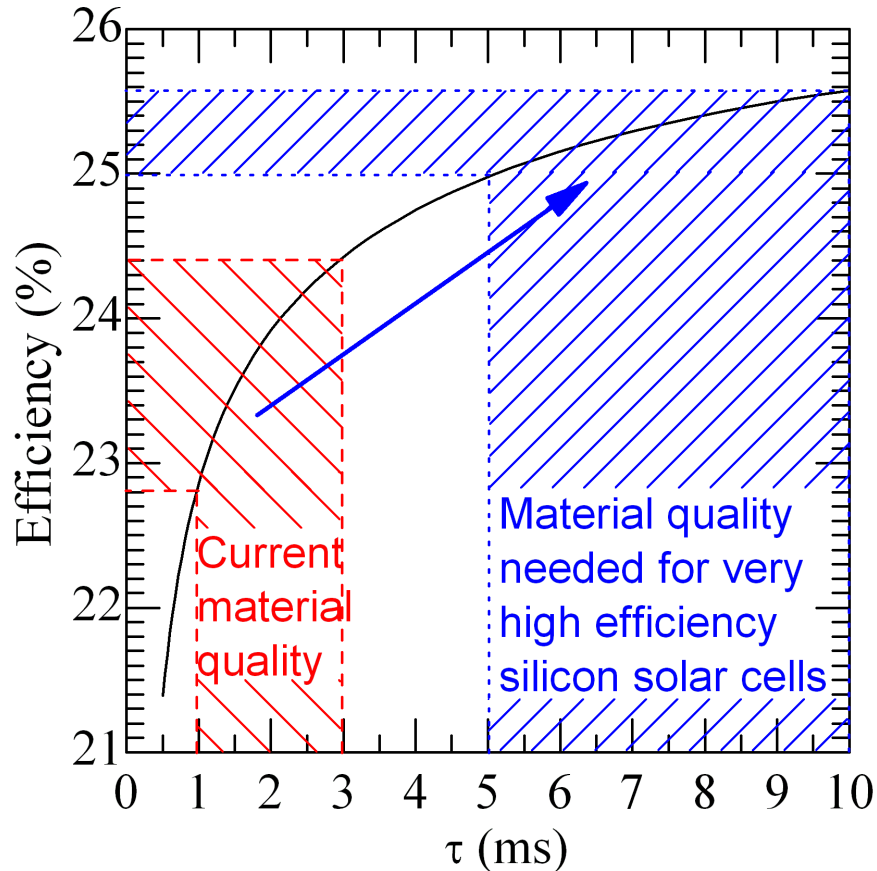


Materials related challenges en route to very high efficiency n-type silicon solar cells

F.E. Rougieux

Research School of Engineering, The Australian National University

What are the lifetime requirement for high efficiency devices?



- Multi milliseconds lifetime for very high efficiency silicon solar cells
- What are the material related challenges to achieve high lifetime?

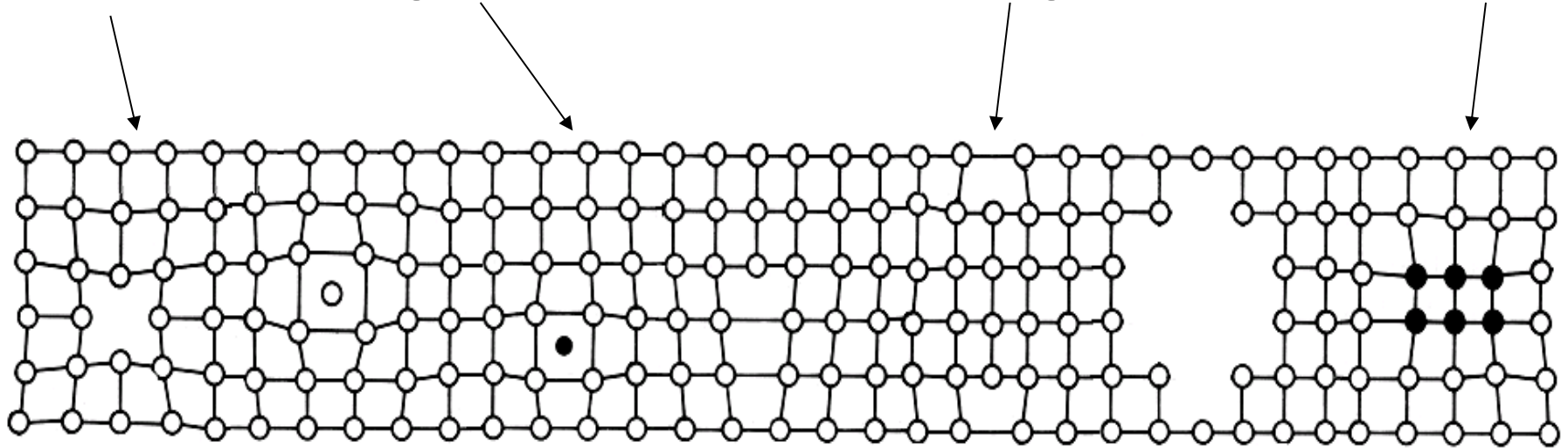
Modified from P. J. Cousins et al. *35th IEEE PVSC*, (2010)

Outline

- **Grown-in extended defects**
- Characterizing as-grown defects
- Grown-in point defects in n-type CZ
- Grown-in point defects in n-type FZ

What grown-in defects are we looking at?

Vacancy Foreign interstitial Stacking Fault Precipitate



Silicon interstitial

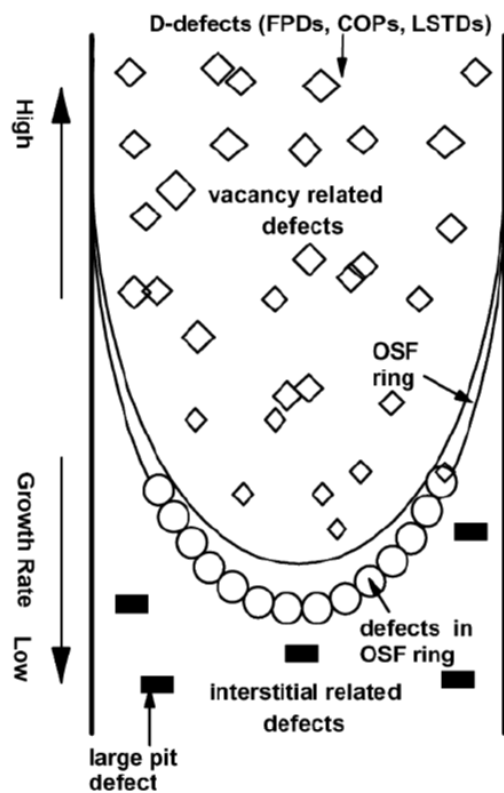
Dislocation

Void

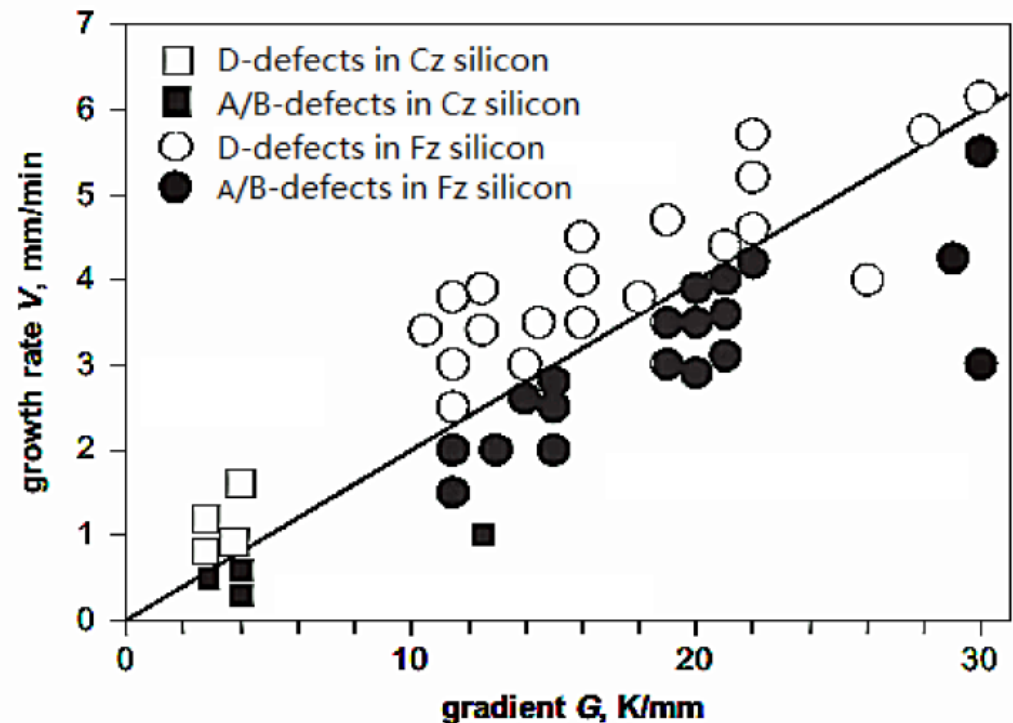
(COP, FPD, D-defects)

Effect of growth rate on defect types

Voronkov criteria v/G

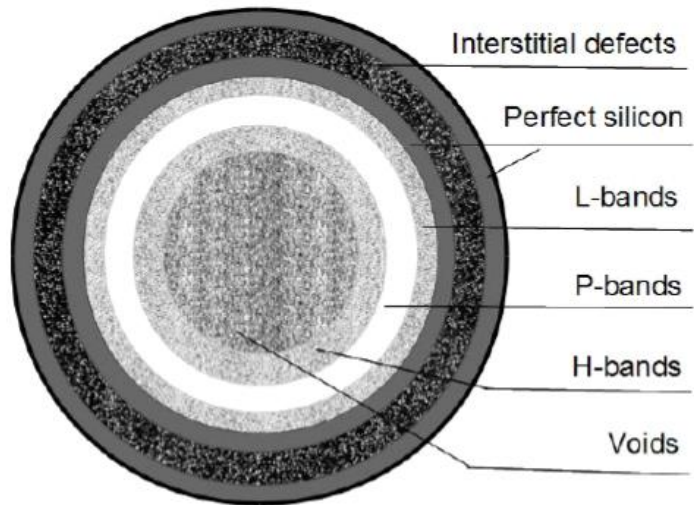


Dornberger et al. J. Cryst. Gr. (2001)



Voronkov et al. J. Cryst. Gr. (2008)

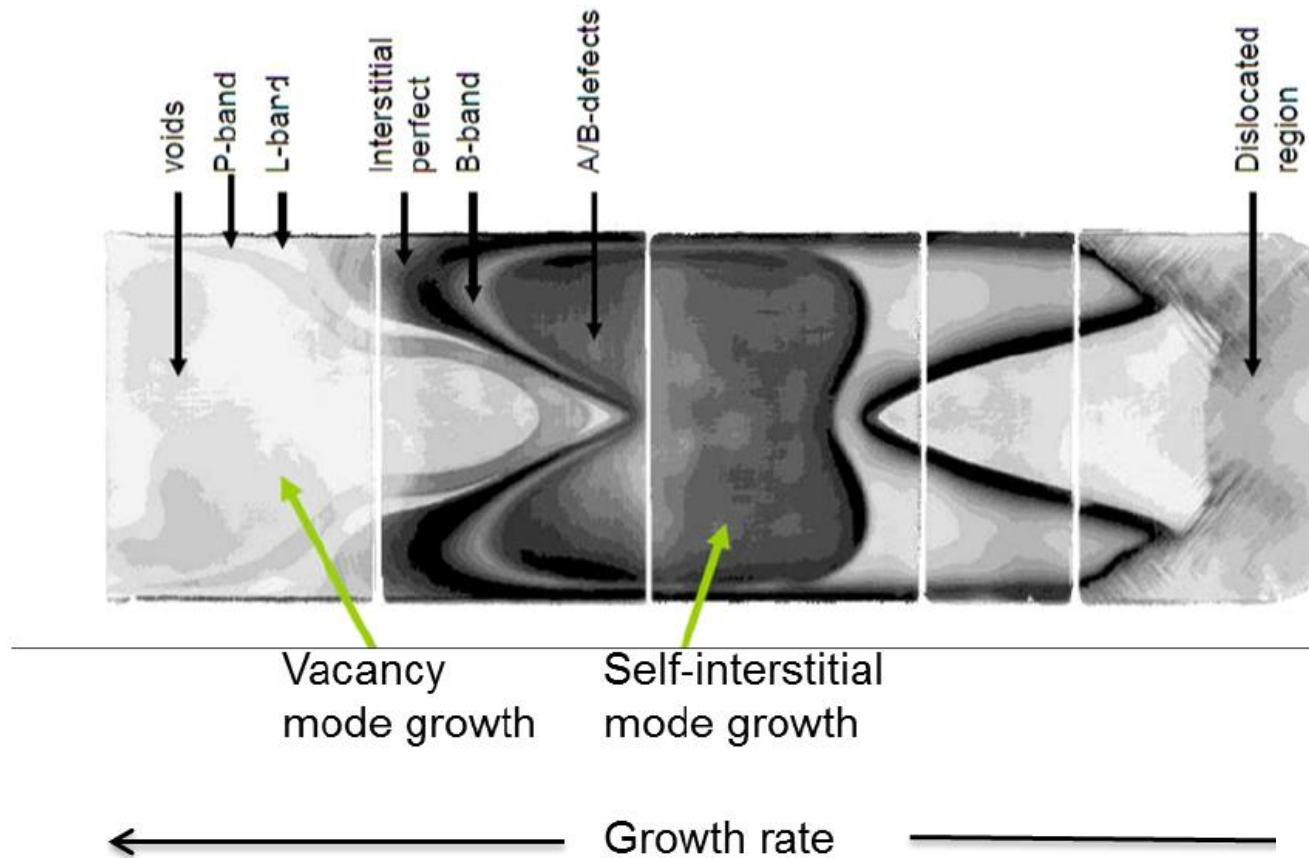
Cross section of a wafer with vacancy rich and interstitial rich silicon



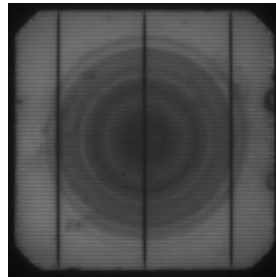
Y. Hu et al 26 EUPVSEC (2011)

- V : growth rate
- G : axial temperature gradient
- High V/G (fast pulling rate): Vacancy mode
- Low V/G (slow pulling rate): Interstitial mode
- Intermediate V/G : P (Particle) band, H (High vacancy) band, L (low vacancy) band

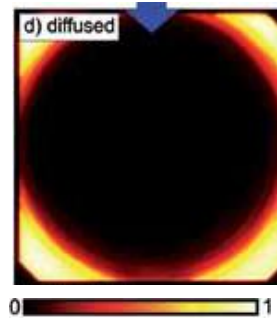
Effect of growth rate on defect distribution



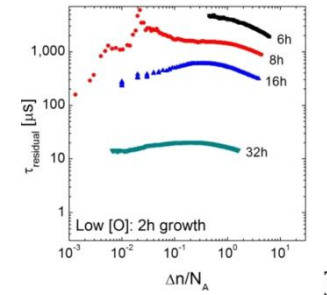
Oxygen precipitates



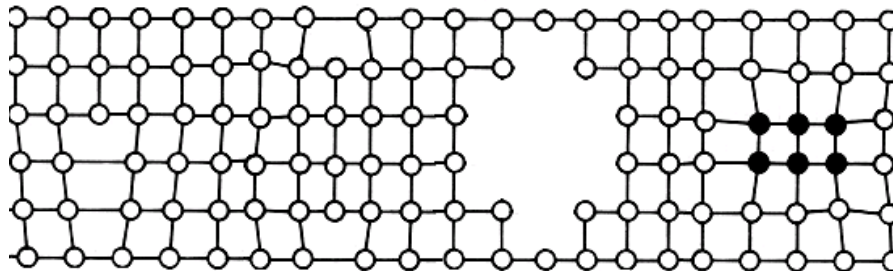
M. Forster et al. N-PV workshop (2014).



J. Haunschild et al. *phys. stat. sol. RRL* (2011)



J. D. Murphy et al. *J. Appl. Phys.* (2012).

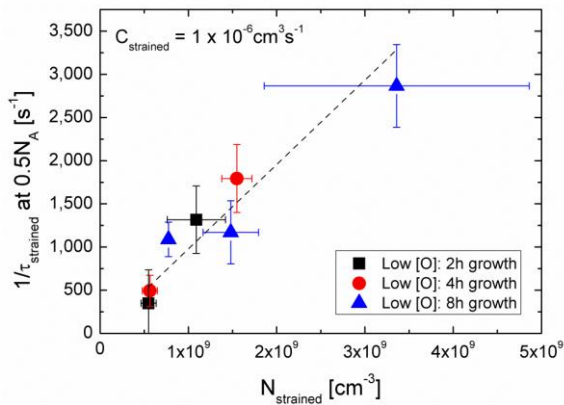


Modified from F. Shimura, "Semiconductor silicon crystal technology" (1989)

Oxygen precipitates and high temperature processing

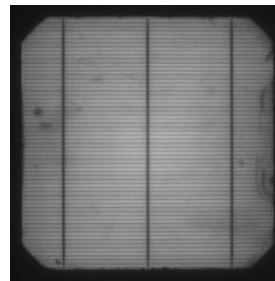
Increased precipitate density

Strained precipitates

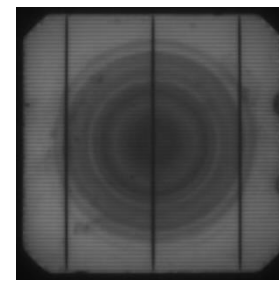


J. D. Murphy et al. *J. Appl. Phys.* (2011).

Metallic decoration

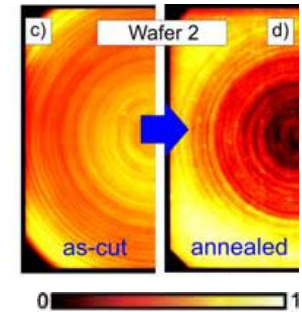


Clean cell process



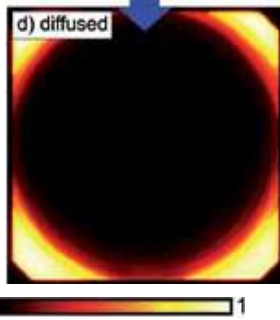
Non-clean cell process

M. Forster et al. N-PV workshop (2014).

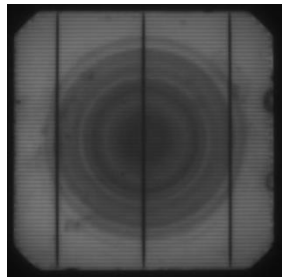


J. Haunschild et al. *phys. stat. sol. RRL* (2011)

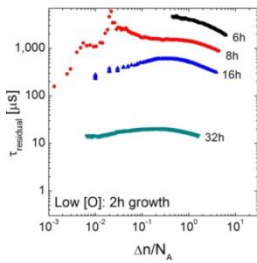
Oxygen precipitates



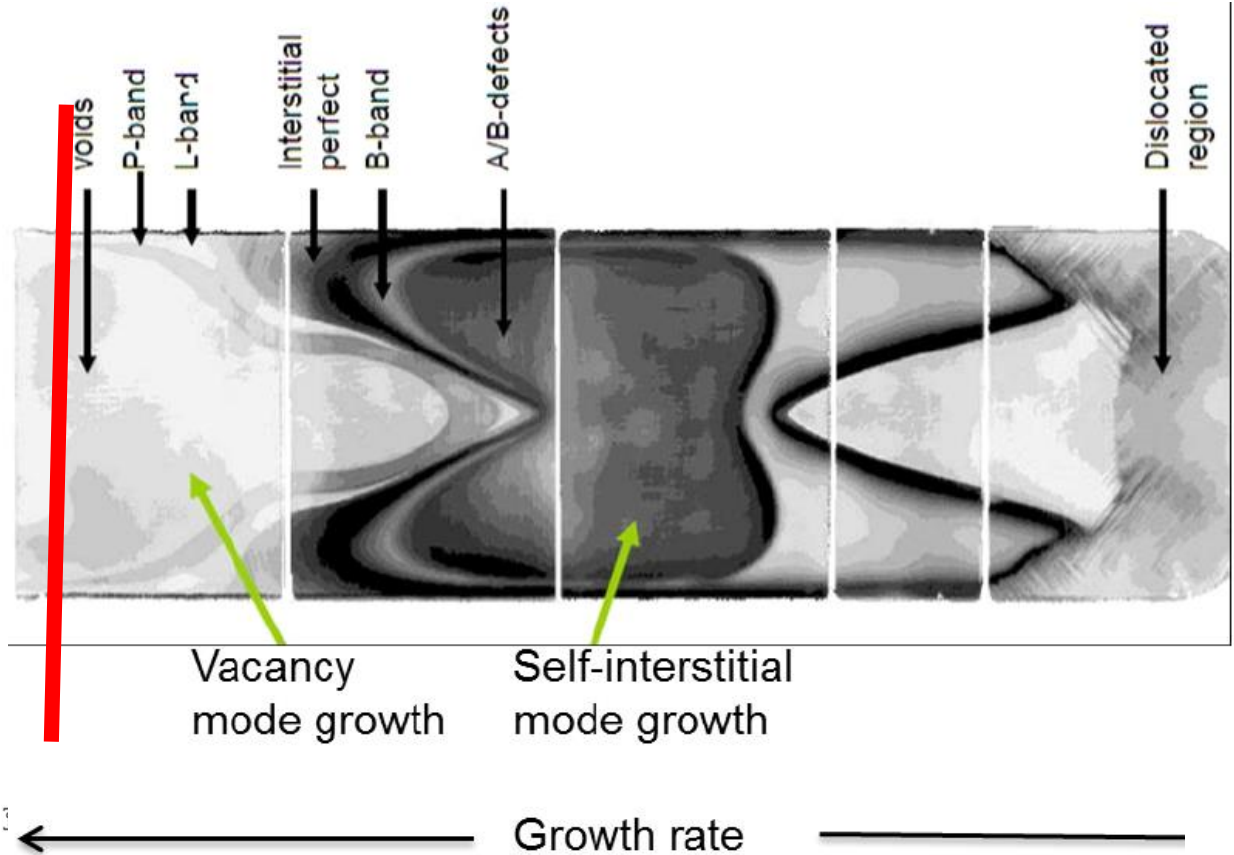
J. Haunschild et al. *phys. stat. sol. RRL* (2011)



M. Forster et al. N-PV workshop (2014).

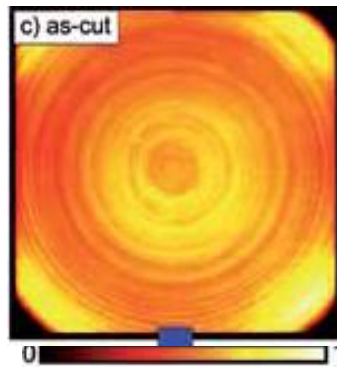


J. D. Murphy et al. *J. Appl. Phys.* (2012).

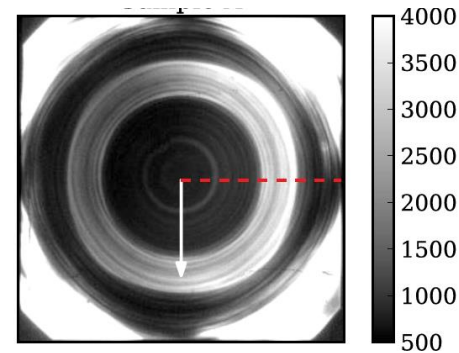


R. Falster *Phys. Stat. Solidi* (2000)

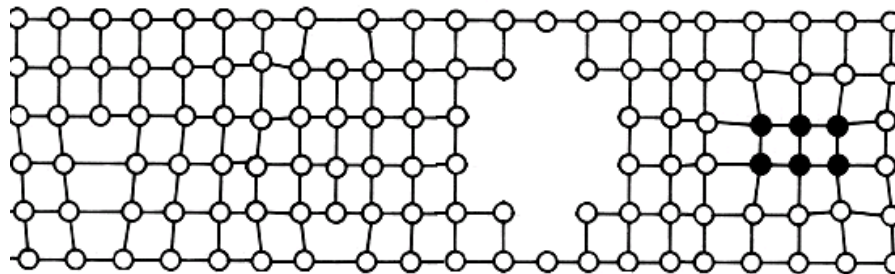
Stacking faults



J. Haunschild et al. *phys. stat. sol. RRL* (2011)

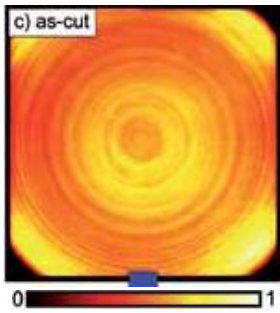


Angelskar et al. *Energy Procedia* (2012)

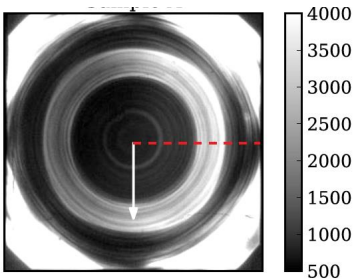


Modified from F. Shimura, "Semiconductor silicon crystal technology" (1989)

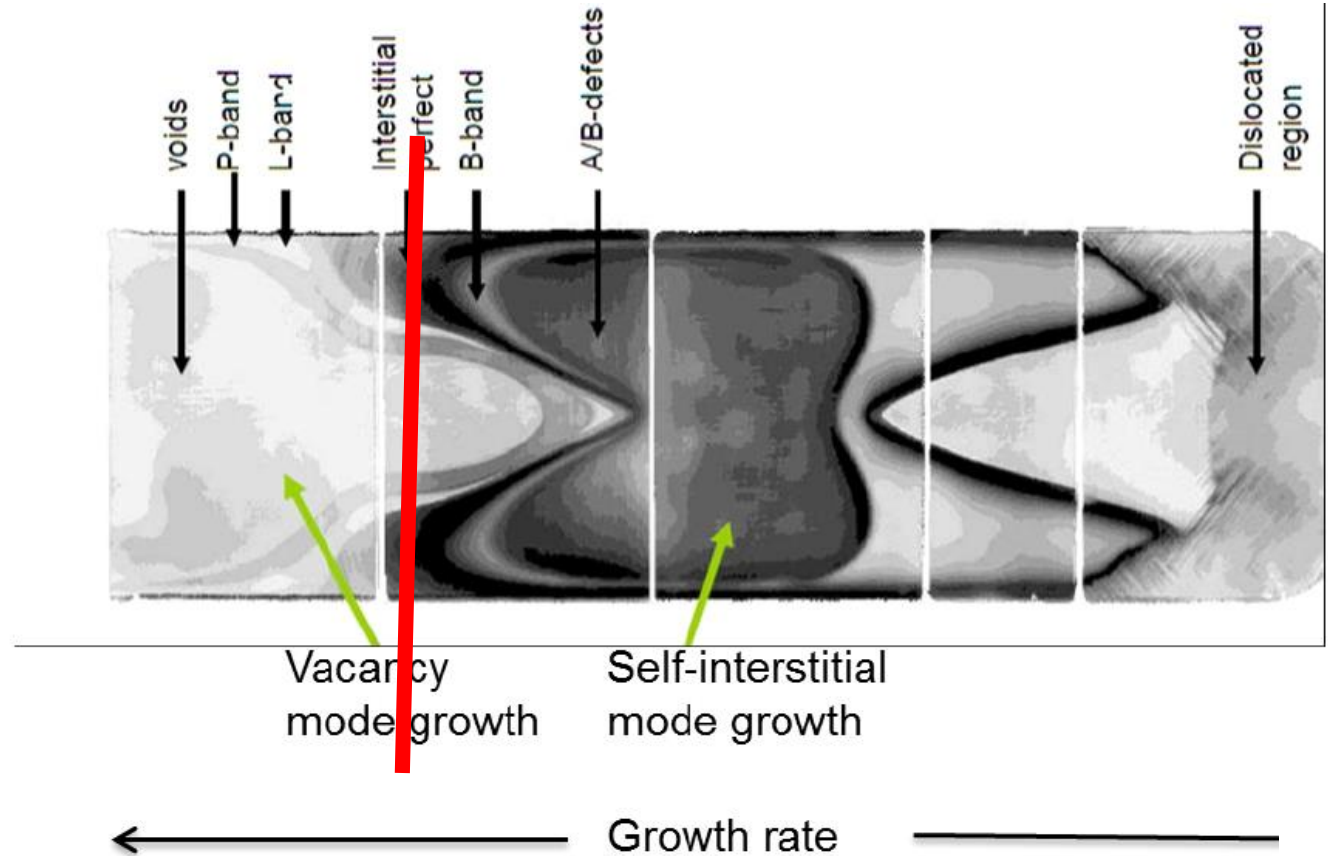
Stacking faults



J. Haunschild et al. *phys. stat. sol. RRL* (2011)

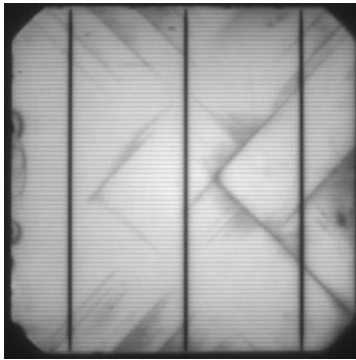


Angelskar et al. *Energy Procedia* (2012)

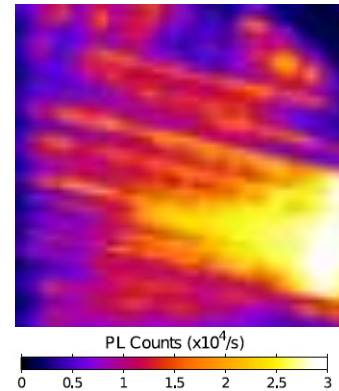


R. Falster *Phys. Stat. Solidi* (2000)

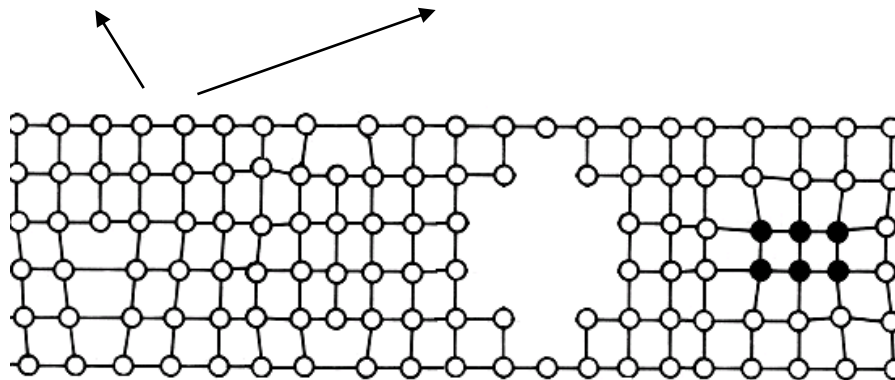
Dislocations



M. Forster et al. N-PV workshop (2014).

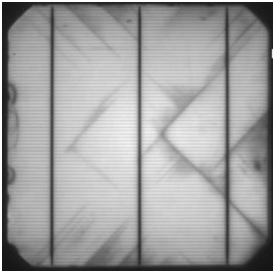


B. Hallam et al. IEEE JPV (2014)

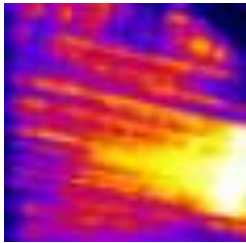


Modified from F. Shimura, "Semiconductor silicon crystal technology" (1989)

Dislocations

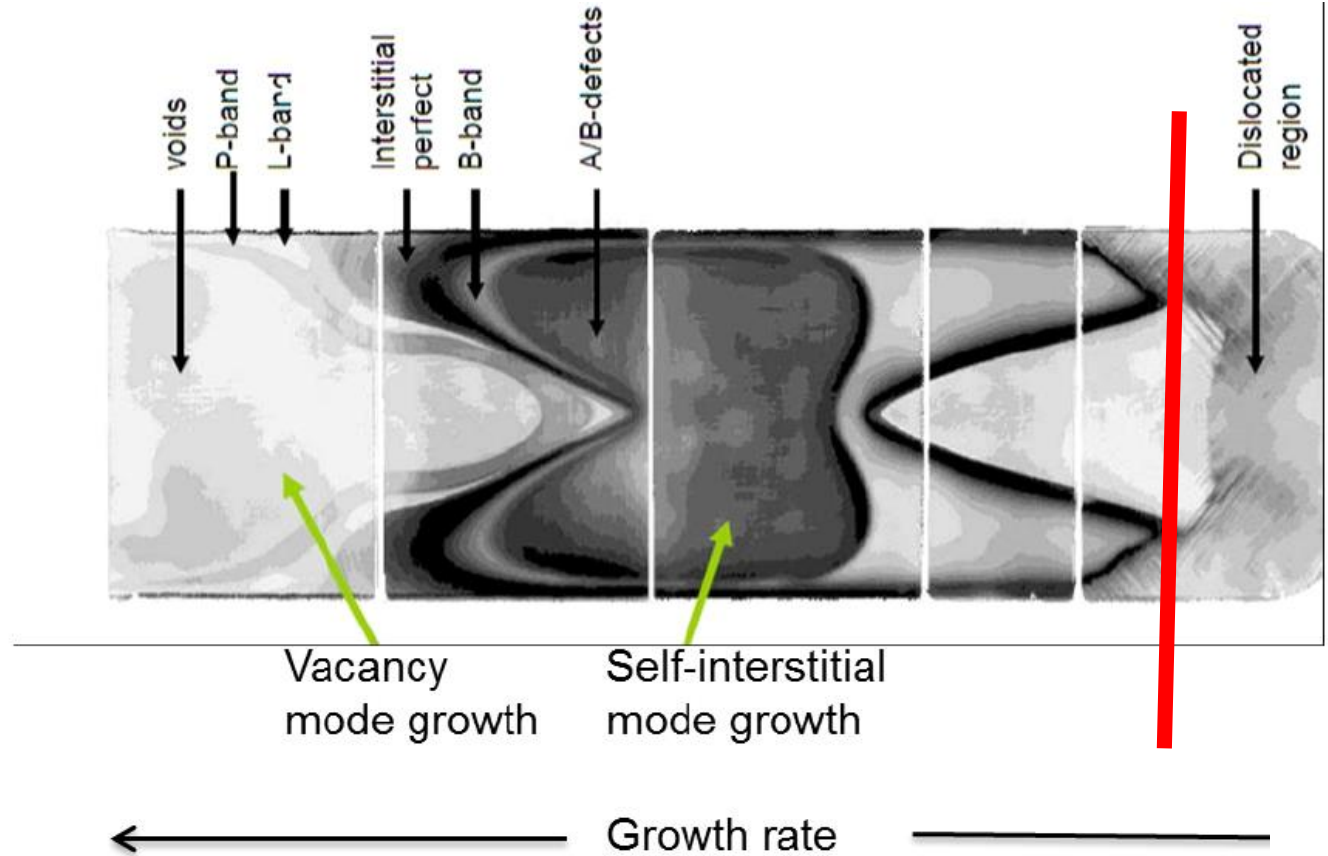


M. Forster et al. N-PV workshop (2014).



PL Counts ($\times 10^4/s$)
0 0.5 1 1.5 2 2.5 3

B. Hallam et al. IEEE JPV (2014)



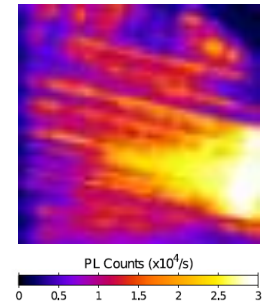
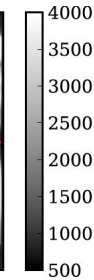
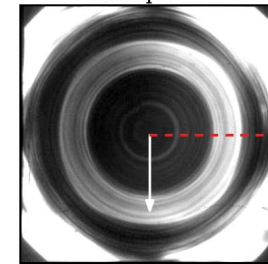
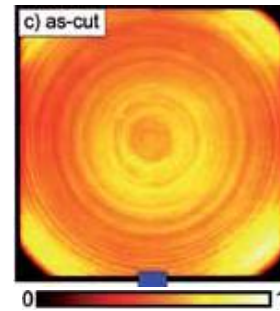
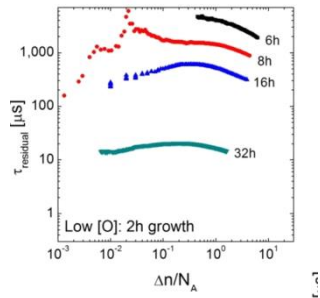
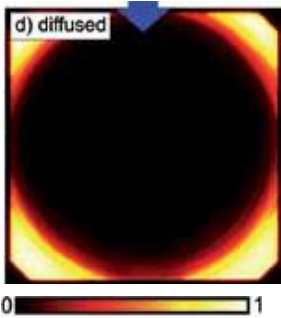
R. Falster Phys. Stat. Solidi (2000)

Grown-in and process-induced **extended** defects

Oxygen precipitates

Stacking faults

Dislocations



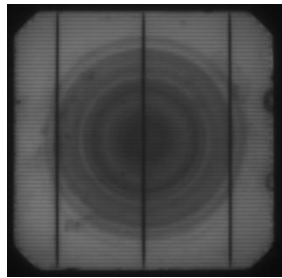
J. Haunschild et al. *phys. stat. sol. RRL* (2011)

J. D. Murphy et al. *J. Appl. Phys.* (2012).

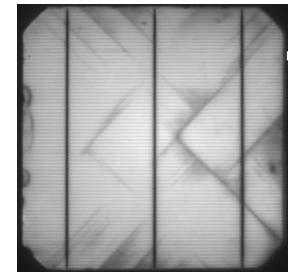
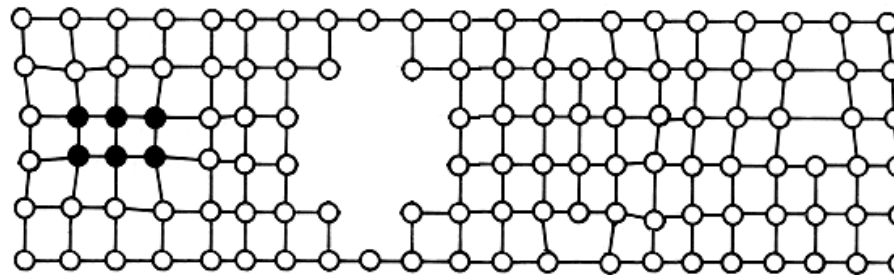
J. Haunschild et al. *phys. stat. sol. RRL* (2011)

Angelskar et al. *Energy Procedia* (2012)

B. Hallam et al. *IEEE JPV* (2014)



M. Forster et al. N-PV workshop (2014).



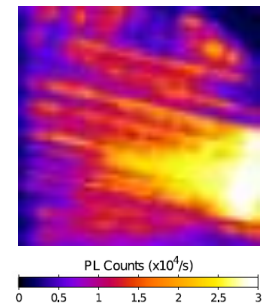
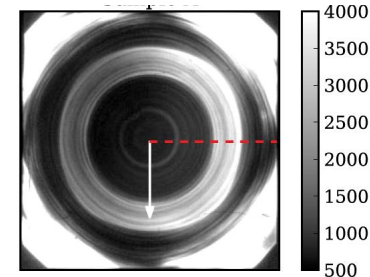
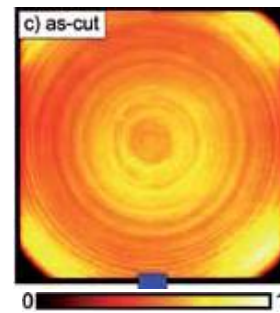
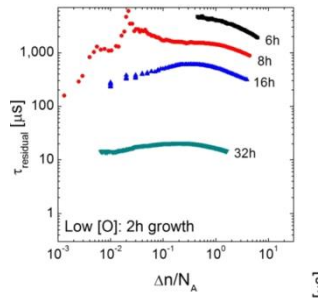
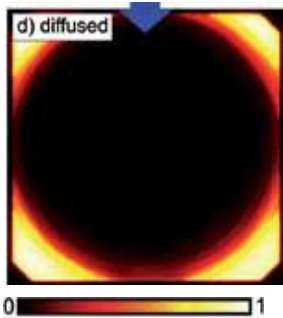
M. Forster et al. N-PV workshop (2014).

Grown-in and process-induced **extended** defects

Oxygen precipitates

Stacking faults

Dislocations



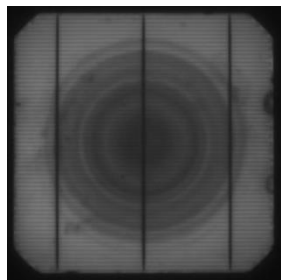
J. Haunschild et al. *phys. stat. sol. RRL* (2011)

J. D. Murphy et al. *J. Appl. Phys.* (2012).

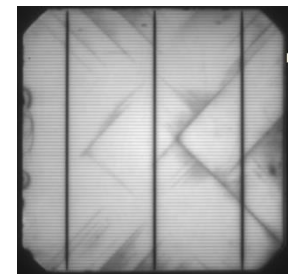
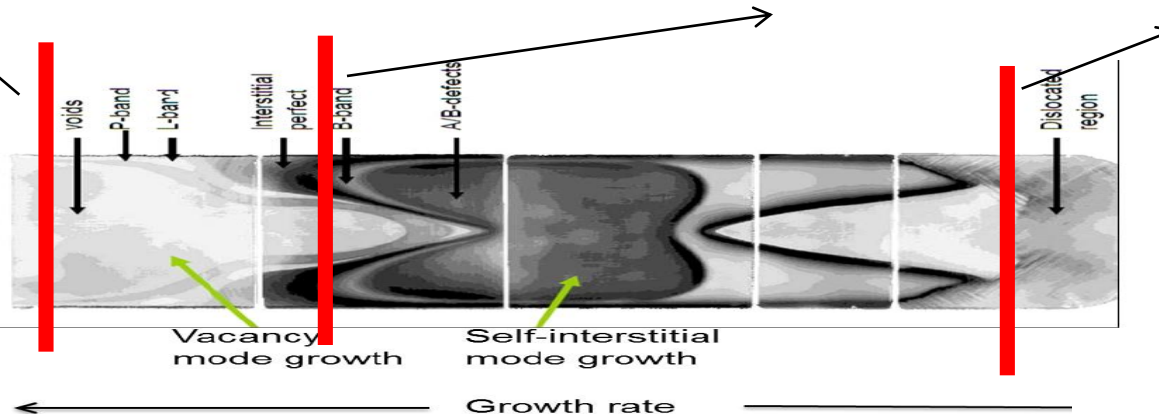
J. Haunschild et al. *phys. stat. sol. RRL* (2011)

Angelskar et al. *Energy Procedia* (2012)

B. Hallam et al. *IEEE JPV* (2014)



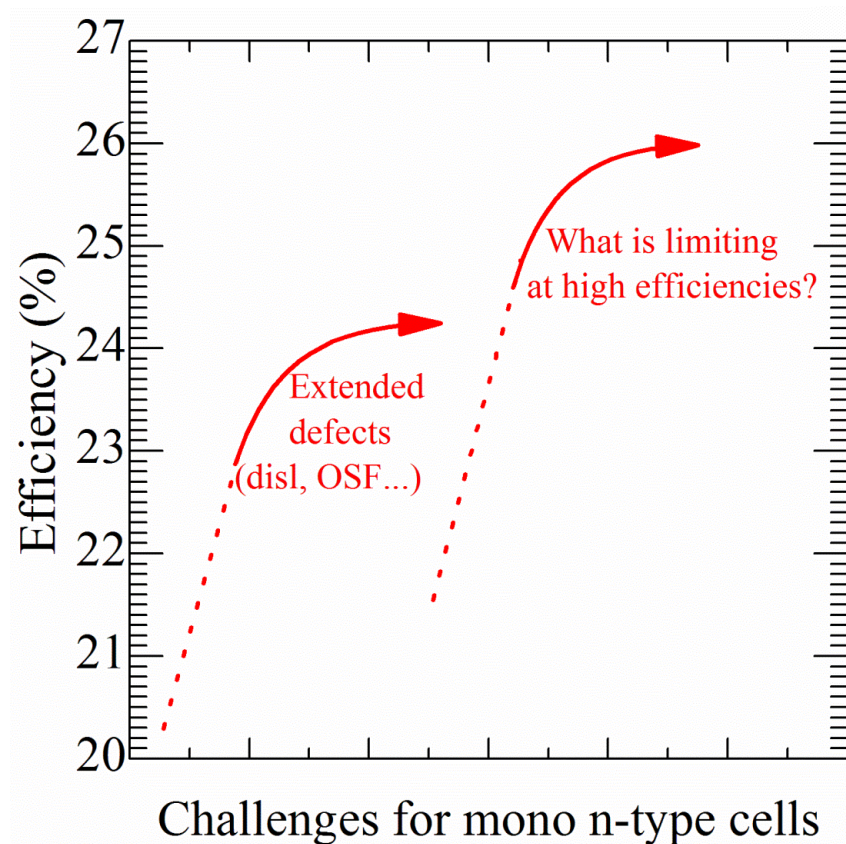
M. Forster et al. N-PV workshop (2014).



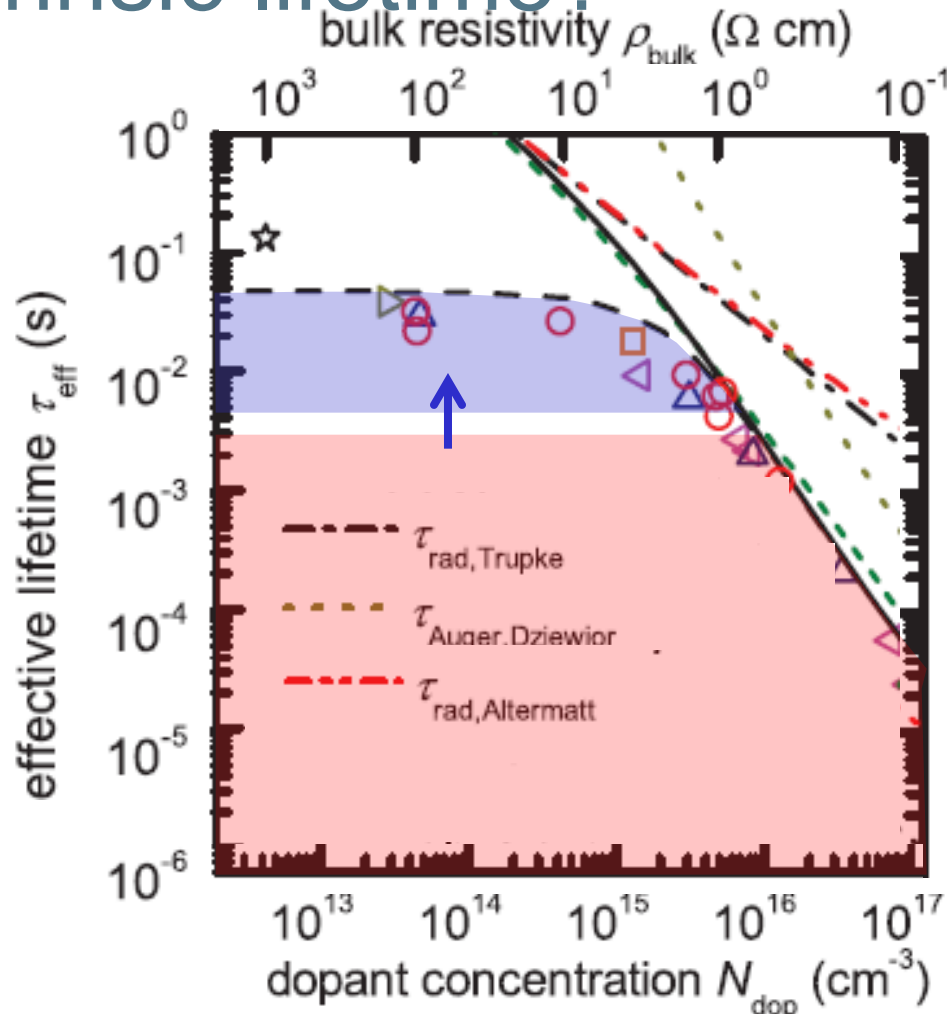
M. Forster et al. N-PV workshop (2014).

R. Falster *Phys. Stat. Solidi* (2000)

Material-related challenges en route to high efficiency n-type solar cells

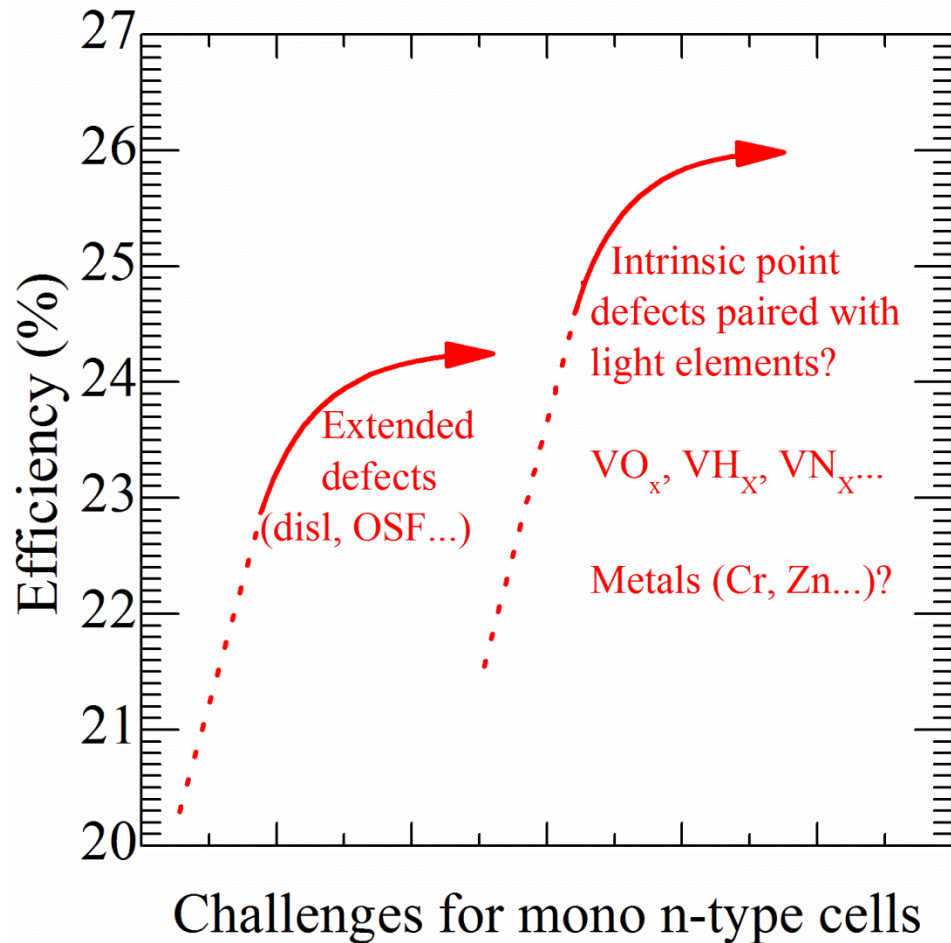


What are the defects between us and the Intrinsic lifetime?



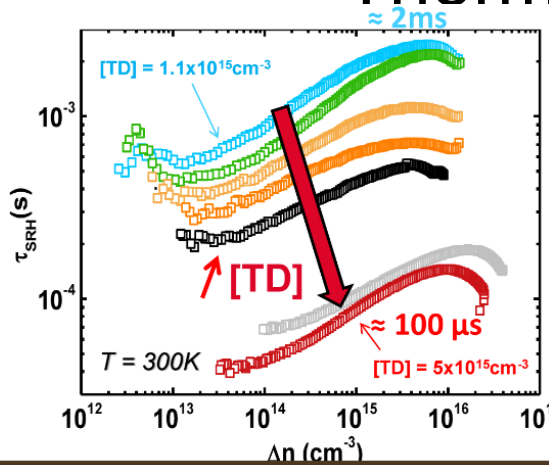
Richter et al. Phys. Rev. B. (2012)

Material-related challenges en route to high efficiency n-type solar cells

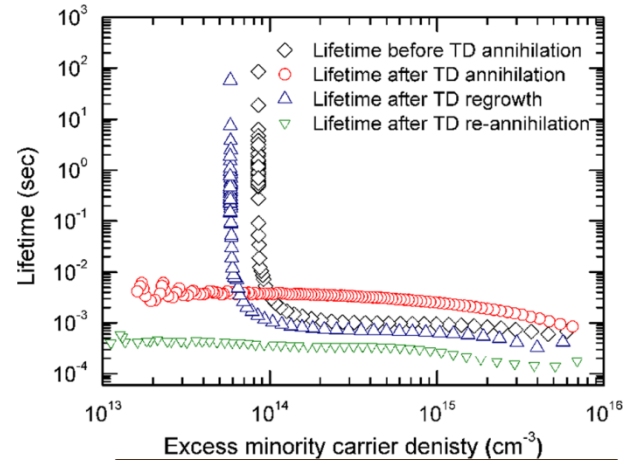


Grown-in and process-induced **point** defects

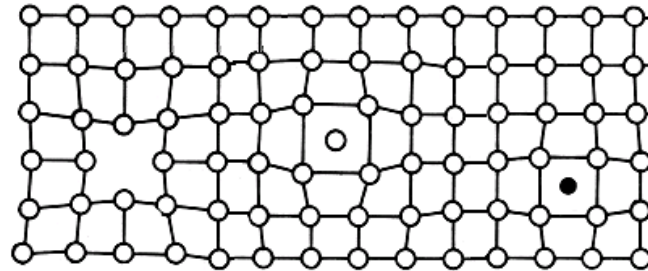
Thermal donors



N.Najid et al. N-PV workshop (2013)



Y. Hu et al. J. Appl. Phys. (2012)



Modified from F. Shimura, "Semiconductor silicon crystal technology" (1989)

Grown-in and process-induced **point** defects

VV?

$C_i C_s$?

VO_x ?

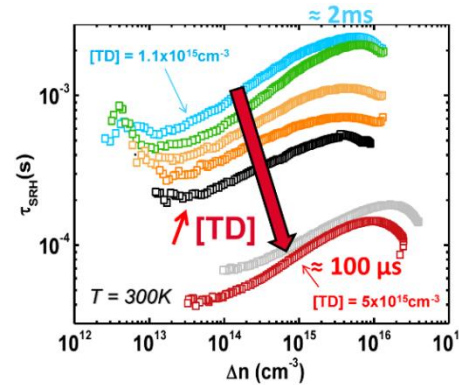
C_i ?

VH_x ?

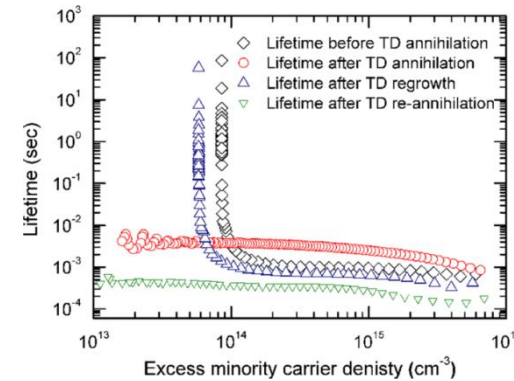
$Si_i H_x$?

...

...

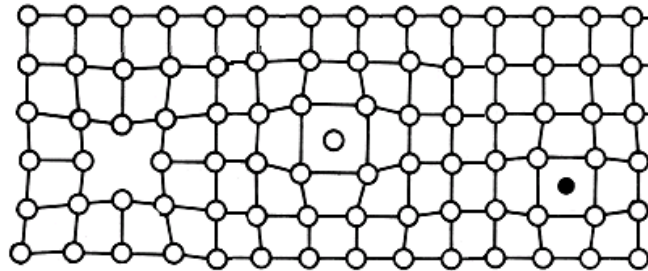


N.Najid et al. N-PV workshop (2013)



Y. Hu et al. J. Appl. Phys. (2012)

Scarce literature on the influence of intrinsic point defects on the lifetime



Outline

- Grown-in extended defects
- **Characterizing as-grown defects**
- Grown-in point defects in n-type CZ
- Grown-in point defects in n-type FZ

Lets have a small exercise

- Lifetime of 1ms
- Assume a midgap defect with a standard capture cross section of $\sigma_p = \sigma_n = 1 \times 10^{-14} \text{ cm}^2$

$$\tau_{p0} = \frac{1}{N_t \sigma_p v_{th}}$$

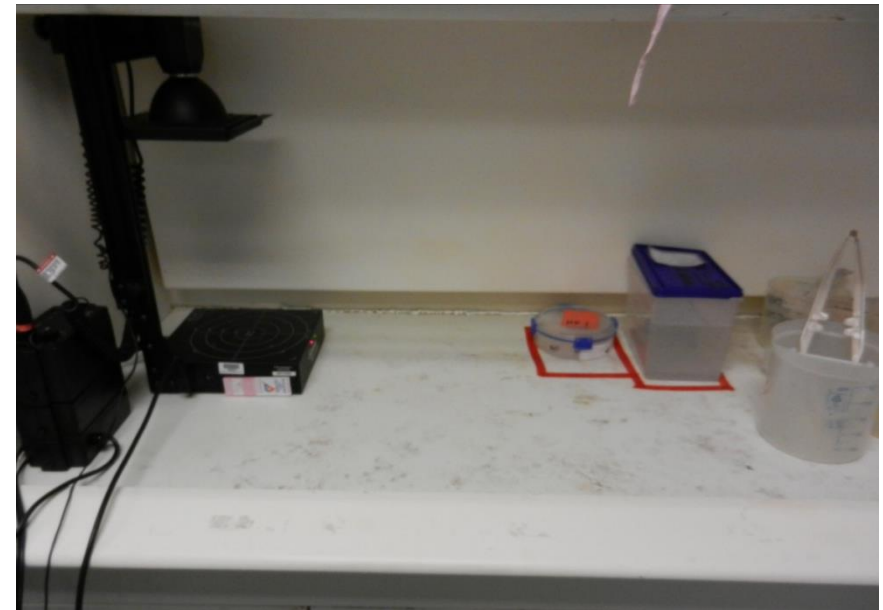
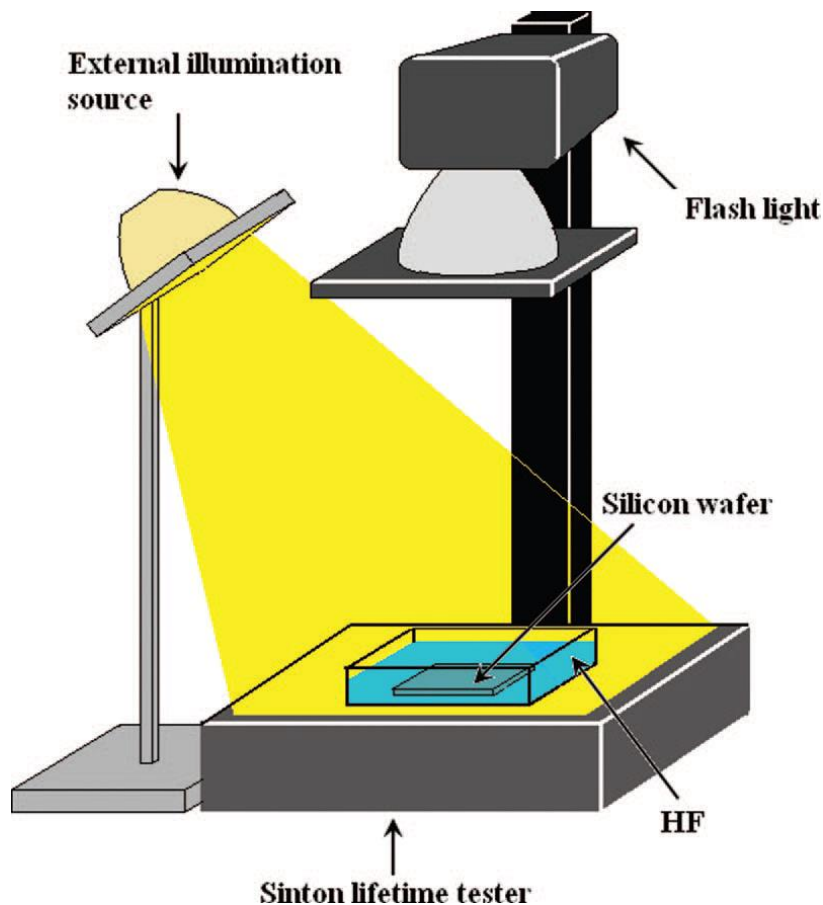
Lets have a small exercise

- Lifetime of 1ms
- Assume a midgap defect with a standard capture cross section of $\sigma_p = \sigma_n = 1 \times 10^{-14}$ cm²
$$\tau_{p0} = \frac{1}{N_t \sigma_p v_{th}}$$
- Defect density $N = 1 \times 10^{10}$ cm⁻³
- Cannot be identified with DLTS or EPR
- We need lifetime spectroscopy to identify the defect

Influence of passivation

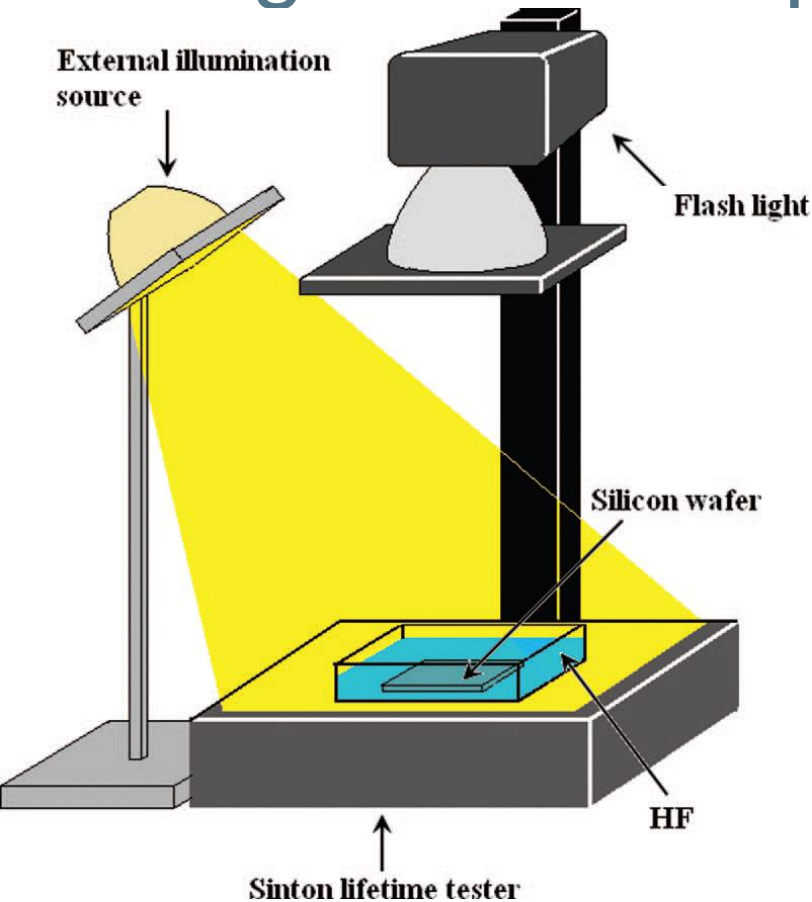
- Using $\text{SiN}_x\text{:H}$ or $\text{Al}_2\text{O}_3\text{:H}$ can potentially anneal or hydrogenate bulk grown-in defects
- We need room temperature passivation
- We use a range of passivation techniques to understand hydrogenation effects

HF passivation to investigate grown-in defects



HF passivation provides room temperature passivation

Value in understanding defect in their as-grown or as-processed state

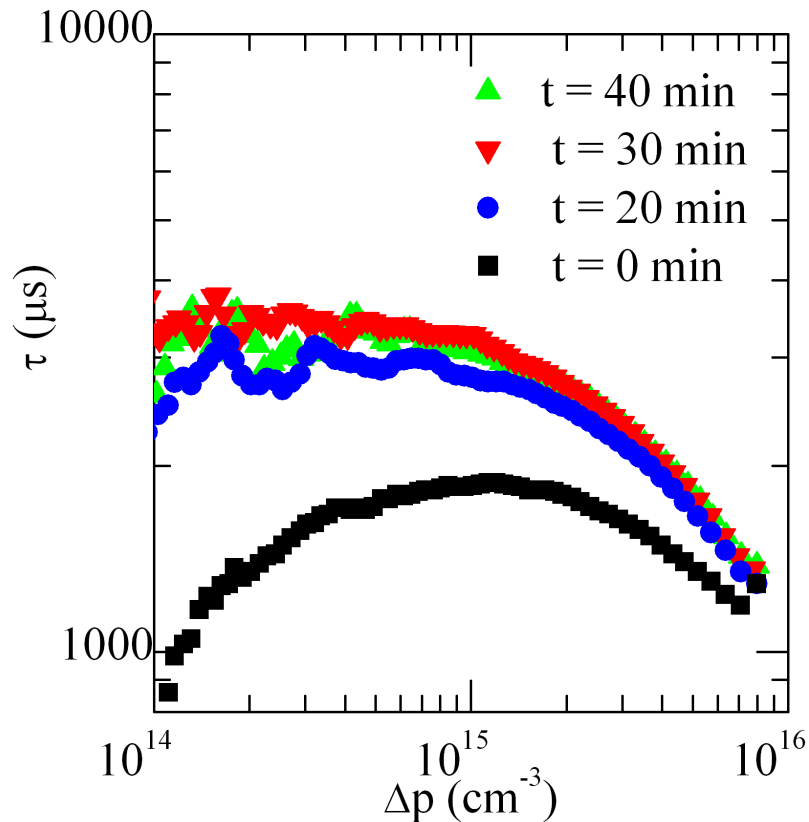


- Represent the “true” growth conditions
 - Using thermal SiO_2 , $\text{SiN}_x\text{:H}$ or $\text{Al}_2\text{O}_3\text{:H}$ can change the state of the defect
 - HF passivation will measure the defect as is
 - $S_{\text{eff}} = 1.1 \pm 0.2 \text{ cm.s}^{-1}$

Outline

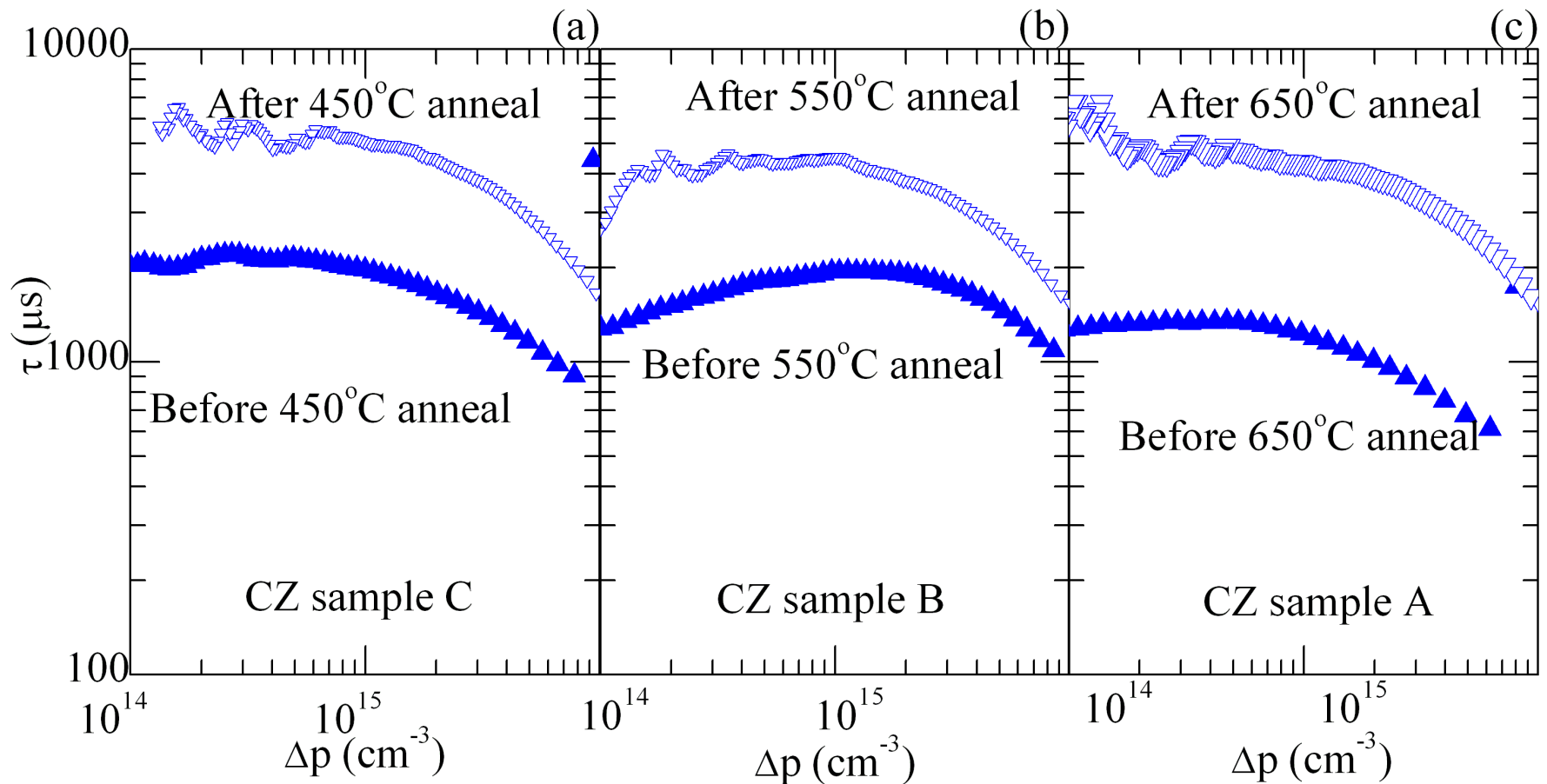
- Grown-in extended defect
- Characterizing as-grown defect
- **Grown-in point defects in n-type CZ**
- Grown-in point defects in n-type FZ

Defects in CZ silicon

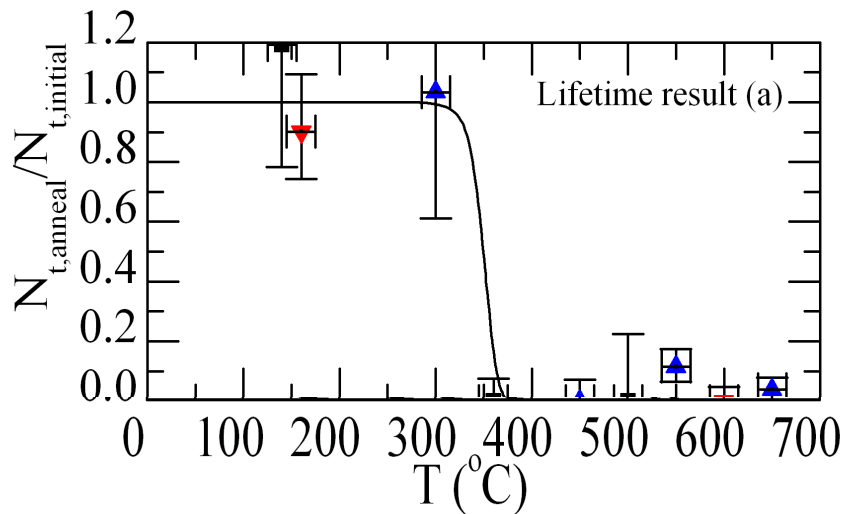


- Anneal at 360°C for different length of time
- The defect is deactivated after 30 min

Defects in CZ silicon

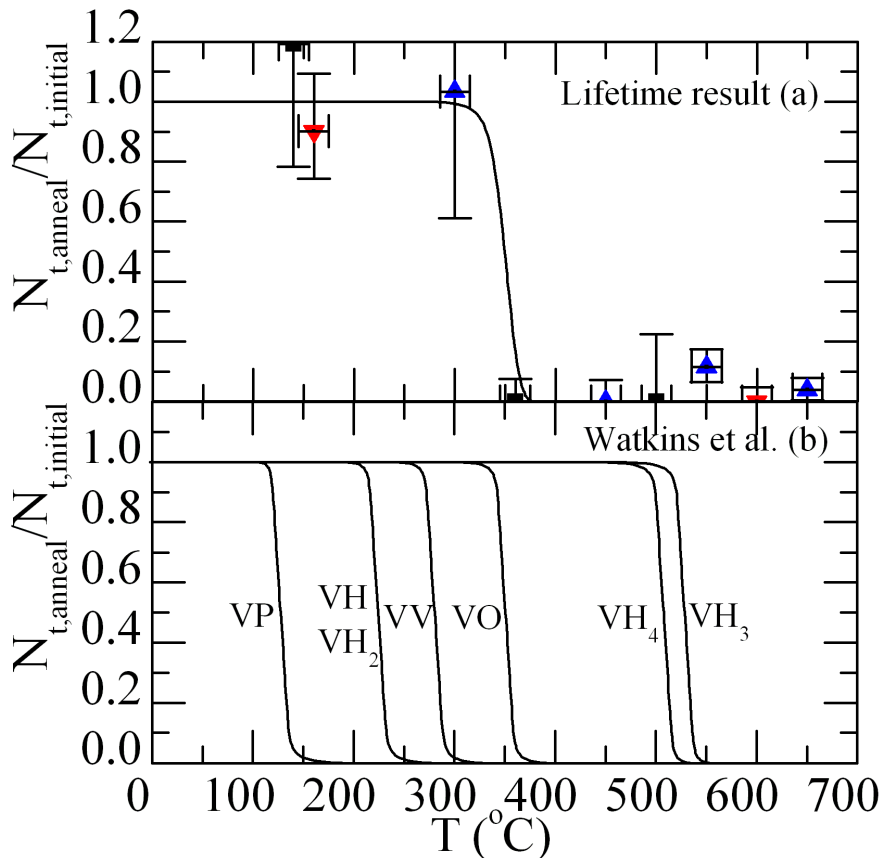


Defect thermal de-activation



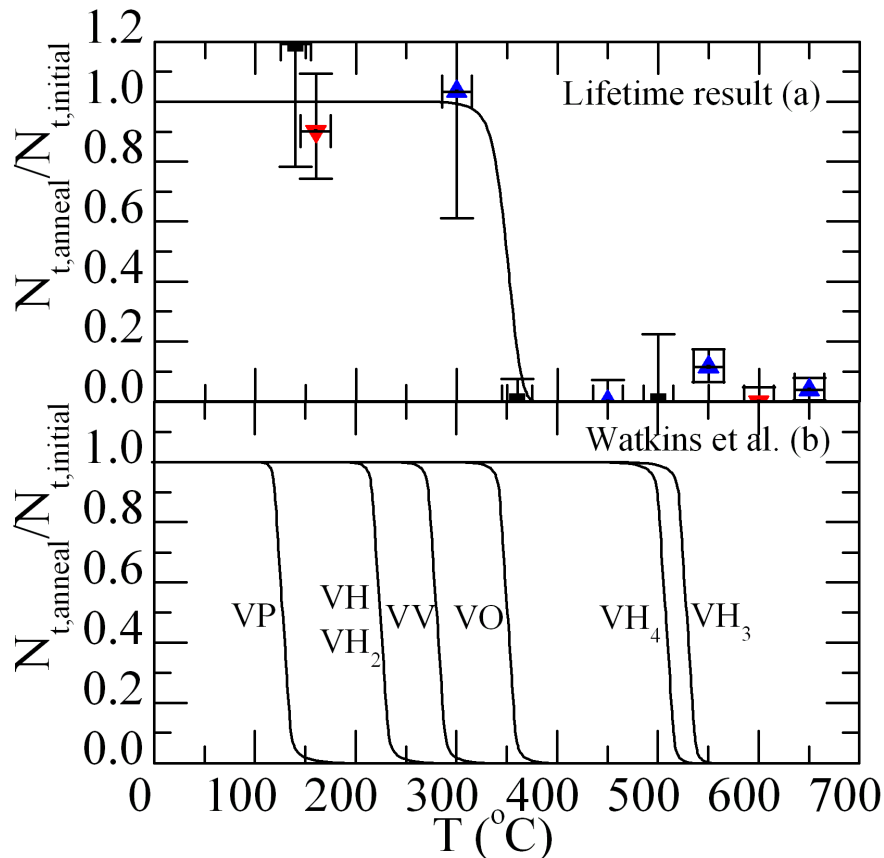
- Isochronal anneal for 30 min
- The defect is deactivated above 360°C

Identification (tentative) of the defect



- The defect is deactivated above 360°C
- The defect could be related to vacancy-oxygen pairs
- Highly influential for heterojunction designs

Defects in CZ silicon



- Oxygen is a problem for precipitates, stacking faults, thermal donors and pairing with vacancies
- Why not use FZ silicon?

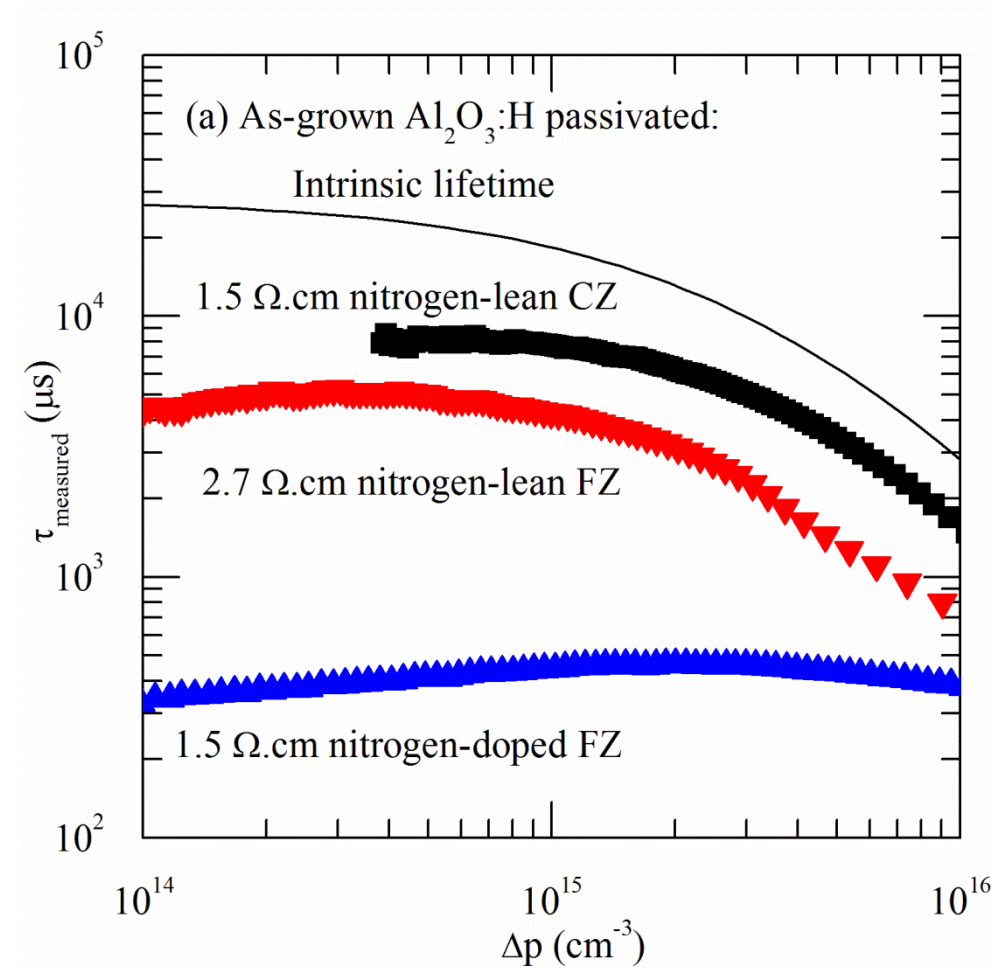
Outline

- Grown-in extended defect
- Characterizing as-grown defect
- Grown-in point defects in n-type CZ
- **Grown-in point defects in n-type FZ**

Why is there nitrogen in FZ silicon?

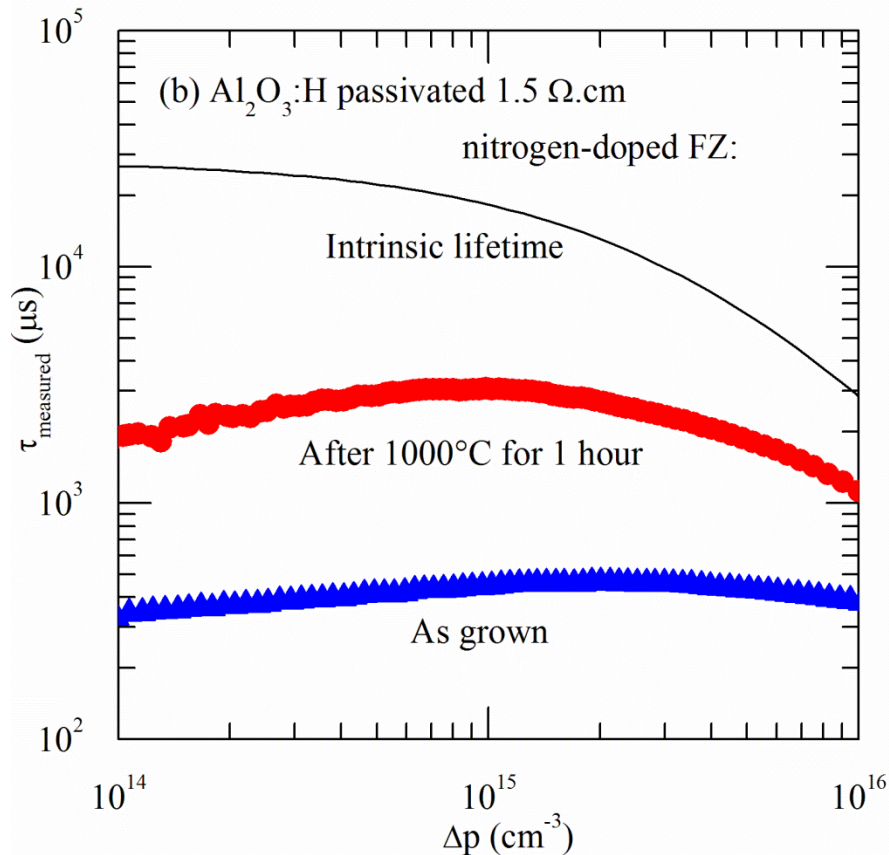
- Mitigates the impact of extended defects.
- Suppresses the formation of vacancy and interstitial aggregates
- $N_2 + V \rightarrow N_2V$
- $N_2V + I \rightarrow N_2$
- Pins dislocations for improved mechanical stability at high temperature

Defects in nitrogen-doped FZ silicon?



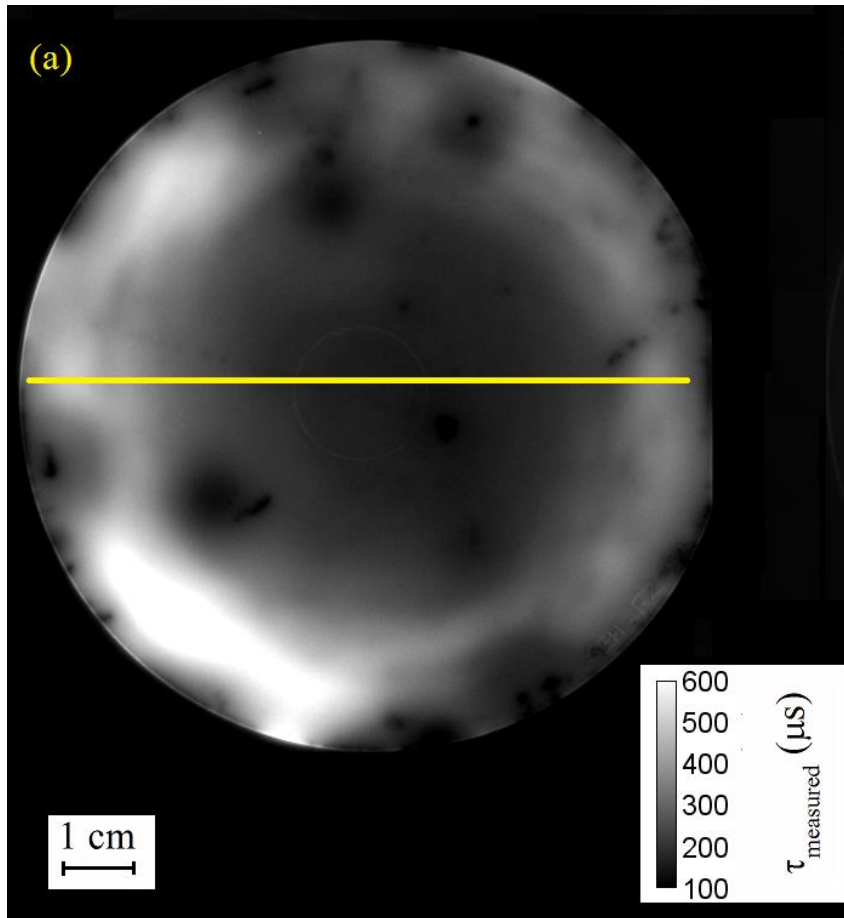
- Nitrogen-doped FZ silicon wafers have lower as-grown lifetime than nitrogen-lean FZ or CZ wafers

Thermal deactivation of defect



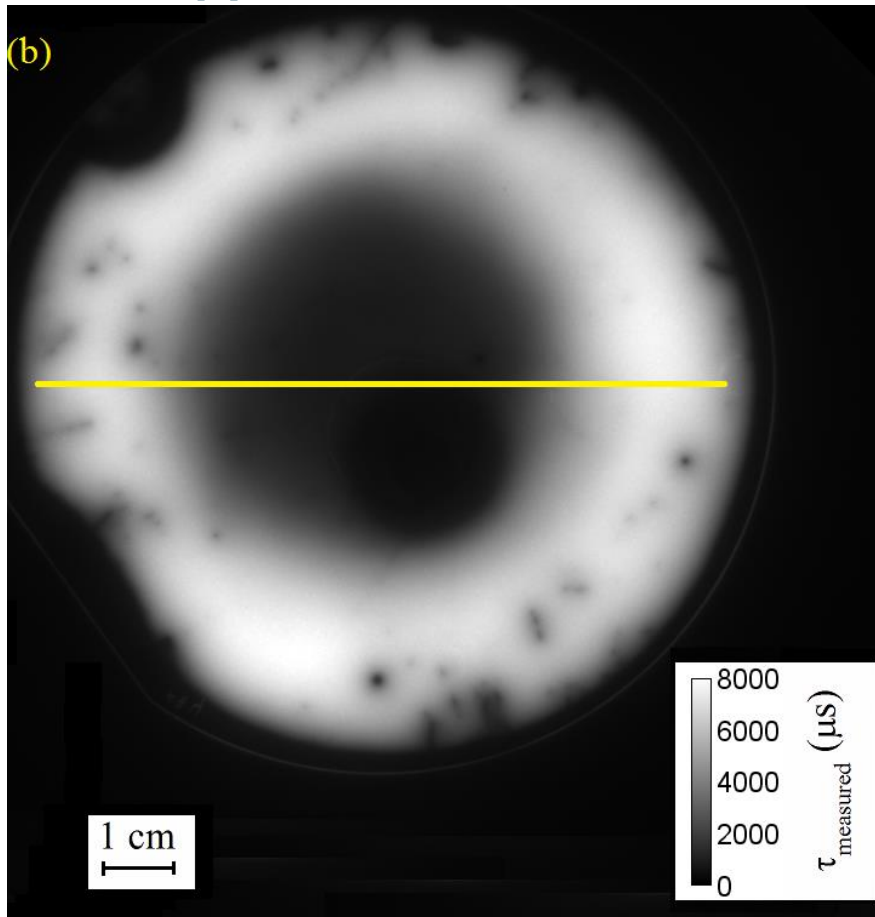
- Lifetime increases significantly after anneal at 1000°C
- Removal or transformation of recombination active defect
- What is the defect?

Spatial distribution of the lifetime $\text{Al}_2\text{O}_3:\text{H}$



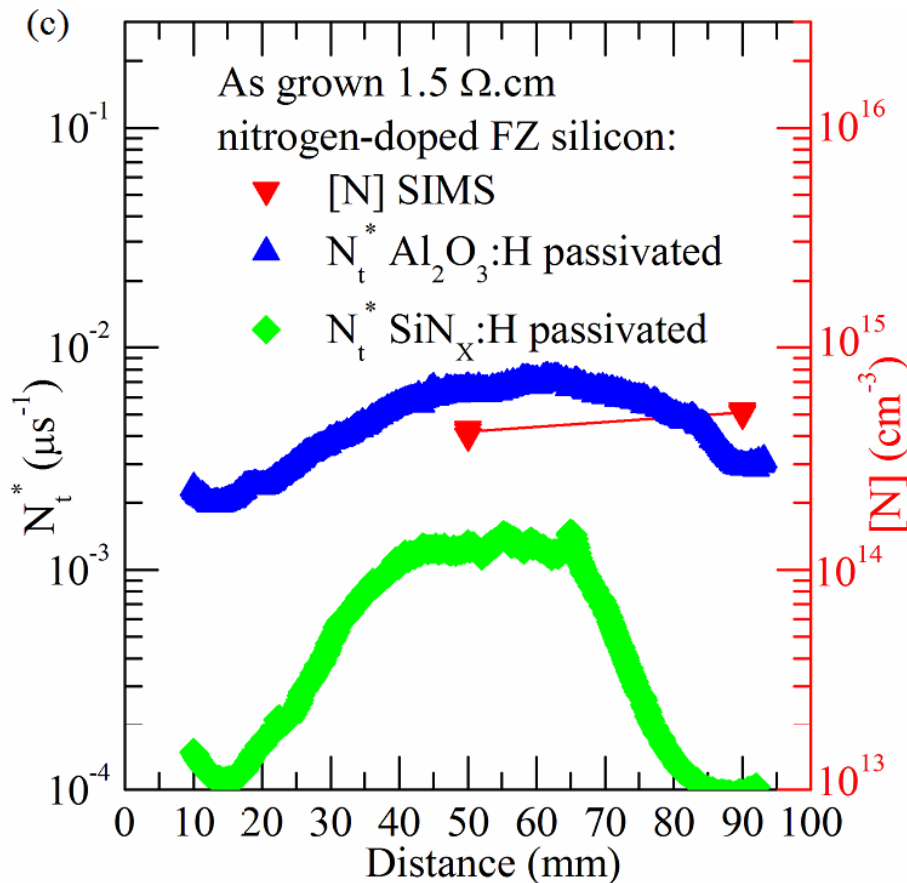
- Higher lifetime around the edges
- Radially symmetric distribution of lifetime

Spatial distribution of the defect lifetime $\text{SiN}_x:\text{H}$



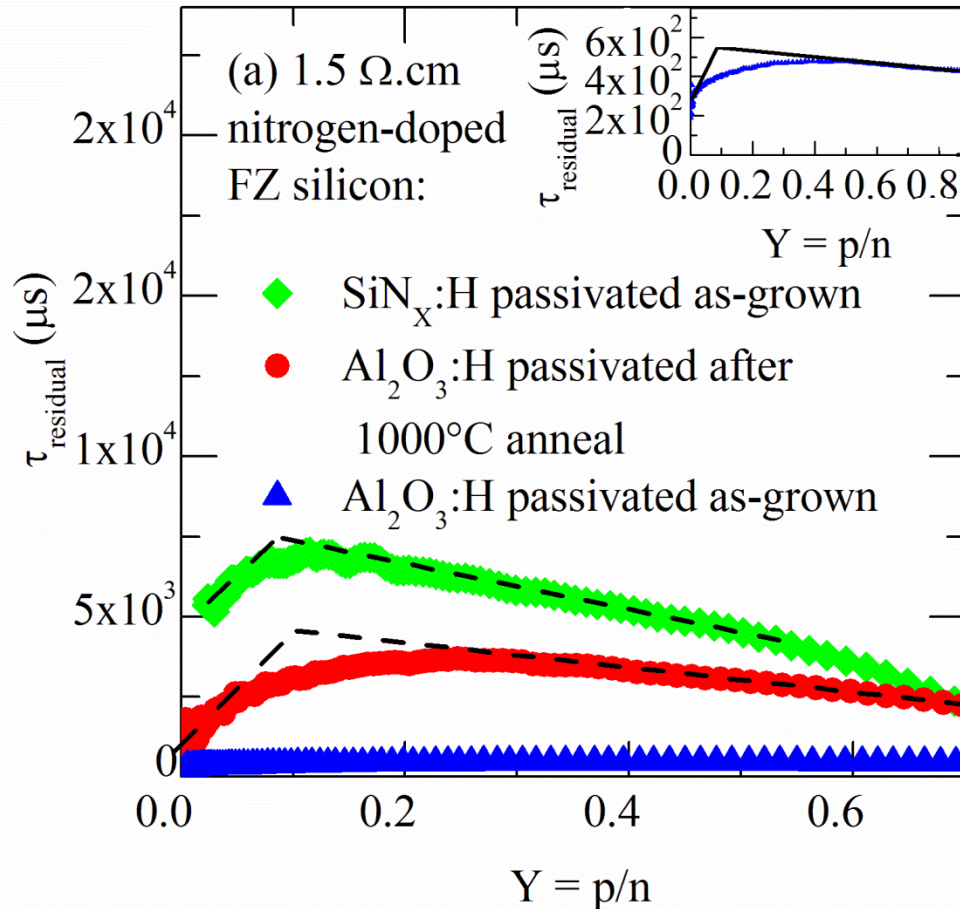
- Higher lifetime around the edges
- Radially symmetric distribution of lifetime
- Higher lifetime than $\text{Al}_2\text{O}_3:\text{H}$
- What does that imply for the defect structure?

Spatial distribution of the defect



- Defect density higher in the centre
- Nitrogen constant laterally
- Radial distribution suggests nitrogen-vacancy point defect
- Is there one or many different defect species?

One or many defect species?

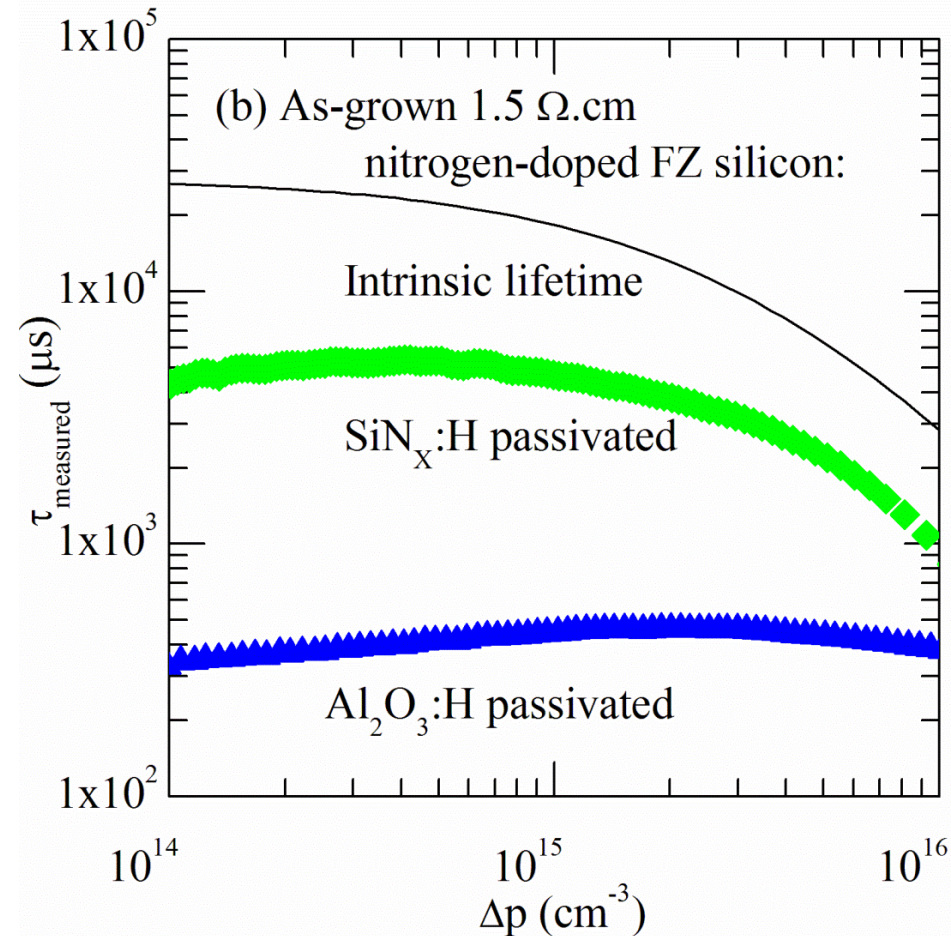


$$\tau_p = \frac{1}{\alpha_p N} \left[1 + \frac{n_1}{n_0} + \frac{p_1}{n_0 Q} + Y \left(\frac{1}{Q} - \frac{n_1}{n_0} - \frac{p_1}{Q n_0} \right) \right]$$

J. D. Murphy et al. J. Appl. Phys. (2012).

- Absence of a single linear trend
- More than one type of defect

Effect of passivating films with different hydrogen contents



- $\text{SiN}_x\text{:H}$ contains 15%-20% total H (complexed and atomic)
- Al_2O_3 contains less than 5% total H
- Increases the lifetime through bulk hydrogenation

Conclusion: Extended defects

- Stacking faults and oxygen precipitates can severely limit the lifetime of n-type monocrystalline silicon
- High temperature processes can increase the recombination activity by changing the precipitate density, having strained precipitates and through metallic decorations
- Dislocations and slip lines are detrimental but should not occur when using high purity feedstocks

Conclusion: Point defects

- We demonstrate that intrinsic point defects paired with light elements can limit the lifetime of high purity silicon wafers
- V_xO_y and V_xN_y complexes are two likely candidate limiting the lifetime of CZ and FZ silicon
- Solutions to increase the lifetime:
 - from 1-2ms to 5ms after annealing above 360°C of CZ silicon
 - from 0.5 ms to 3-5ms after annealing above 1000°C or hydrogenation of FZ silicon

What is a control wafer?

- Standard high temperature and passivation processes are likely to affect the states or concentrations of defects through hydrogenation or annealing
- There is no such things as a perfect and stable control
- One must use multiple controls in order to rightfully interpret enhanced surface passivation or cell parameters

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Thank you for your attention