The Norwegian Research Centre for Solar Cell Technology

CENTRE FOR ENVIRONMENT-FRIENDLY ENERGY RESEARCH

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Challenges in GD-MS analysis of PV silicon materials

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EW-GDS

3rd-4th September 2012

Why do we need to measure impurities in PV silicon?

Silicon value chain

Role of impurities in solar cell silicon

⇒ Quantitative measurements **?**

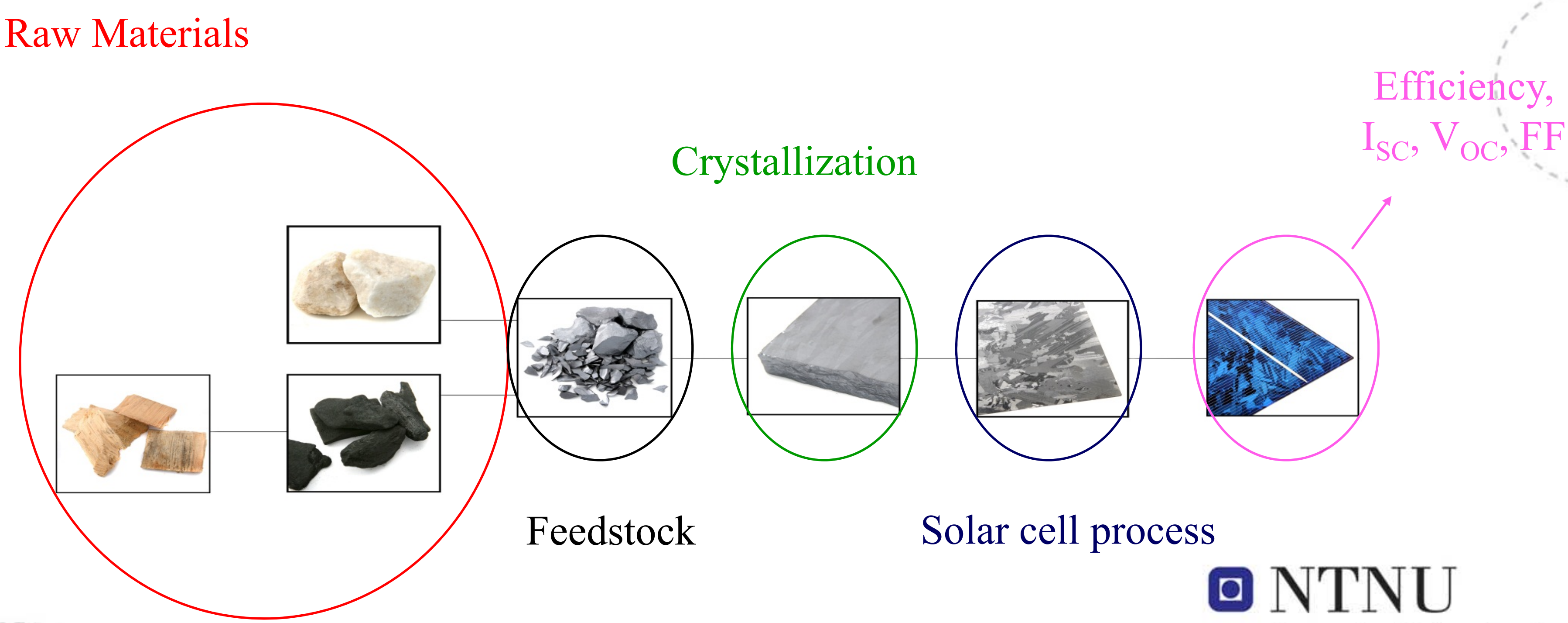
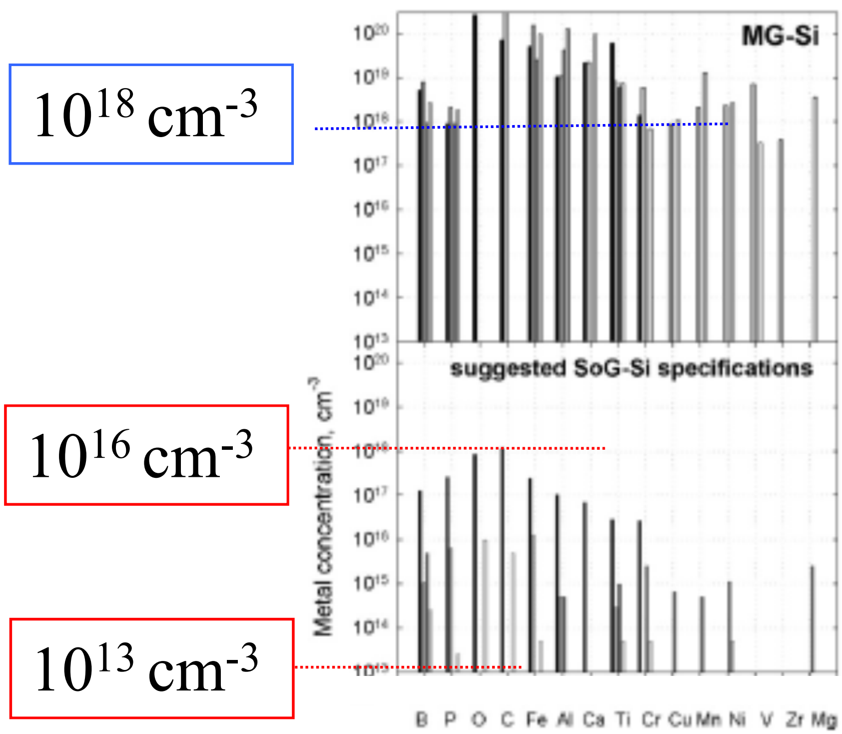
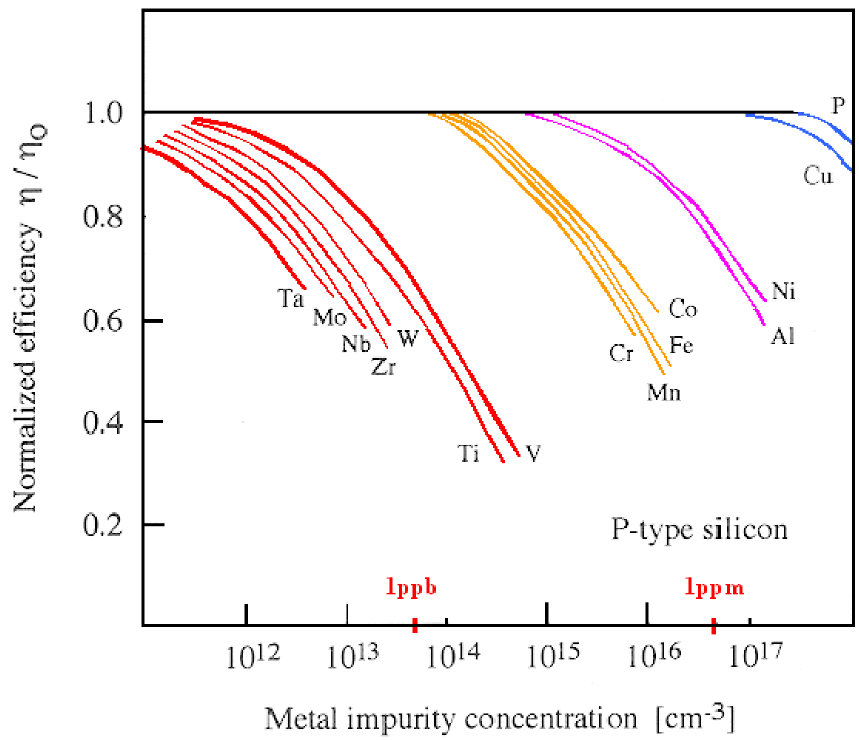


Photo: Melinda Gaal

Why do we need to measure impurities in PV silicon?



Istratov et al., Mat Sc Eng B (2006)



Davis et al. (1980), IEEE Transactions

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Outline

- Trace element analysis in PV silicon
  - Occurrence in the matrix
  - Quantification of trace elements
- Applications of GD-MS for PV silicon:
  - Concentration of doping elements
  - Concentration of metal impurities
- Summary

Silicon for photovoltaics

- Si is a **semicondutor** material ⇔ the concentration of doping elements influences the possibility to perform GD-MS analyses

- Typical concentrations of doping elements (p-type solar cells) are in the range **110 – 300 ppba** ⇔ resistivity in the range 1 – 2.5 Ω cm

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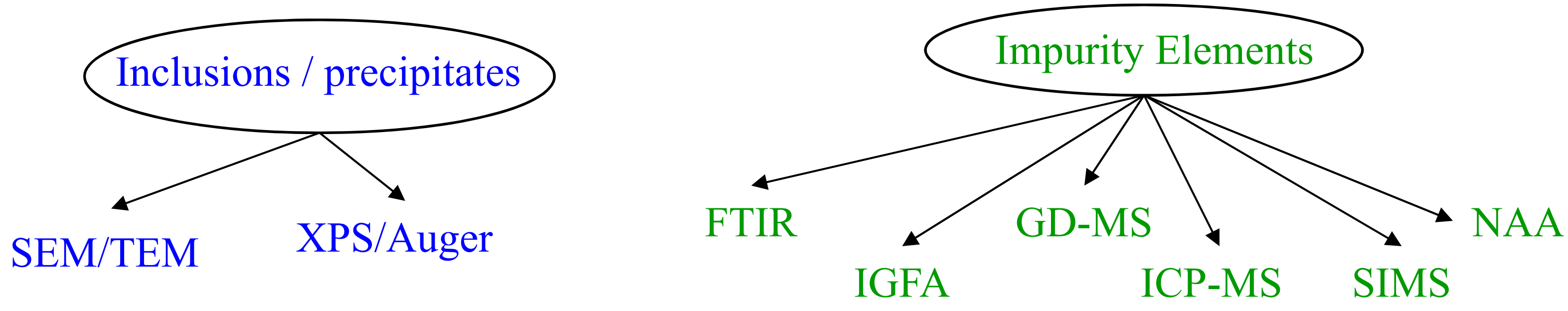
Analytical methods for trace elements analysis in PV silicon

- ❑ Impurities are present in Si for photovoltacis in 2 states:
  - Dissolved into the Si matrix: O_i, C_s, Fe_i, …
  - As precipitates: metal- based, Si_3N_4, SiC …
- ❑ Impurities can be affected by macro- and micro-segregation ⇔ different techniques are available / suitable to measure the impurities



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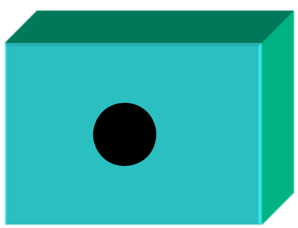
Experimental setup

Flat samples - sample size:
max. Ø 70 mm, 40 mm height
min. Ø 20 mm



Analysed area: Ø ~ 8mm

⇩

Bulk measurement, average over a wide area

Thermo ELEMENT GD

Sputtering rate = 20 nm/sec

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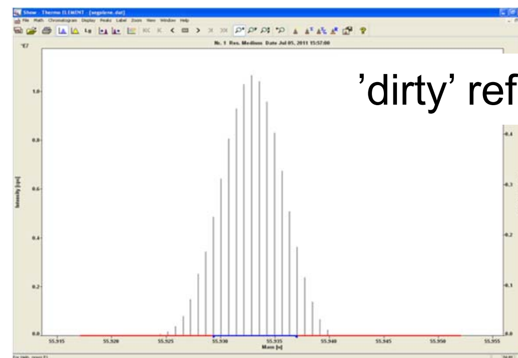
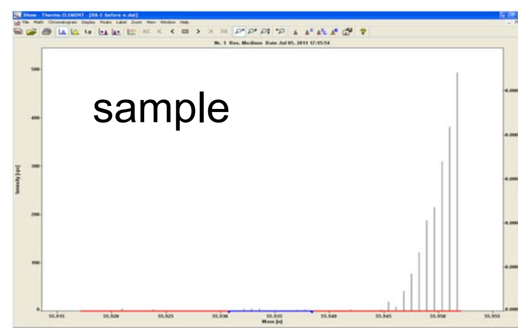
Quantification of trace elements

The quantification of the concentration of the elements is done according to:

$$C_X = \frac{(I_X)}{(I_M)} \cdot \frac{(A_M)}{(A_X)} \cdot RSF$$





C_X: concentration of element (isotope)
C_M: concentration of matrix (Si^{28})
I_X: intensity (cps) of element
I_M: intensity (cps) of matrix
A_X: abundance of element (isotope)
A_M: abundance of matrix (Si^{28})
RSF: relative sensitivity factor (element-specific)

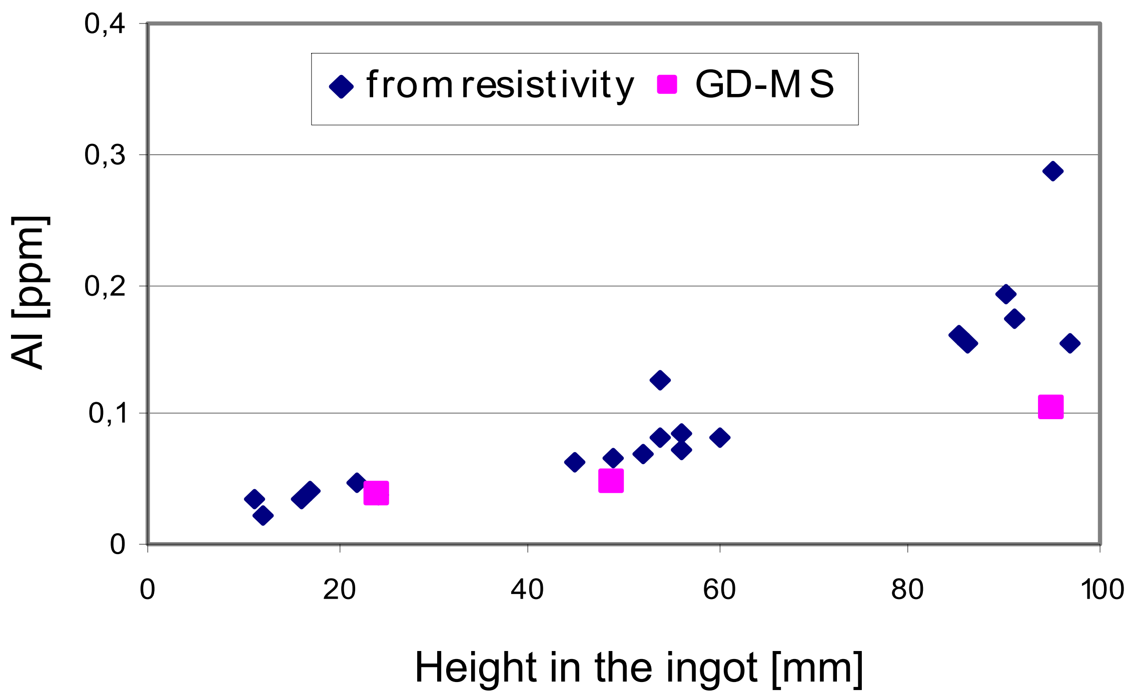
Ion Beam Ratio (IBR) = I_X / I_{Si}

Applications of GD-MS for PV silicon materials

- Concentration of doping elements:
  - Indirect measurement of resistivity
  - Comparison with direct measurement of resistivity
- Concentration of metal impurities:
  - Important to understand their effect on the electronic properties of Si

Applications - Dopant concentration

mc-Si with Al doping, p-type semiconductor



ASTM F723-99

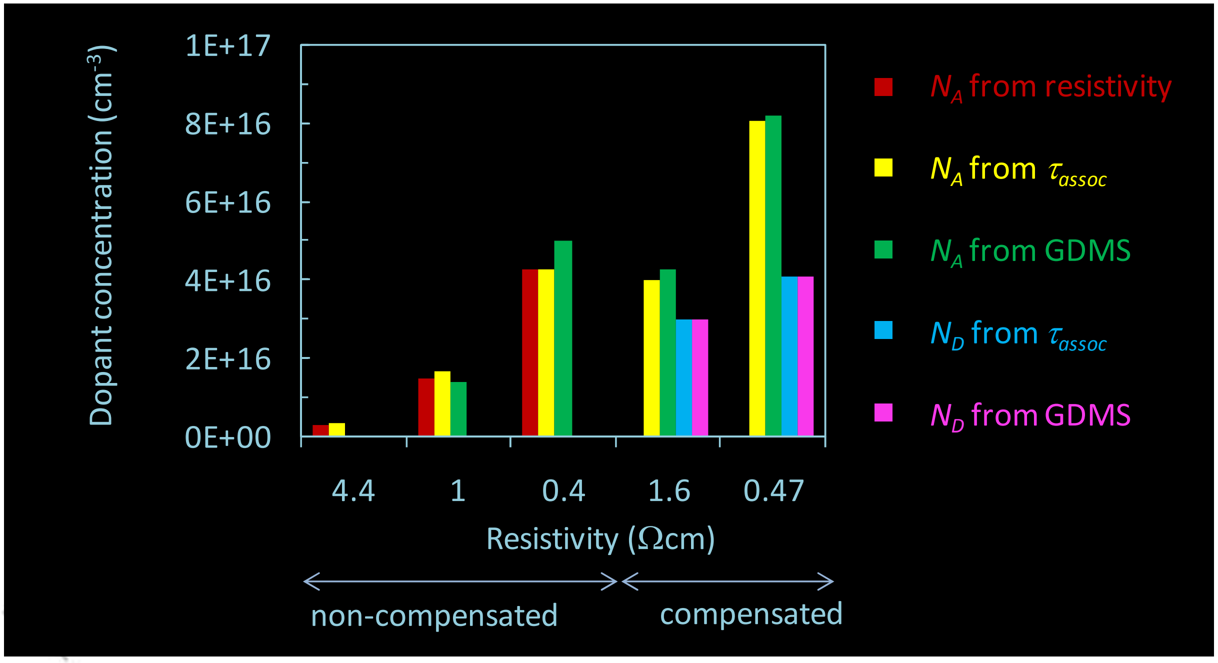
$$N_{acceptor} = \frac{c_1}{\rho} + \frac{c_2}{f(\rho)}$$

Di Sabatino et al., EUPVSEC (2007)

Applications - Dopant concentration from Fe-acceptor pairing

B and P by GDMS ⇩

Minority carrier lifetime before and after light soaking (Fe-B pairs dissociate) ⇨ calculate B, N_A and P, N_D ⇨ comparison



Macdonald et al., EUPVSEC (2008)

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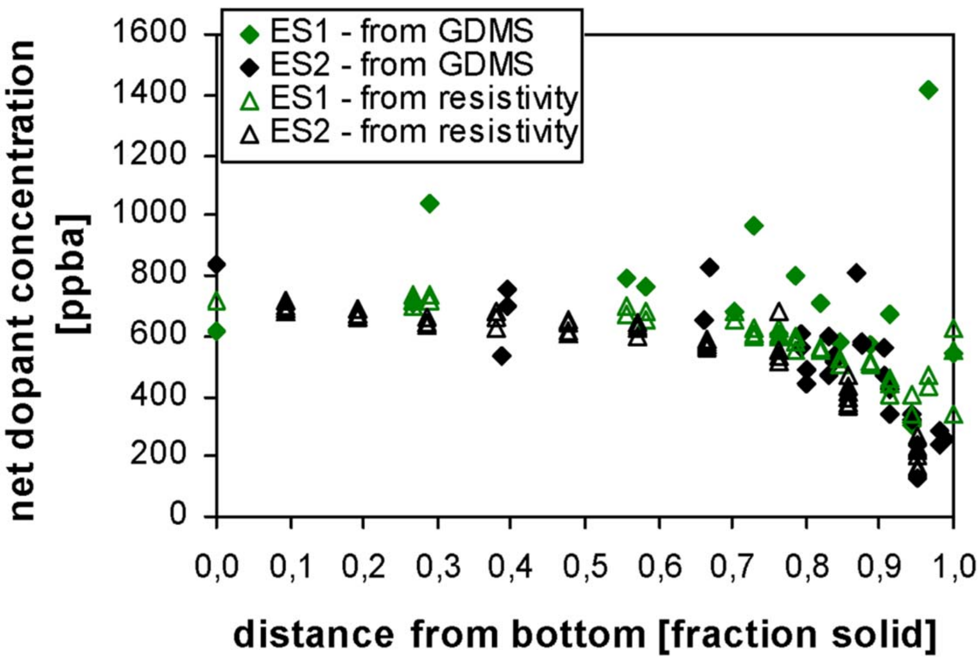
Applications - Net doping in compensated silicon

Compensation ⬄ high content of acceptor (B) and donor (P) species

conversion equation from ASTM F723-99 for p- or n- type may be applied to the net doping



Modanese et al., PiP (2011)

⇩

developed method by GDMS

⇩

$$N_{NET} = (B+Al) - (P)$$

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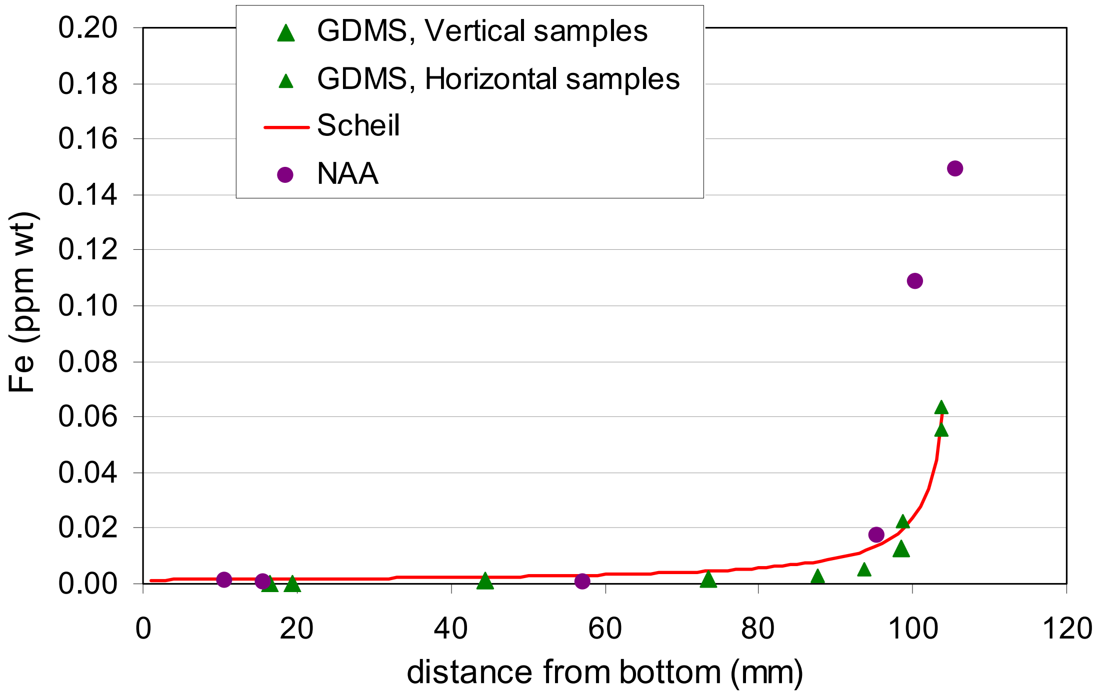
Applications - Fe addition



- ❑ 50 ppmw Fe were added to the Si melt
- ❑ Given the low segregation coefficient (C_{sol} / C_{liq} ≈ 10^{-5}), most of the Fe segregates towards the top of the ingot (last to solidify) ⇔ non-homogeneous distribution

Kvande et al., JAP (2008)

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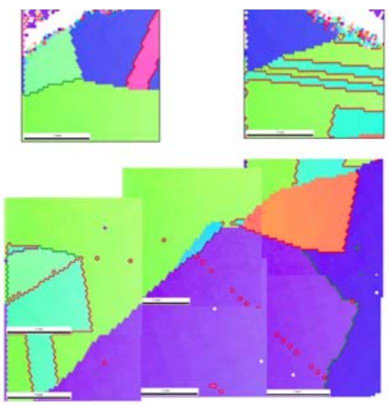
Applications - Study of grain boundaries

Metal impurities in PV Si can form precipitates:

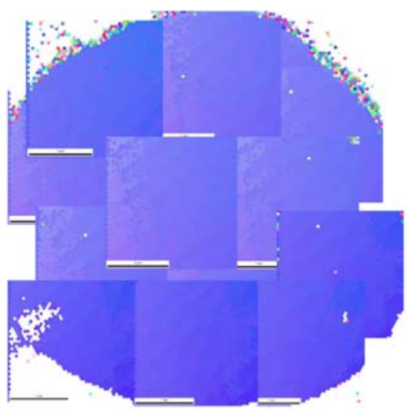
- they are detrimental for electronic properties
- they usually segregate at grain boundaries

⇨ **Is there any difference due to sample microstructure** (i.e. random grain boundary, single grain, twin boundary)**?**

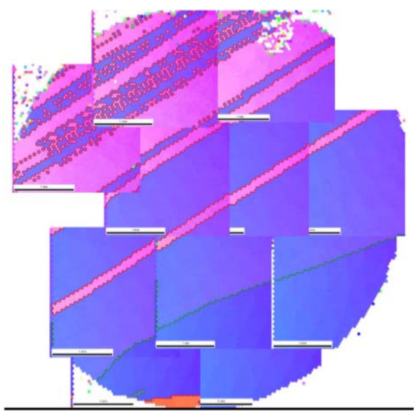
Selected areas:
- SG1: single grain, area 1
- GB1: (random) grain boundary, area 1
- TB1: twin boundary, area 1



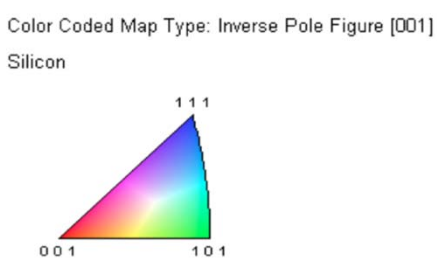
GB1



SG1



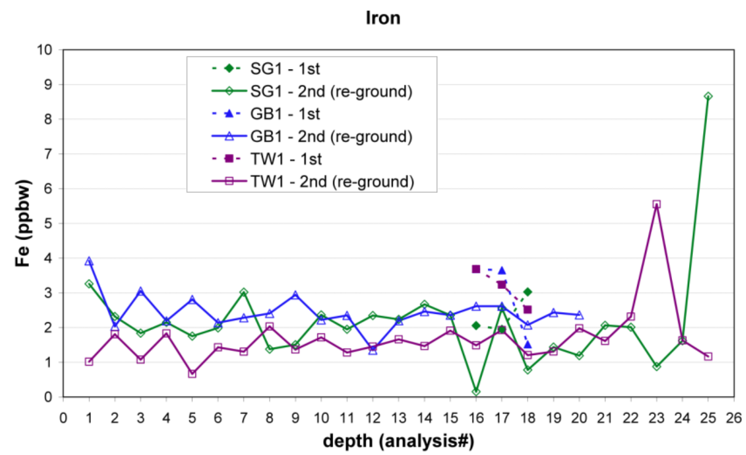
TB1



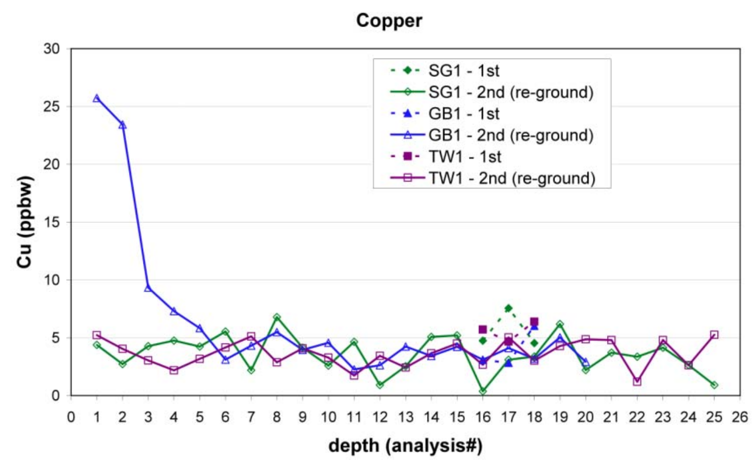
Applications - Study of grain boundaries (continue)

Selected impurities in mc-Si: Fe and Cu

Selected areas:
- SG1: single grain, area 1
- GB1: (random) grain boundary, area 1
- TB1: twin boundary, area 1



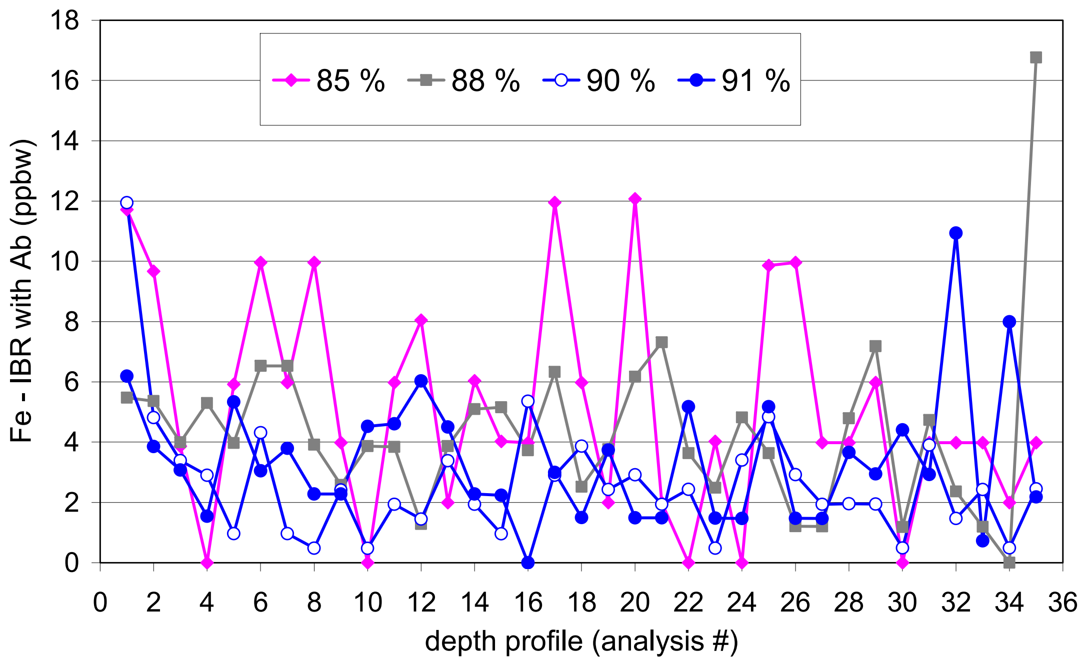
➢ No clear evidence of precipitates ⇔ too low concentrations **?**



No pre-sputtering!

Applications - Depth profiling and investigation of precipitates

- p-type Si ingot, with 50 ppmw (1.25×10^{18} cm^{-3}) Fe and 128 ppbw (1.66×10^{16} cm^{-3}) B added to the melt (prior to casting)



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Sample	Si28 (cps)		Fe56 (ppbw)	
	AVG	STDEV	AVG	STDEV
85%	$1.01x10^{9}$	$9.64x10^{6}$	5.2	3.6
88%	$1.61x10^{9}$	$6.77x10^{7}$	4.3	2.9
90%	$4.15x10^{9}$	$2.56x10^{7}$	2.6	2.1
91%	$2.69x10^{9}$	$5.13x10^{7}$	3.4	2.2

- Non-homogeneous Fe concentration
- Averaging over several repeated analyses
- Low Fe levels, although the impact on electronic properties is strong at these low concentrations

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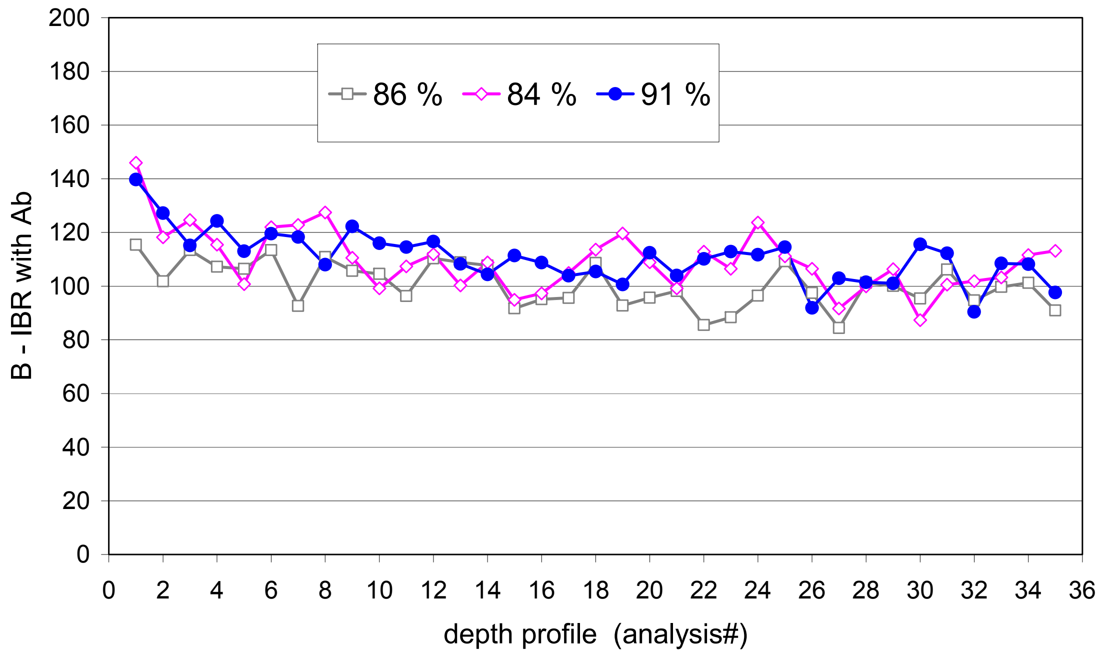

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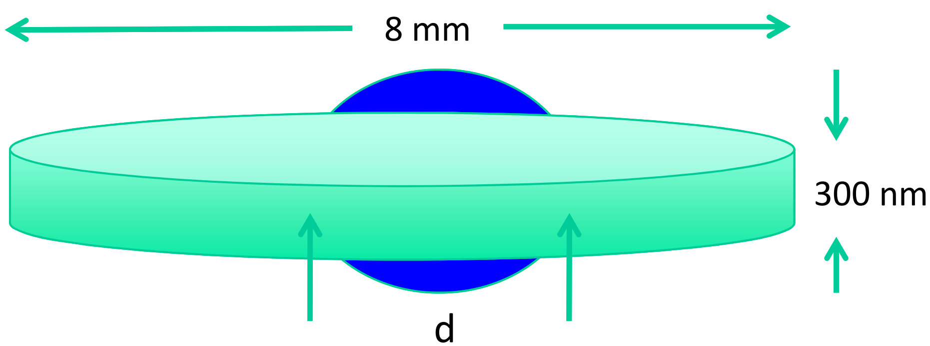
Applications - Depth profiling and investigation of precipitates

❑ p-type Si ingot, with 50 ppmw (1.25×10^{18} cm^{-3}) Fe and 128 ppbw (1.66×10^{16} cm^{-3}) B added to the melt (prior to casting)

Sample	Si28 (cps)		B11 (ppbw)	
	AVG	STDEV	AVG	STDEV
84%	4.57×10^9	4.93×10^7	109	11.6
86%	4.28×10^9	2.72×10^8	101	8.2
91%	5.51×10^9	6.48×10^7	111	10.0

- Homogeneous B concentration
- Compared to Fe, lower number of analyses required
- Important to have a precise quantification due to the B impact on the conductivity

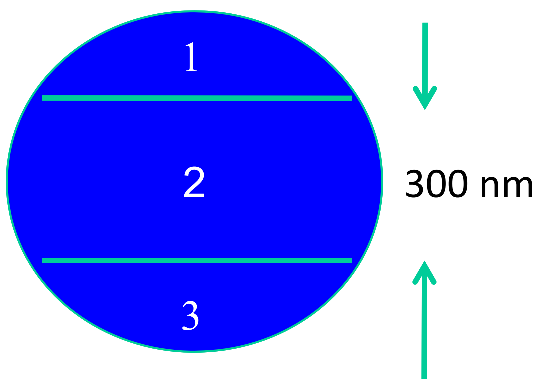
Challenges in the study of GB and dislocations

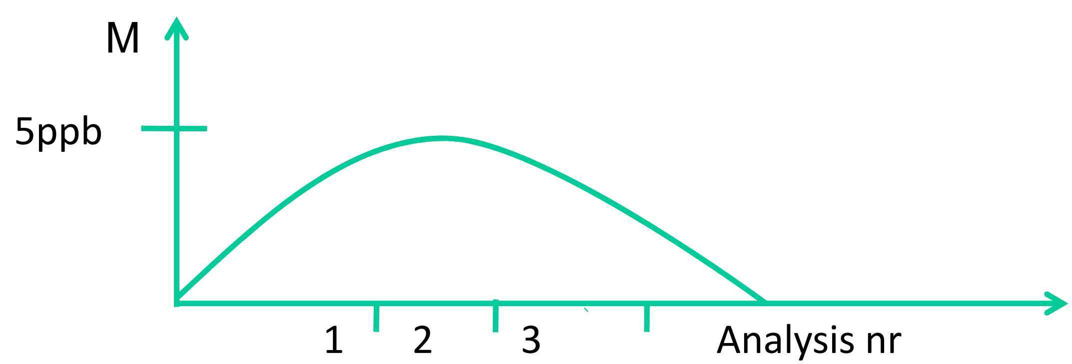


Conclusion:

- ❑ 300 nm particle with 0.5% M ⇔ 0.5×10^{-9}, below LoD!

- ❑ Estimation of the size of precipitates for detection ⇔ to give 5 ppb M, a single particle should have Ø = 660 nm!





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Concluding remarks

- GDMS can provide **reproducible** measurements of doping and trace elements in silicon for photovoltaics, with **precise quantification** down to **low-ppb** levels
- Applications for PV Si - examples:
  - Concentration of **doping elements**: doping, net doping
  - Concentration of **metallic impurities**: segregation profile, relation to micro- and macro-segregation
- Further work: tuning of measurements for precipitates analysis