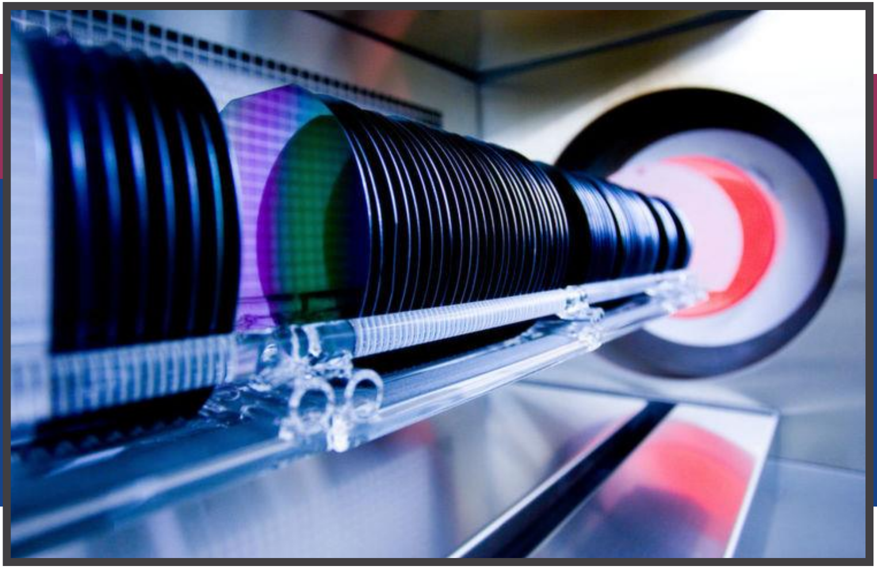
TECHNISCHE UNIVERSITÄT ILMENAU

CiS Forschungsinstitut für Mikrosensorik GmbH



The A_{Si}-Si$_i$-defect - a possible candidate to explain acceptor removal in LGADs

21.06.2022, 40th RD50 Workshop

Kevin Lauer, Katharina Peh, Aaron Flötotto, Dirk Schulze, Wichard Beenken, Erich Runge, Stefan Krischok, Thomas Ortlepp

ZUSE-GEMEINSCHAFT
FORSCHUNG, DIE ANKOMMT.
GRÜNDUNGSMITGLIED

Overview

1. **Motivation** (light-induced degradation, boron removal LGAD)
2. **A_{Si}-Si_i-defect model**
3. **B_{Si}-Si_i-defect responsible for acceptor removal in LGADs?**
4. **Outlook on DFT calculations of A_{Si}-Si_i-defect**
5. **Summary**

Motivation
(light-induced degradation LID, boron removal LGAD)

Light-induced degradation (LID) of silicon

- First observed in n-in-p solar cells for space application after electron irradiation and subsequent illumination
- Later found to appear even in unirradiated solar cells
- Defect known since nearly 50 years
- Microscopic structure and composition of responsible defect is still an open question

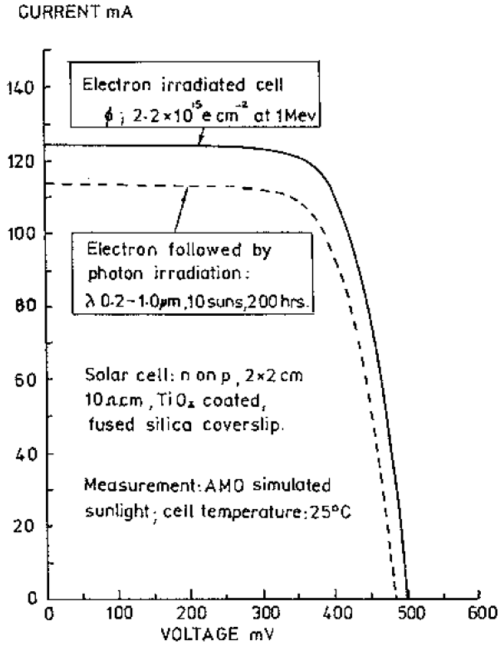
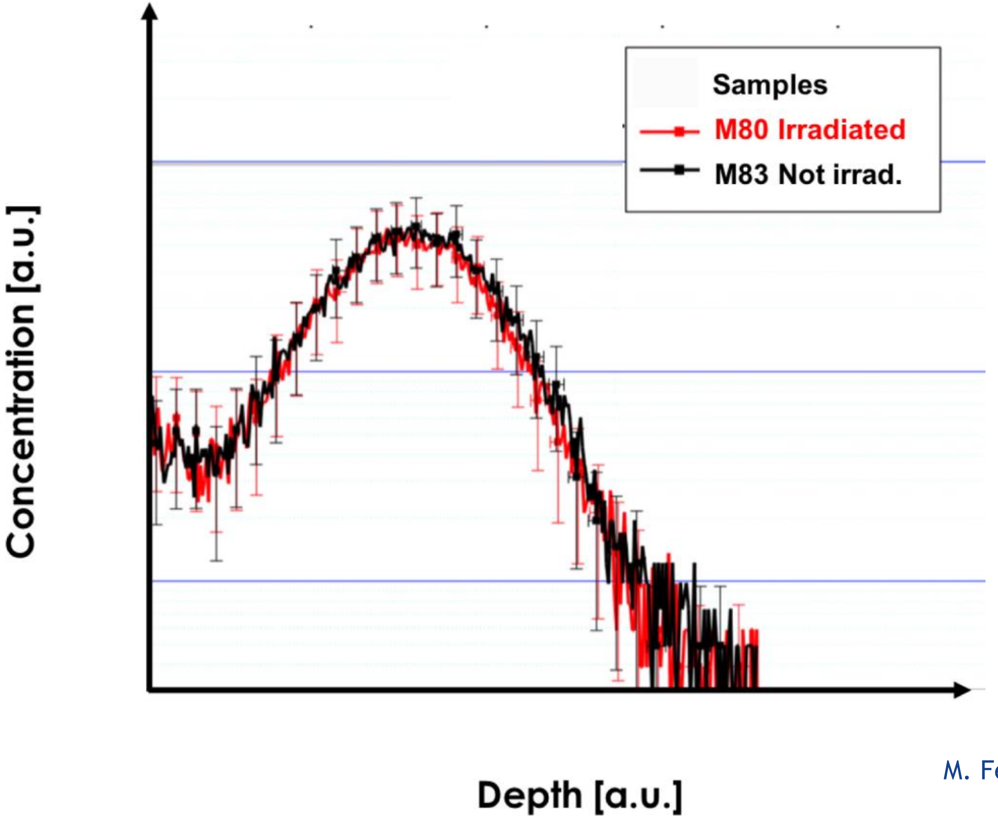


Fig 1 Solar cell V-I performance degradation following sequential electron-photon irradiation

R. L. Crabb, Proceedings of the 9th IEEE Photovoltaic Specialists Conference, New York, 329 (1972)

Boron removal in low gain avalanche detectors



- LGAD looses gain after irradiation
- Gain layer seems to be removed
- Actually, boron atoms are not "removed"
- SIMS profiles do not show any macroscopic migration of the boron

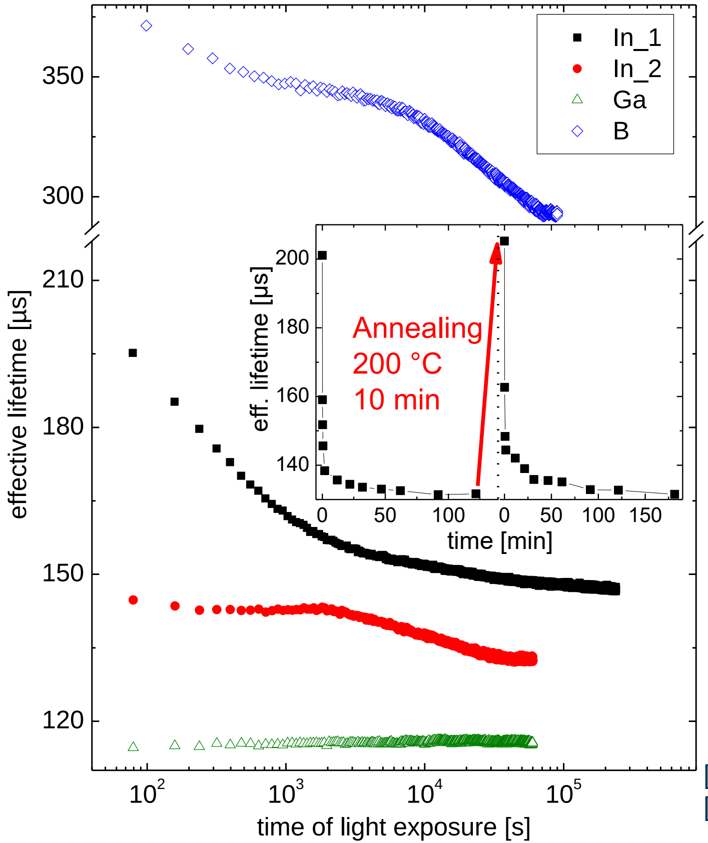
=> Defect reactions take place

- Which?

M. Ferrero et al., NIMA **919**, 16 (2019).

Preliminary A_{Si}-Si_i-defect model

LID in indium doped silicon



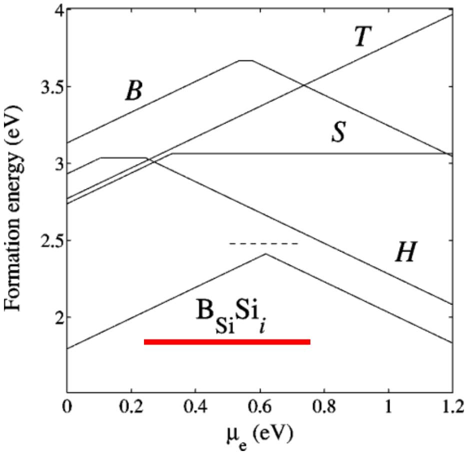
- LID occurs in indium-doped silicon [1,2]
- Fast and slow component visible
- Degradation is fully reversible

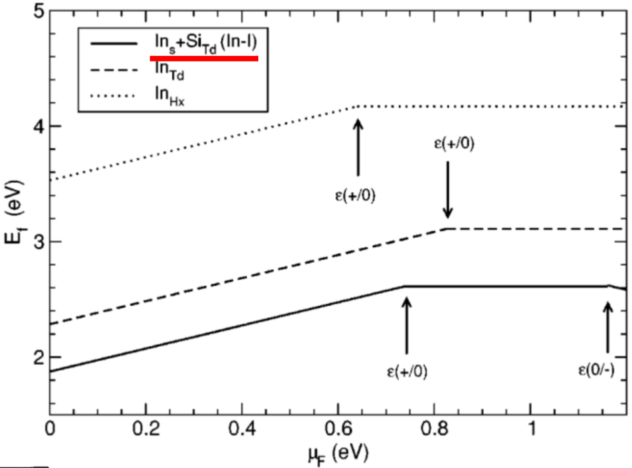
- Why does the defect occur in boron and indium and not in gallium doped silicon?

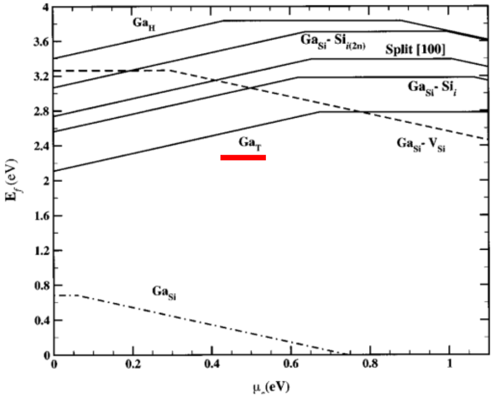
sample	method/ orientation	dopant	ρ (Ω cm)	N_A (10^{15} cm^{-3})	[O_i] (10^{17} cm^{-3})
B	CZ/100	boron	5.80	2.4	9.84
Ga	CZ/100	gallium	3.41	4.1	8.39
In_1	CZ/100	indium	7.82	1.8	17.68
In_2	FZ/111	indium	8.61	1.6	0.11

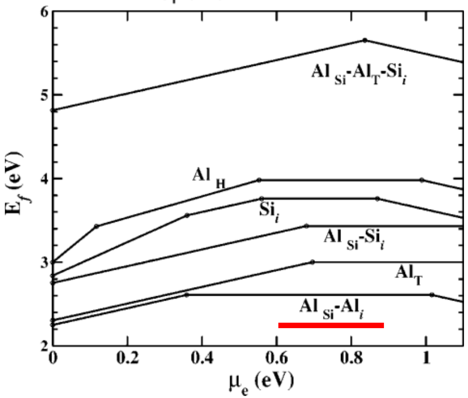
[1] C. Möller and K. Lauer, phys. stat. sol. RRL **7**, 461 (2013)
[2] M.J. Binns et al., in 42nd IEEE Photovoltaic Specialist Conference (PVSC), (IEEE, 2015), p. 1.

Basic idea for defect model









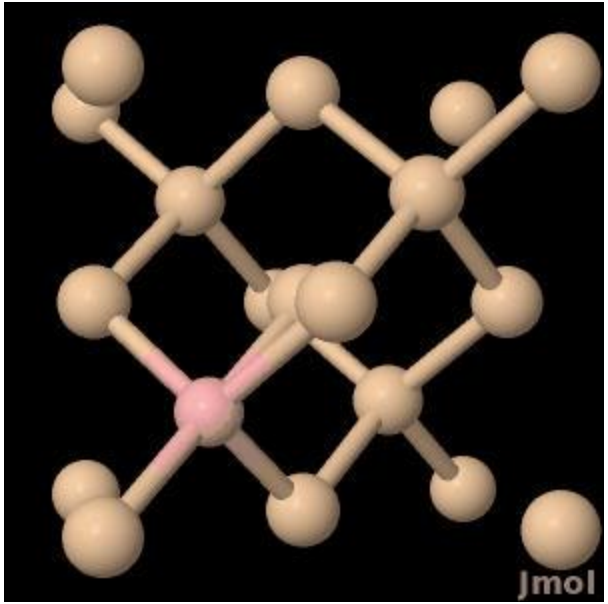
- Configuration of interstitial acceptor atom with lowest formation energy varies
- Gallium on tetrahedral position
- Boron and indium forming an acceptor silicon interstitial pair (A_{Si}-Si_i)

=> A_{Si}-Si_i responsible for observed LID phenomenon?

M. Hakala et al., Phys. Rev. B **61**, 8155 (2000)
C. Melis et al., Appl. Phys. Lett. **85**,4902 (2004)
P. Alippi et al., Phys. Rev. B **69**, 085213 (2004)
P. Schirra et al., Phys. Rev. B **70**, 245201 (2005)

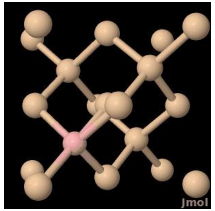
Preliminary A_{Si}-Si_i defect model

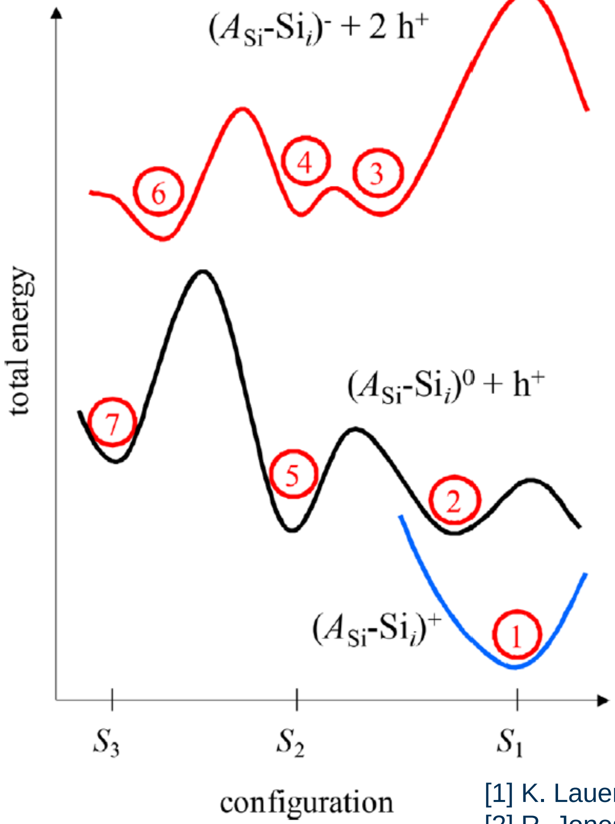
- B_{Si}-Si_i-defect [1] also known as BI [2] or B_i defect
- Boron diffusion mediated by this defect
- A_{Si}: acceptor atom is close to its substitutional position
- Silicon interstitial is moving around (e.g. tetrahedral, hexagonal or split interstitial position)



[1] M. Hakala, M. J. Puska, and R. M. Nieminen, Physical Review B **61**, 8155 (2000).
[2] S. Mirabella, D. De Salvador, E. Napolitani, E. Bruno, and F. Priolo, J. Appl. Phys. **113**, 031101 (2013)

Preliminary A_{Si}-Si_i defect model



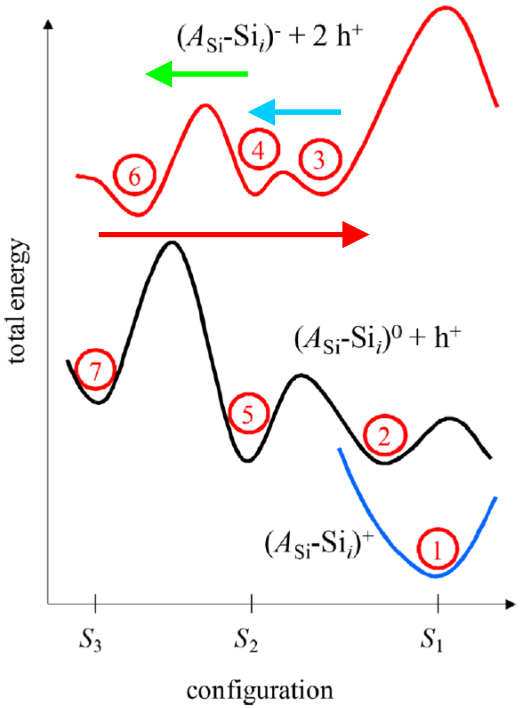


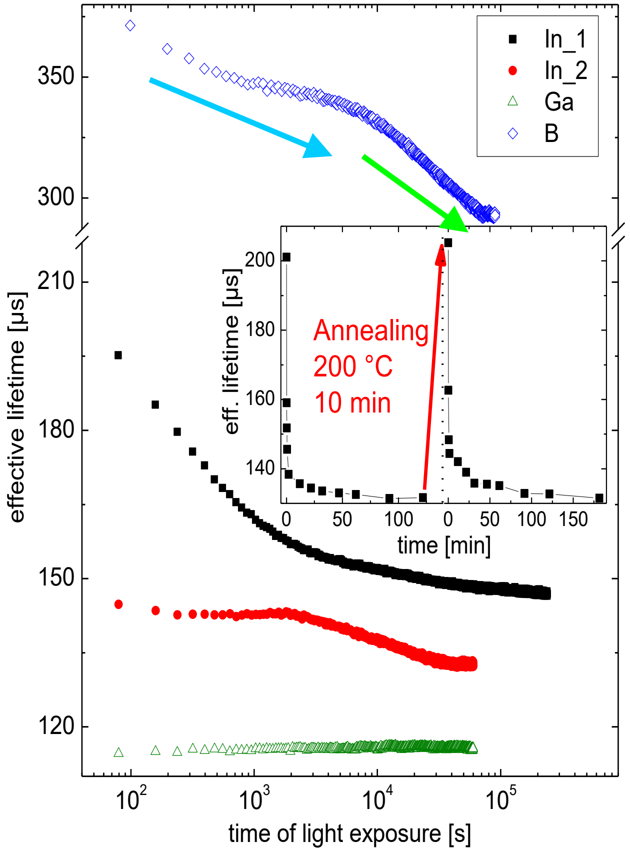
- Configuration coordinate total (electronic + elastic) energy diagram [1] deduced from simulation results of the silicon interstitial [2]
- Three charge states (+, 0, -) and three configurations (S_1, S_2 and S_3) of A_{Si}-Si_i possible
- Energy barriers between configurations (e.g. $E_{3,4}$, $E_{4,6}$)

- Negative charge state: configuration S_3 energetically favored
- Neutral charge state: configuration S_2 and S_1 energetically favored

[1] K. Lauer, C. Möller, C. Tessmann, D. Schulze, and N.V. Abrosimov, Physica Status Solidi (c) 14, 1600033 (2017).
[2] R. Jones, A. Carvalho, J.P. Goss, and P.R. Briddon, Materials Science and Engineering: B 159–160, 112 (2009).

Preliminary A_{Si}-Si_i defect model, LID cycle



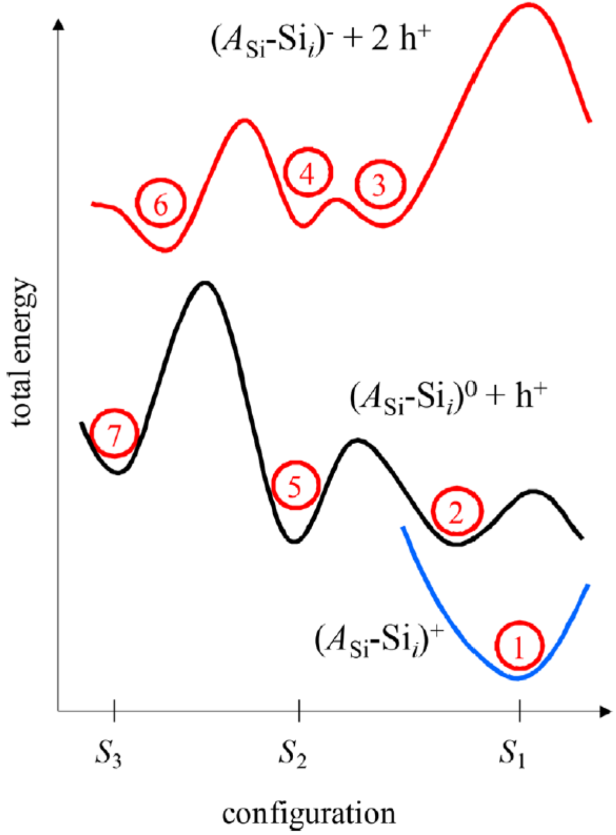


- Transition 1 to 3: defect captures electrons under illumination
- Transition 3 to 4: thermally stimulated, fast component of LID (FRC)
- Transition 4 to 6: thermally stimulated, slow component of LID (SRC)
- Transition 7 to 1: thermally stimulated, recovery of defect, without illumination

B_{Si}-Si_i-defect responsible for acceptor removal in LGADs?

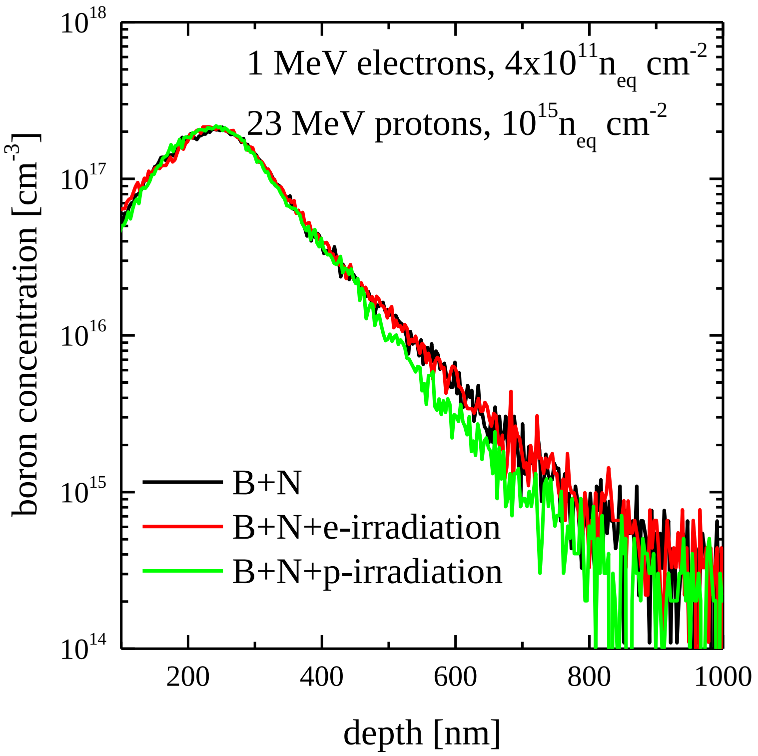
Explanation by B_{Si}-Si_i-defect

- Irradiation generates silicon interstitials
- Positively charged silicon interstitials move to negatively charged boron acceptors (Coulomb attraction)
- B_{Si}-Si_i-defect is formed
- B_{Si}-Si_i-defect is donor in its ground state (configuration S_1)
- Due to charge carrier generation while irradiation some B_{Si}-Si_i-defects might be in configuration S_2 (neutral)
- Loss of acceptors in both cases
- => "acceptor removal" in LGADs can be explained



Comparison to B_i-O_i-explanation approach

- B_i generation as before
- B_s leaves substitutional position, diffuses to O_i and forms B_i-O_i-defect
- Therefore B_i (or B_{Si}-Si_i) has to diffuse fast at room temperature
- Only observed under heavy extrinsic conditions while sputtering for SIMS analysis [1]
- Our SIMS investigations show no fast diffusion of B [2, GADEST 2022] necessary for B_i-O_i-formation
- For FZ silicon with $[O_i] \approx 10^{15}cm^{-3}$ => ~50nm of B diffusion necessary



[1] E. Napolitani, D. De Salvador, R. Storti, A. Carnera, S. Mirabella, and F. Priolo, Physical Review Letters 93, (2004).
[2] K. Lauer, K. Peh, S. Krischok, S. Reiß, E. Hiller, and T. Ortlepp, Physica Status Solidi (a) 10.1002/pssa.202200177

Outlook on DFT calculations of A_{Si}-Si_i-defect

DFT calculation of stable A_{Si}-Si_i-defects

- **Five** different stable configurations for the neutral B_{Si}-Si_i-defect found so far

					E-E_{Bulk} [eV]	
	Si	X	defect symmetry		X=B	X=In
A	i	s	C3v	ditrigonal	-3.34	1.39
B	i	i	C1h	domatic	-3.19	--
C	s	i	Td	tetrahedral	-2.56	1.88
D	s	i	S6	rhombohedral	-2.9	--
E	i	i	C2v	rhombic	-2.96	1.49

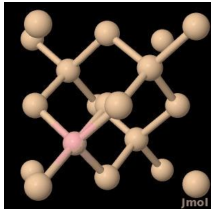
- Each configuration is a separate defect with DLTS levels and so on…

Open questions

- What is the electronic transition responsible for the observed E_c−0.25eV level [1] (sometimes related to B_i-O_i) within the A_{Si}-Si_i-defect model?
- Is a metastability (similar to the LID) visible for the E_c−0.25eV level?
- Planned: DFT calculations of energy barriers in-between different configurations and for different charge states

[1] L. Vines, E.V. Monakhov, A.Yu. Kuznetsov, R. Kozłowski, P. Kaminski, and B.G. Svensson, Physical Review B 78, 085205 (2008).

Summary



- Preliminary A_{Si}-Si_i-defect model developed to explain LID and P line
- Consist of 3 charge states and 3 configurations
- B_{Si}-Si_i-defect formed by capturing of Si_i by B_s during irradiation
- B_{Si}-Si_i-defect is donor in its ground state => indeed defect candidate to explain acceptor removal in LGADs
- Five different configurations of B_{Si}-Si_i-defect found by DFT => meta stability possible
- Main message: B_i is not only one defect. There are at least five B_{Si}-Si_i-defects, where one or more could be responsible for “acceptor removal”.

Thank you for your kind attention!

Dr. Kevin Lauer
klauer@cismst.de, Kevin.Lauer@TU-Ilmenau.de

Thanks to: Christian Möller (CiS), Carsten Ahrens (Infineon), Jan Vanhellemont (U Ghent), Nikolay Abrosimov (IKZ)

This work was supported by the projects SimASiSii and PAK 981/1 of the Deutsche Forschungsgemeinschaft (DFG KR 2228/11-1, LA 4623/1-1, RU 1383/6-1, RU 1383/8-1) and the project DELGAD of the BMWi (49MF190042).

Forschungsinstitut für Mikrosensorik GmbH

Konrad-Zuse-Str. 14
99099 Erfurt, Germany
www.cismst.de

Telefon: +49 361 6631211
Telefax: +49 361 6631413
E-Mail: info@cismst.de

Backup

Light-induced degradation (LID) of silicon

- Efficiency of n-in-p solar cells reduced by about 10% (relative) due to this defect (commercial problem)
- Microscopic structure and composition of responsible defect is still an open question

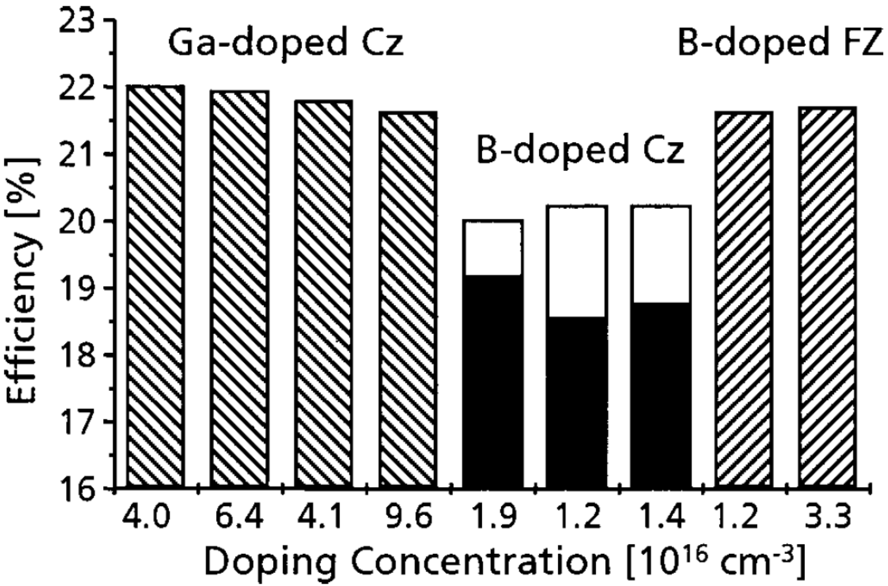


FIG. 6. Solar cell results using the RP-PERC structure on different materials. The open columns show the results for boron-doped Cz before degradation.

S.W. Glunz, S. Rein, J.Y. Lee, and W. Warta, J. Appl. Phys. 90, 2397 (2001).

In_{Si}-Si_i-defect identified as cause of P line in indium doped silicon

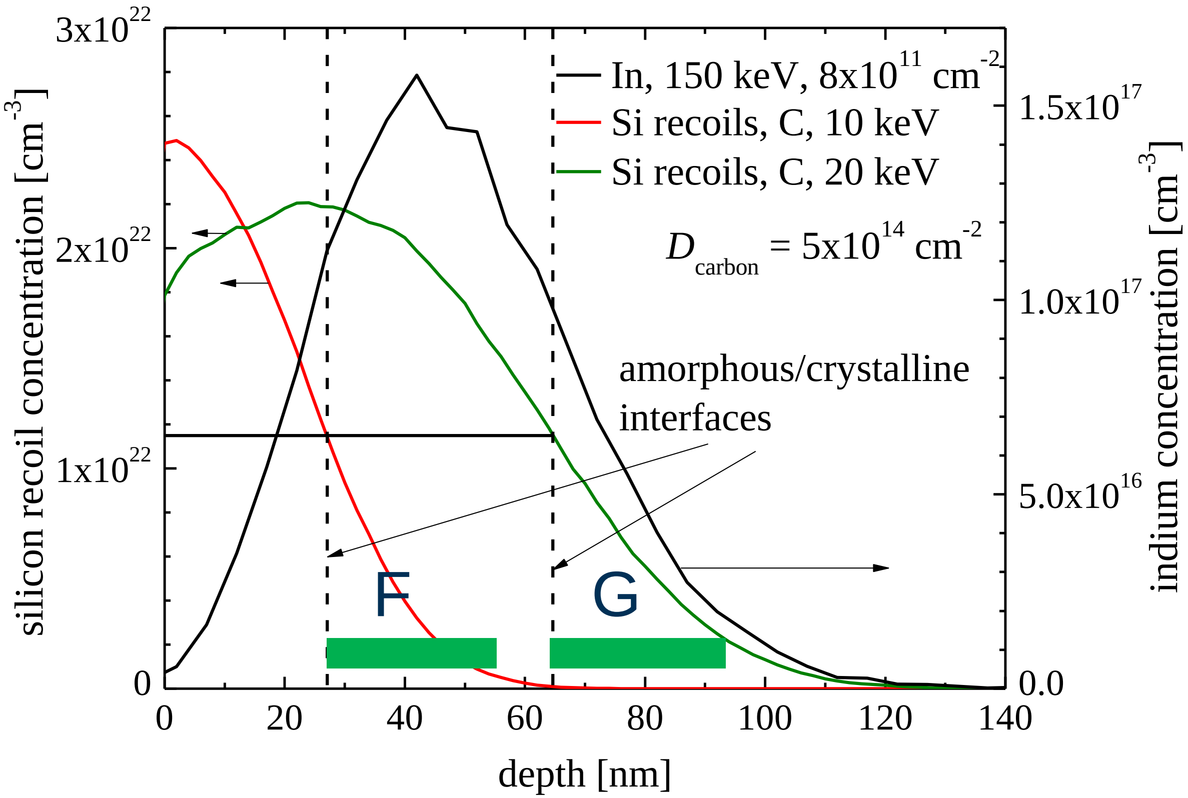
Samples / Experiment

- FZ silicon wafers, diameter 200mm, thickness 750µm
- Low temperature FTIR:
  - $[B_s] = 3x10^{13} cm^{-3}$
  - $[O_i] = 4x10^{14} cm^{-3}$
  - $[C_s] < 7x10^{14} cm^{-3}$
  - $[N_{2i}] = 3x10^{14} cm^{-3}$
- Implantation parameters varied
- After implantation same thermal budget for all samples
- SiN_x/SiO_x stack deposited at end of processing sequence

TABLE I. Parameters of indium and carbon implantation. The radius of the measurement position is given as well.

wafer	implantation				sample	
	indium		carbon		1	2
	dose (cm^{-2})	energy (keV)	dose (cm^{-2})	energy (keV)	radius (mm)	
A	-	-	-	-	79	-
B	1.6×10^{12}	150	-	-	73	-
C	1.6×10^{12}	150	5.0×10^{14}	10	91	93
D	1.6×10^{12}	150	5.0×10^{14}	20	75	97
E	8.0×10^{11}	150	-	-	85	-
F	8.0×10^{11}	150	5.0×10^{14}	10	50	93
G	8.0×10^{11}	150	5.0×10^{14}	20	74	93

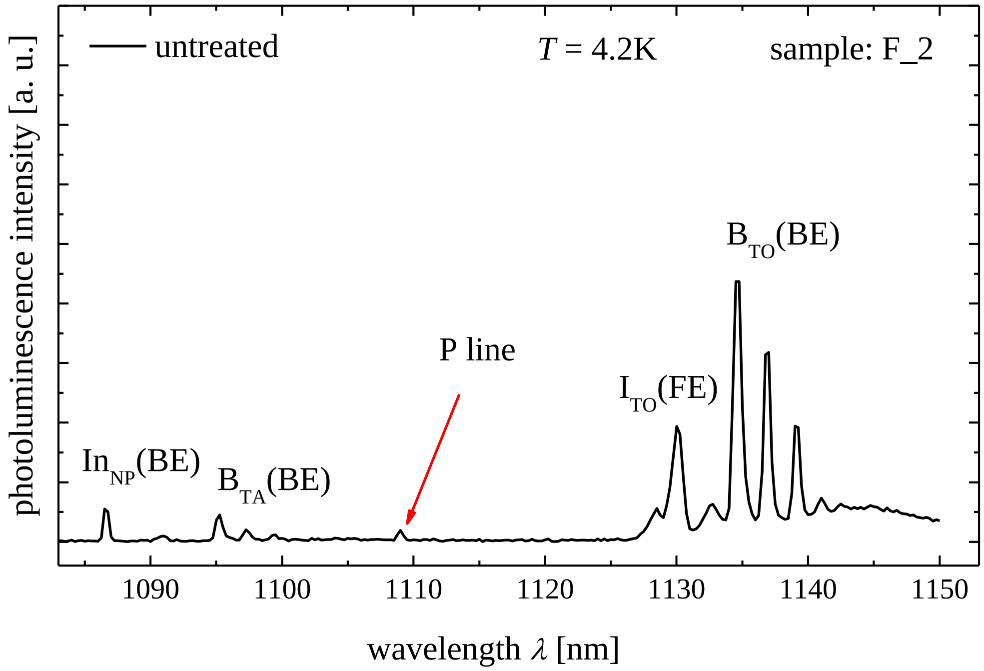
Experiment, SRIM calculation

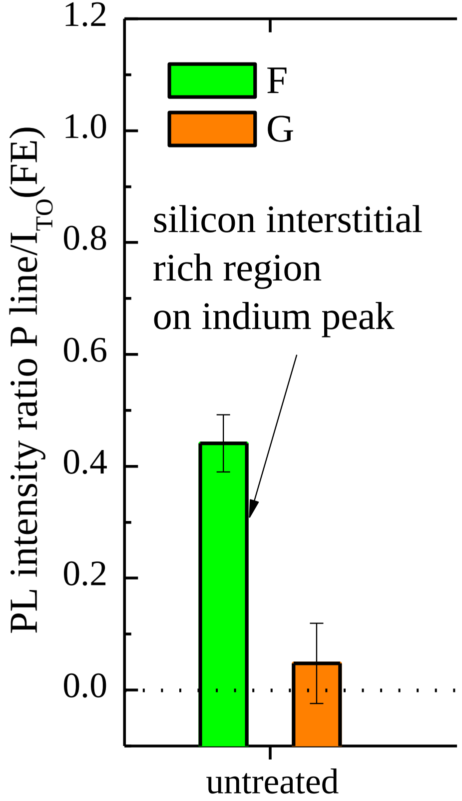


- Amorphous silicon re-crystallizes => no defects remain
- Beneath a/c interface: excess of silicon interstitials
- Evident due to formation of end-of-range defects (EOR)

- Silicon interstitial rich (SIR) region placed on indium peak (sample F) or behind indium peak (sample G) by varying carbon implantation energy
- Investigation of interaction of indium and silicon interstitial atoms possible

Photoluminescence (PL) spectroscopy

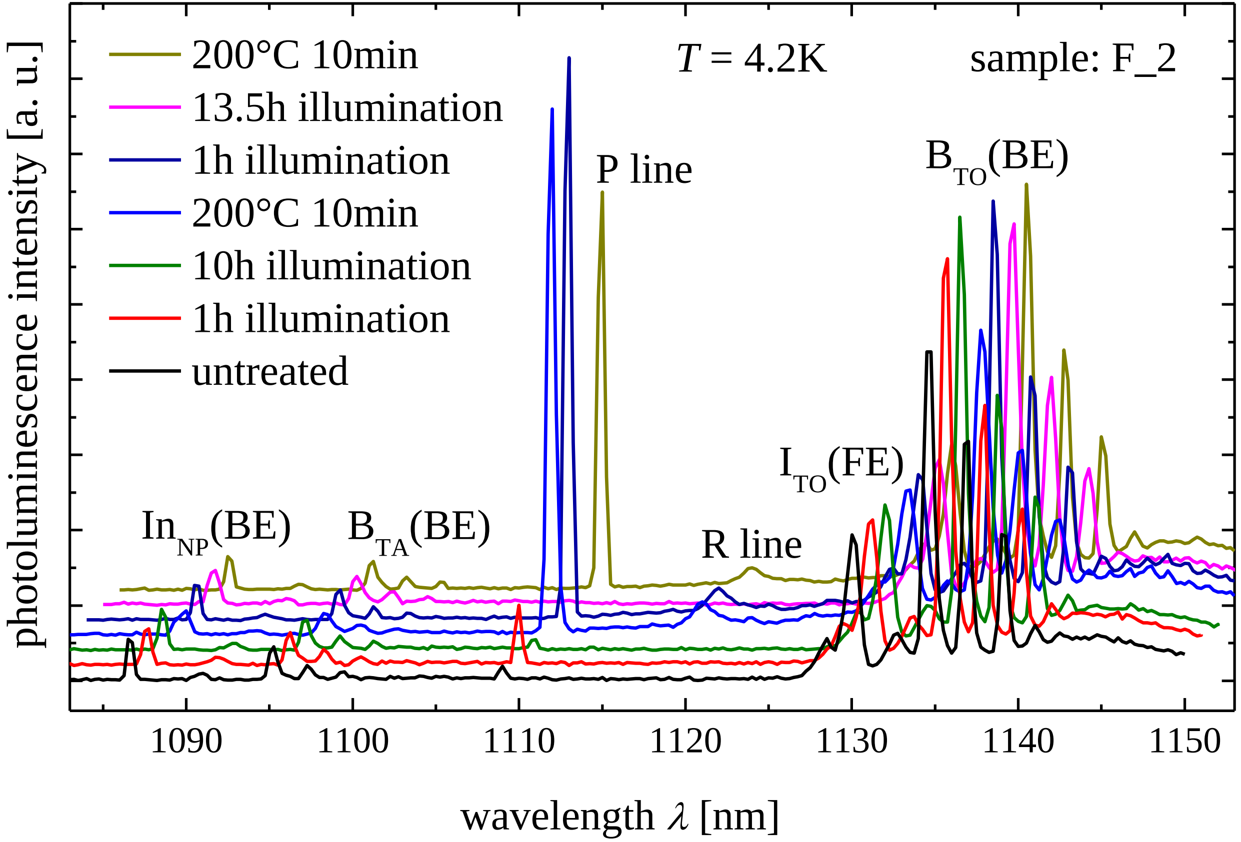




- P line appears in samples with SIR on indium peak
- Idea: In_{Si}-Si_i-defect responsible for P line

=> P line has to follow well known LID annealing and illumination cycle

LID cycle of P line



- P line follows well known LID annealing and illumination cycle

K. Lauer, C. Möller, D. Schulze, and C. Ahrens, AIP Advances 5, 017101 (2015).

Implications of the A_{Si}-Si_i-defect model
(Migration of interstitial boron, dependency of LID density on $[O_i]^2$, hydrogen passivation)

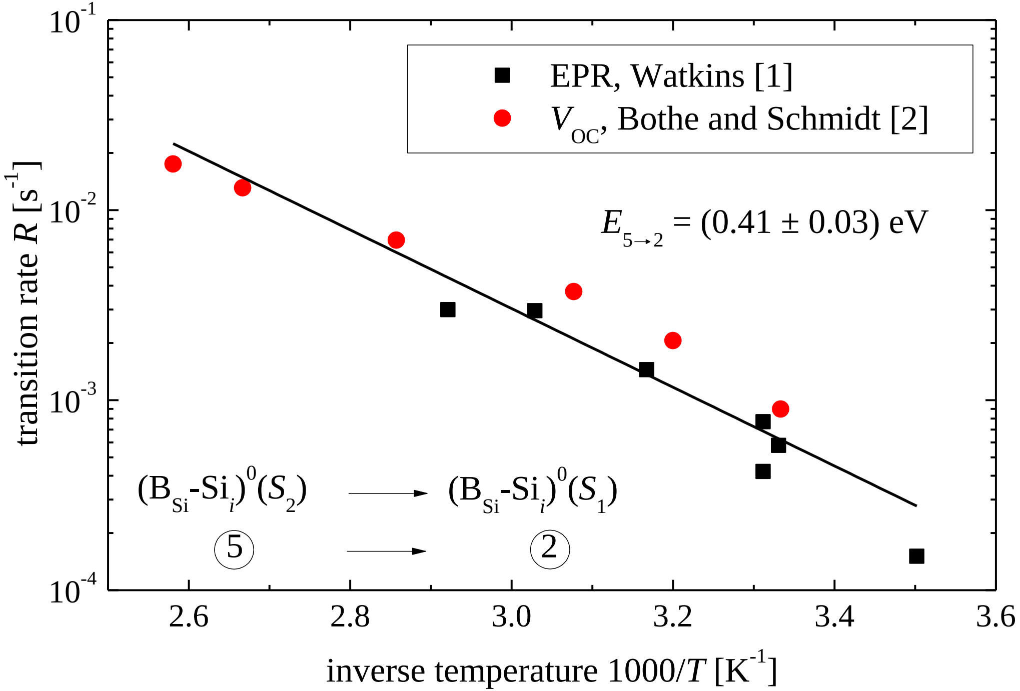
Migration of interstitial boron at room temperature?

Common understanding of B_i, which is the B_{Si}-Si_i-defect [1]:

- Trapping self-interstitials by B_s produces the interstitial boron species, B_i, which is mobile above ~240 K [2,3] and can be trapped by other defects e.g. B_iB_s or B_iO_i
- In contradiction to A_{Si}-Si_i-defect model since LID remains after high temperature anneals
- Problem: In these papers [2,3] there is no "direct evidence" that migration of boron is the cause for the disappearance of Si-G28 or DLTS peaks!
- The annealing kinetics of these signals are still an open question [4].

[1] E. Tarnow, Europhys. Lett. 16, 449 (1991).
[2] G. Watkins, Physical Review B 12, 5824 (1975).
[3] J. Troxell et al., Phys. Rev. B 22, 921 (1980).
[4] R. Harris et al., Mat. Sci. For. 10-12, 163 (1986)

Migration of interstitial boron at room temperature?



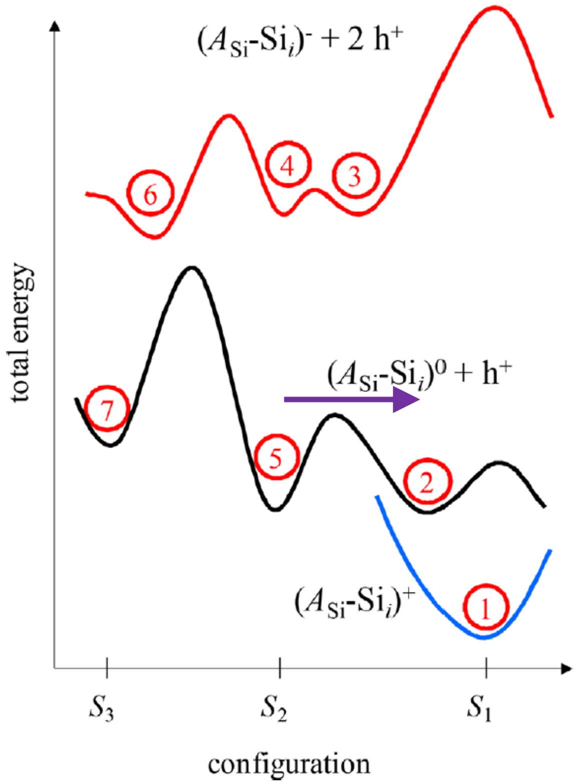
K. Lauer, C. Möller, D. Schulze, and C. Ahrens, AIP Advances 5, 017101 (2015).

- Disappearance of Si-G28 (EPR signal) coincides with annihilation of fast LID component (V_{OC} signal)

=> A_{Si}-Si_i-defect model in agreement with experimental data of boron interstitial defect

[1] G. Watkins, Physical Review B 12, 5824 (1975).
[2] K. Bothe and J. Schmidt, J. Appl. Phys. **99**, 013701 (2006).

Migration of interstitial boron at room temperature?



- Disappearance of Si-G28 (EPR signal) coincides with annihilation of fast LID component (V_{OC} signal)

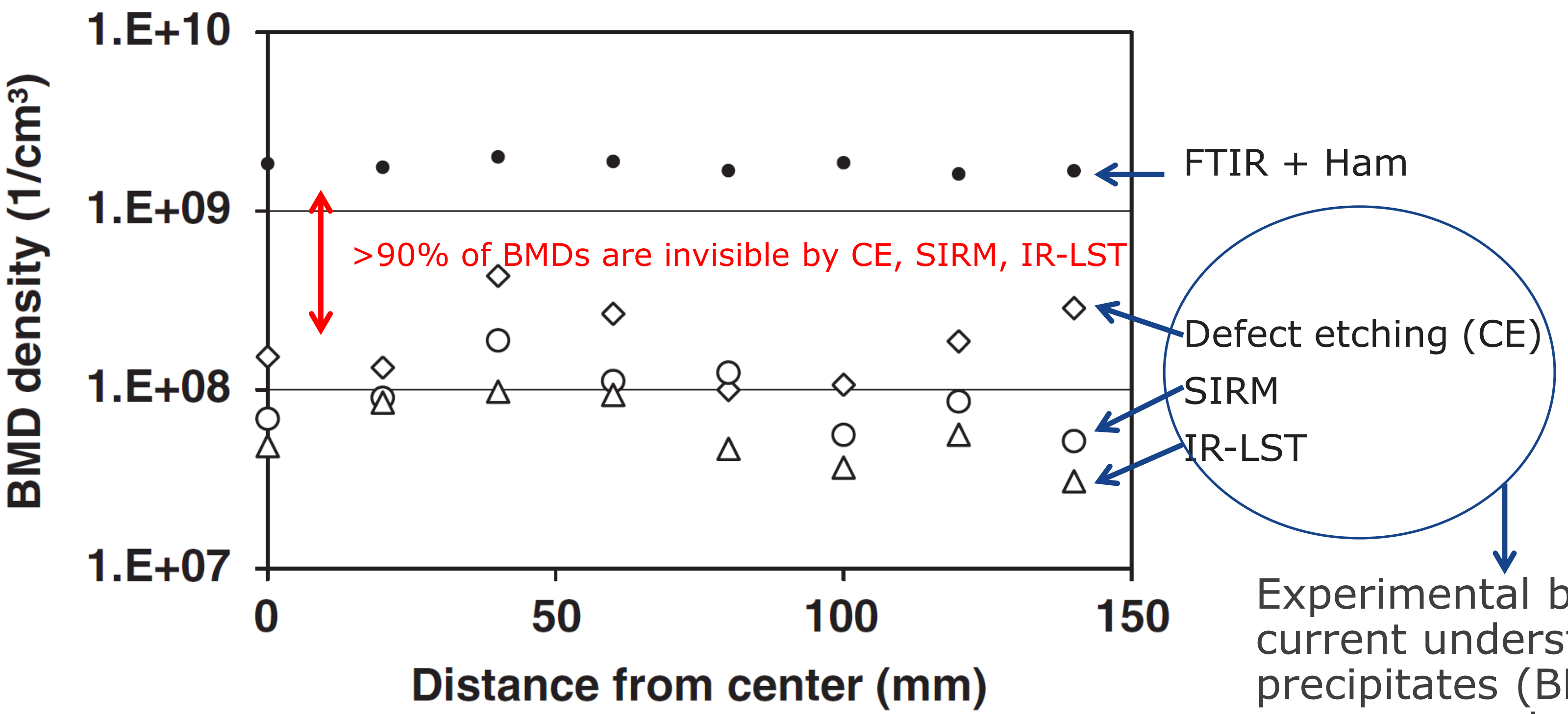
=> A_{Si}-Si_i-defect model in agreement with experimental data of boron interstitial defect

Dependency of A_{Si}-Si_i-defect density on $[O_i]^2$

- LID defect density experimentally found to be proportional to $[O_i]^2$
- Hence LID often labeled as boron-oxygen (BO) defect complex
- Explanation in frame of A_{Si}-Si_i-defect model :
  - O_i forms precipitates during crystal cooling [1]
  - For two precipitating oxygen atoms approximately one silicon atom is released [2]
  - Si_i migrates to substitutional acceptor atom and forms A_{Si}-Si_i-defect [3,4]
- Consequence:
  - Oxygen precipitate density in as grown crystals must be proportional to $[O_i]^2$
- Can this be excluded by present available experimental data?
- No!

[1] J. Vanhellemont et al., Electrochem. Soc. Proc. 98-13, 101 (1998).
[2] U. Gösele et al., Appl. Phys. A 28, 79–92 (1982)
[3] V. Akhemetov et al. Phys. Status Solidi A 72, 61 (1982)
[4] A. Bean et al. J. Phys. C 5, 379 (1972)

Measurement of bulk micro defects (BMD)



Experimental basis for current understanding of precipitates (BMD) in as-grown crystals

G. Kissinger et al., Mat. Sci. Sem. Proc. 9, 236 (2006).

Dependency of A_{Si}-Si_i-defect density on $[O_i]^2$

- Relation of invisible precipitate density on $[O_i]$ is not yet investigated experimentally.

- Theory of homogenous oxygen nucleation predicts a $[O_i]^2$ dependency [1]

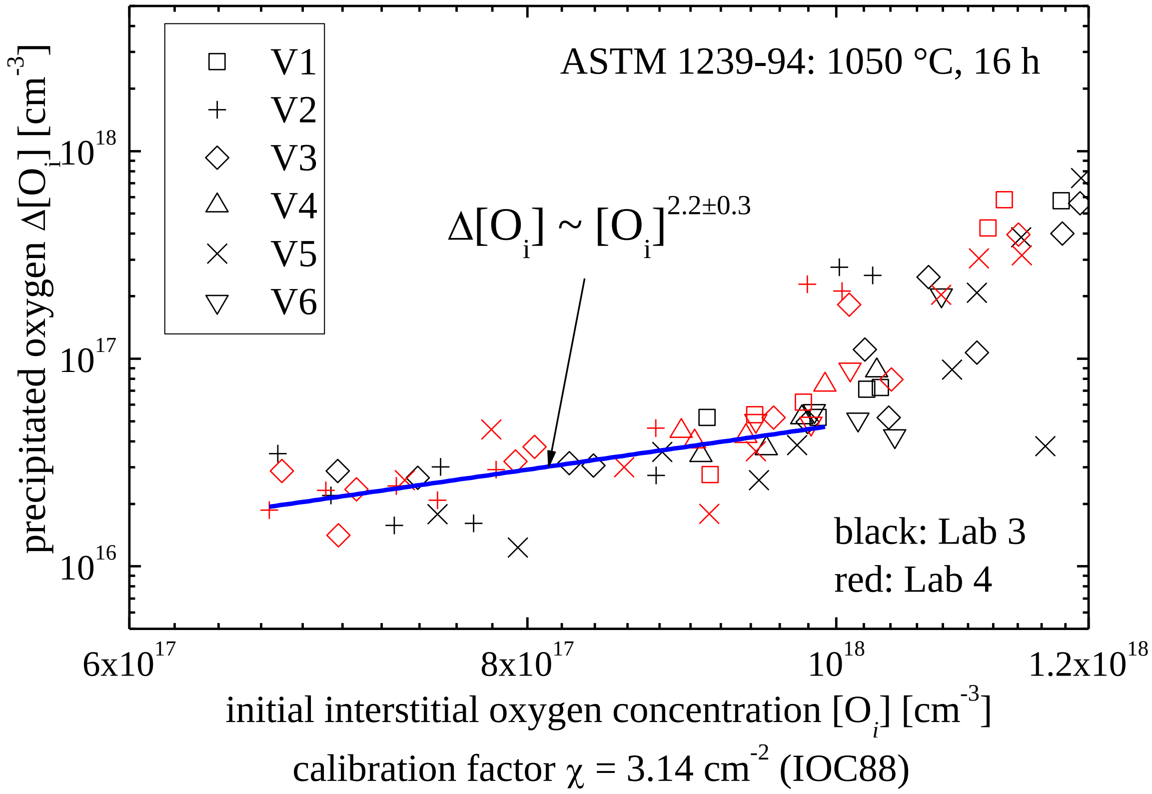
  - => An $[O_i]^2$ dependency of the majority of the oxygen precipitate density in as-grown silicon cannot be excluded and is even expected from theory.

=> An indirect involvement of oxygen in the LID defect cannot be excluded by present available experimental data on oxygen clustering during crystal cooling!

- Interesting: Thermal donor generation rate depends on $[O_i]^2$ as well.

[1] T. Tan et al., in „Oxygen in Silicon“ (1994)

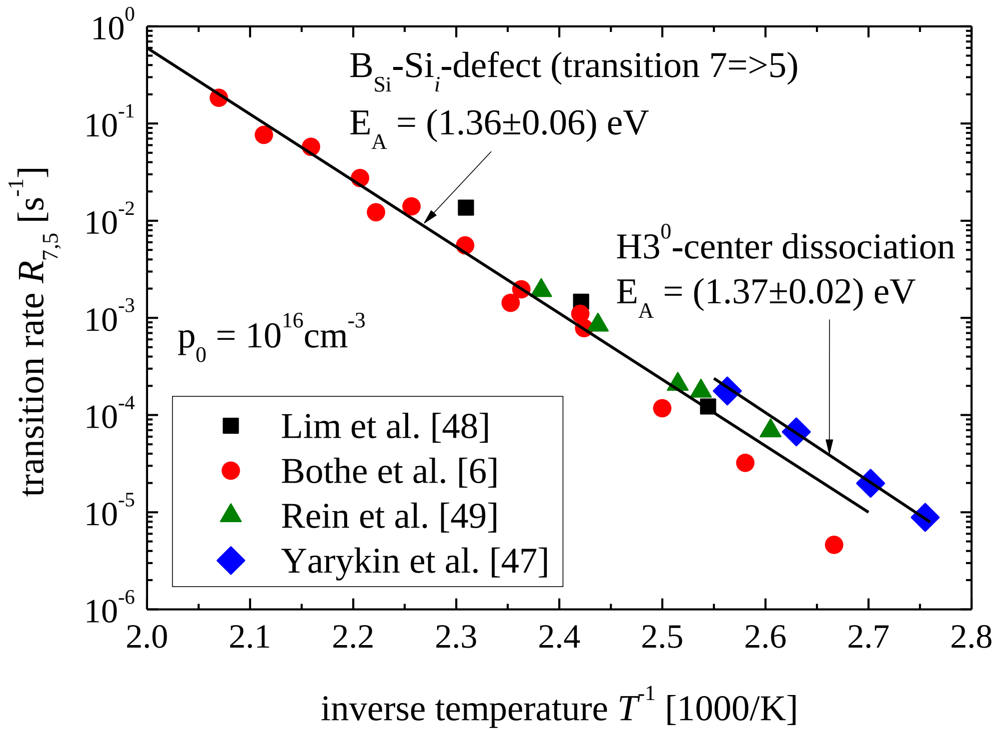
Oxygen precipitation by annealing steps



- Precipitated oxygen concentration shows in relevant region a quadratic dependency on interstitial oxygen concentration

K. Lauer, C. Möller, D. Schulze, C. Ahrens, and J. Vanhellemont, Solid State Phenomena 242, 90 (2015).

Hydrogen passivation



- LID can be deactivated by thermal annealing and illumination when hydrogen is available
- H3 center could be identified with B_{Si}-Si_i-H defect

K. Lauer, C. Möller, D. Schulze, C. Ahrens, and J. Vanhellemont, Solid State Phenomena 242, 90 (2015).