Faculty of Engineering \ School of Photovoltaic and Renewable Energy Engineering
Advanced Hydrogenation Group

Understanding the boron-oxygen defect: properties, kinetics and deactivation mechanisms

SPREE Seminar

University of New South Wales
Sydney, Australia

9 November 2017

Nitin Nampalli

Supervisors: Malcolm Abbott, Stuart Wenham,
Matthew Edwards

Motivation

- *p*-type silicon dominant for forseeable future

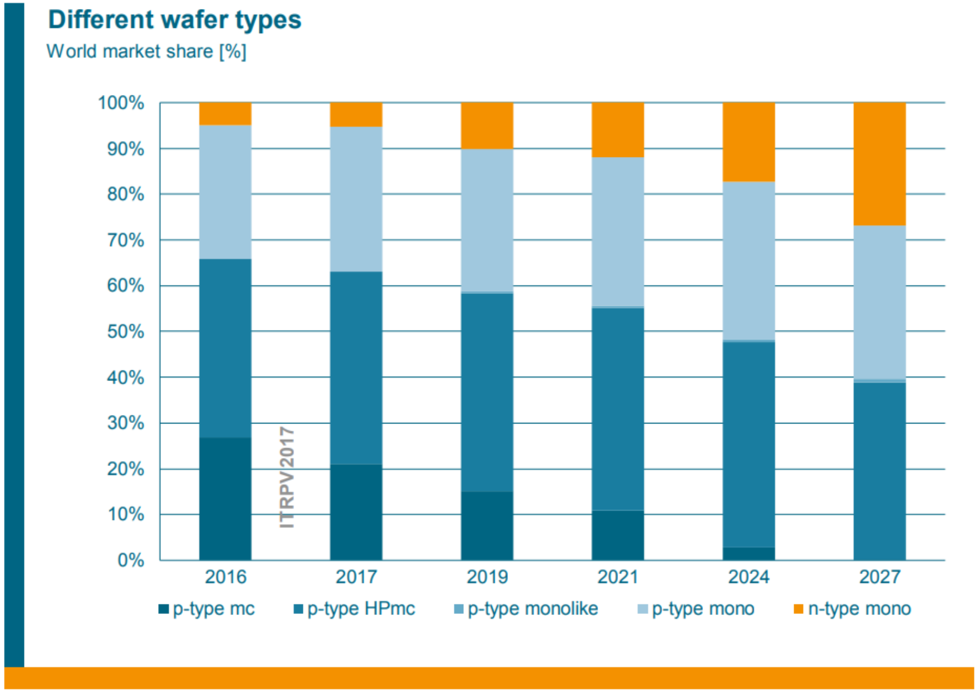


Fig. 36: World market shares for different wafer types.

International Technology Roadmap for Photovoltaics, 8th Edition, 2017.

Motivation

- *p*-type silicon dominant for forseeable future
- PERC cells seeing an increasing market share

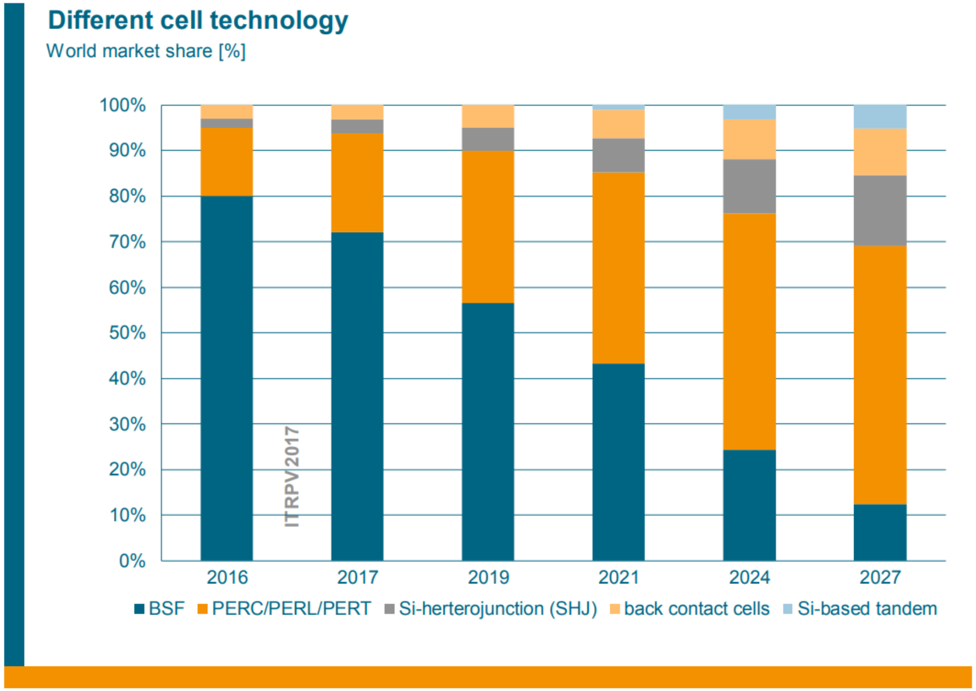


Fig. 41: Worldwide market shares for different cell technologies.

International Technology Roadmap for Photovoltaics, 8th Edition, 2017.

Motivation

- *p*-type silicon dominant for forseeable future
- PERC cells seeing an increasing market share
- Surface passivation quality is improving

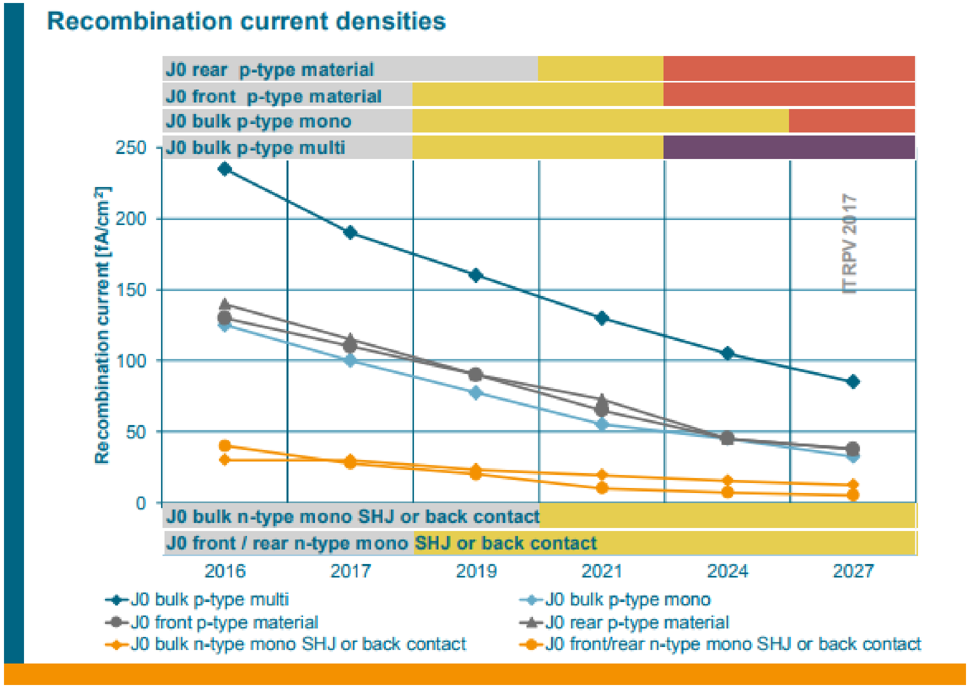


Fig. 25: Predicted trend for recombination currents J0bulk, J0front, J0rear for p-type and n-type cell concepts.

International Technology Roadmap for Photovoltaics, 8th Edition, 2017.

Motivation

- *p*-type silicon dominant for forseeable future
- PERC cells seeing an increasing market share
- Surface passivation quality is improving

→ Strong imperative to:

(a) Improve bulk quality

(b) Minimise cell degradation

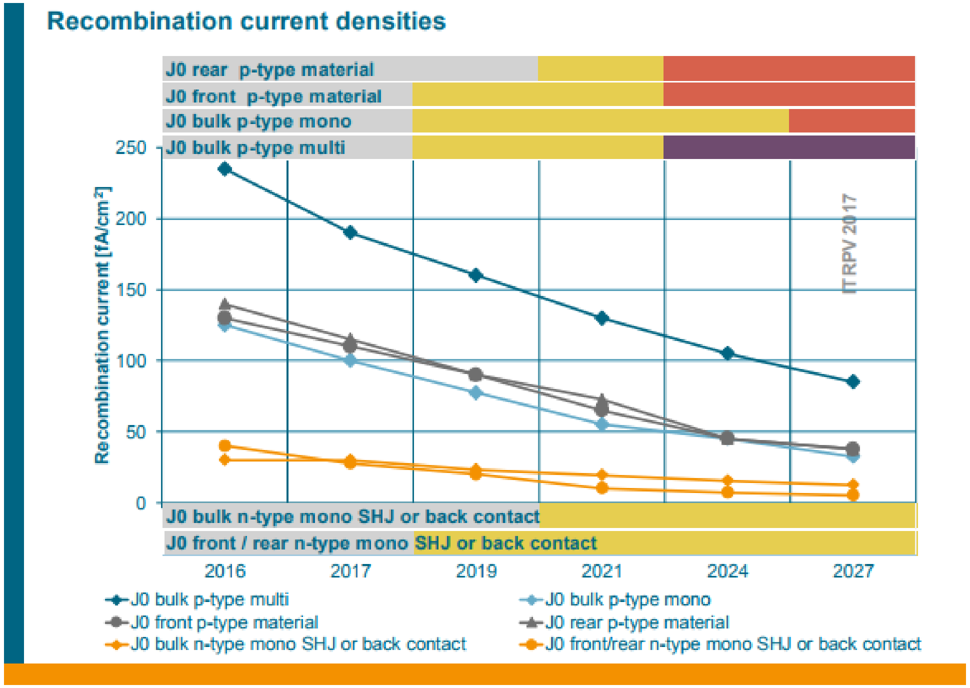


Fig. 25: Predicted trend for recombination currents J0bulk, J0front, J0rear for p-type and n-type cell concepts.

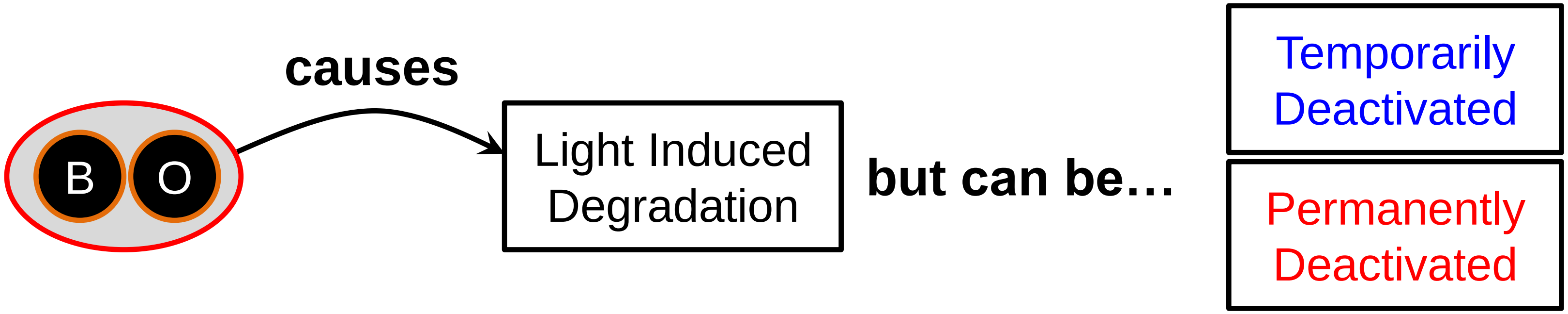
International Technology Roadmap for Photovoltaics, 8th Edition, 2017.

Motivation

- Boron-oxygen defects are the most important source of LID in commercial Cz solar cells
- Cell efficiency loss:
  - – PERC: 1-12$\%_{rel}$
  - – Al-BSF: 1-6$\%_{rel}$
  - – For a cell manufacturer producing 1,000 MW_p/year:
    - 60-120 MW_p/year in lost production
    - <u>USD $12-24 million/year in lost savings</u>

Mitigation of BO defects is of vital importance

The boron-oxygen defect



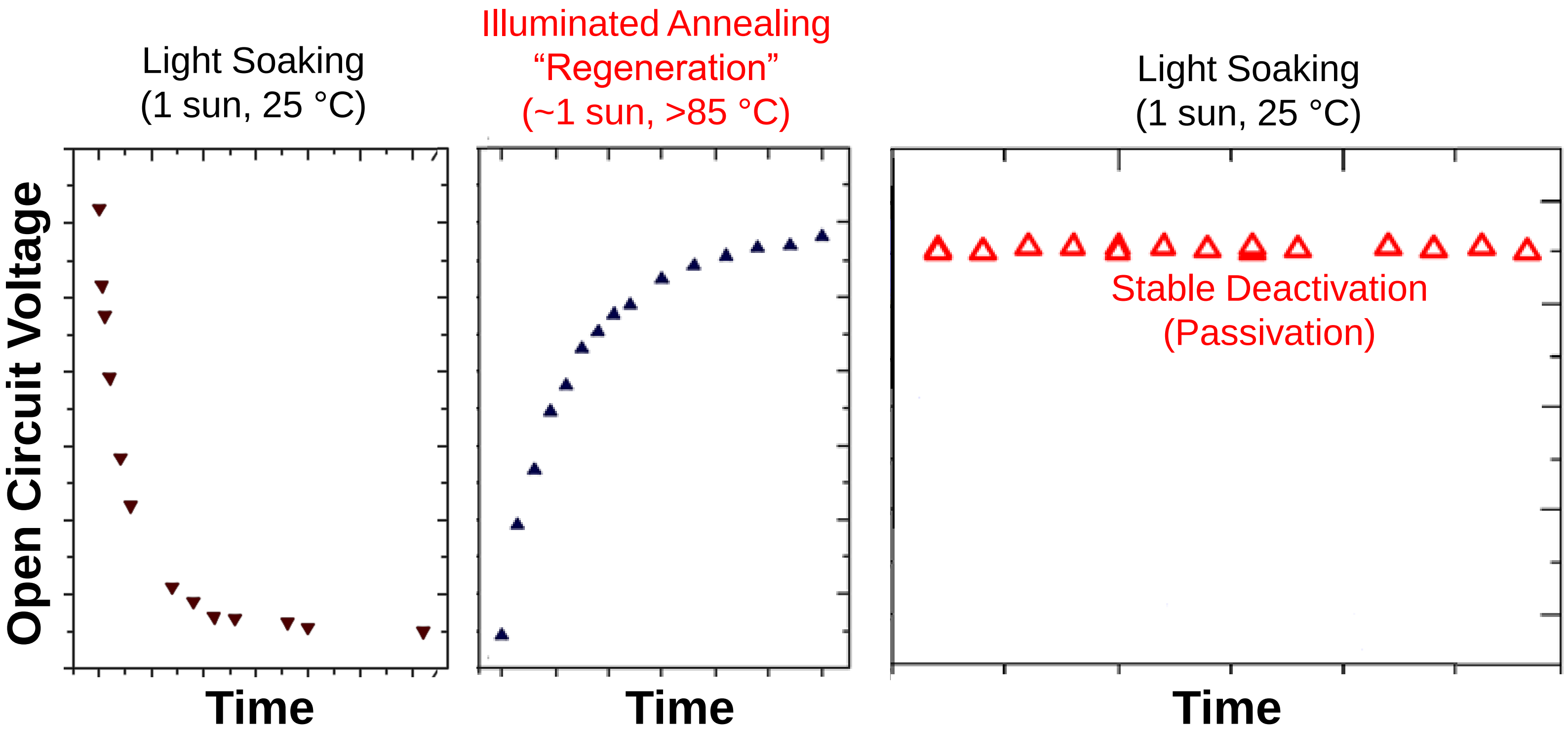
causes

Light Induced Degradation

but can be…

Temporarily Deactivated

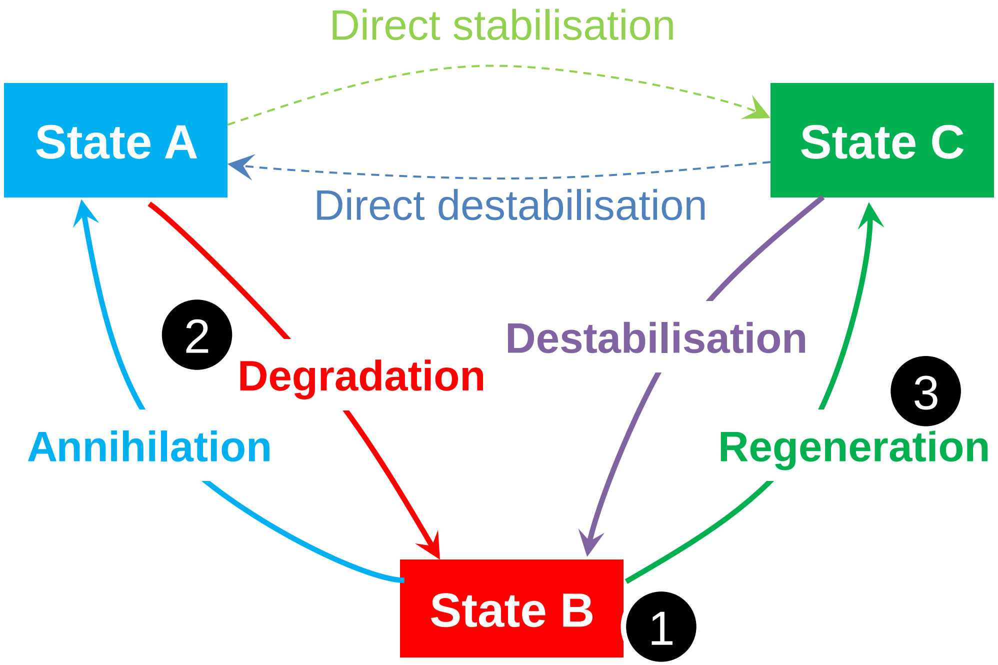
Permanently Deactivated



The boron-oxygen defect

- Behaviour described by 3-state model

- Focus of this work:
  1. Recombination properties
  2. Reaction kinetics
  3. Deactivation mechanisms



Recombination properties of the boron-oxygen defect

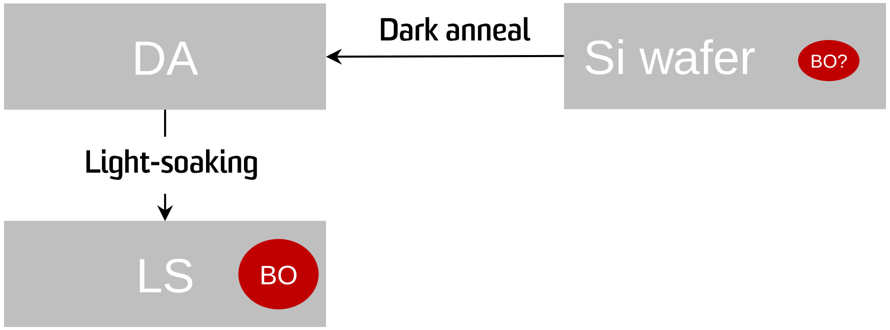
Never Stand Still

Engineering

Recombination properties of BO

$$\frac{1}{\tau_{eff,DA}} = \frac{1}{\tau_{surf}} + \frac{1}{\tau_{bulk,non-BO}}$$

$$\frac{1}{\tau_{eff,LS}} = \frac{1}{\tau_{surf}} + \frac{1}{\tau_{bulk,non-BO}} + \frac{1}{\tau_{SRH,BO}}$$


Si wafer
BO?
Dark anneal
DA
Light-soaking
LS
BO

$$p_1 = n_{i,eff} \times e^{\left(\frac{E_i - E_{trap}}{k_B T}\right)}$$

$$\tau_{n0} = \frac{1}{N_{trap}\,\sigma_n \cdot v_{th,e}}$$

$$\frac{1}{\tau_{SRH}} = \frac{\left(np - n_i^2\right)}{\Delta n \cdot \left[\boldsymbol{\tau_{p0}}(n + \boldsymbol{n_1}) + \boldsymbol{\tau_{n0}}(p + \boldsymbol{p_1})\right]}$$

$$\tau_{p0} = \frac{1}{N_{trap}\,\sigma_p \cdot v_{th,h}}$$

$$k = \frac{\sigma_n}{\sigma_p}$$

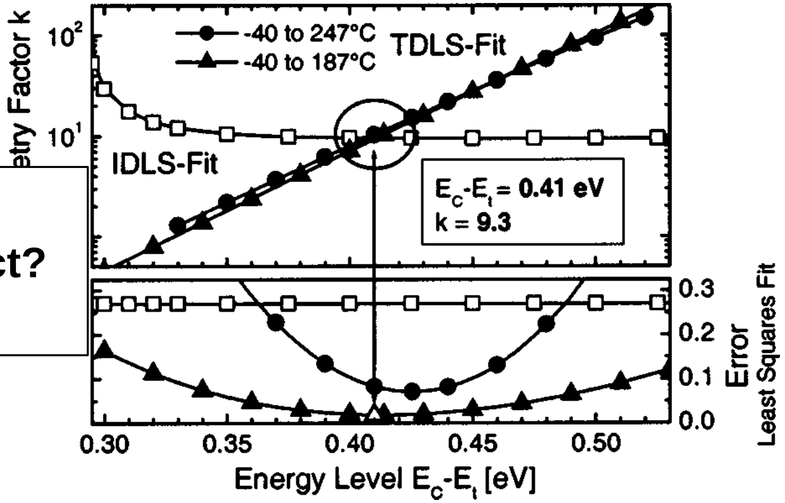
Recombination properties of BO

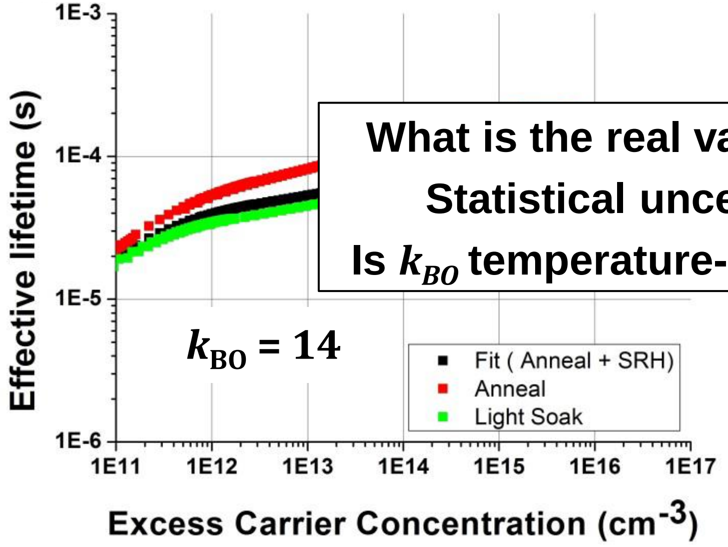
***N*$_{\text{trap}}$**

***E*$_{\text{trap}}$** →

k →

Is the value of $E_{trap,BO}$ correct?



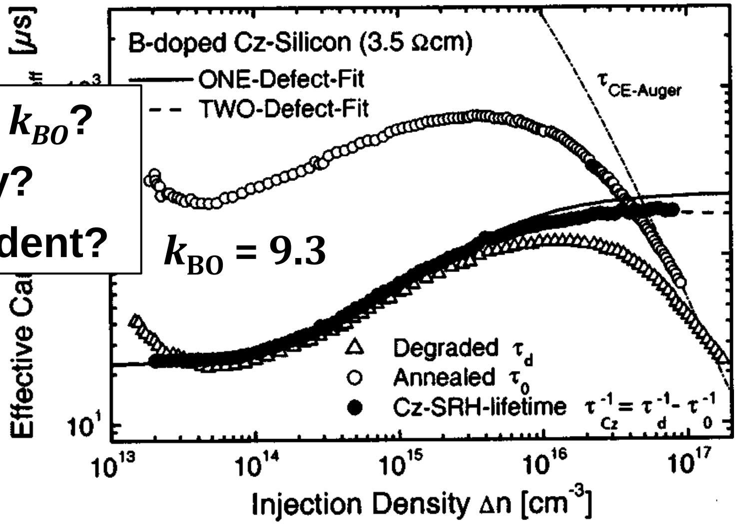


k_{BO} = 14

What is the real value of k_{BO}?

Statistical uncertainty?

Is k_{BO} temperature-dependent?



k_{BO} = 9.3

S. Rein and S. Glunz, Applied Physics Letters 82(7), pp.1054-1056, 2003.
X. Wang et al., Energy Procedia 55, pp.169-178, 2014.

Recombination properties of BO

N_{trap}

E_{trap}

k

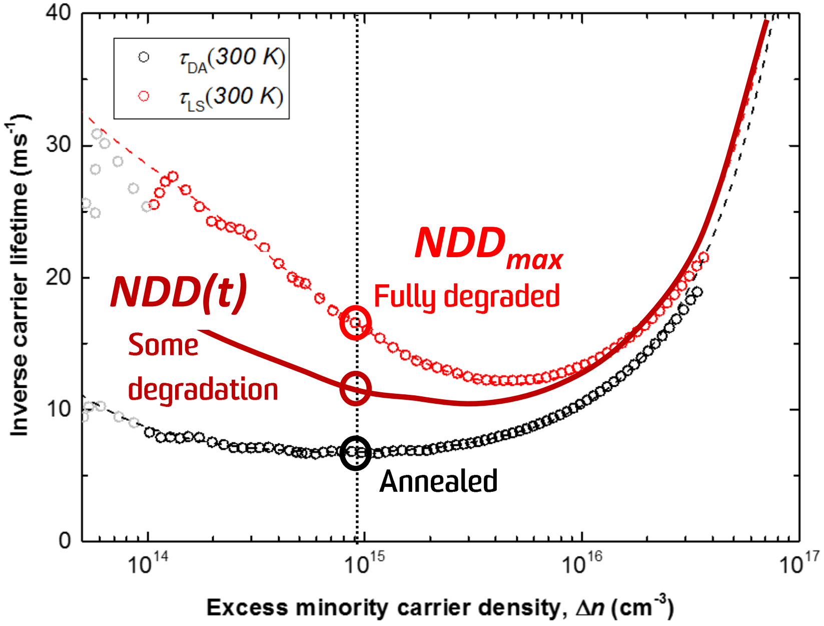
$$N_{trap} = \frac{1}{\tau_{n0} \cdot \boxed{\sigma_n} \cdot v_{th,e}}$$ → **Value unknown! (for BO)**

At low injection ($\Delta n = 0.1 \times N_A$):

$$N_{trap} \propto \frac{1}{\tau_{SRH,BO}}$$

$$\propto \left(\frac{1}{\tau_{LS}} - \frac{1}{\tau_{DA}}\right) = NDD$$

(Normalised Defect Density)



Recombination properties of BO

N_{trap} → Affected by processing conditions

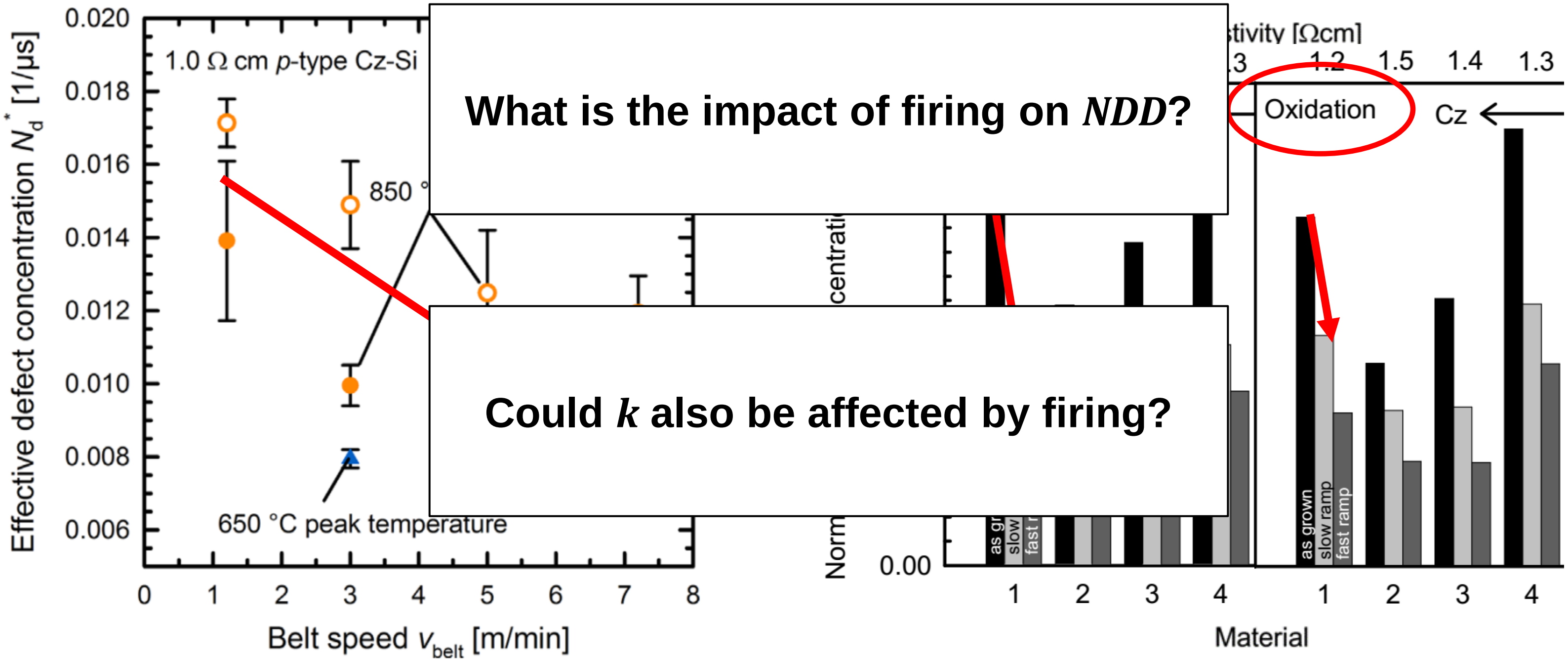
E_{trap} ?? ↗

Affected by processing conditions → Low temperatures (< 300 ºC) (Light soaking, dark annealing, etc)

Affected by processing conditions → High temperatures (> 400 ˚C)

↓

Offers opportunity for reducing BO during cell fabrication



What is the impact of firing on *NDD*?

Could *k* also be affected by firing?

K. Bothe et al., Solid State Phenomena 95-96, p. 223-228 (2004)
D. Walter et al., Solar Energy Materials and Solar Cells 131, p. 51-57 (2014)

Recombination properties of BO

- SRH properties of the BO defect (k , E_{trap})
- Impact of firing on k
- Impact of firing on defect density

Recombination properties of BO

- SRH properties of the BO defect (k, E_{trap})

- Impact of firing on k

- Impact of firing on defect density

SRH Recombination Properties

Methods for determining recombination properties:

- **IDLS**: **I**njection-**D**ependent **L**ifetime **S**pectroscopy
  - A common characterization method
  - Good sensitivity to k (if E_{trap} is known)
  - Low sensitivity to E_{trap} (for mid-gap defects)

- **TDLS**: **T**emperature-**D**ependent **L**ifetime **S**pectroscopy
  - Good sensitivity to E_{trap}, k
  - Analysis at single injection level (Δn)

- **TIDLS**: **T**emperature- and **I**njection-**D**ependent **L**ifetime **S**pectroscopy
  - Best sensitivity to E_{trap}, k
  - Analysis over full range of Δn

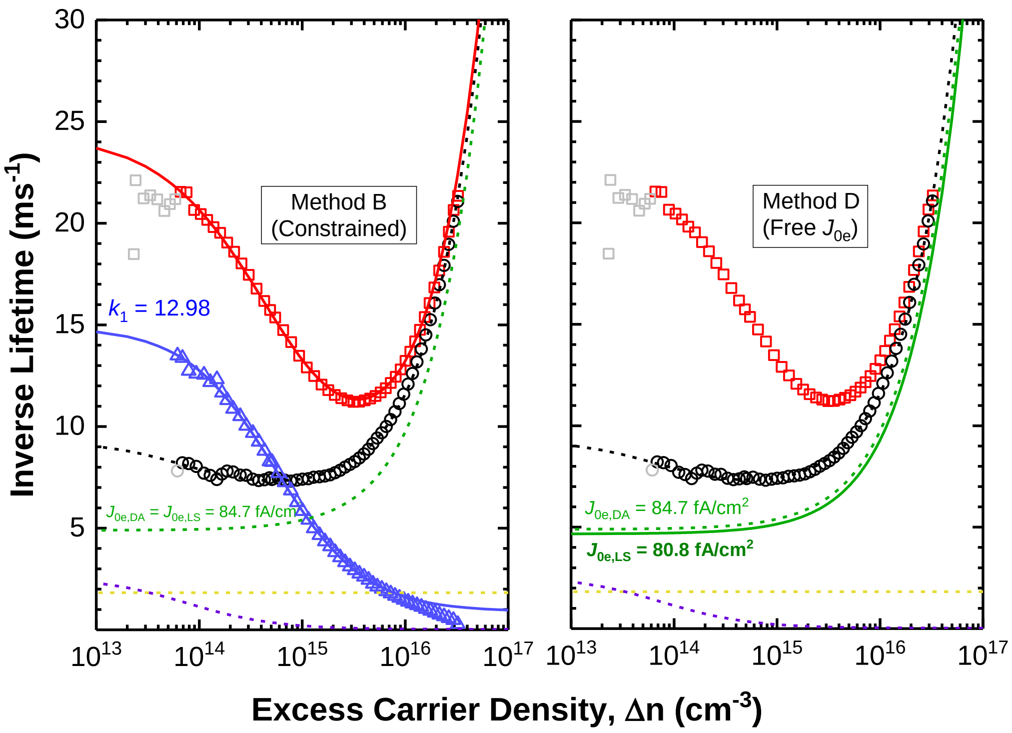
SRH Recombination Properties

IDLS analysis

$$\frac{1}{\tau_{DA}} = \frac{1}{\tau_{surf}} + \frac{1}{\tau_{bulk,fixed}} + \frac{1}{\tau_{SRH,non-BO}}$$

$$\frac{1}{\tau_{LS}} = \frac{1}{\tau_{surf}} + \frac{1}{\tau_{bulk,fixed}} + \frac{1}{\tau_{SRH,non-BO}} + \frac{1}{\tau_{SRH,BO}}$$

Allow this to vary



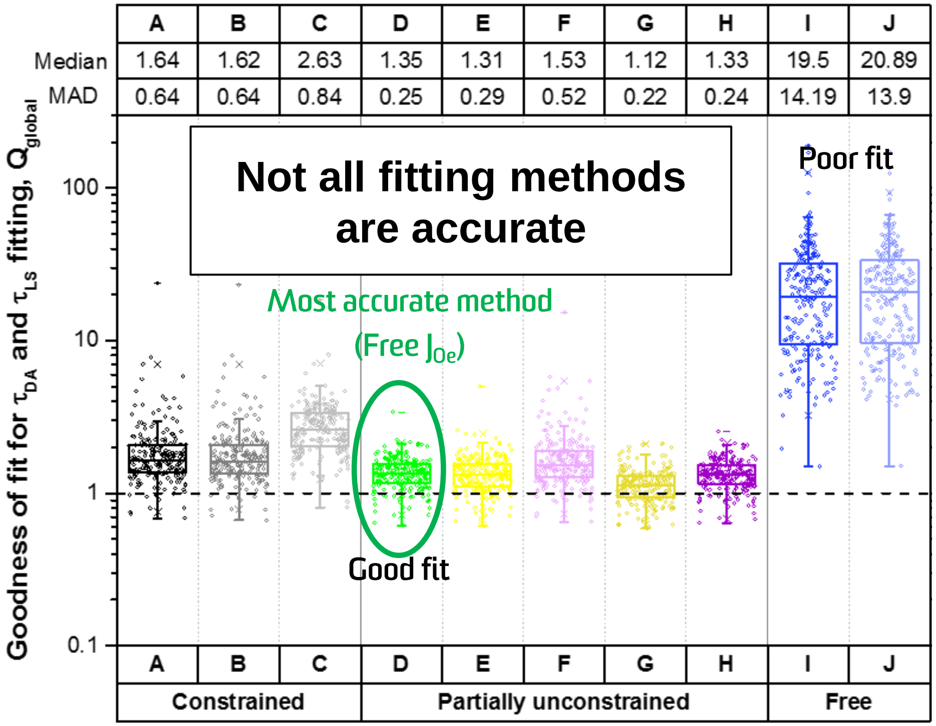
N. Nampalli et al., Frontiers in Energy 11(1), 2017.

SRH Recombination Properties

IDLS analysis

$$\frac{1}{\tau_{DA}} = \frac{1}{\tau_{surf}} + \frac{1}{\tau_{bulk,fixed}} + \frac{1}{\tau_{SRH,non-BO}}$$

$$\frac{1}{\tau_{LS}} = \frac{1}{\tau_{surf}} + \frac{1}{\tau_{bulk,fixed}} + \frac{1}{\tau_{SRH,non-BO}} + \frac{1}{\tau_{SRH,BO}}$$



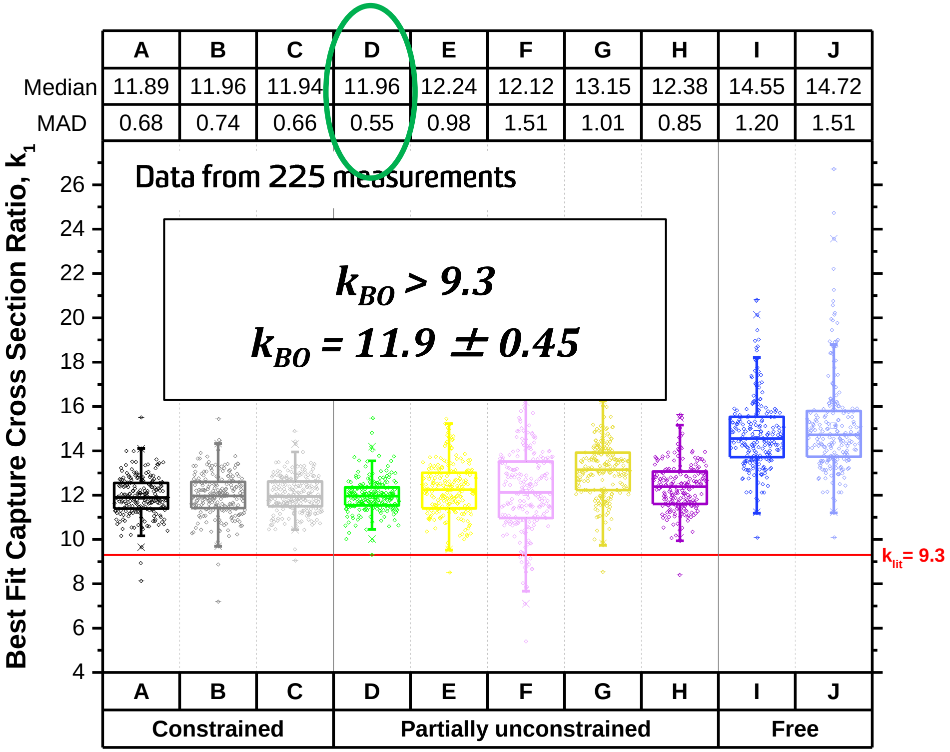
	A	B	C	D	E	F	G	H	I	J
Median	1.64	1.62	2.63	1.35	1.31	1.53	1.12	1.33	19.5	20.89
MAD	0.64	0.64	0.84	0.25	0.29	0.52	0.22	0.24	14.19	13.9

Not all fitting methods are accurate

Poor fit

Most accurate method (Free J_{0e})

Good fit



	A	B	C	D	E	F	G	H	I	J
Median	11.89	11.96	11.94	11.96	12.24	12.12	13.15	12.38	14.55	14.72
MAD	0.68	0.74	0.66	0.55	0.98	1.51	1.01	0.85	1.20	1.51

Data from 225 measurements

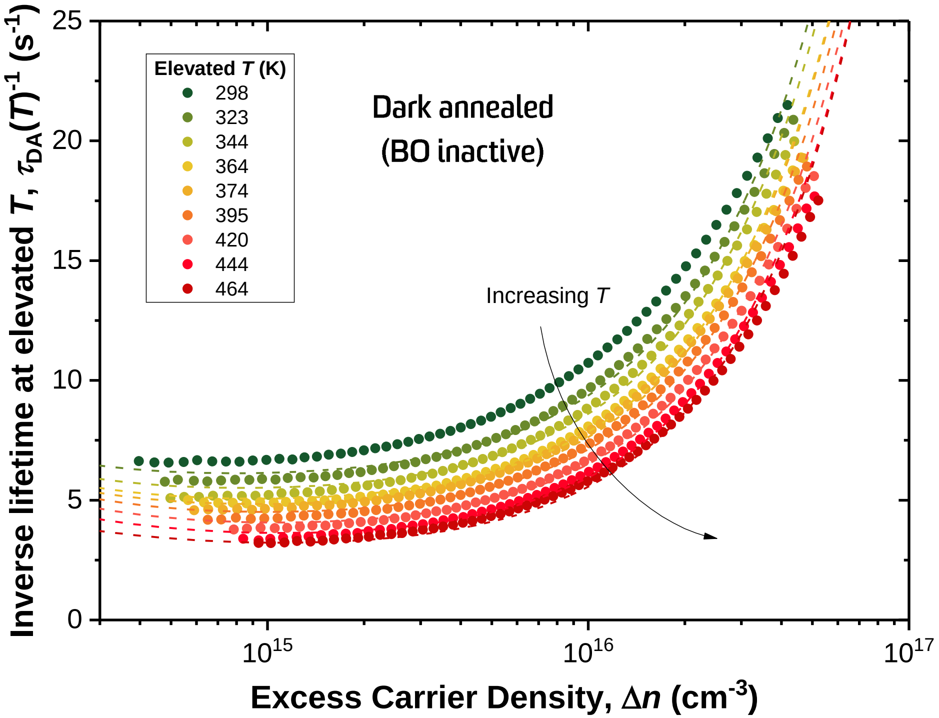
$k_{BO} > 9.3$

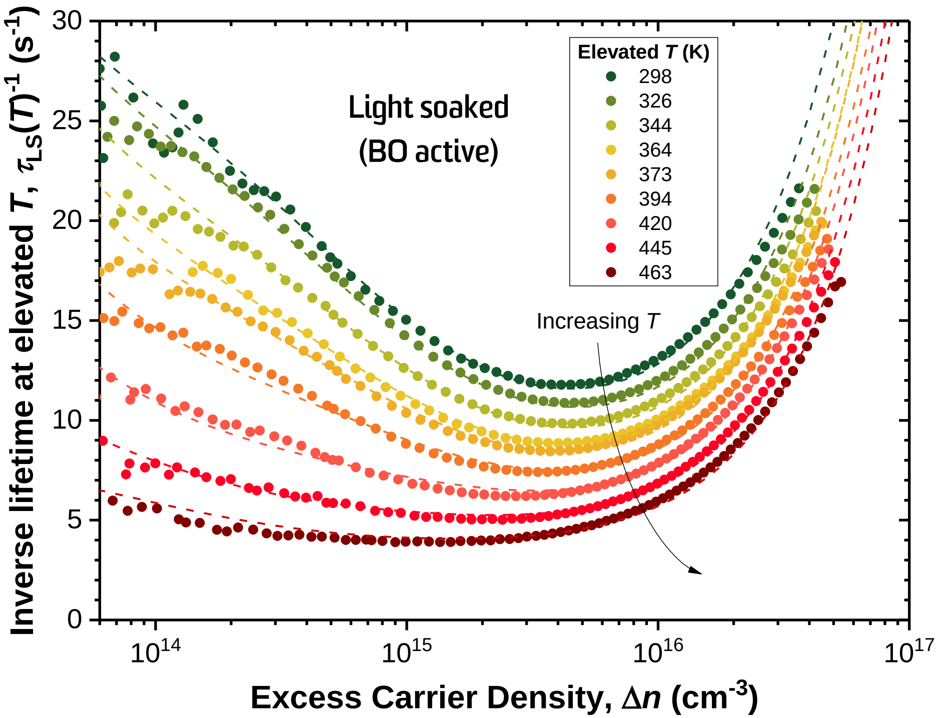
$k_{BO} = 11.9 \pm 0.45$

N. Nampalli et al., Frontiers in Energy 11(1), 2017.

SRH Recombination Properties

TIDLS analysis



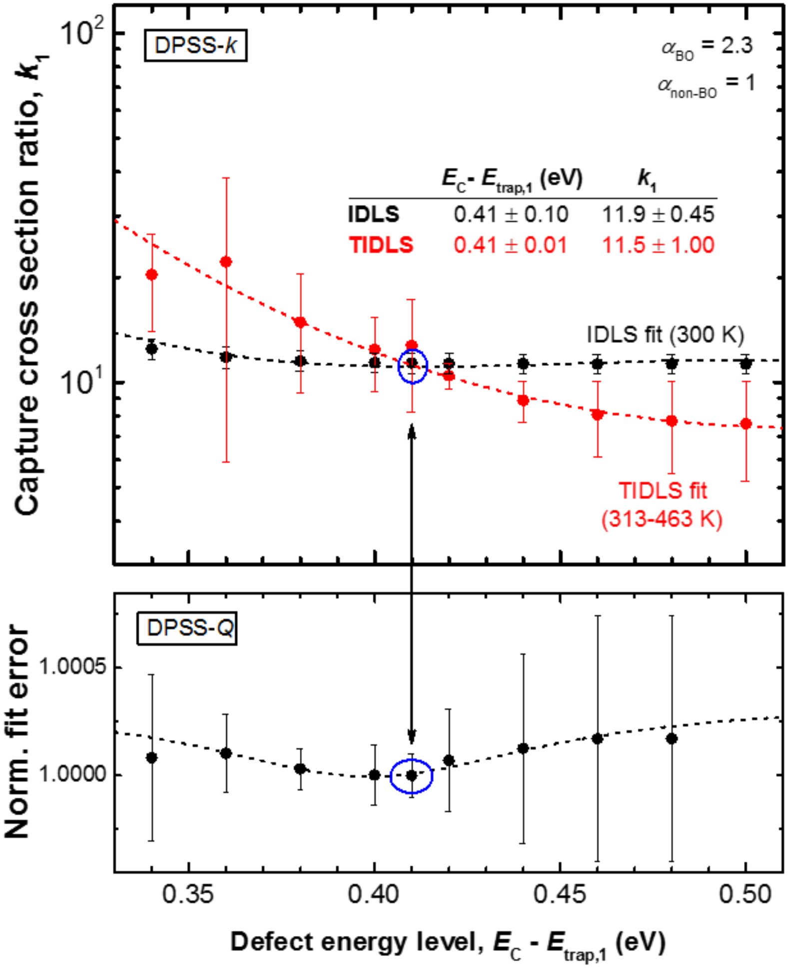


SRH Recombination Properties

TIDLS analysis

- Determine E_{trap}, k

$$E_C - E_{trap} = 0.41 \pm 0.10$$
$$k_{BO} = 11.5 \pm 1.00$$



SRH Recombination Properties

TIDLS analysis

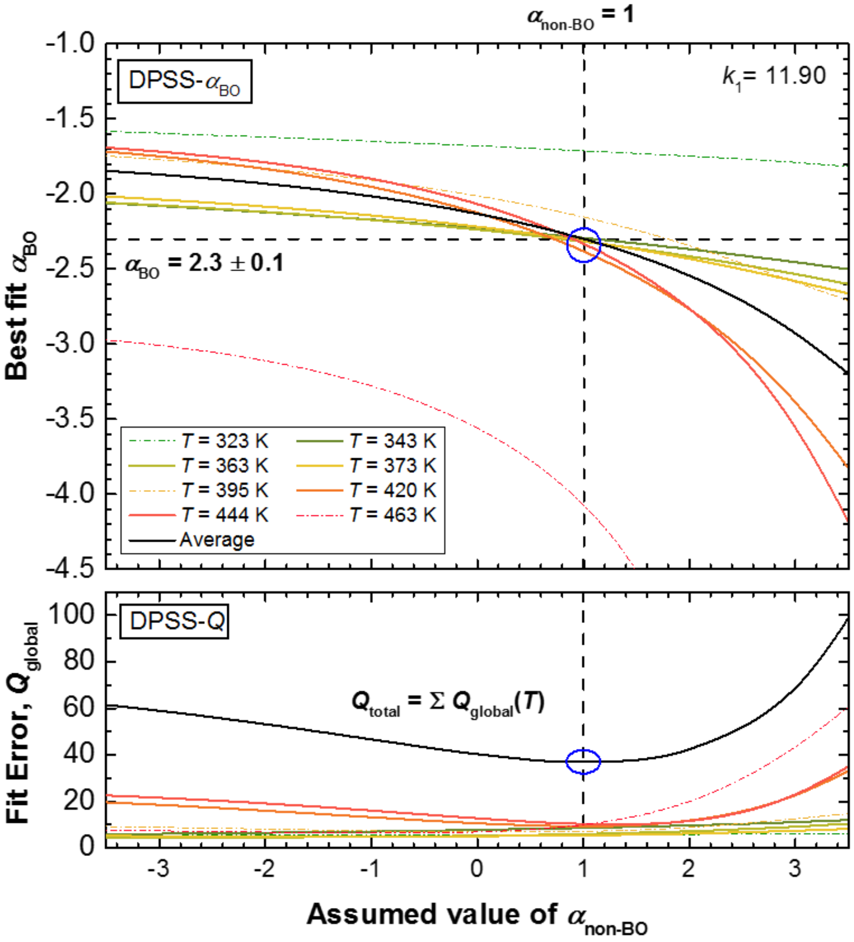
- Determine E_{trap}, k

$$E_C - E_{trap} = 0.41 \pm 0.10$$
$$k_{BO} = 11.5 \pm 1.00$$

- T-dependence of $\tau_{SRH,BO}$

$$\alpha_{BO} = -2.3$$

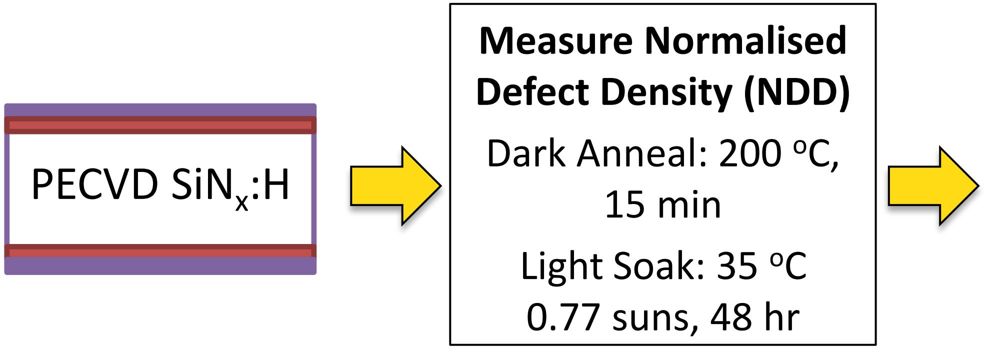
$$\sigma_{n/p}(T) \propto T^{-2.3}$$



Recombination properties of BO

- SRH properties of the BO defect (k , E_{trap})
- Impact of firing on k
- Impact of firing on defect density

Impact of firing – Experiment details



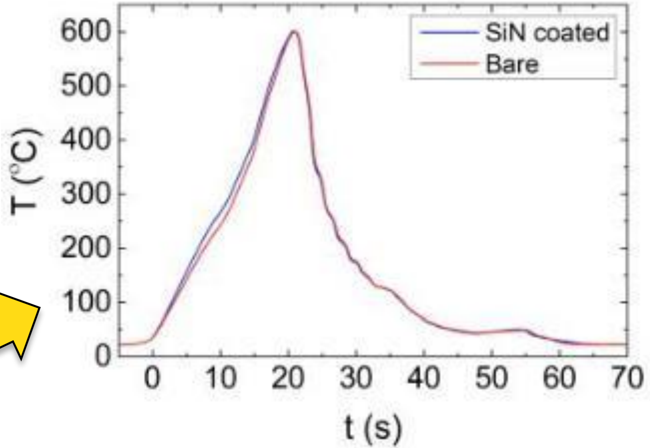
PECVD SiN_x:H

Measure Normalised Defect Density (NDD)

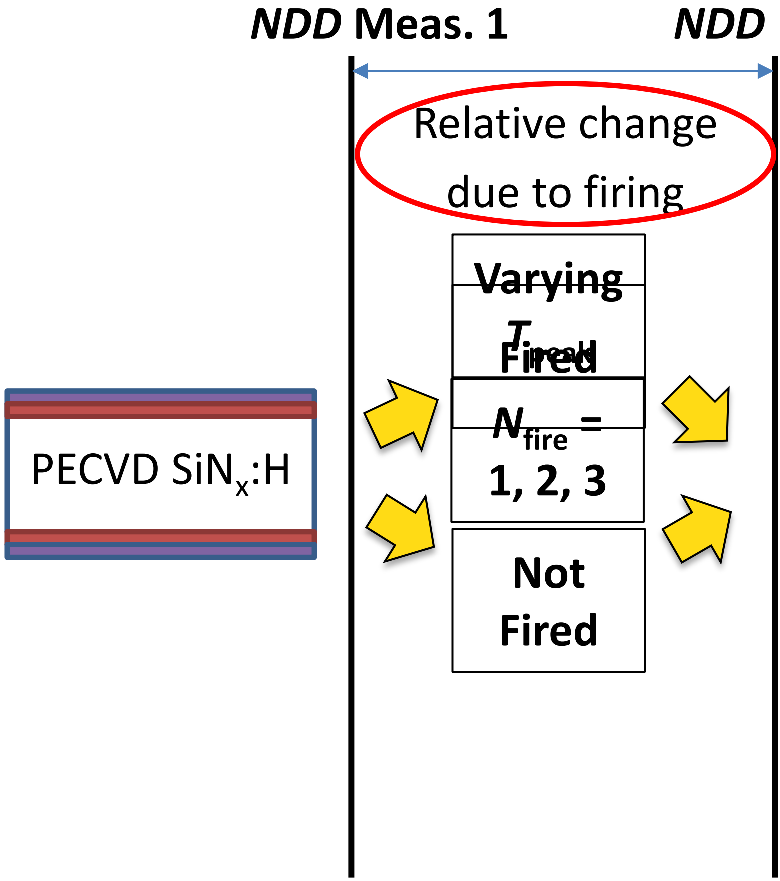
Dark Anneal: 200 °C, 15 min

Light Soak: 35 °C 0.77 suns, 48 hr

***NDD* Meas. 1**



Impact of firing – Experiment details



***NDD* Meas. 1**

***NDD* Meas. 2**

Relative change due to firing

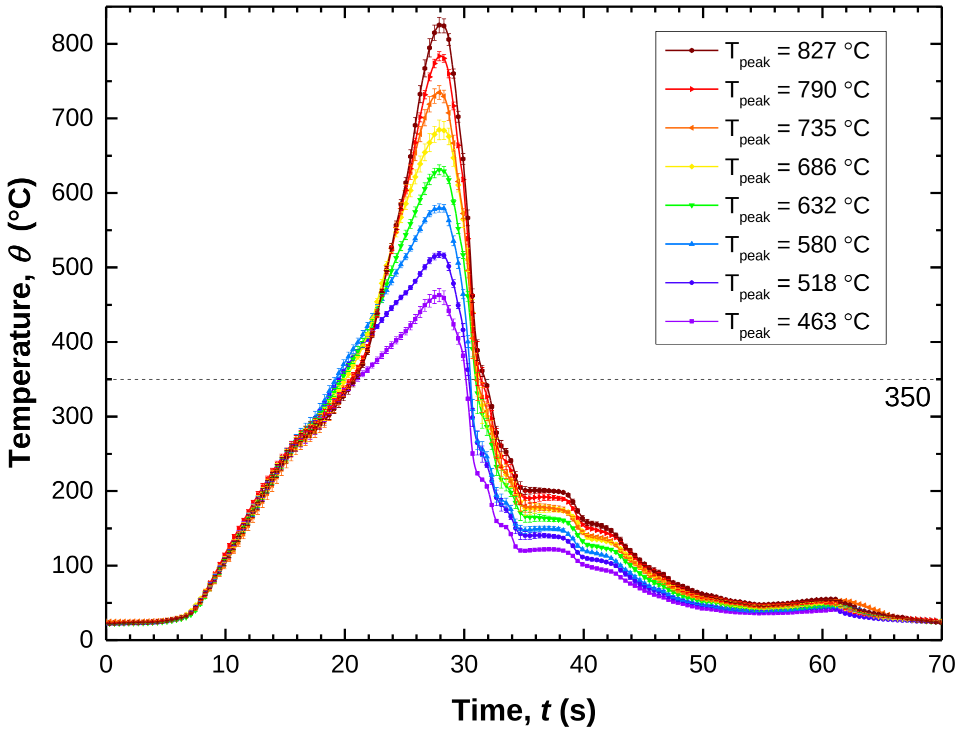
PECVD SiN$_x$:H

Varying T_{peak}

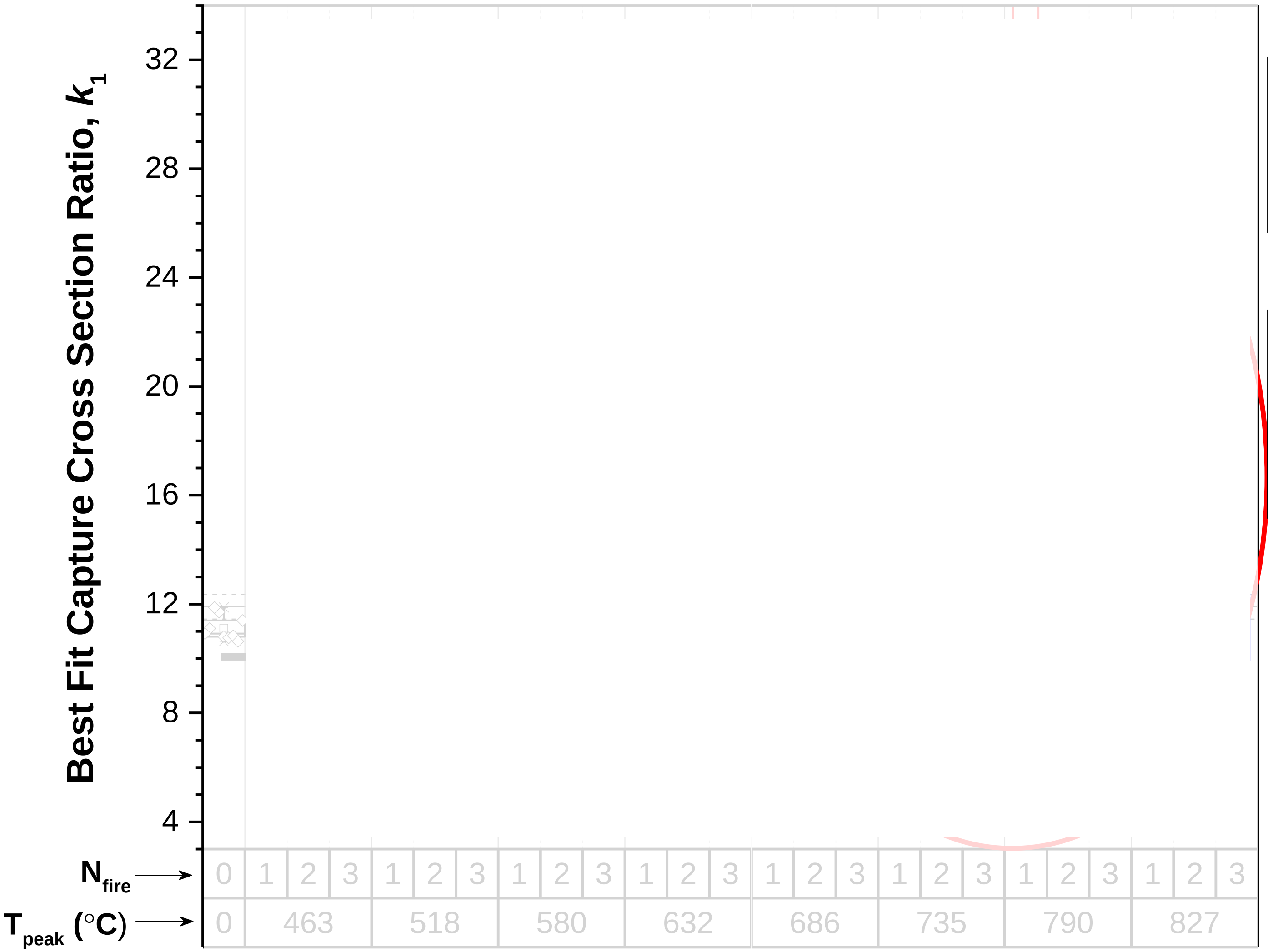
Fired

N_{fire} = 1, 2, 3

Not Fired



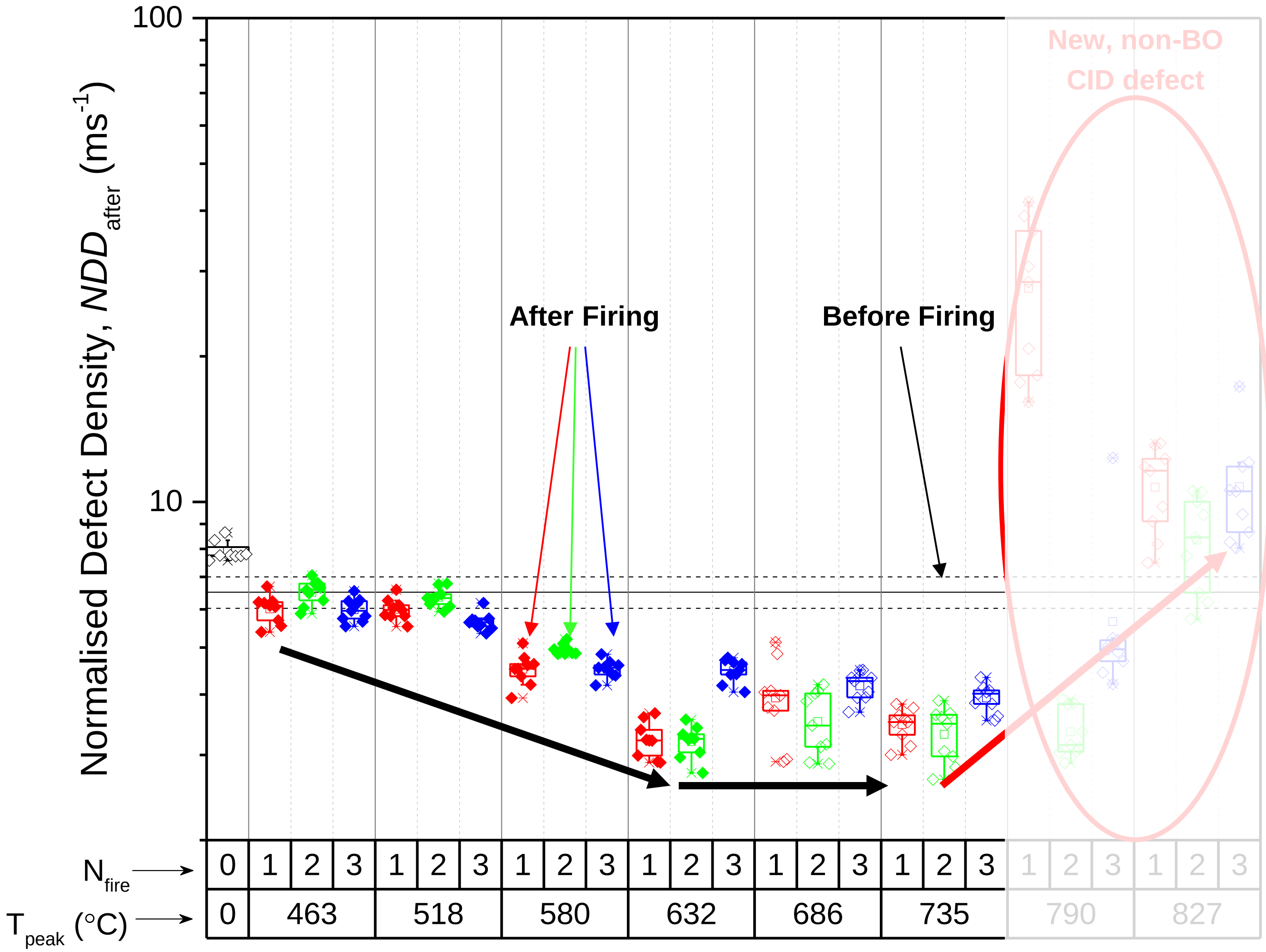
Impact of firing on k_{BO}



Firing has no impact on k_{BO}

Evidence of a new CID defect in Cz silicon (firing activated)

Impact of firing on NDD_{BO}



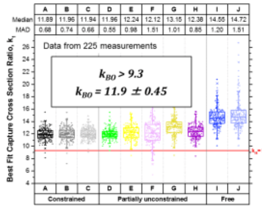
Firing reduces NDD_{BO}

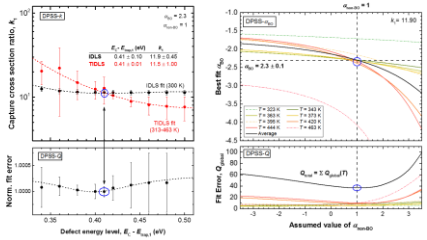
Firing multiple times has no impact

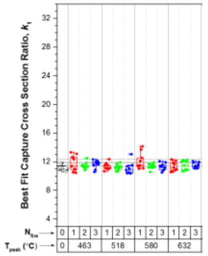
(Cooling rate is critical)

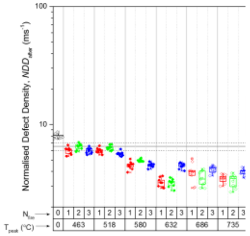
Summary – Properties of the BO defect

- SRH properties of BO:
  - Determined $k_{\mathrm{BO}} = 11.9$ (> 9.3)
  - Confirmed that $E_{\mathrm{trap}} = E_{\mathrm{C}} - 0.41$ eV
  - Determined that $\sigma_{\mathrm{n/p}}(T) \propto T^{-2.3}$
- Impact of firing on BO properties:
  - Confirmed that k_{BO} is not affected by firing
  - Demonstrated that firing reduces NDD_{BO}
  - Firing can induce other (non-BO) CID defects in Cz silicon







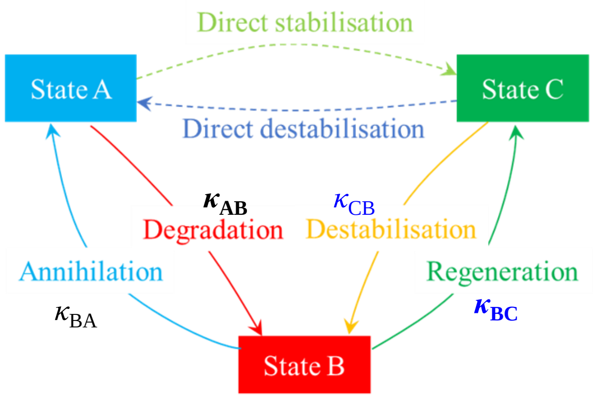


Transition kinetics of the BO system

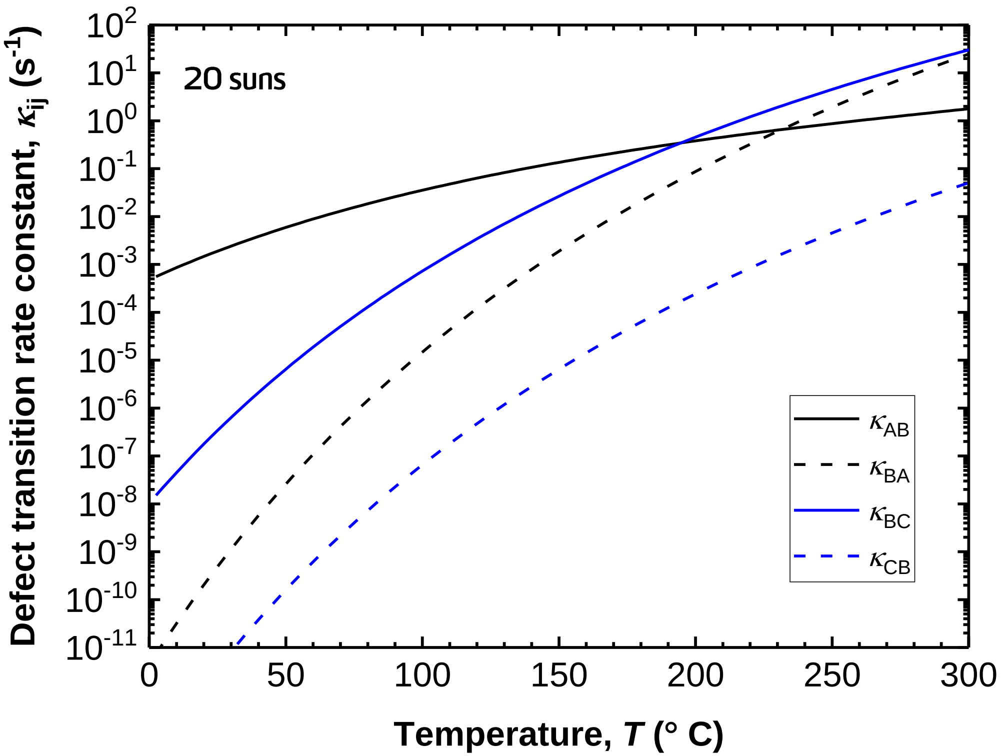
Never Stand Still

Engineering

Transition kinetics of the BO system



Dependence of transition rates on *T* and illumination (*Δn*) are of vital importance!



Transition kinetics of the BO system

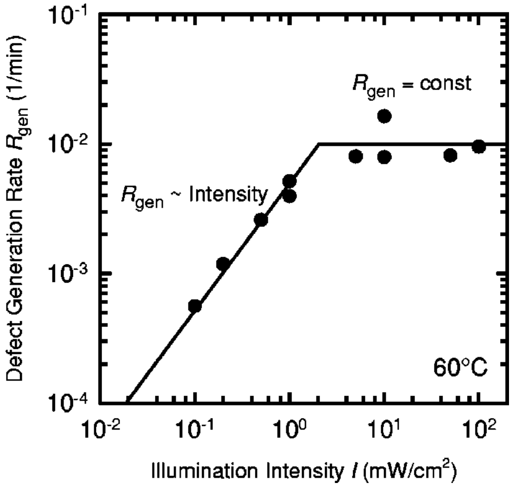
- Degradation:
  - κ_{AB} appears to be independent of illumination intensity (>0.1 suns)
  - Other studies show $\kappa_{deg} \propto (p_0)^2$

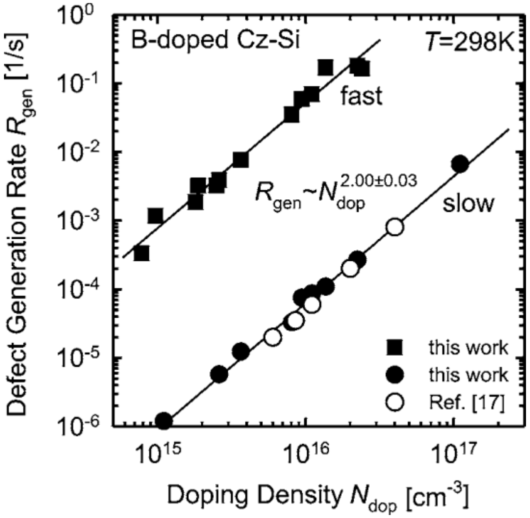
Which is true?

$$\boldsymbol{\kappa_{AB} \propto (p_0)^2}$$

$$\boldsymbol{\kappa_{AB} \propto p \cdot p_0}$$

$$\boldsymbol{\kappa_{AB} \propto (p)^2}$$



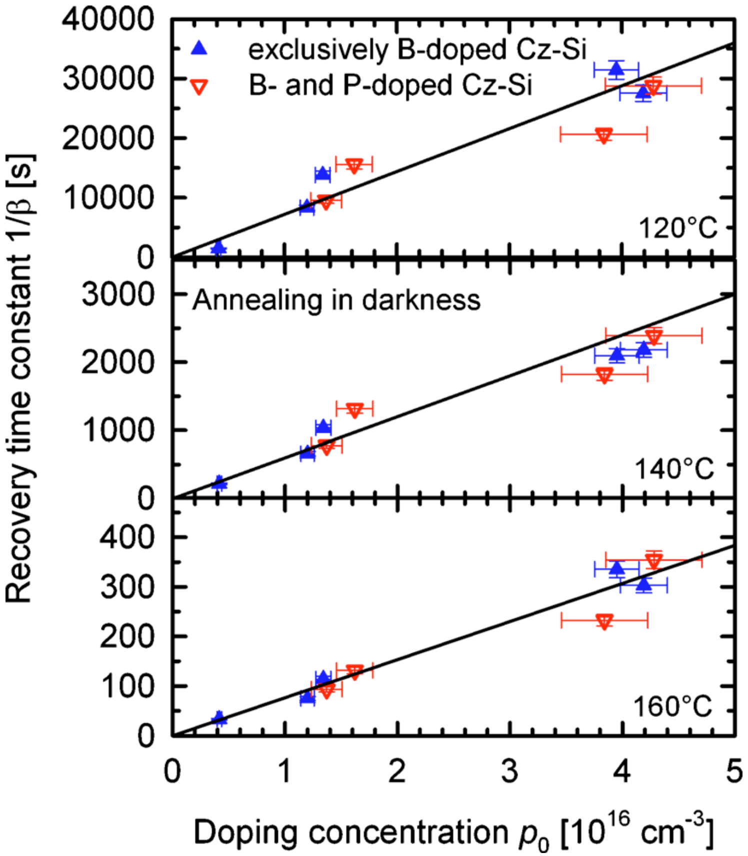


J. Schmidt and K. Bothe, Physical Review B 69, p.024107, 2004.
K. Bothe and J. Schmidt, Journal of Applied Physics 99, p. 013701, 2006.

Transition kinetics of the BO system

- Annealing:
  - Known to occur in dark (no carrier dependence assumed)
  - But…one study showed $\kappa_{BA} \propto \frac{1}{p_0}$ for compensated Si

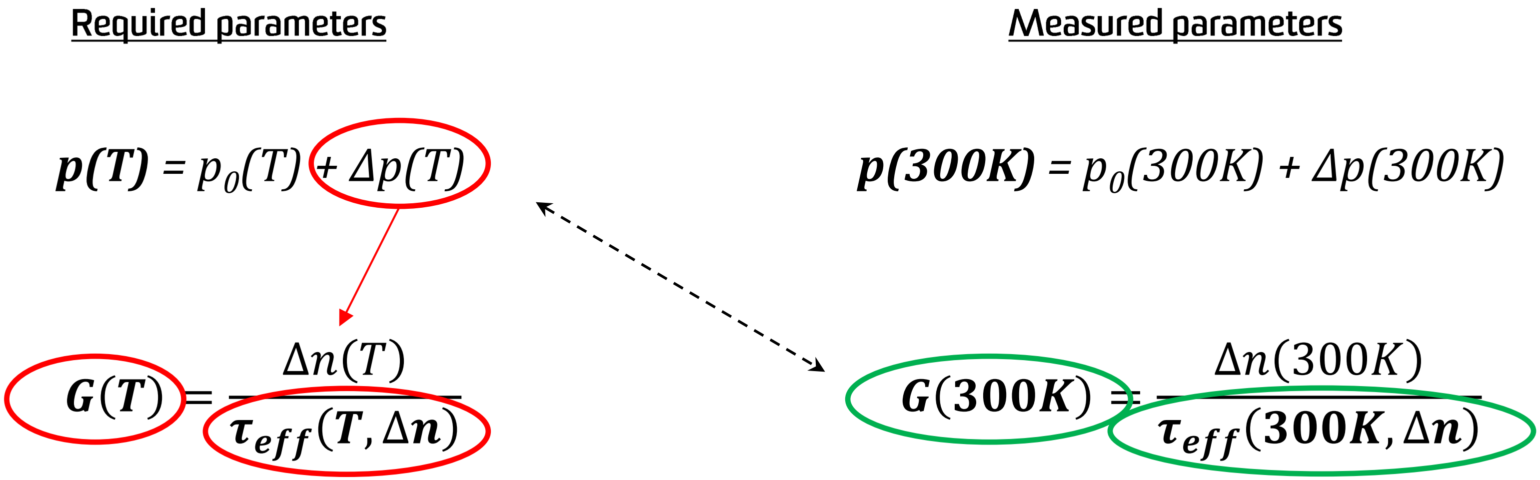
Does κ_{BA} have a carrier dependence?



B. Lim et al., Applied Physics Letters 98, p.162104, 2011.

Issue with reaction rate studies

- **Process *T* ≠ Measurement *T*** !



Required parameters

$\boldsymbol{p(T)} = p_0(T) + \Delta p(T)$

$$\boldsymbol{G(T)} = \frac{\Delta n(T)}{\boldsymbol{\tau_{eff}(T, \Delta n)}}$$

Measured parameters

$\boldsymbol{p(300K)} = p_0(300K) + \Delta p(300K)$

$$\boldsymbol{G(300K)} = \frac{\Delta n(300K)}{\boldsymbol{\tau_{eff}(300K, \Delta n)}}$$

Need a method to determine $\boldsymbol{\Delta n(T)}$ from $\boldsymbol{\tau_{eff}(300K)}$ and $\boldsymbol{G(300K)}$

Reaction kinetics of the BO system

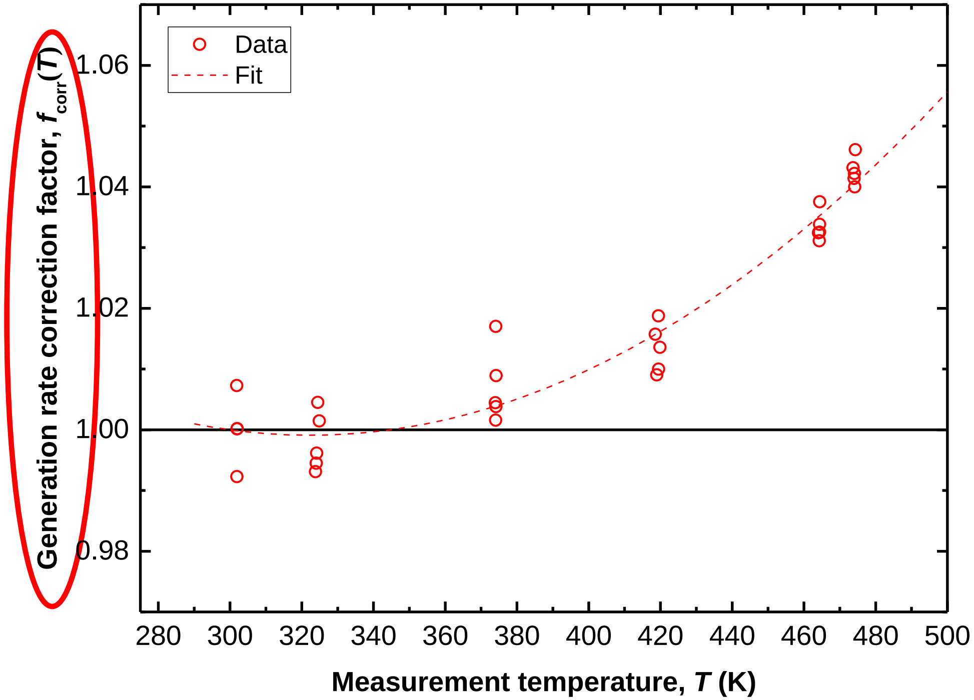
- Model to obtain $\tau_{\mathrm{eff}}(T)$ from $\tau_{\mathrm{eff}}(300\ K)$

- Temporary deactivation (annealing) kinetics

- Degradation kinetics

Temperature dependence of lifetime

$$\boxed{G(T)} = \frac{\Delta n(T)}{\tau_{eff}(T,\Delta n)}$$



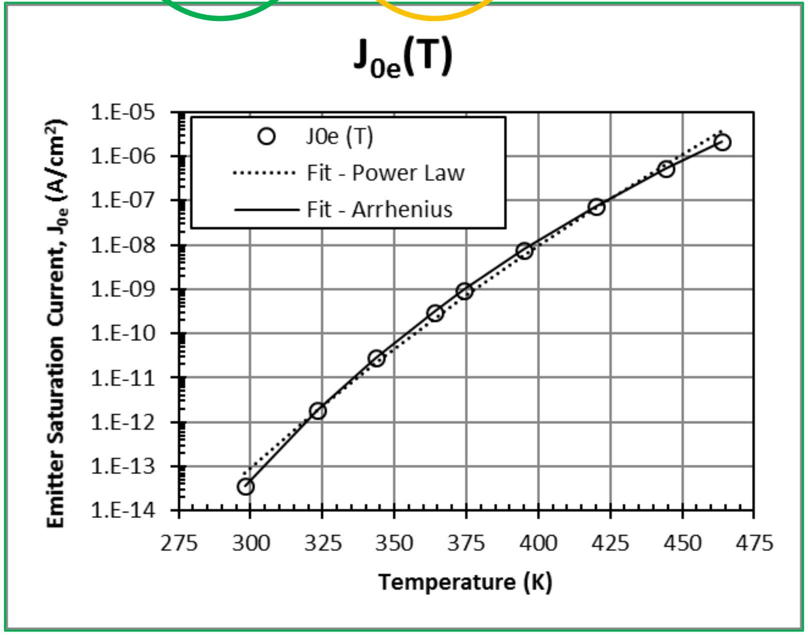
Temperature dependence of lifetime

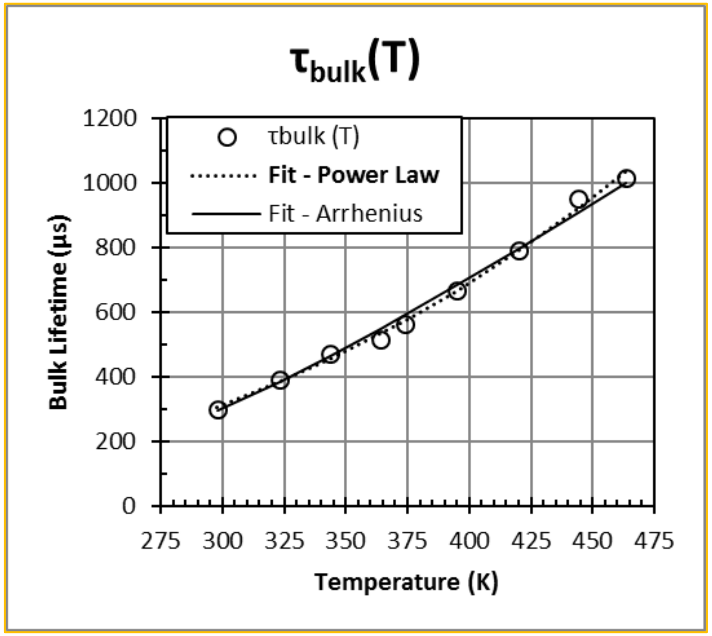
$$G(T) = \frac{\Delta n(T)}{\tau_{eff}(T,\Delta n)}$$

$$\frac{1}{\boldsymbol{\tau_{DA}(T,\Delta n)}} = \frac{1}{\tau_{surf}(T,\Delta n)} + \frac{1}{\tau_{bulk,fixed}(T)} + \frac{1}{\tau_{SRH,non-BO}(T)}$$

$$\frac{1}{\boldsymbol{\tau_{LS}(T,\Delta n)}} = \frac{1}{\tau_{surf}(T,\Delta n)} + \frac{1}{\tau_{bulk,fixed}(T)} + \frac{1}{\tau_{SRH,non-BO}(T)} + \frac{1}{\tau_{SRH,BO}(T,\Delta n)}$$

Step 1: Fit $\boldsymbol{\tau_{DA}(T,\Delta n)}$ and $\boldsymbol{\tau_{LS}(T,\Delta n)}$
at each temperature





Temperature dependence of lifetime

$$G(T) = \frac{\Delta n(T)}{\boxed{\tau_{eff}(T, \Delta n)}}$$

$$\frac{1}{\boldsymbol{\tau_{DA}(T, \Delta n)}} = \frac{1}{\tau_{surf}(T, \Delta n)} + \frac{1}{\tau_{bulk,fixed}(T)} + \frac{1}{\tau_{SRH,non-BO}(T)}$$

$$\frac{1}{\boldsymbol{\tau_{LS}(T, \Delta n)}} = \frac{1}{\tau_{surf}(T, \Delta n)} + \frac{1}{\tau_{bulk,fixed}(T)} + \frac{1}{\tau_{SRH,non-BO}(T)} + \frac{1}{\tau_{SRH,BO}(T, \Delta n)}$$

$$\tau_{SRH,BO}(T, \Delta n) \rightarrow \tau_{n0,BO}(T)$$

$$\tau_{SRH,non-BO}(T) \rightarrow \tau_{n0,non-BO}(T)$$

$$\tau_{bulk,fixed}(T) \rightarrow \tau_{bulk,fixed}(T)$$

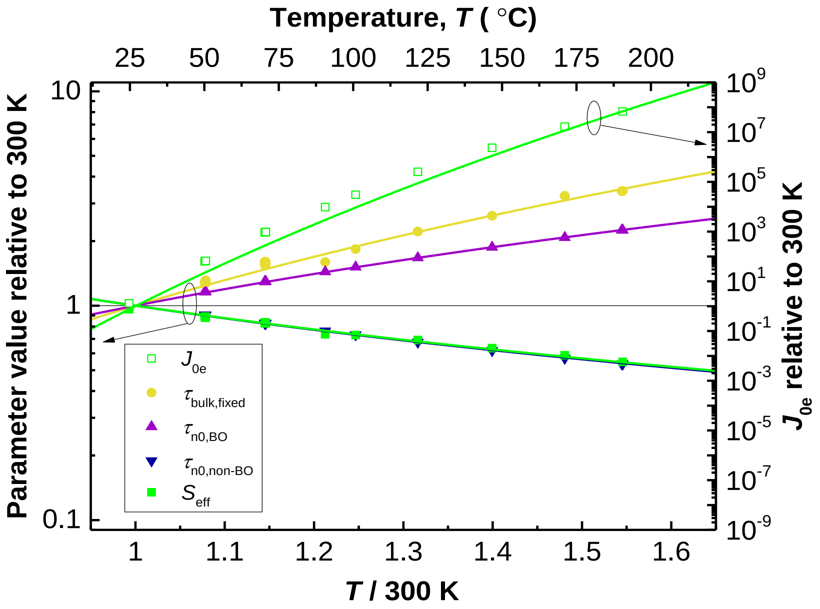
$$\frac{1}{\tau_{surf}(T, \Delta n)} \rightarrow \frac{1}{\tau_{surf}(T, \Delta n)}$$

$$\frac{1}{\tau_{surf}(T, \Delta n)}$$

Step 2: Apply this relation for each fitted parameter:

$$\boldsymbol{Param(T) = Param(300K) \times \left(\frac{T}{300}\right)^{\alpha_{param}}}$$

Temperature dependence of lifetime



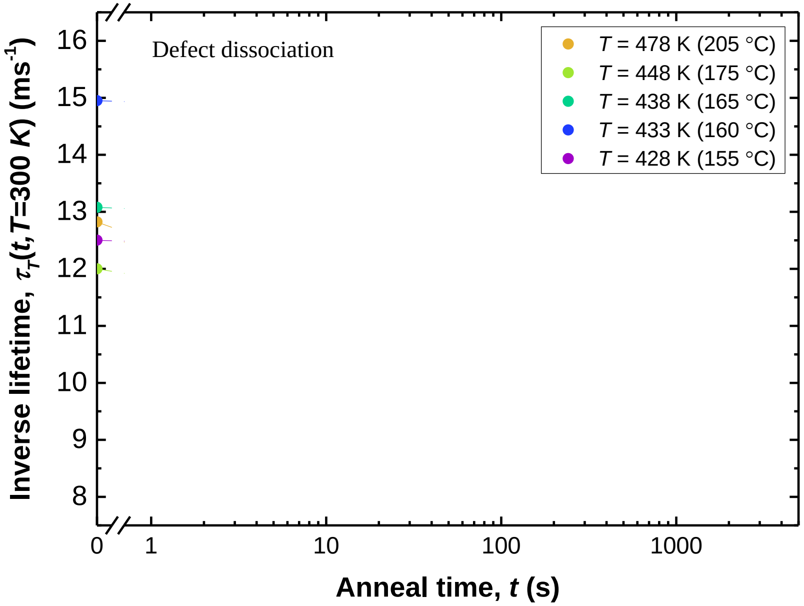
Parameter	Relevant lifetime component	Exponent of temperature dependence	Value for α_{param}
$\tau_{bulk,fixed}$*	$\tau_{bulk,fixed}(T)$	α_b	2.880 ± 0.032
S_{eff}	$\tau_{surf}(T)$	α_{Seff}	-1.395 ± 0.030
J_{0e}	$\tau_{surf}(T)$	α_{J0e}	41.449 ± 0.044
$\tau_{n0,BO}$	$\tau_{SRH, BO}(T)$	$\alpha_{n0,BO}$	1.870 ± 0.003
$\tau_{n0,non\text{-}BO}$*	$\tau_{SRH,non\text{-}BO}(T)$	$\alpha_{n0,non\text{-}BO}$	-1.420 ± 0.006

** may be specific to wafers used in this study*

Reaction kinetics of the BO system

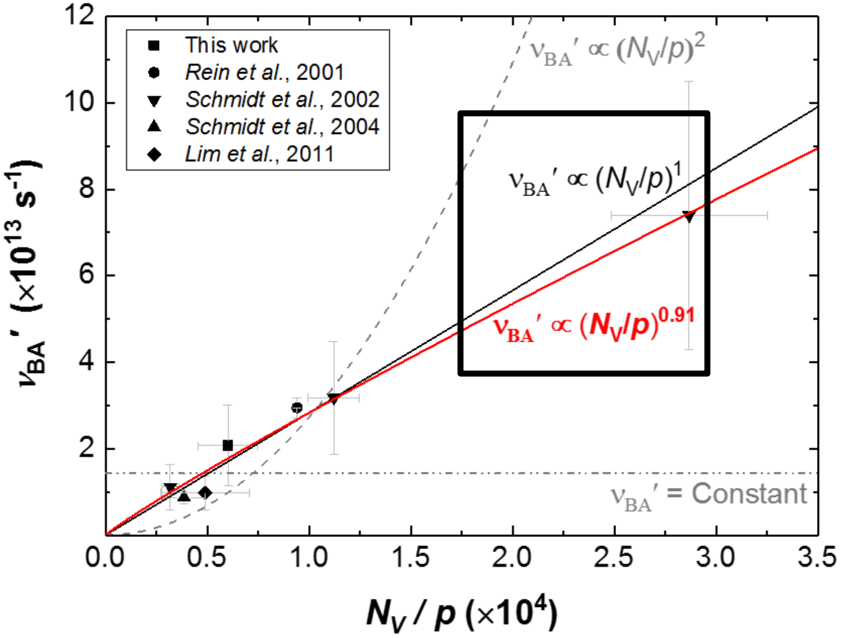
- Model to obtain $\tau_{\mathrm{eff}}(T)$ from $\tau_{\mathrm{eff}}(300\ K)$
- Temporary deactivation (annealing) kinetics
- Degradation kinetics

Annealing kinetics



Rates extracted

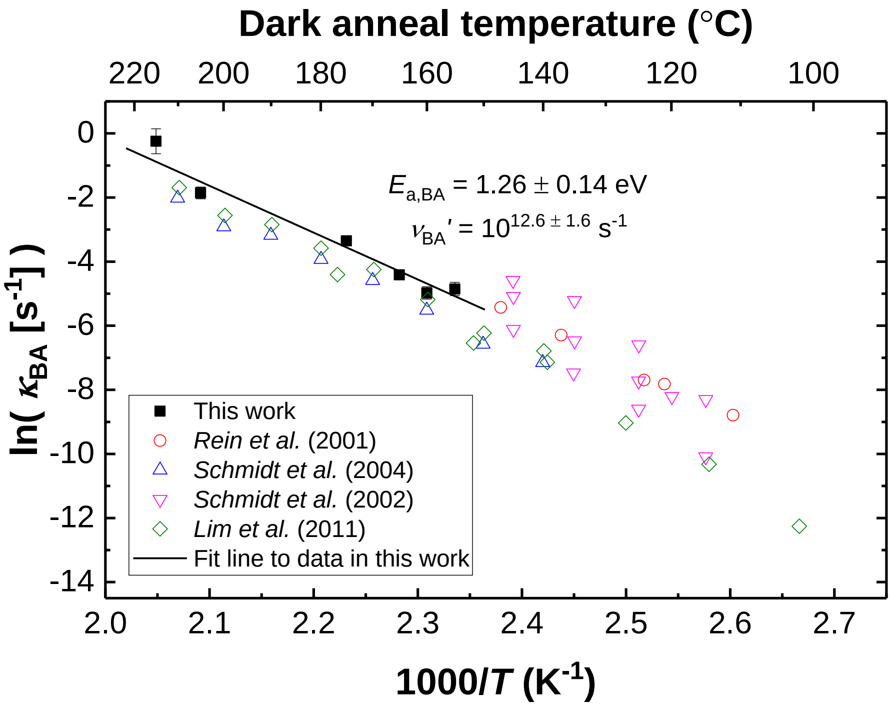
$$\kappa_{\mathrm{BA}} \propto \left[\frac{1}{p(T)}\right]$$

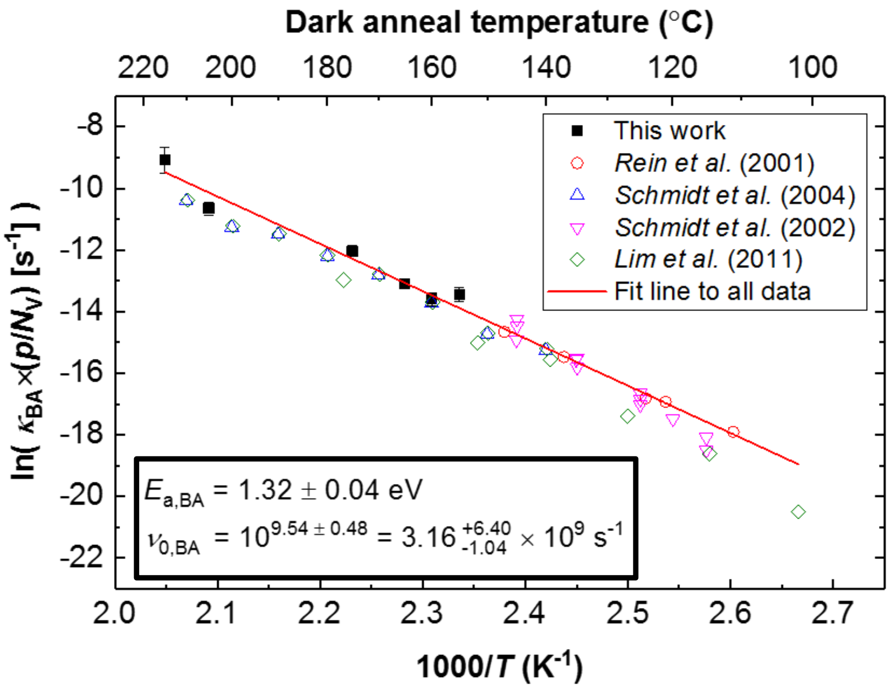


Annealing kinetics

κ_{BA} - not normalised

κ_{BA} – normalised to $(p/\mathrm{N_V})^{-1}$





$$\kappa_{\mathrm{BA}} = \nu_{BA}' \cdot e^{\frac{-E_{a,BA}}{k_B T}}$$

$$\kappa_{\mathrm{BA}} = \nu_{0,BA} \cdot \left[\frac{N_C(T)}{p(T)}\right] \cdot e^{\frac{-E_{a,BA}}{k_B T}}$$

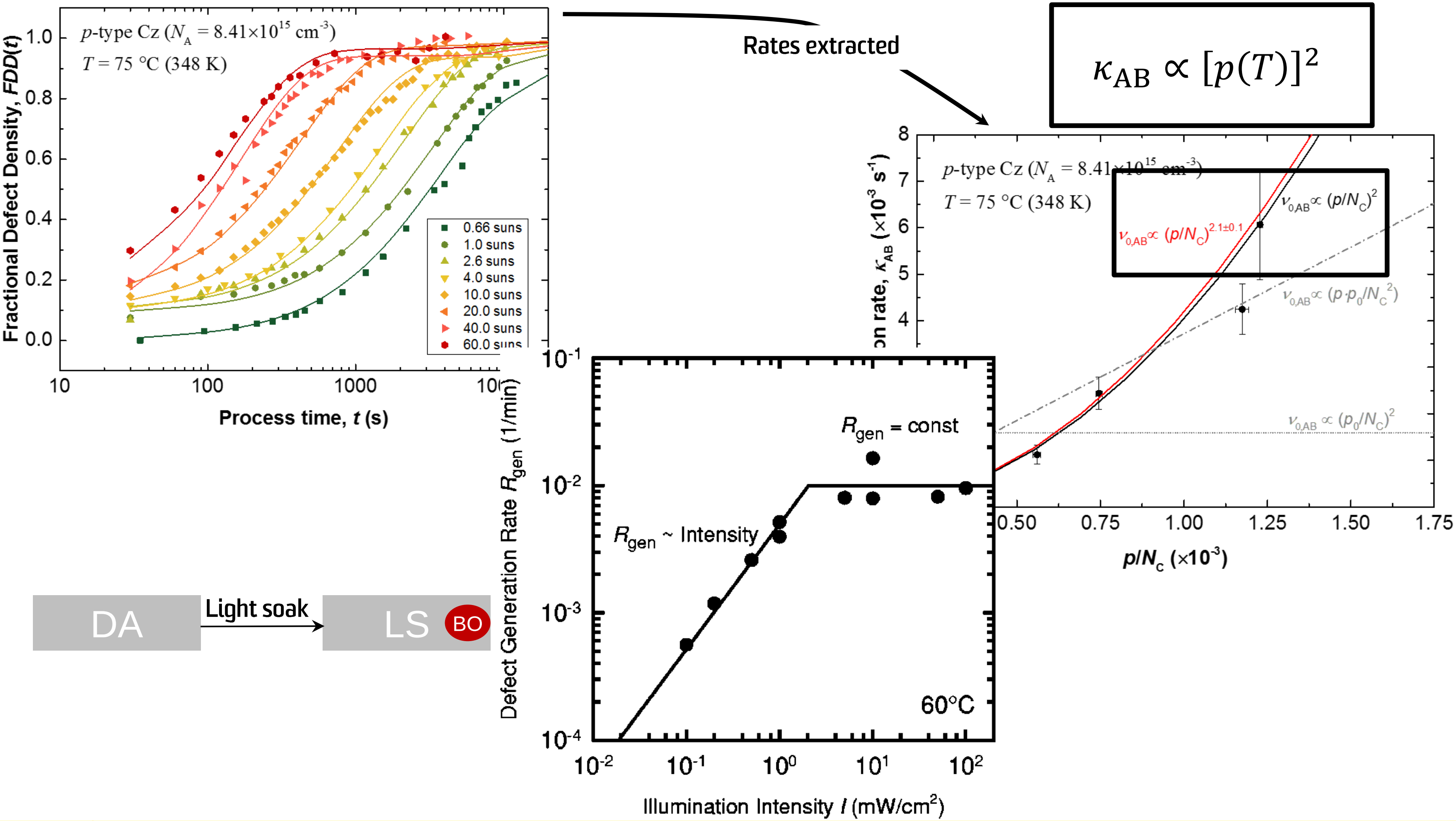
Reaction kinetics of the BO system

- Model to obtain $\tau_{eff}(T)$ from $\tau_{eff}(300\ K)$

- Temporary deactivation (annealing) kinetics

- Degradation kinetics

Degradation kinetics



Rates extracted

$$\kappa_{AB} \propto [p(T)]^2$$

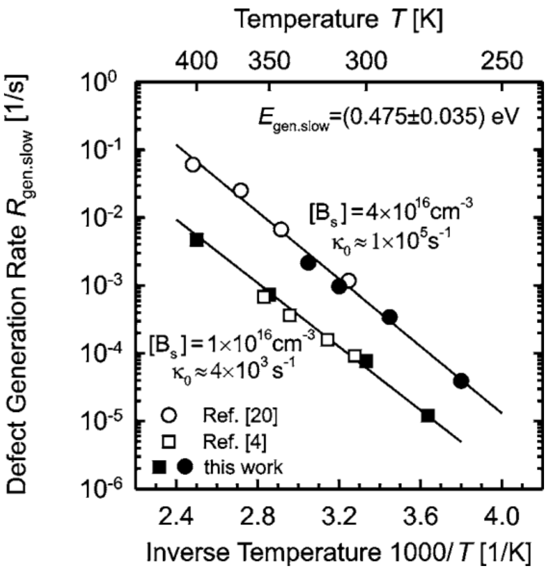
DA $\xrightarrow{\text{Light soak}}$ LS BO

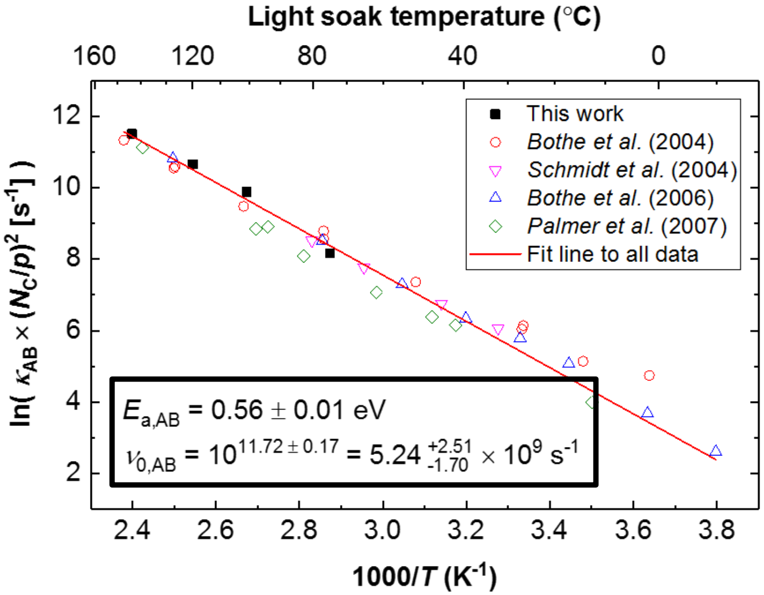
J. Schmidt and K. Bothe, Physical Review B 69, p.024107, 2004.

Degradation kinetics

κ_{AB} - not normalised
(Bothe and Schmidt, 2004)

κ_{AB} – normalised to $(p/\mathrm{N_C})^2$
(This work)





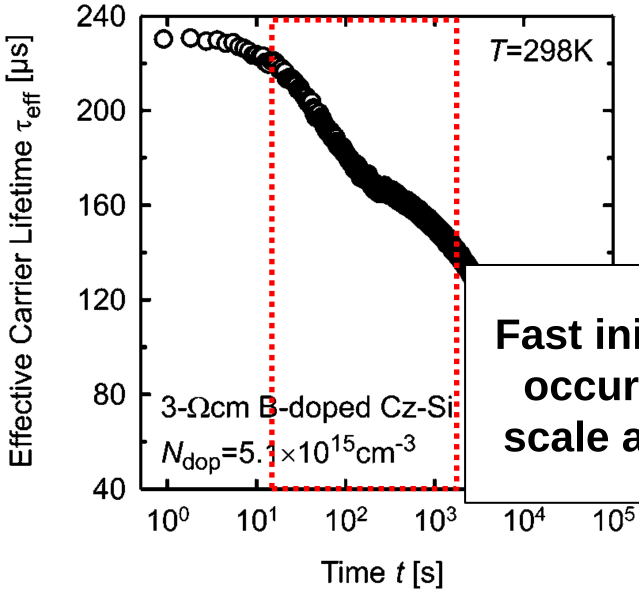
$$\kappa_{\mathrm{AB}} = \nu_{AB}' \cdot e^{\frac{-E_{a,AB}}{k_B T}}$$

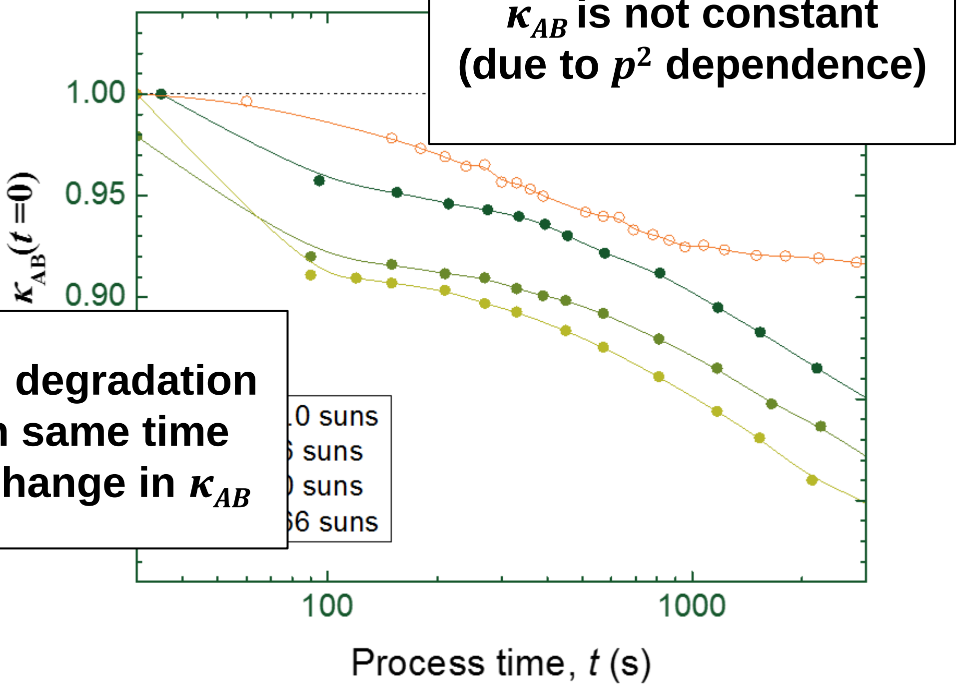
$$\kappa_{\mathrm{AB}} = \nu_{0,AB} \cdot \left[\frac{p(T)}{N_C(T)}\right]^2 \cdot e^{\frac{-E_{a,AB}}{k_B T}}$$

K. Bothe and J. Schmidt, Journal of Applied Physics 99, p. 013701, 2006.

Implications of degradation kinetics

- Fast initial degradation (“FRC”)
  - May be partially related to *p*^{2} dependence





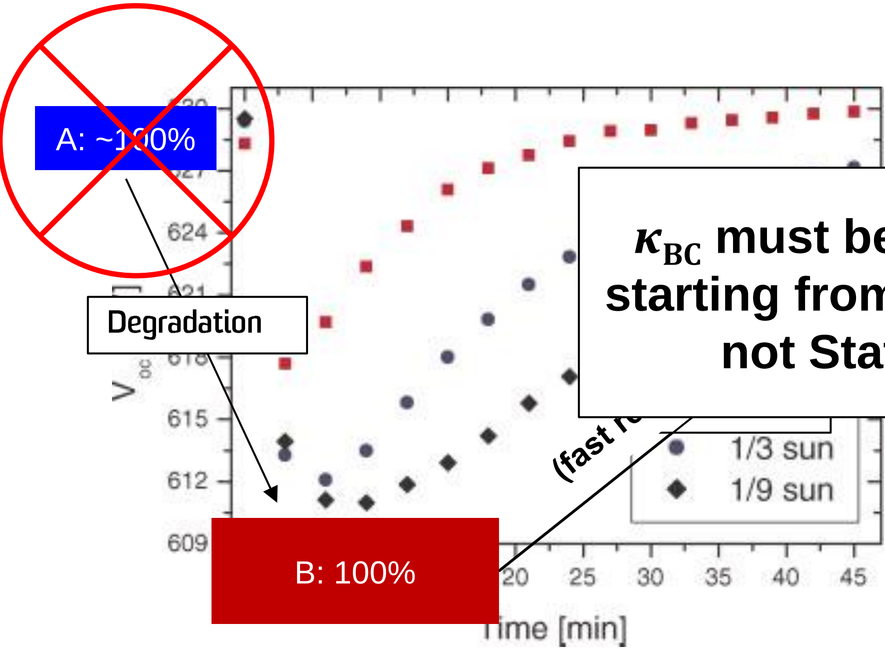
κ_{AB} is not constant (due to p^2 dependence)

Fast initial degradation occurs in same time scale as change in κ_{AB}

K. Bothe and J. Schmidt, Journal of Applied Physics 99, p. 013701, 2006.

Implications of degradation kinetics

- Regeneration rates
  - Regen (B → C) occurs only after degradation (A → B)
  - κ_{BC} will be limited by κ_{AB}

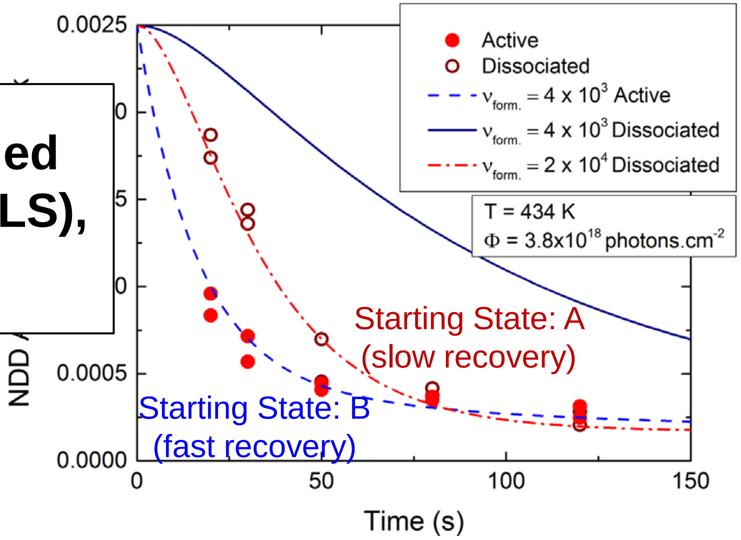


A: ~100%

Degradation

B: 100%

κ_{BC} must be determined starting from State B (LS), not State A (DA)



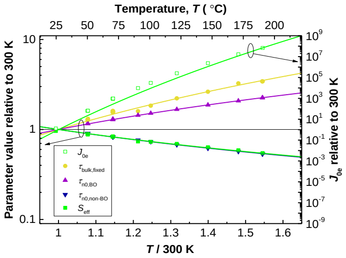
Starting State: A
(slow recovery)

Starting State: B
(fast recovery)

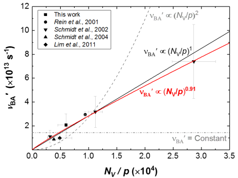
A. Herguth et al., Progress in Photovoltaics: Research and applications 16, pp.135-140, 2008
P. Hamer et al., Solar Energy Materials and Solar Cells 145, pp.440-446, 2016

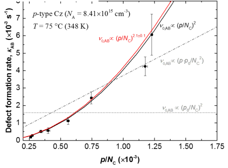
Summary – Reaction Kinetics

- Developed parameterization to obtain $\tau_{eff}(T)$ from $\tau_{eff}(300\ K)$

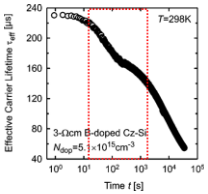


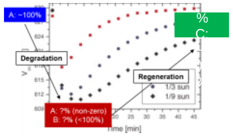
- Carrier dependence confirmed for annealing (A → B), degradation (B → A)





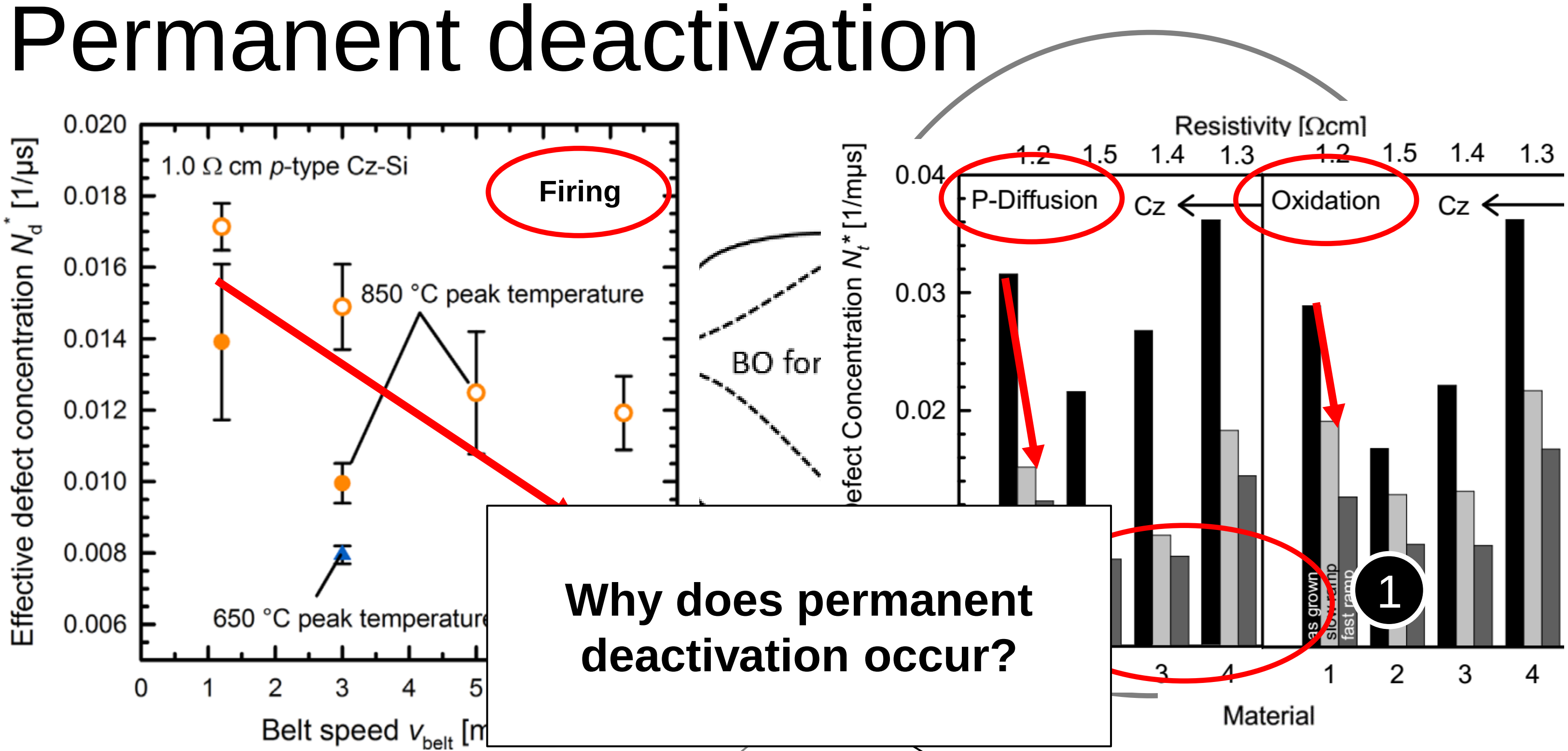
- Carrier dependence explains other observed kinetics phenomena



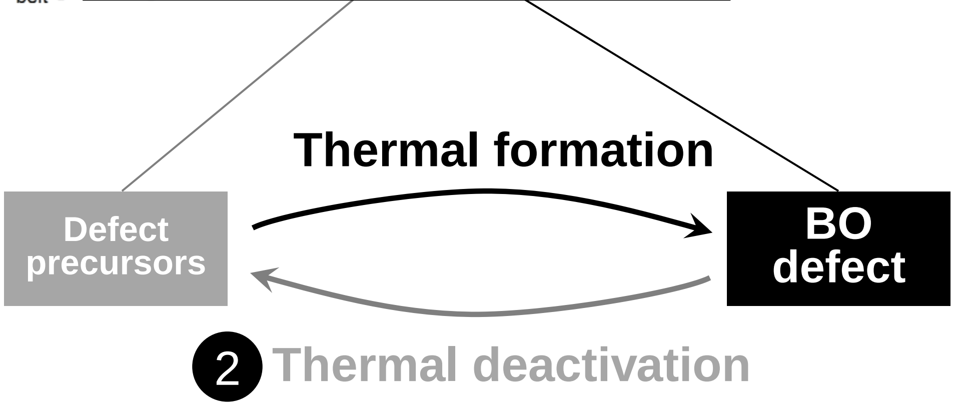


Mechanisms for permanent deactivation of BO defects

Permanent deactivation



Why does permanent deactivation occur?



Thermal formation

Defect precursors

BO defect

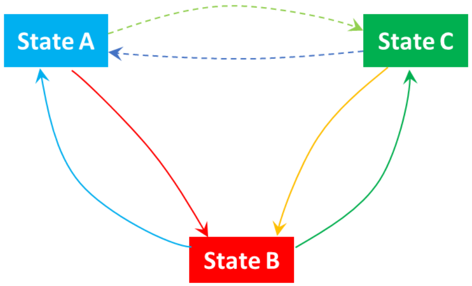
② **Thermal deactivation**

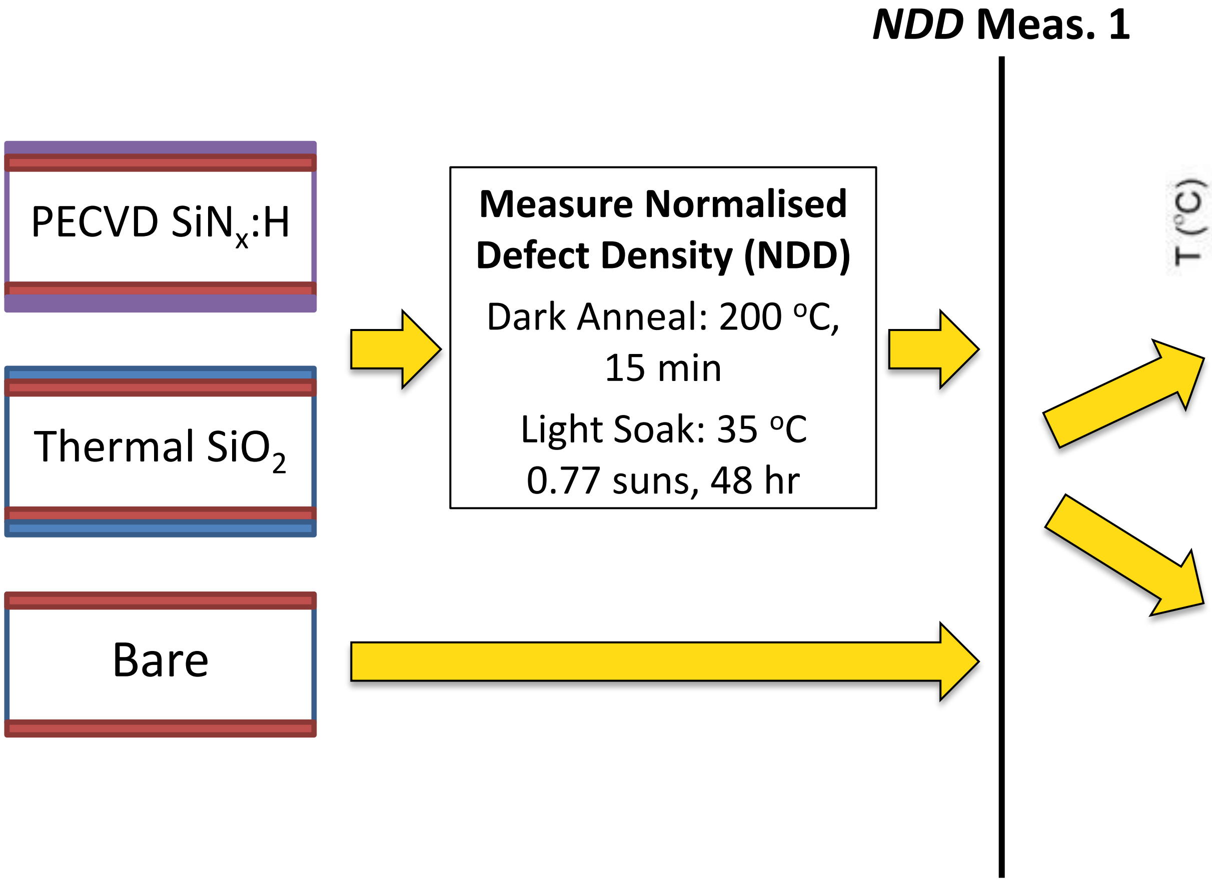
D. Walter et al., Solar Energy Materials and Solar Cells 131, p. 51-57 (2014)
K. Bothe et al., Solid State Phenomena 95-96, p. 223-228 (2004)
V. Voronkov and R. Falster, Physica Status Solidi C 13(10-12), p. 712-717 (2016)

Deactivation mechanisms

- Why does regeneration occur?
- Why does thermal deactivation occur?
- Are they related?

Experimental Details





PECVD SiN_x:H

Thermal SiO_2

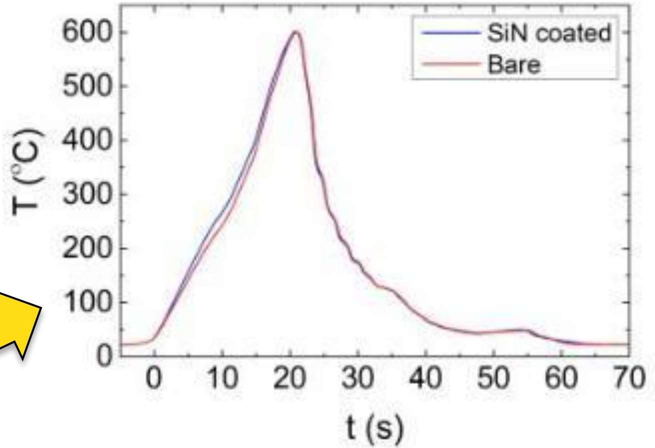
Bare

Measure Normalised Defect Density (NDD)

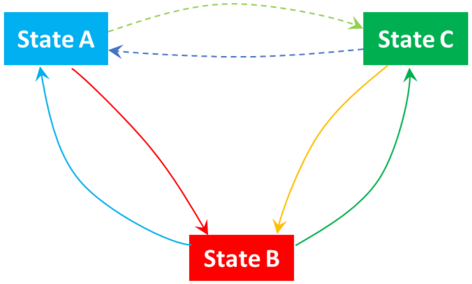
Dark Anneal: 200 ºC, 15 min

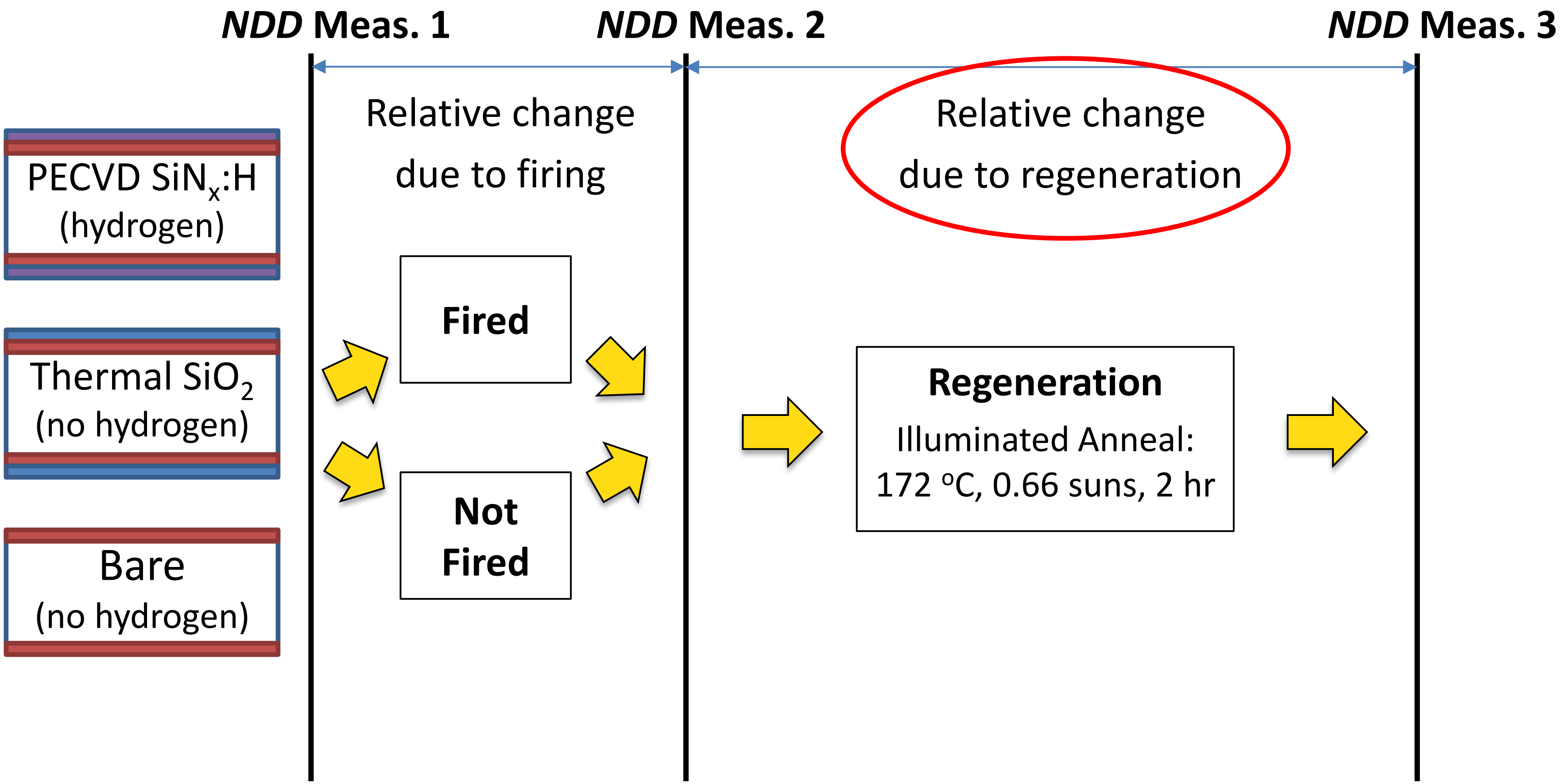
Light Soak: 35 ºC 0.77 suns, 48 hr

***NDD* Meas. 1**



Regeneration





***NDD* Meas. 1**

***NDD* Meas. 2**

***NDD* Meas. 3**

PECVD SiN_x:H
(hydrogen)

Thermal SiO_2
(no hydrogen)

Bare
(no hydrogen)

Relative change
due to firing

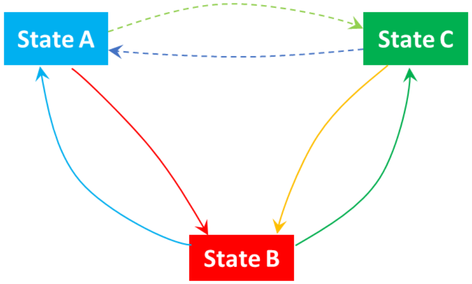
Fired

Not Fired

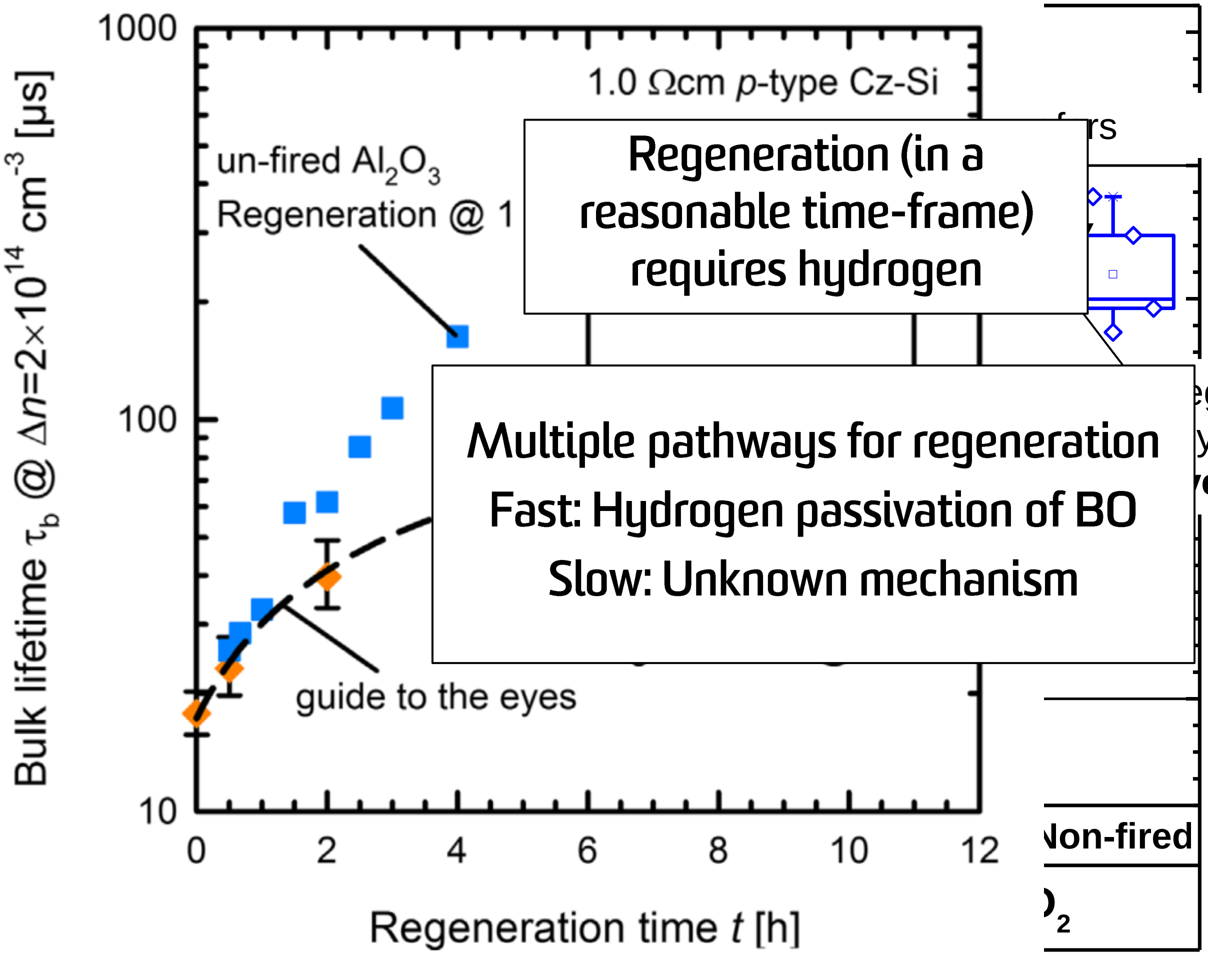
Relative change
due to regeneration

Regeneration

Illuminated Anneal:
172 °C, 0.66 suns, 2 hr



Regeneration



Regeneration (in a reasonable time-frame) requires hydrogen

Multiple pathways for regeneration

Fast: Hydrogen passivation of BO

Slow: Unknown mechanism

egeneration observed in ydrogen-lean samples **ery long time scales**)

D. Walter and J. Schmidt, Solar Energy Materials and Solar Cells 158, p.91-97 (2016)

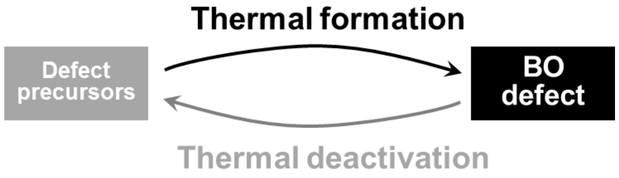
Deactivation mechanisms

- Why does regeneration occur?

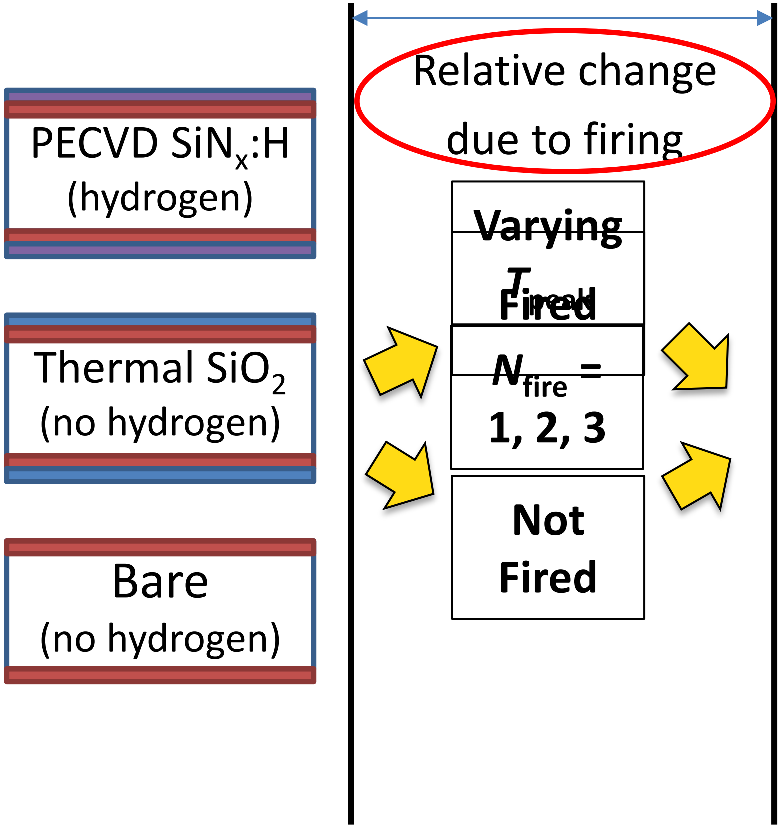
- Why does thermal deactivation occur?

- Are they related?

Thermal deactivation



***NDD* Meas. 1** ***NDD* Meas. 2** ***NDD* Meas. 3**



Relative change due to firing

PECVD SiN_x:H (hydrogen)

Thermal SiO_2 (no hydrogen)

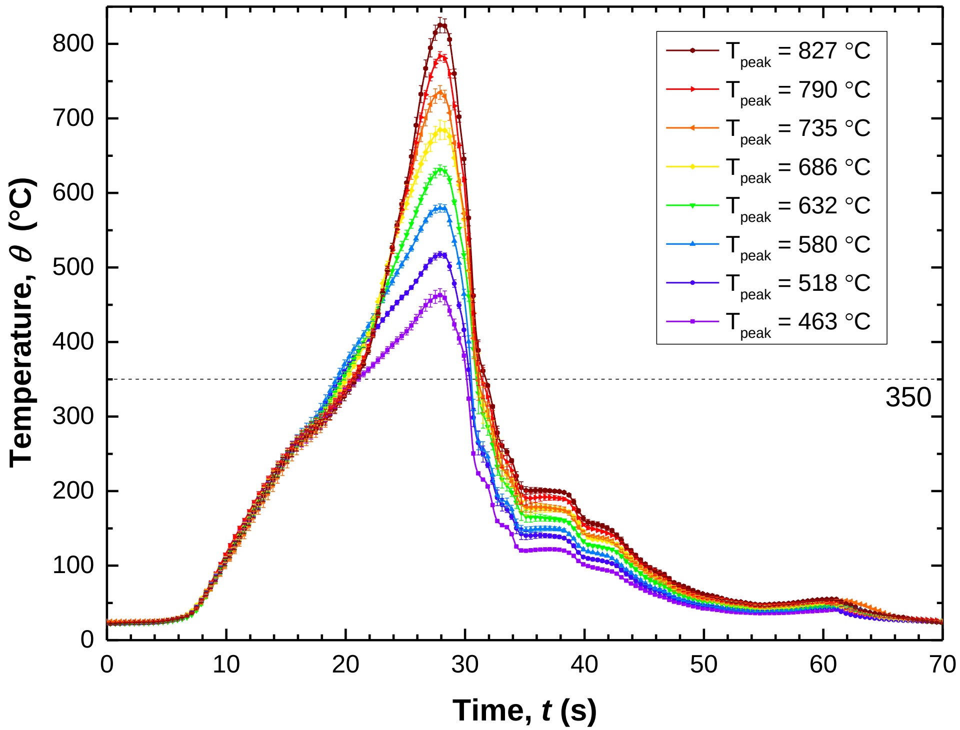
Bare (no hydrogen)

Varying T_{peak}

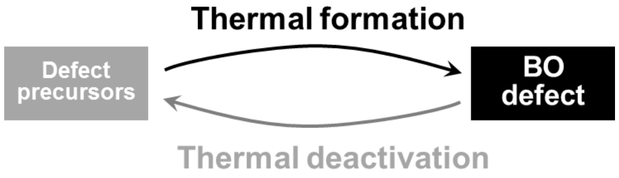
Fired

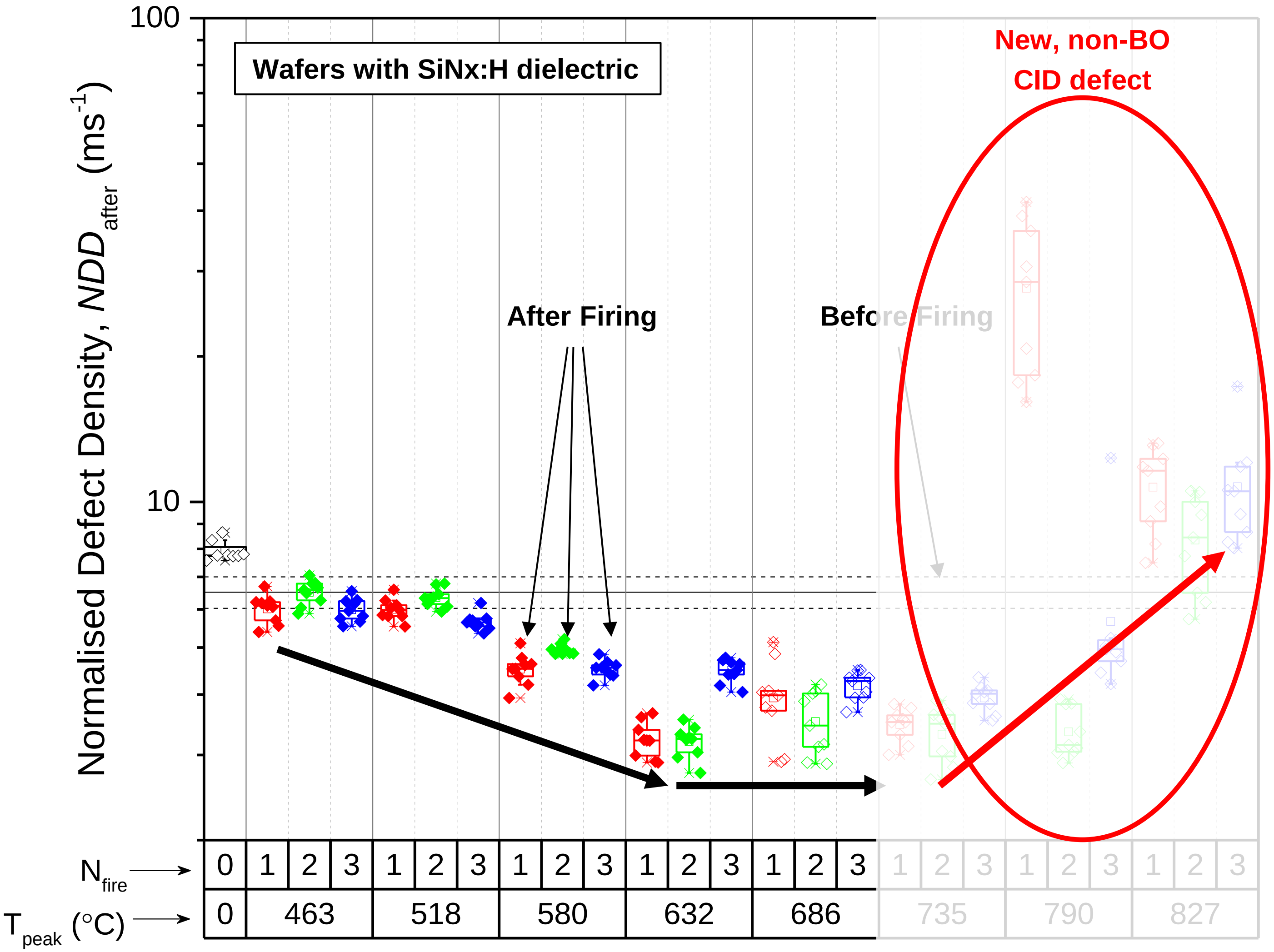
N_{fire} = 1, 2, 3

Not Fired



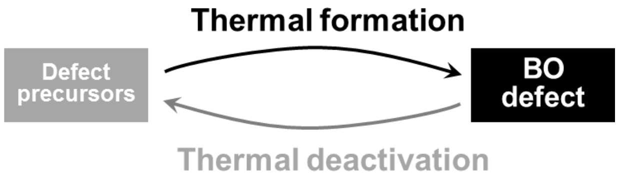
Thermal deactivation

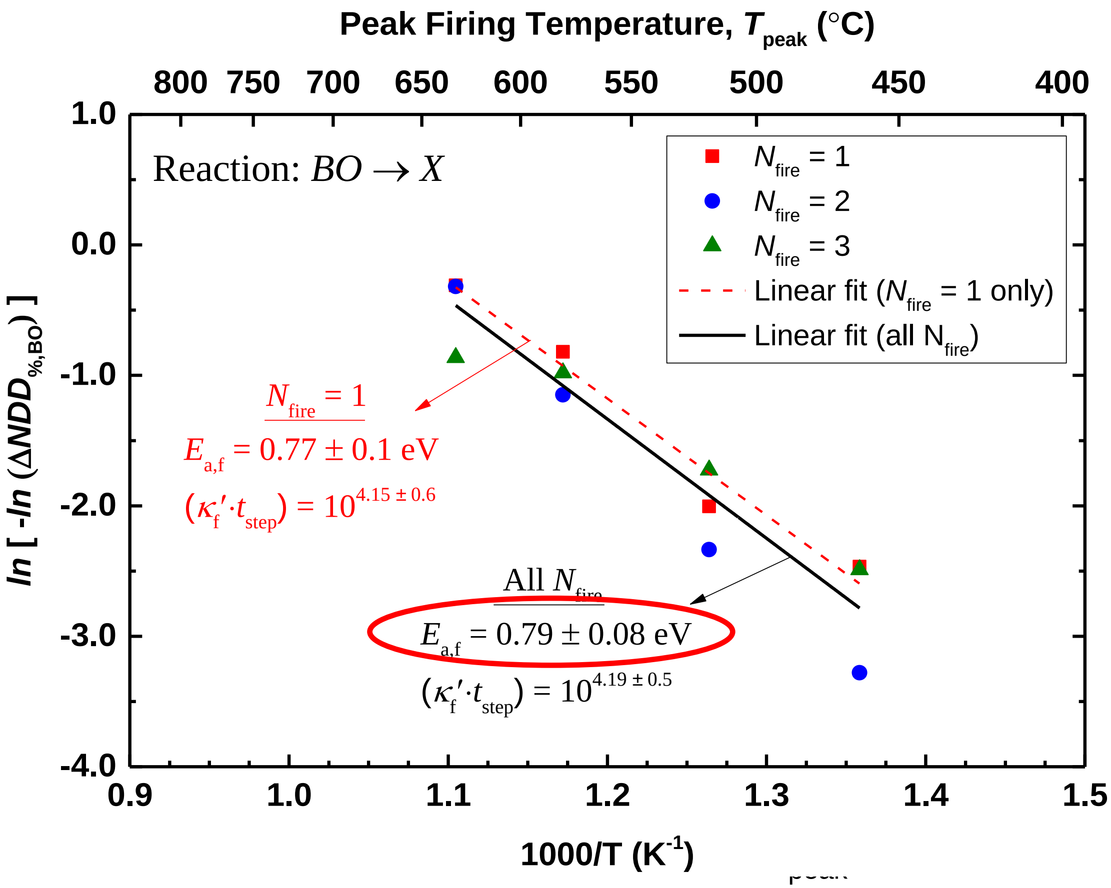




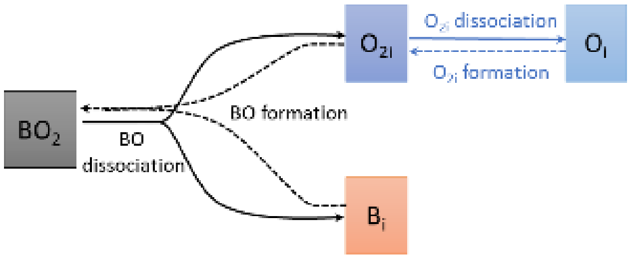
BO → X ?

Thermal deactivation



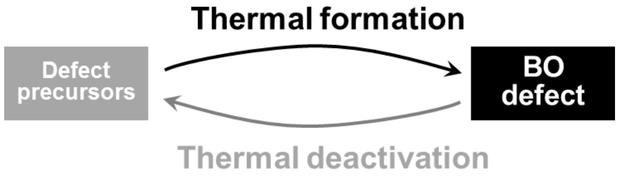


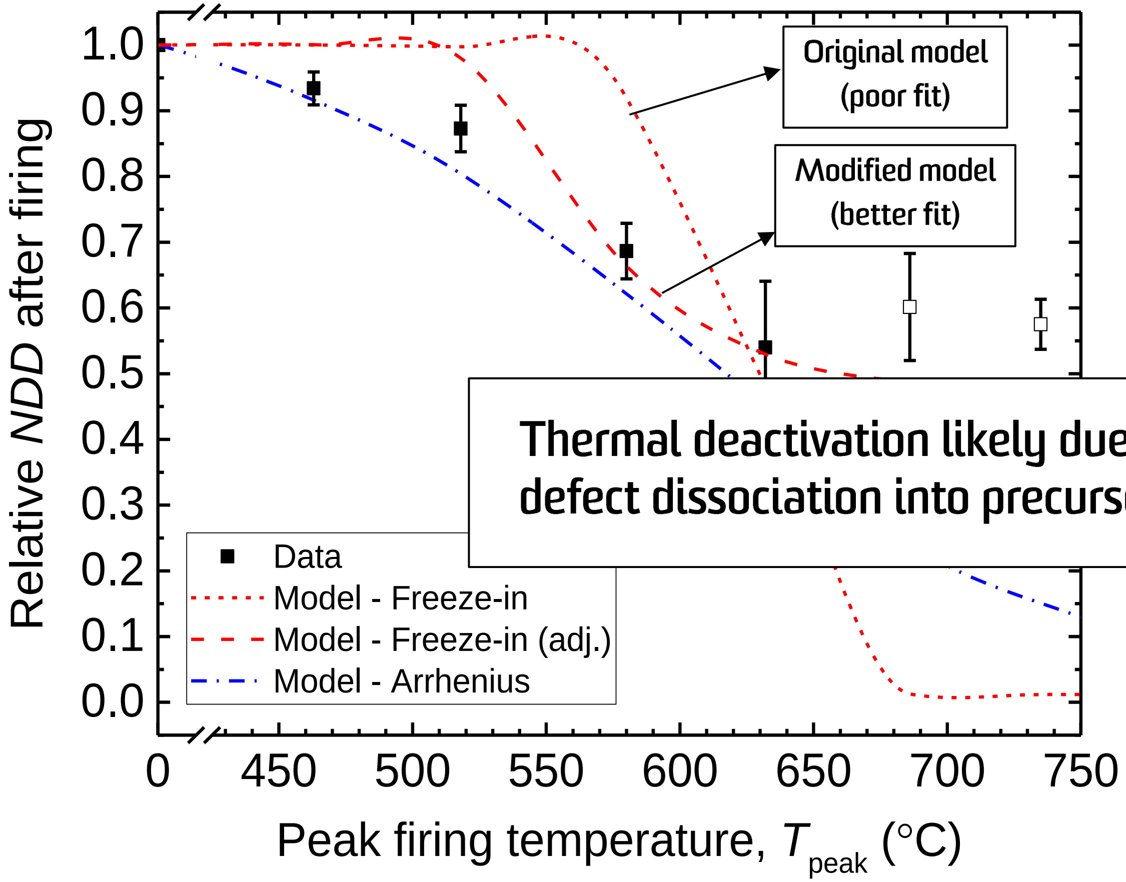
~~BO → X ?~~



V. Voronkov and R. Falster, Physica Status Solidi C 13(10-12), p. 712-717 (2016)

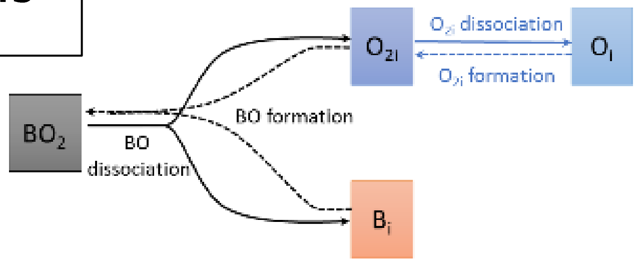
Thermal deactivation





Thermal deactivation likely due to defect dissociation into precursors

~~BO → X ?~~



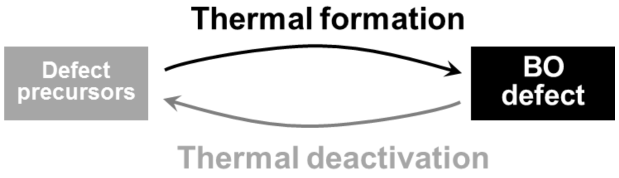
Fits OK, but needs adjustment

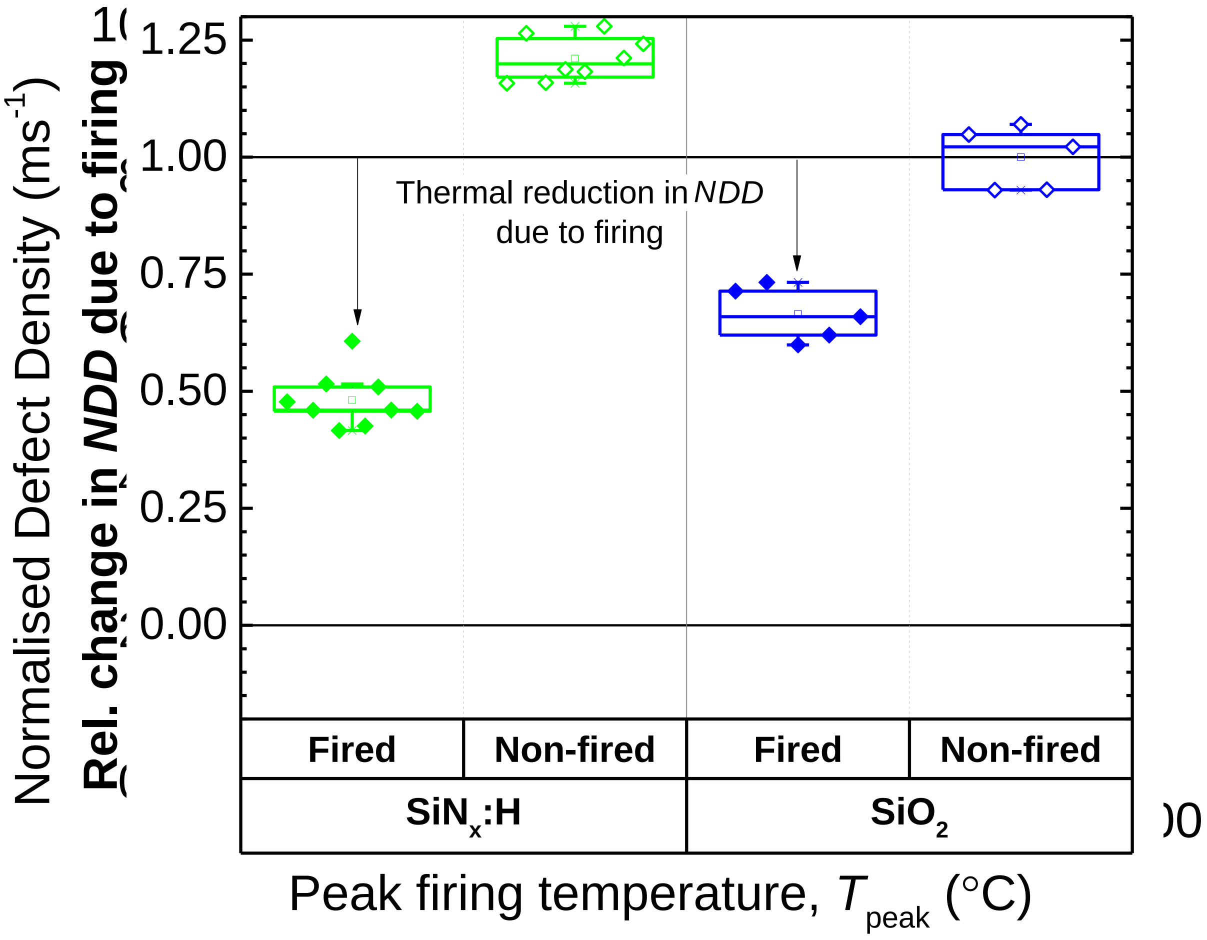
V. Voronkov and R. Falster, Physica Status Solidi C 13(10-12), p. 712-717 (2016)

Deactivation mechanisms

- Why does regeneration occur?
- Why does thermal deactivation occur?
- Are they related?

Thermal deactivation



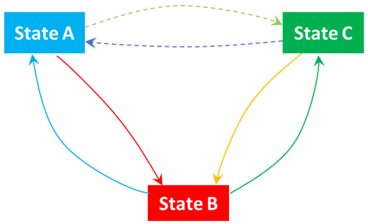


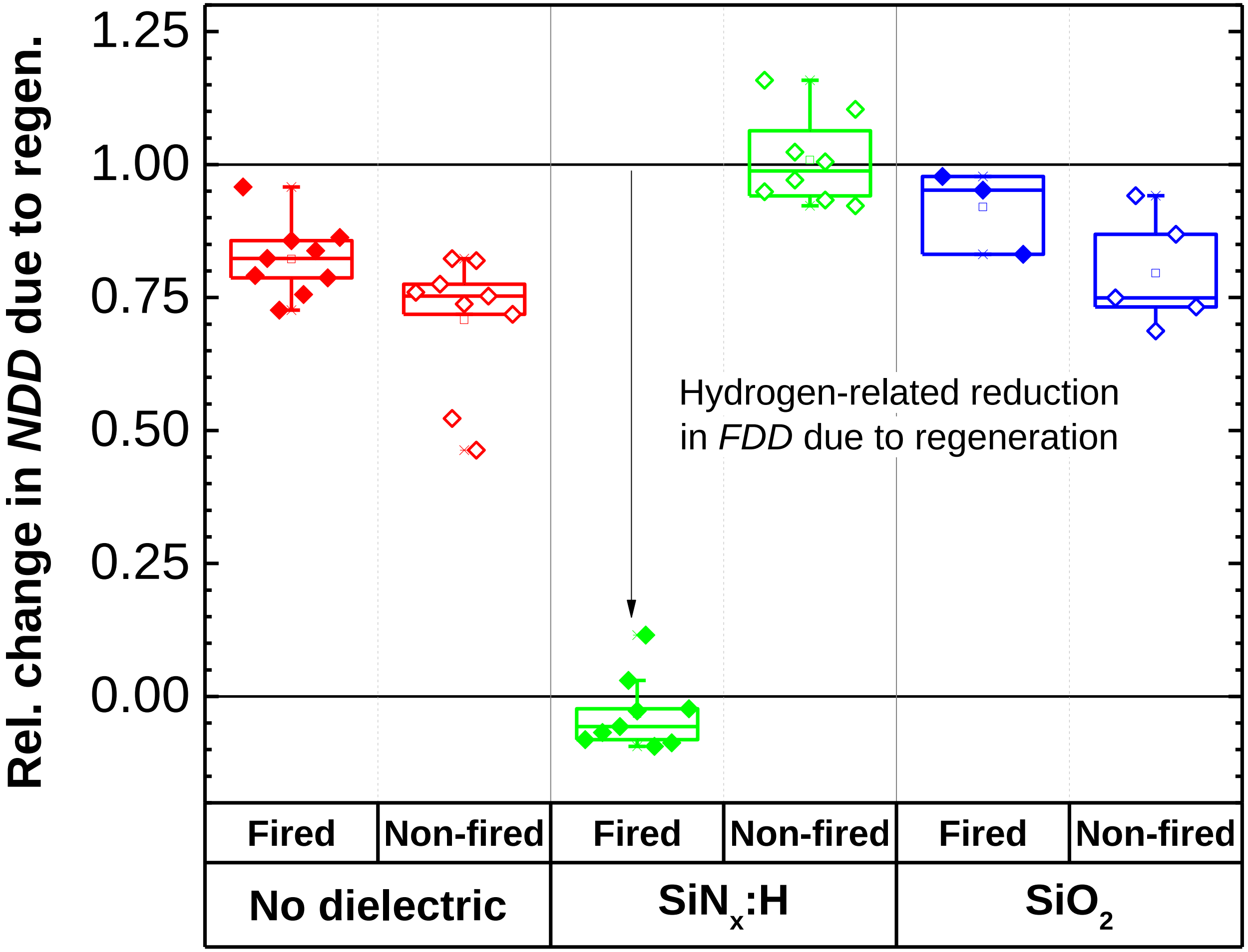
Impact of dielectric

Similar thermal reduction in oxide & nitride passivated samples

(i.e. Thermal deactivation is not hydrogen-related)

Regeneration





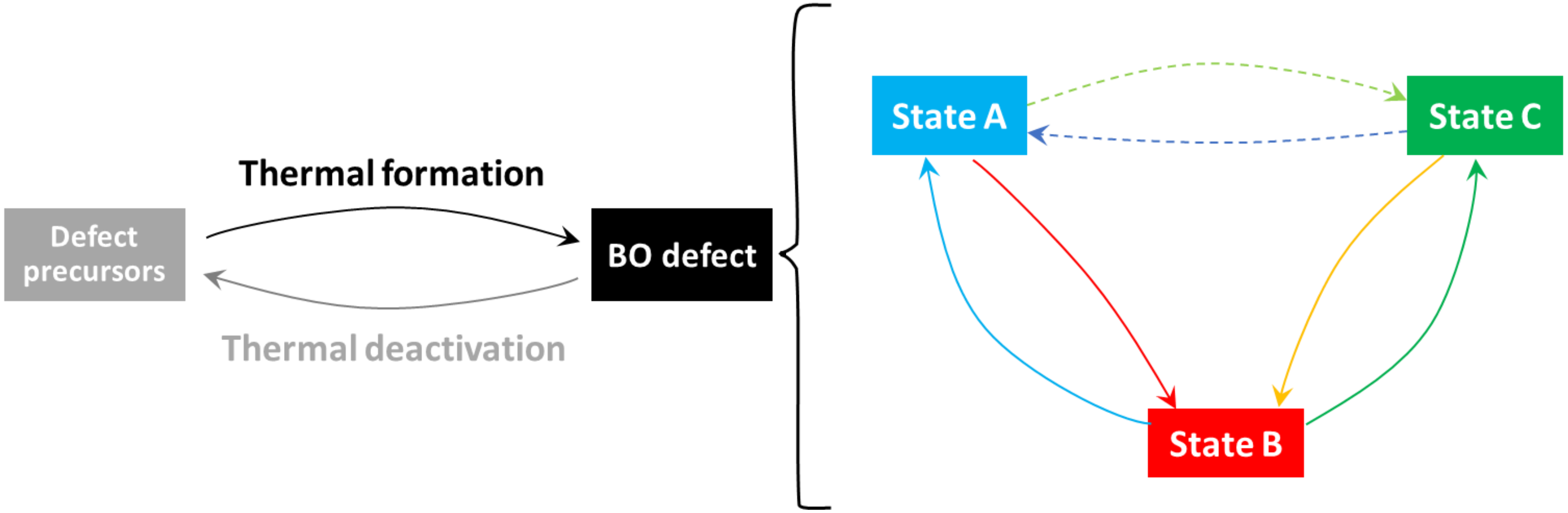
Similar thermal reduction in oxide & nitride passivated samples

(i.e. Thermal deactivation is not hydrogen-related)

Regeneration only occurs in nitride passivated samples

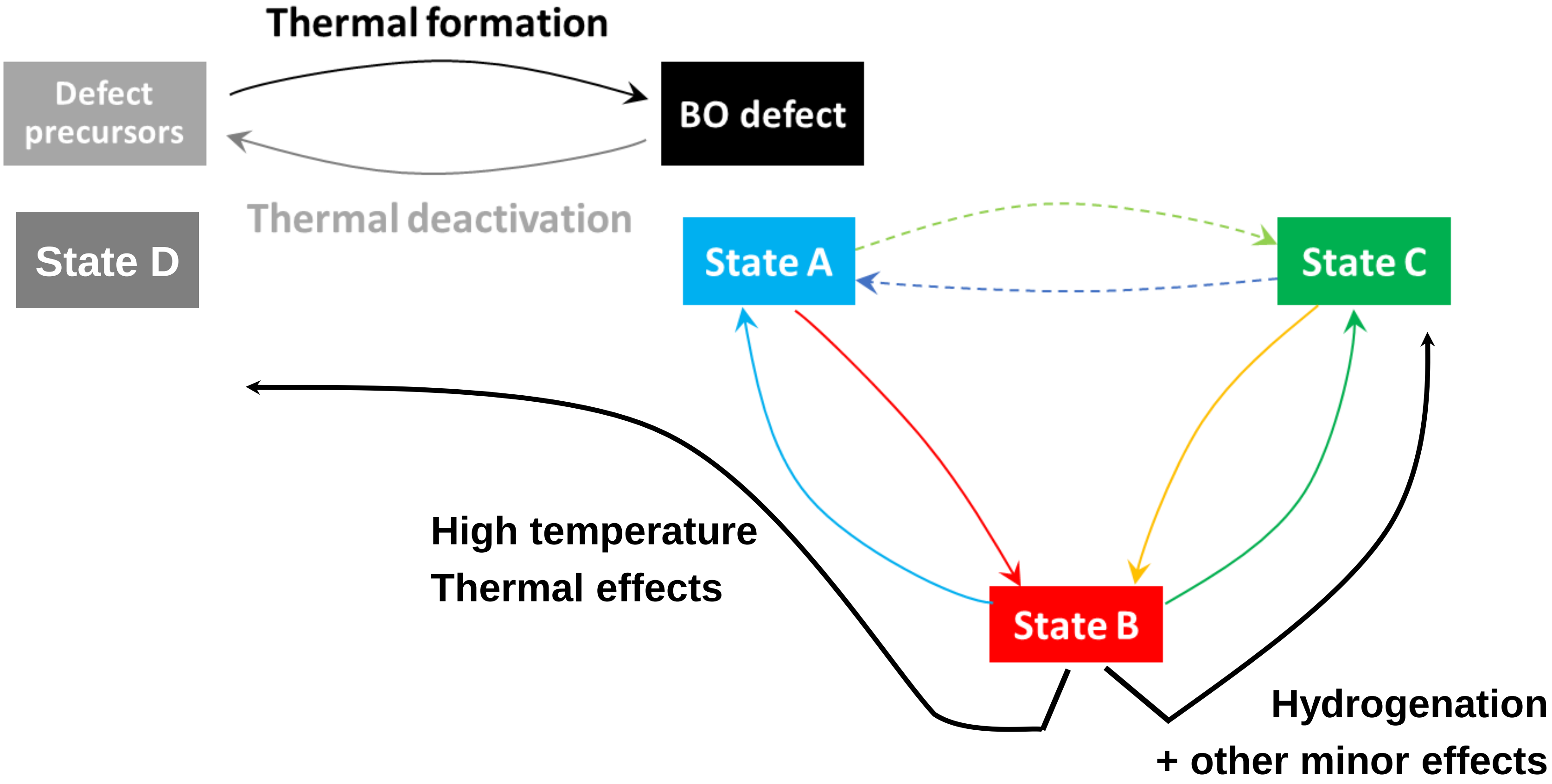
(i.e. Regen is hydrogen-related)

Revision to 3 state model?



Can they be combined?

4 state model



Thermal formation

Defect precursors

BO defect

Thermal deactivation

State D

State A

State C

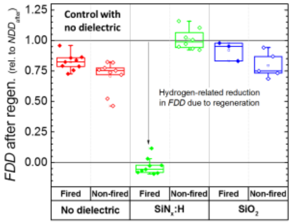
State B

High temperature
Thermal effects

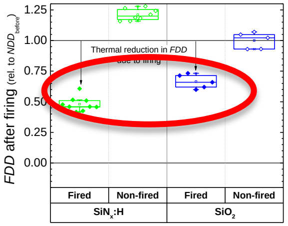
Hydrogenation
+ other minor effects

Summary – Permanent deactivation

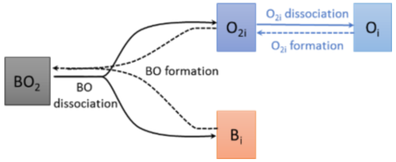
- Effective regeneration requires sufficient quantities of hydrogen. Regeneration could involve other mechanisms (slower).



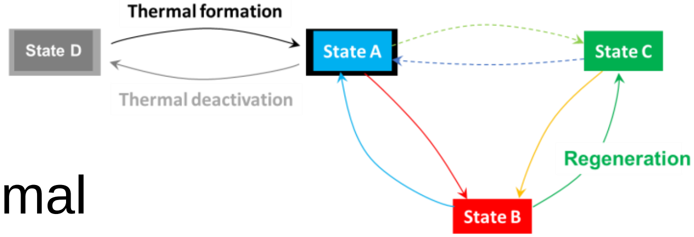
- Thermal deactivation occurs independent of regeneration. Likely not hydrogen-related.



- Thermal deactivation is likely to be defect dissociation



- 4-state model proposed to account for thermal deactivation



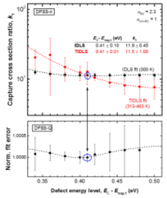
Implications of this work

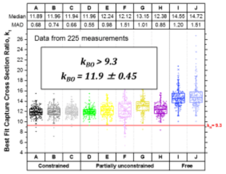
Never Stand Still

Engineering

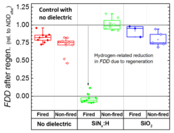
Implications

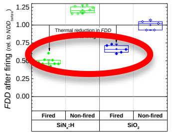
1. Improved understanding of the BO defect



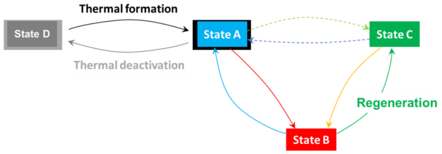


- Recombination properties





- Mechanism of permanent deactivation



- 4-state model

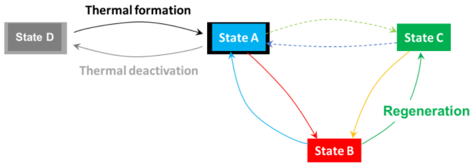
Impact:

- Easier identification of the BO defect

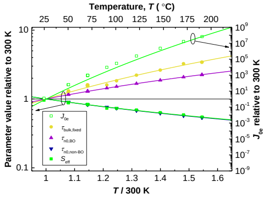
- Multiple, tailored solutions to mitigate BO defect

Implications

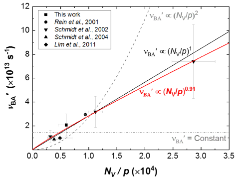
2. Accurate reaction kinetics modelling for BO

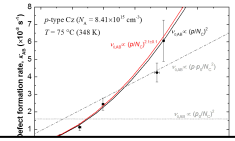


- 4-state model



- Conversion from $\tau_{\mathrm{eff}}(300K)$ to $\tau_{\mathrm{eff}}(T)$





- Carrier dependence of reactions

Impact:
- Better estimate of regeneration time-scales for industrial wafers / solar cells

Acknowledgements

- Funding sources
  - Australian Renewable Energy Agency (ARENA)
  - Australian Center for Advanced Photovoltaics (ACAP)
  - UK Institution of Engineering and Technology (IET) / A.F. Harvey Engineering Prize.
  - Commercial partners (ARENA 1-A060)

CanadianSolar

MEYER BURGER

Sunport

科嶠工業股份有限公司
ASIA NEO TECH INDUSTRIAL CO., LTD

CECENERGY
PTE LTD

ACAP

tindo solar

TW SOLAR

DR Laser

LONGi 隆基

APOLLON SOLAR

Sunrise
Global Solar Energy

ARENA

Australian Government
Australian Renewable Energy Agency

FOLUNGWIN

KUTTLER
AUTOMATION SYSTEMS

SCHMID

ROTH & RAU
CELL & COATING SYSTEMS

CSUN
energy for the future

SUNTECH
BE UNLIMITED

Acknowledgements

- Supervisors: Malcolm Abbott, Stuart Wenham, Matt Edwards

- Hydrogenation group

- Laboratory:
  - MAiA processing team
  - LDOT team
  - Others

- Admin staff:
  - TETB
  - SPREE

- Friends and family

Thank you for your attention

nnampalli@gmail.com

Motivation

- *p*-type silicon dominant for forseeable future
- PERC cells seeing an increasing market share
- Surface passivation quality is improving
- “Reliable kWh” is increasingly important

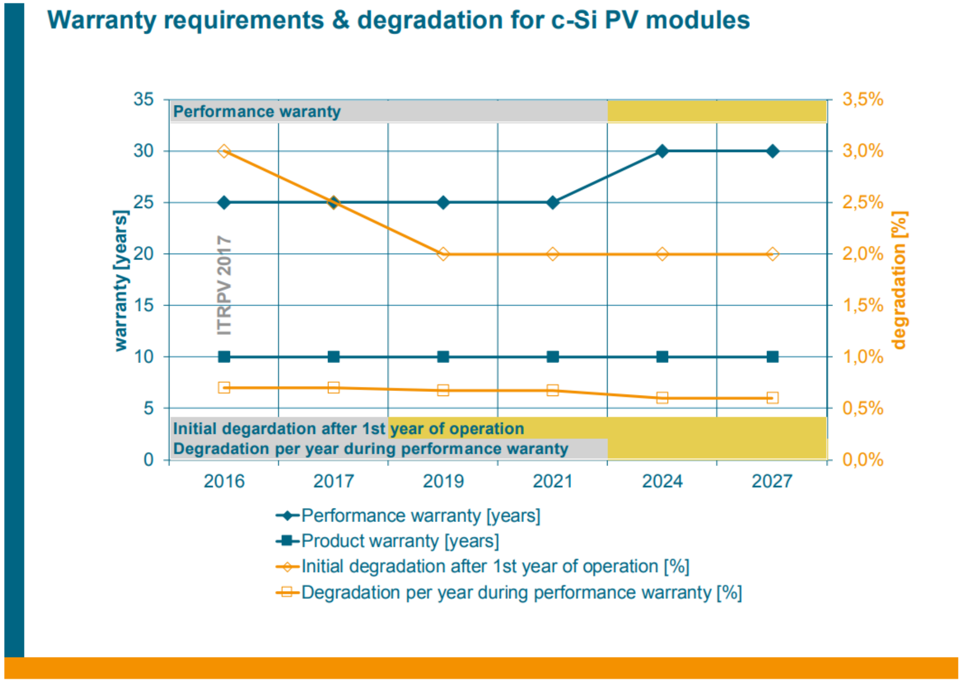


Fig. 48: Expected trend for product warranties and degradation of c-Si PV modules

International Technology Roadmap for Photovoltaics, 8th Edition, 2017.