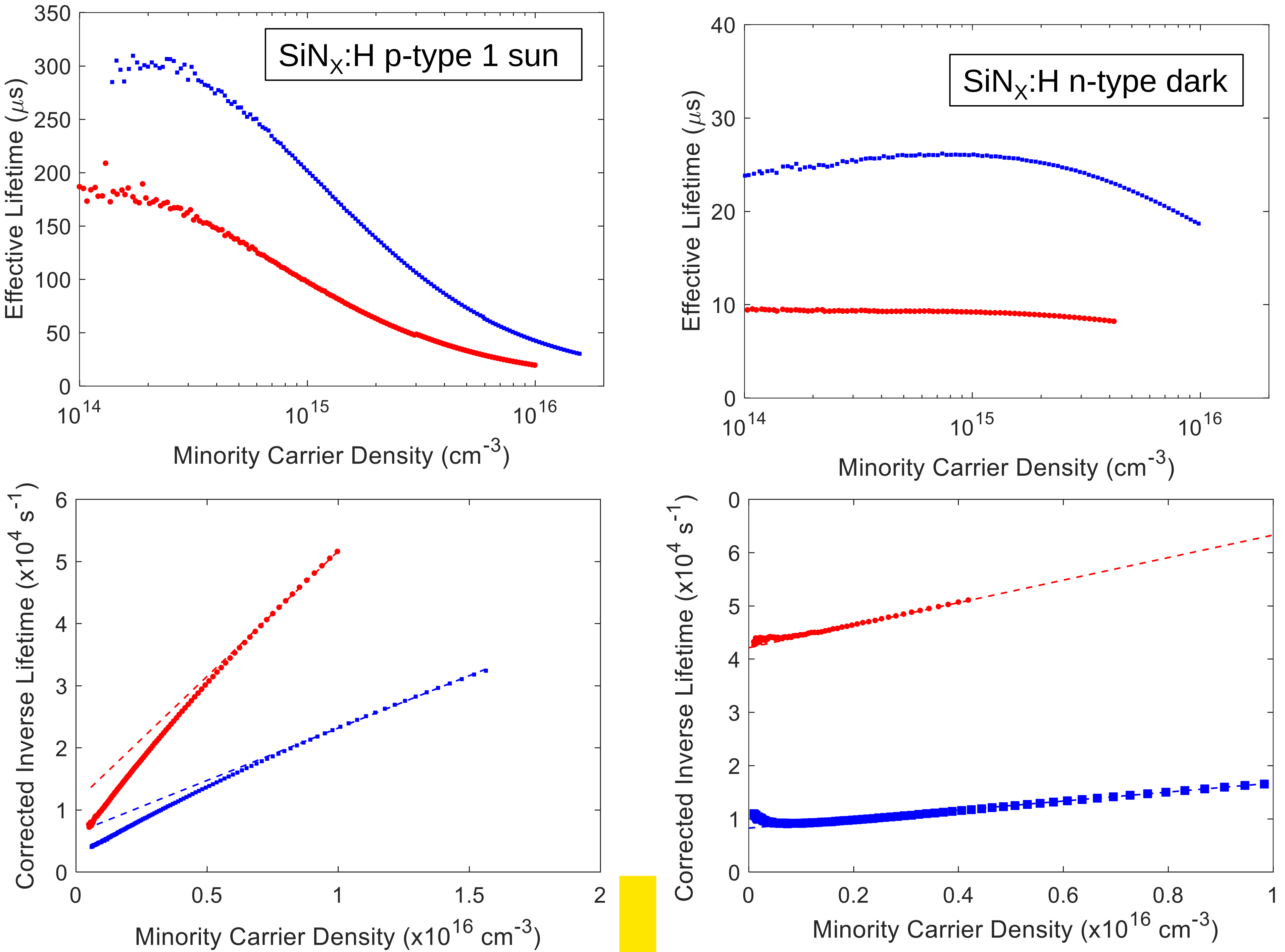


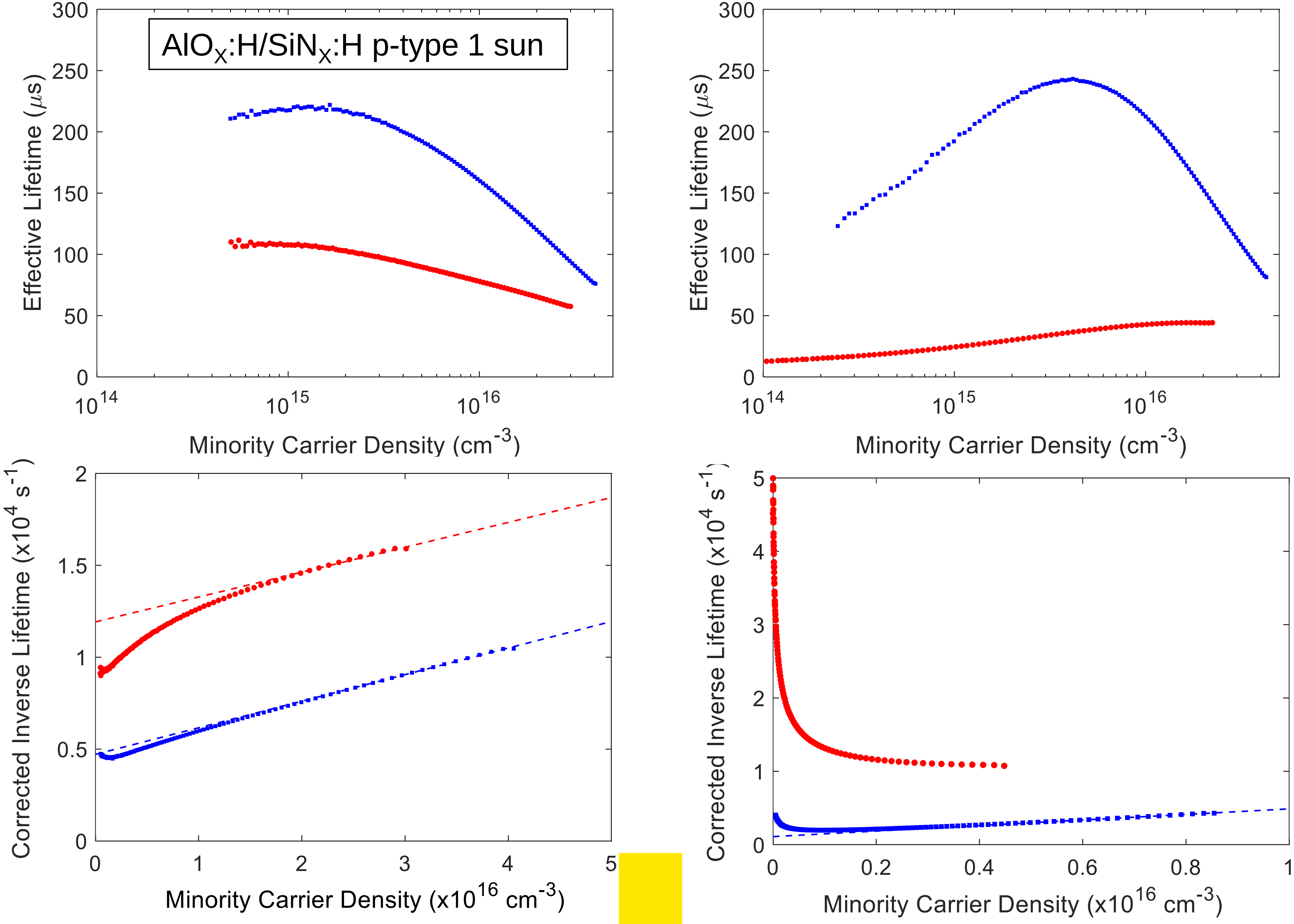
Phosphorous doping profile (from eCV) used in simulations



Left Axis: Fractional concentrations of hydrogen in each charge state for Q_f=2×10^{12} on P-diffused 2 Ω.cm p-type silicon under light soaking at 175^{o}C. **Right Axis**: Carrier concentrations during the process.

- Defects on n-type side of metallurgical junction but over 100 nm from surface
- Electric field and competition with dopant traps of particular importance


SiN$_X$:H p-type 1 sun
Effective Lifetime (μs)
350
300
250
200
150
100
50
0
10^{14}
10^{15}
10^{16}
Minority Carrier Density (cm^{-3})
SiN$_X$:H n-type dark
Effective Lifetime (μs)
40
30
20
10
0
10^{14}
10^{15}
10^{16}
Minority Carrier Density (cm^{-3})
Corrected Inverse Lifetime (x10^4 s^{-1})
6
5
4
3
2
1
0
0
0.5
1
1.5
2
Minority Carrier Density (x10^{16} cm^{-3})
Corrected Inverse Lifetime (x10^4 s^{-1})
0
6
5
4
3
2
1
0
0
0.2
0.4
0.6
0.8
1
Minority Carrier Density (x10^{16} cm^{-3})


AlO$_X$:H/SiN$_X$:H p-type 1 sun
Effective Lifetime (μs)
0
50
100
150
200
250
300
10^{14}
10^{15}
10^{16}
Minority Carrier Density (cm^{-3})
Effective Lifetime (μs)
0
50
100
150
200
250
300
10^{14}
10^{15}
10^{16}
Minority Carrier Density (cm^{-3})
Corrected Inverse Lifetime (x10^4 s^{-1})
0
0.5
1
1.5
2
0
1
2
3
4
5
Minority Carrier Density (x10^{16} cm^{-3})
Corrected Inverse Lifetime (x10^4 s^{-1})
0
1
2
3
4
5
0
0.2
0.4
0.6
0.8
1
Minority Carrier Density (x10^{16} cm^{-3})

AlO_X:H is a different cat

- Cannot fit with J_0
- On p-type no region where hydrogen related defects should form
- Very distinctive injection level dependence different in p- and n-type
- Degradation in AlO_X:H passivated samples primarily loss of field effect passivation
- Boron deactivation? Autodoping?

SPECULATION

τ_{eff} before (τ_{noCC}) and after (τ_{CC}) corona charging and Q_f before (Initial) and after (Final) LID treatment [1].

Sample	Dielectric	Side	Initial $\boldsymbol{\tau_{CC}\ \{\tau_{noCC}\}}$ (µs)	Final $\boldsymbol{\tau_{CC}\ \{\tau_{noCC}\}}$ (µs)	Initial Q_f (q/cm²)	Final Q_f (q/cm²)
1 Ω.cm p-type FZ	AlO_X:H/SiN_X:H	Front	143 {1830}	≥ 300 {710}	-3.6×10^{12}	-8×10^{11}
1 Ω.cm p-type FZ	AlO_X:H/SiN_X:H	Rear	136 {1830}	≥ 260 {710}	-2.5×10^{12}	-8×10^{11}
2 Ω.cm n-type FZ	AlO_X:H/SiN_X:H	Front			-3.9×10^{12}	-1.9×10^{12}
1 Ω.cm p-type FZ	SiN_X:H	Front			$+3.5\times10^{12}$	$+3.5\times10^{12}$

[1] Sperber, D. *et al.* (2018) Sol. Energy Mat. Sol. Cells, 188, 112-118

UNSW SYDNEY

Summary

- The redistribution of hydrogen towards silicon surfaces during post-firing thermal processes has been simulated
- Two effects which may be related to this redistribution have been identified
- Both display characteristics associated with known hydrogen behaviours
- Both have the *potential* to affect solar cell performance

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