Materialaspekte multikristalliner Solarzellen aus umg-Si-Feedstock

Kai Petter, Q-Cells SE

FAHL Academia, Oppurg, 29. September 09

Overview

- **Introduction: Impurity concentration in different Silicon Qualities**
- **Production of multicrystalline Ingots and Wafers**
  - Ingot Growth
  - Sawing process
  - Segregation – an important process
- **Companies that produce umg-Si / SOG-Si and their processes**
  - Elkem
  - BSI
  - 6N Silicon
- **Influence of impurities**
  - Dopants
  - Metals
  - Alcaline Metals
  - O / C / N
- **Summary and conclusions**

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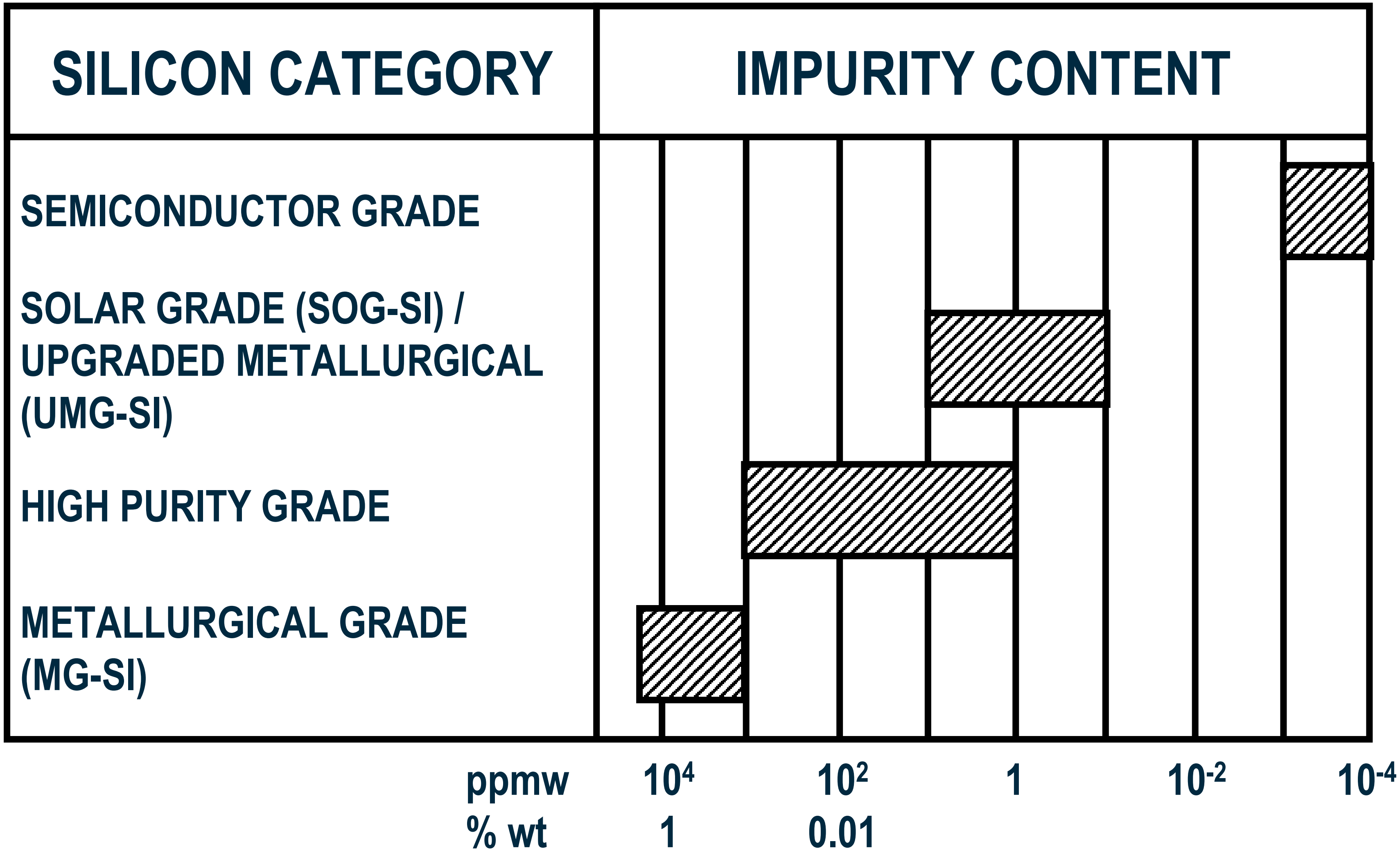
Impurity concentration in different Silicon Qualities



Semiconductor vs. Solar Grade Silicon

Advantages of Semiconductor Grade Silicon:

- Processing from Feedstock to Cell is well known
- Quality is high enough for all high efficiency cell concepts

Advantages of SOG-SI / UMG-SI:

- Energy consumption and payback time lower (→ „greener“ product)
- Lower production and investment costs
- Ramp up of factories and capacities faster → Reaction time to changes in market conditions shorter
- „second source“ to Semiconductor Grade Silicon

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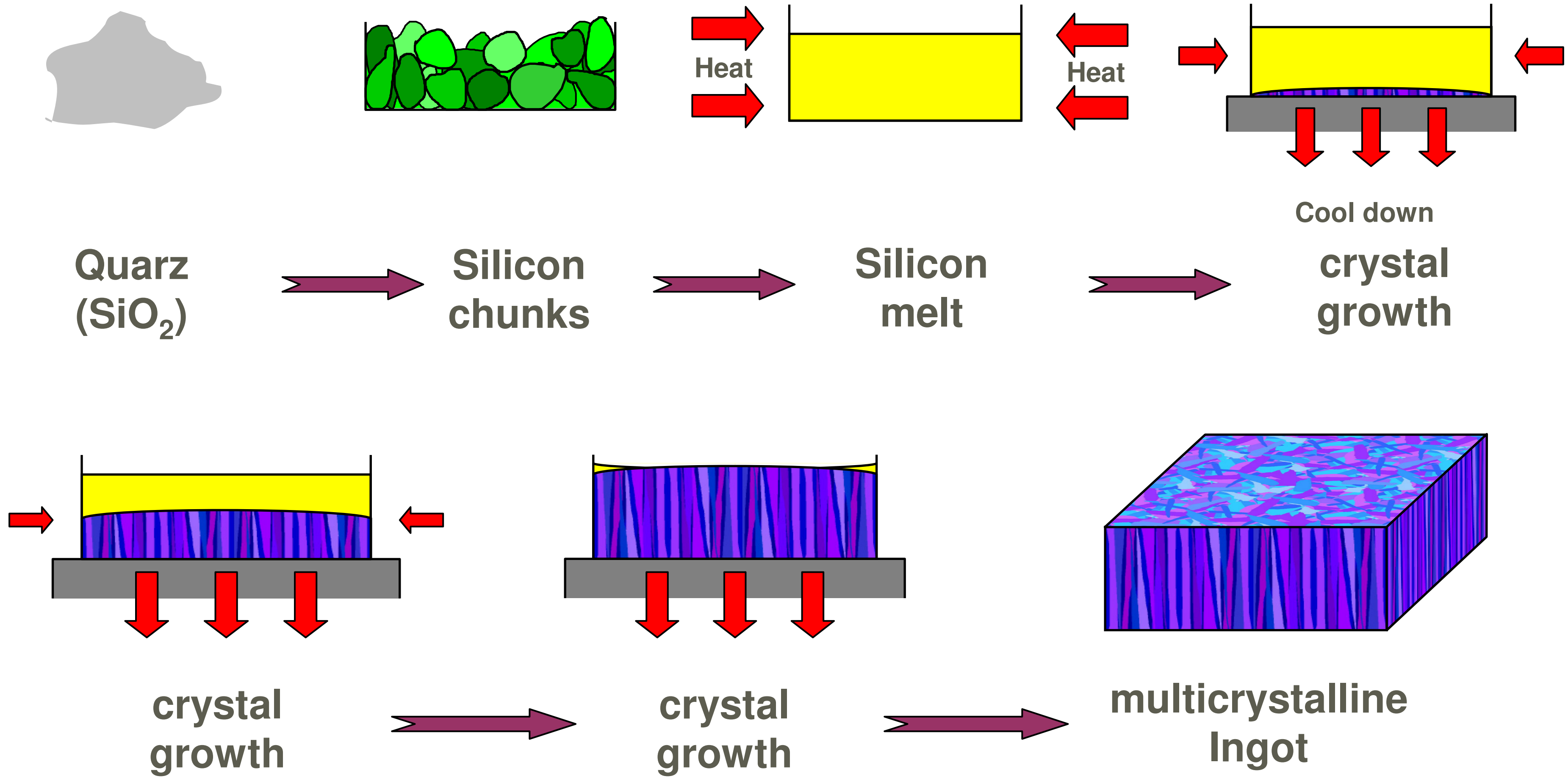
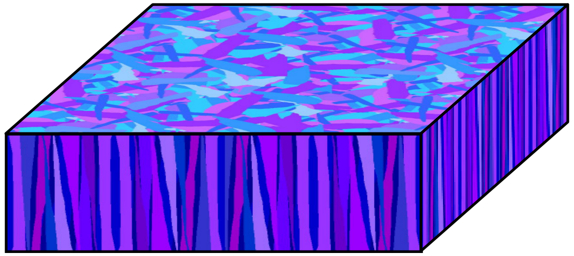
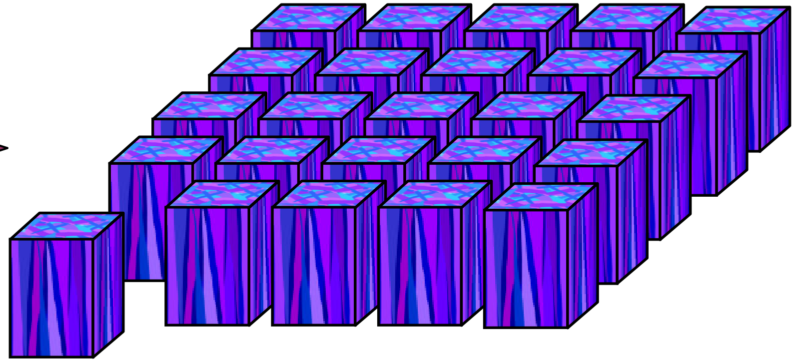
Crystallisation: multicrystalline Ingot



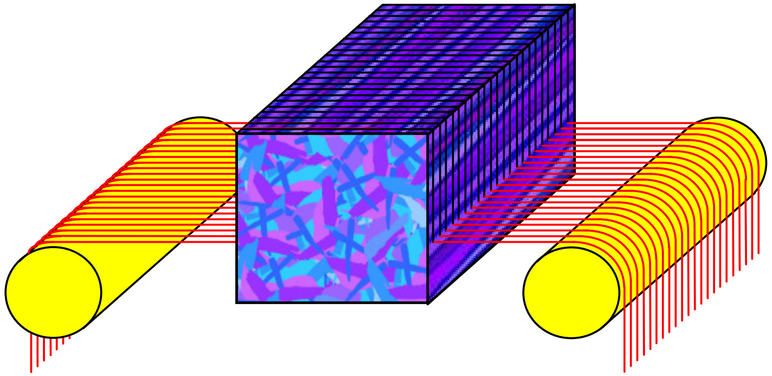
Wire - sawing: multicrystalline wafers



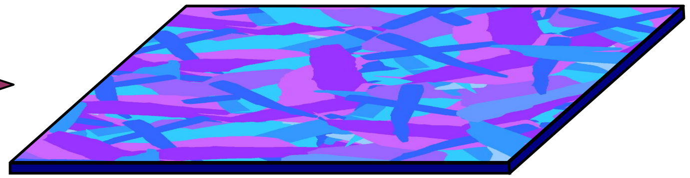
Ingot
~ 80 x 80 x 30 cm
400 kg



Sawing into bricks

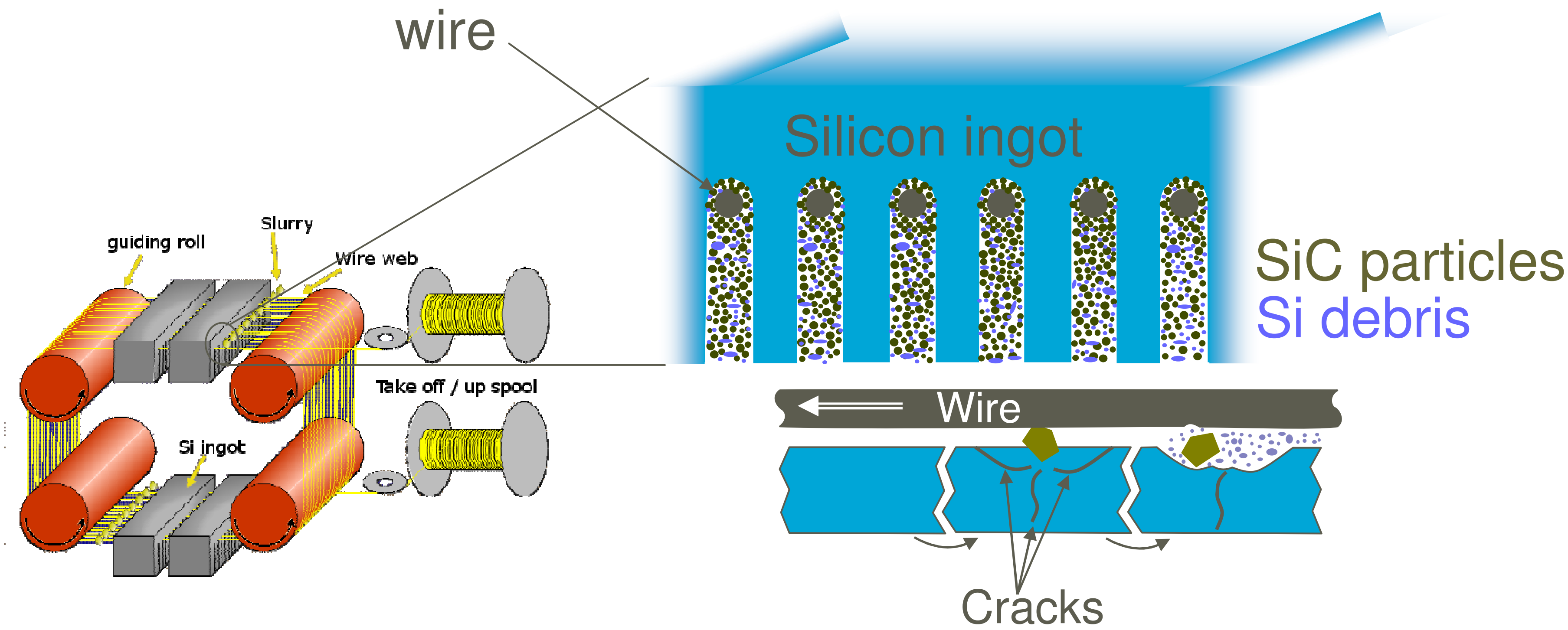


Sawing into wafers
per brick ~ 600 wafers



Multicrystalline Silicon Wafer
156 x 156 mm
Thickness 180 µm

The principle of wire-sawing



A steel wire is wound around wire-guides

Some Slurry (PEG + SiC) is poured on the wires

The SiC particles wear the silicon ingot out → slices wafers

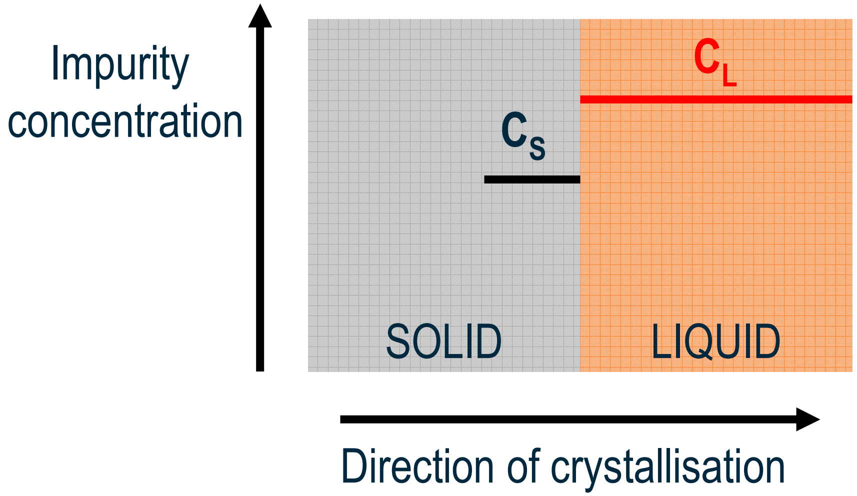
This process induces cracks in the wafers → they become brittle

Segregation – a central process

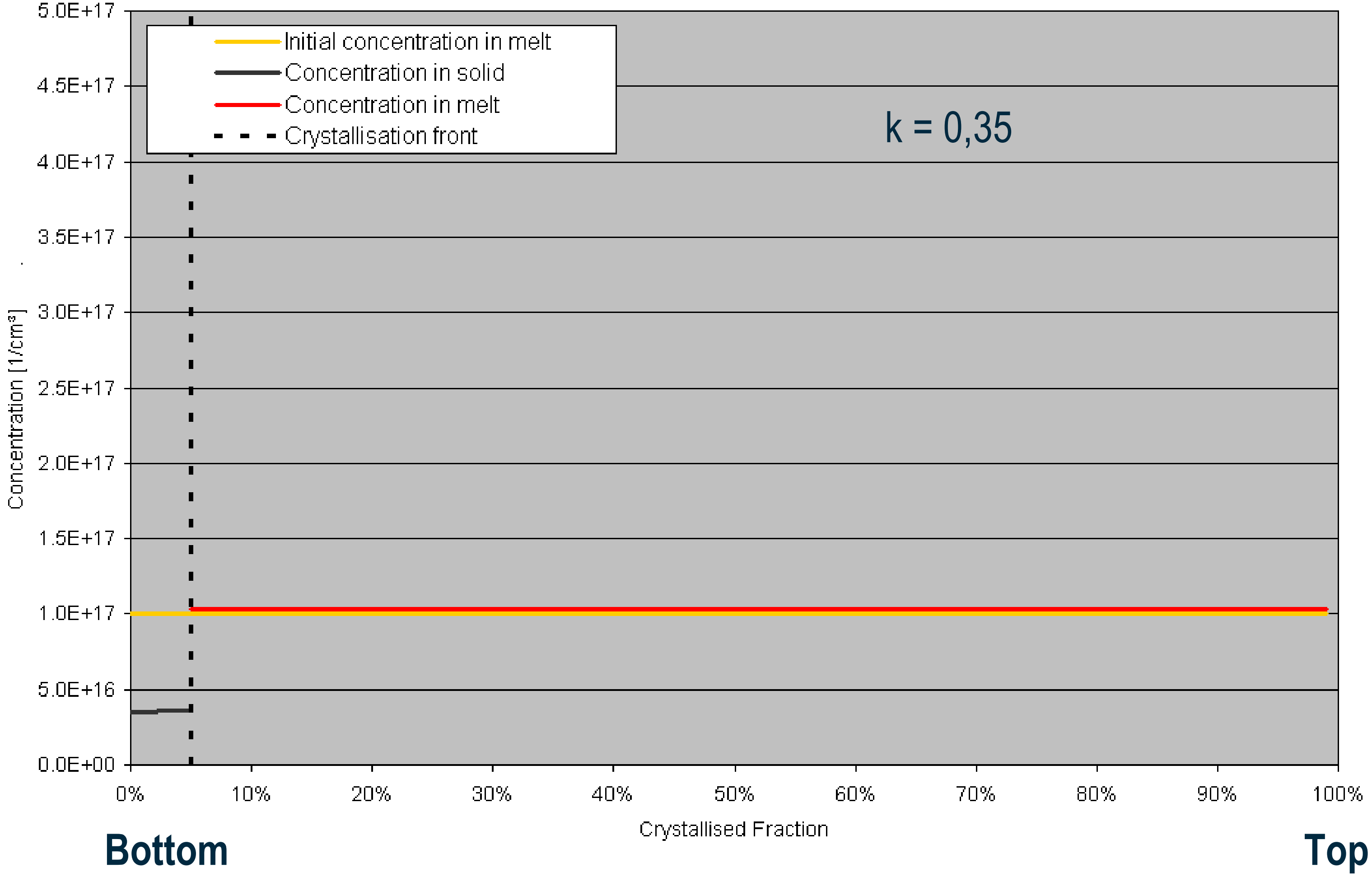
At the growth front, the concentration incorpotated in the crystallised phase is different to the concentration in the melt
The Segregation coefficient k is defined as:

$$k = \frac{C_S}{C_L}$$

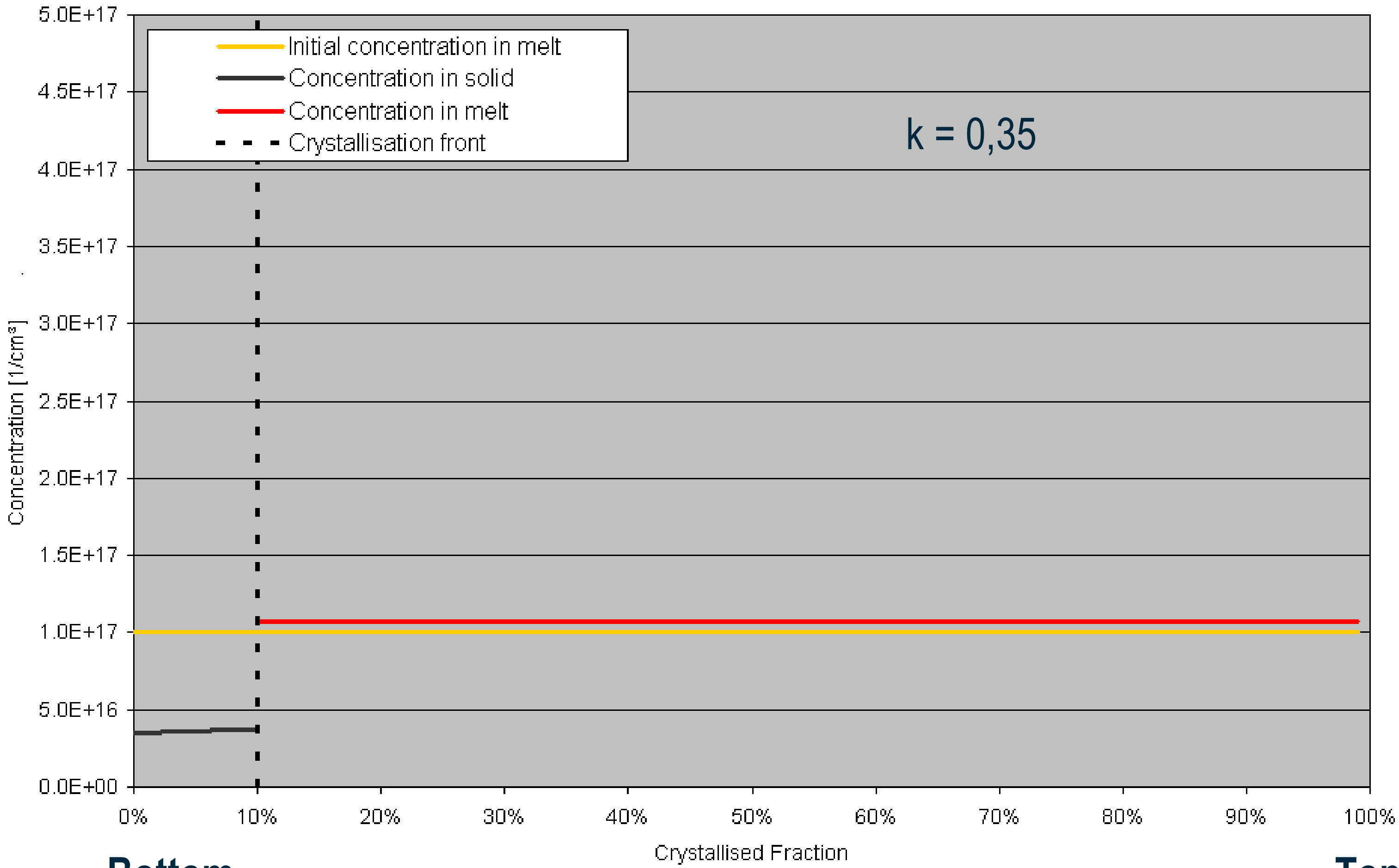
C_L concentration in the melt
C_S concentration in the solid



Segregation



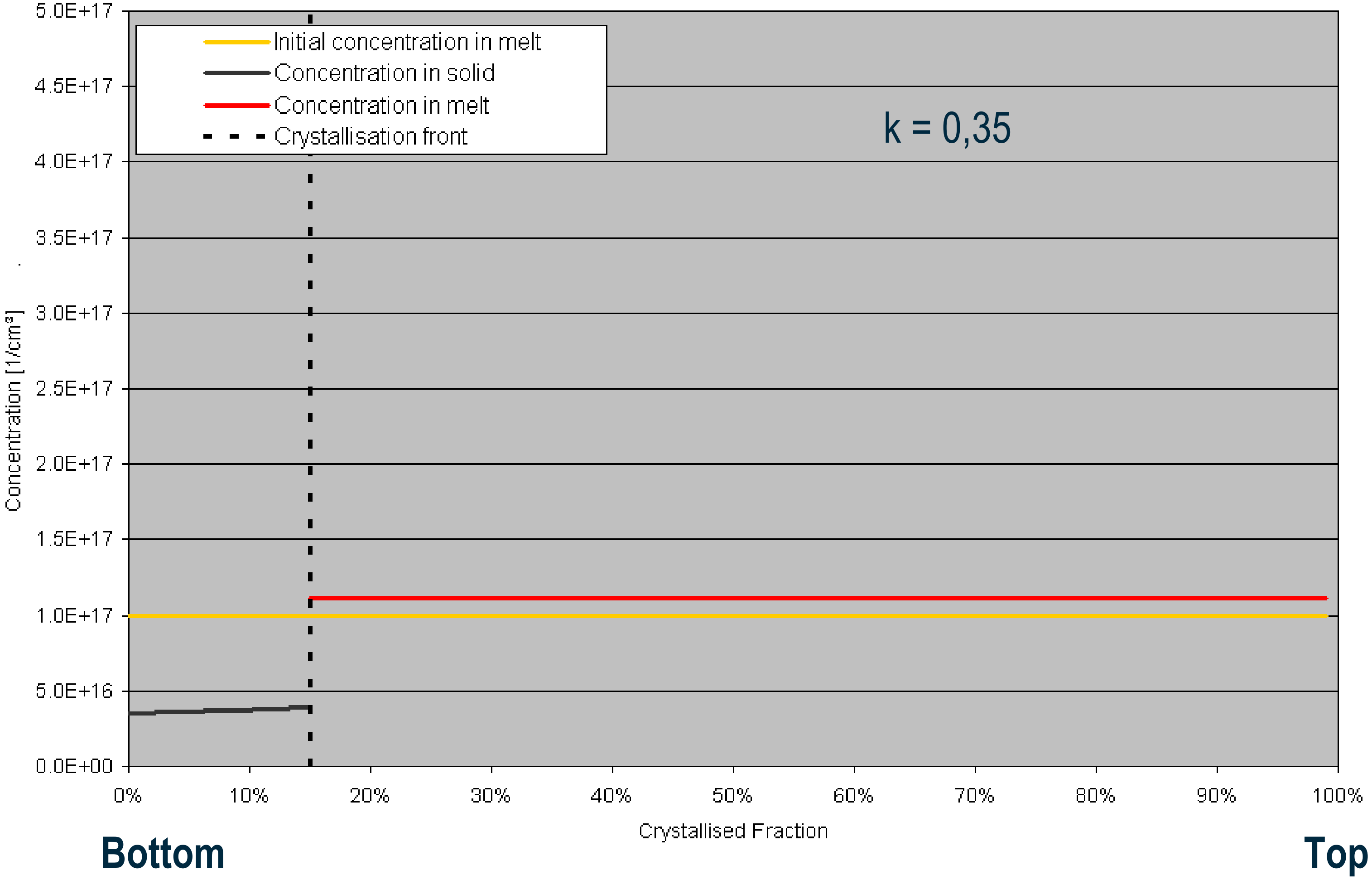
Segregation



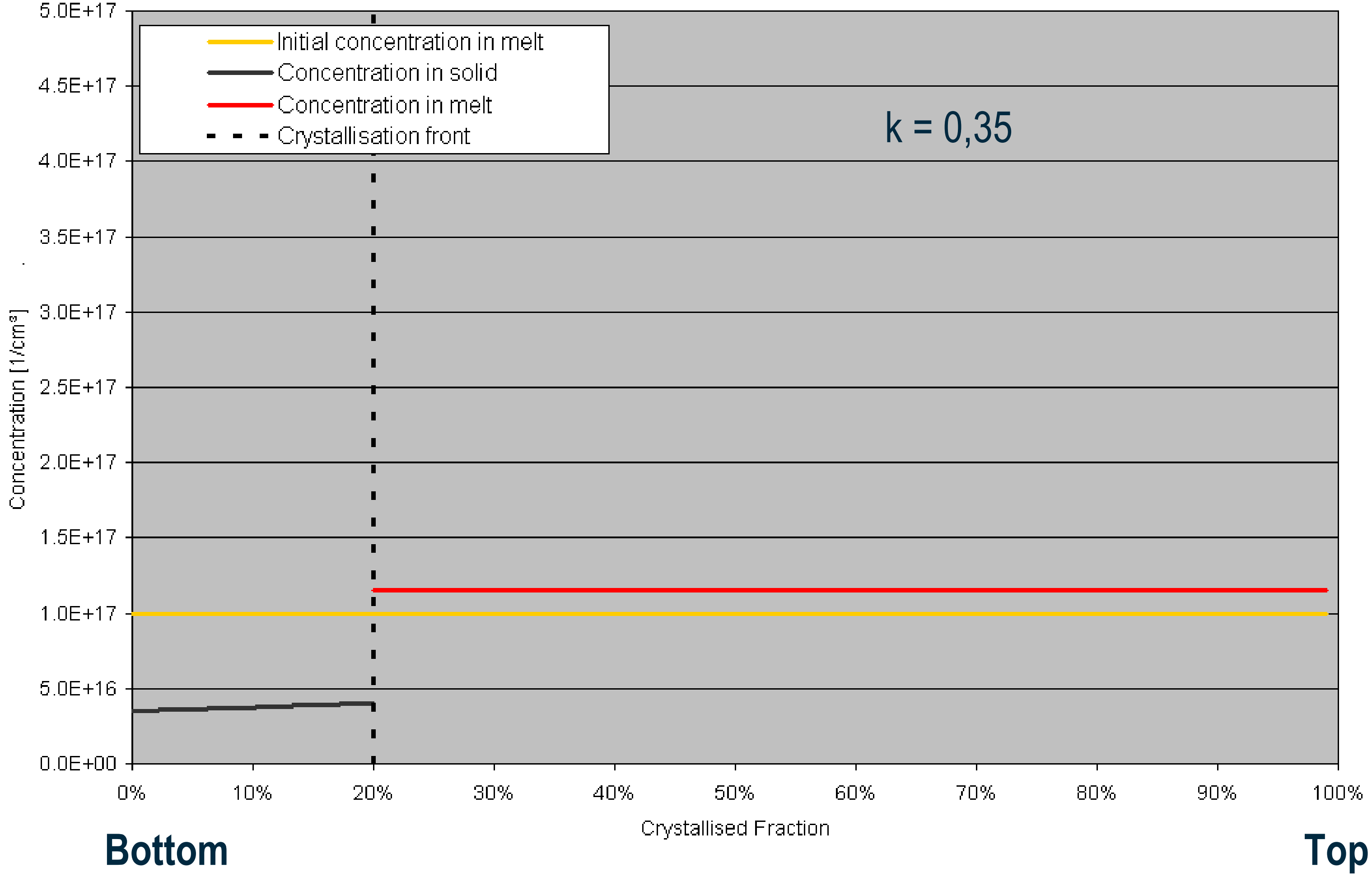
Bottom

Top

Segregation



Segregation



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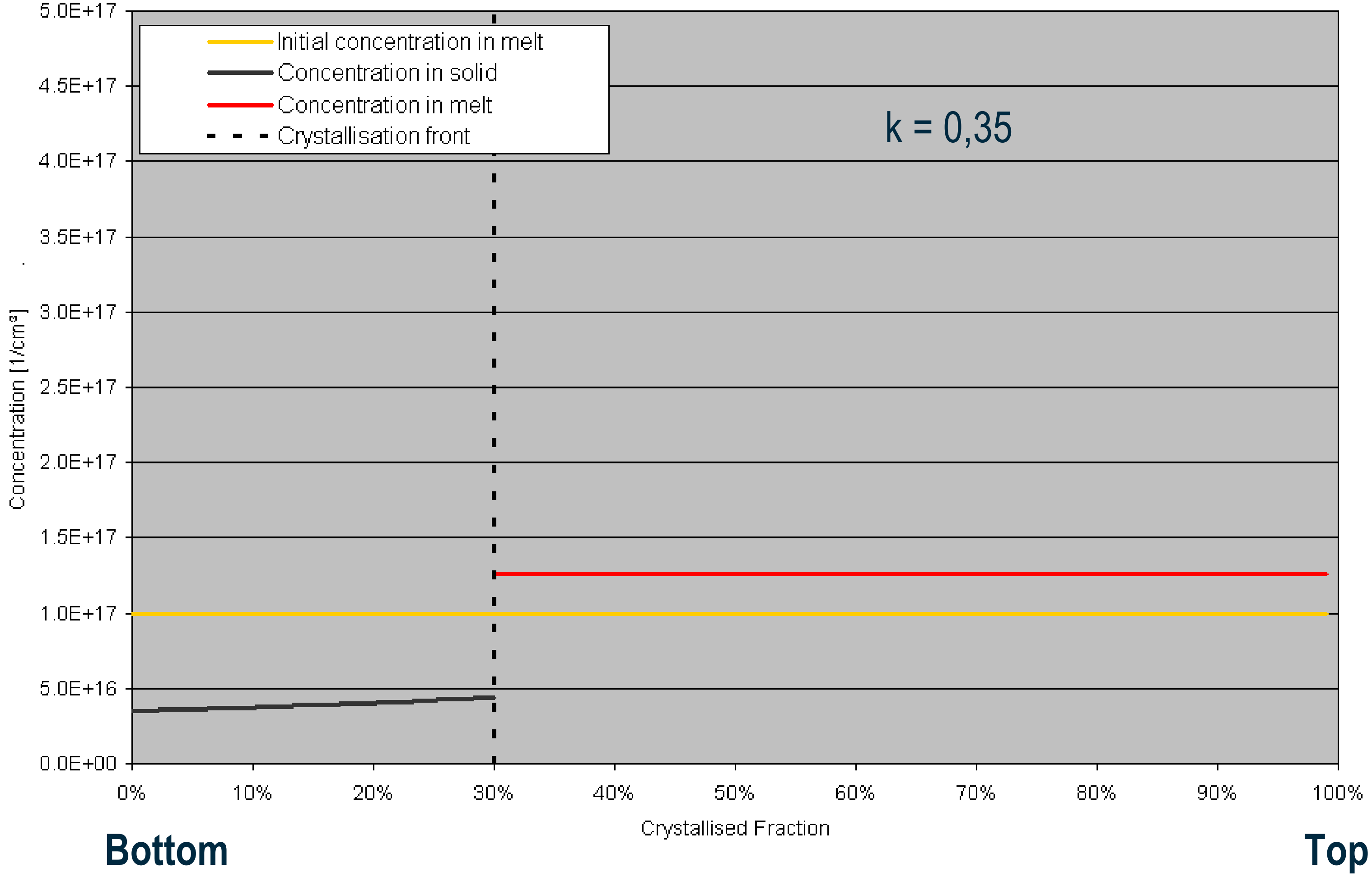

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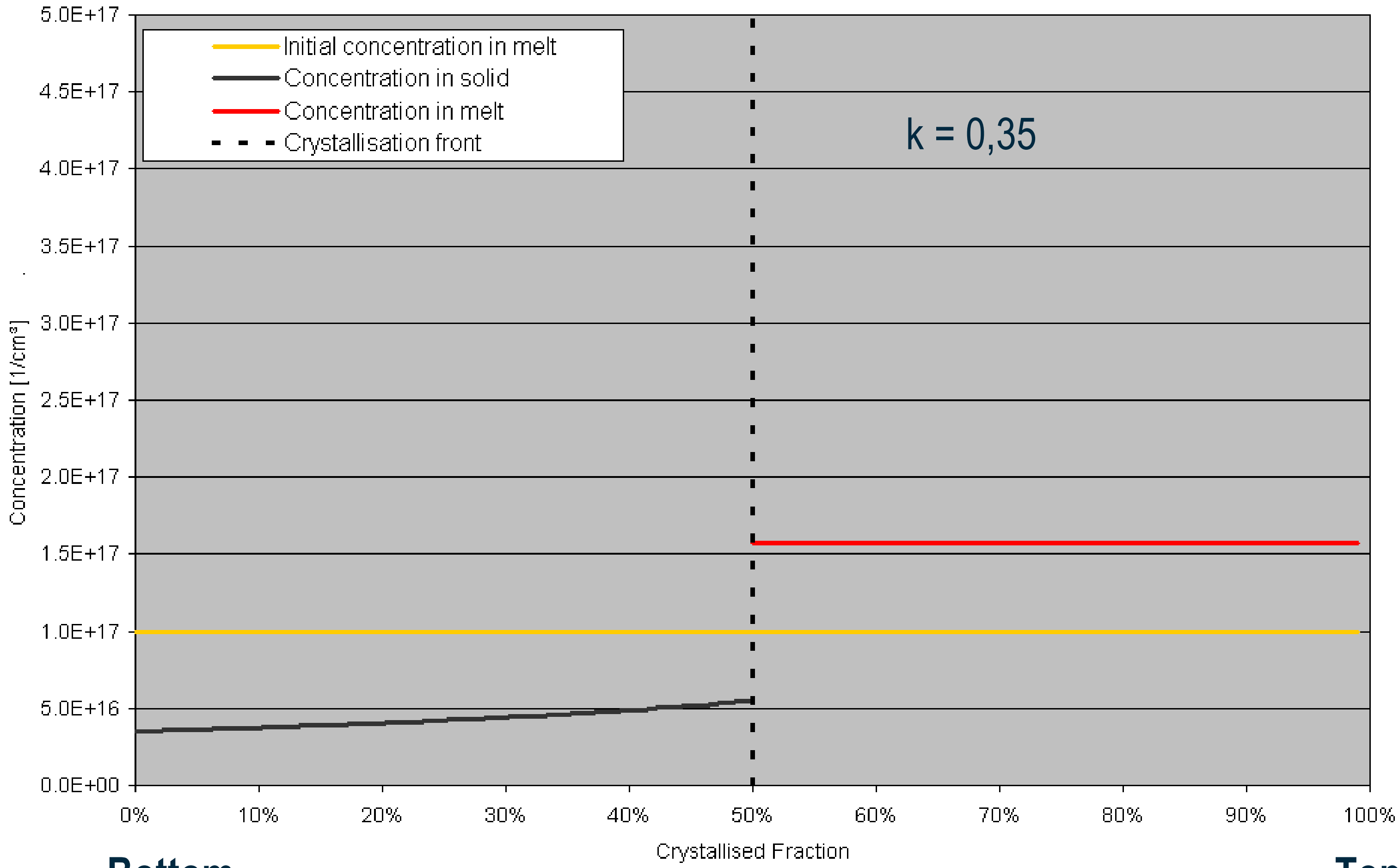
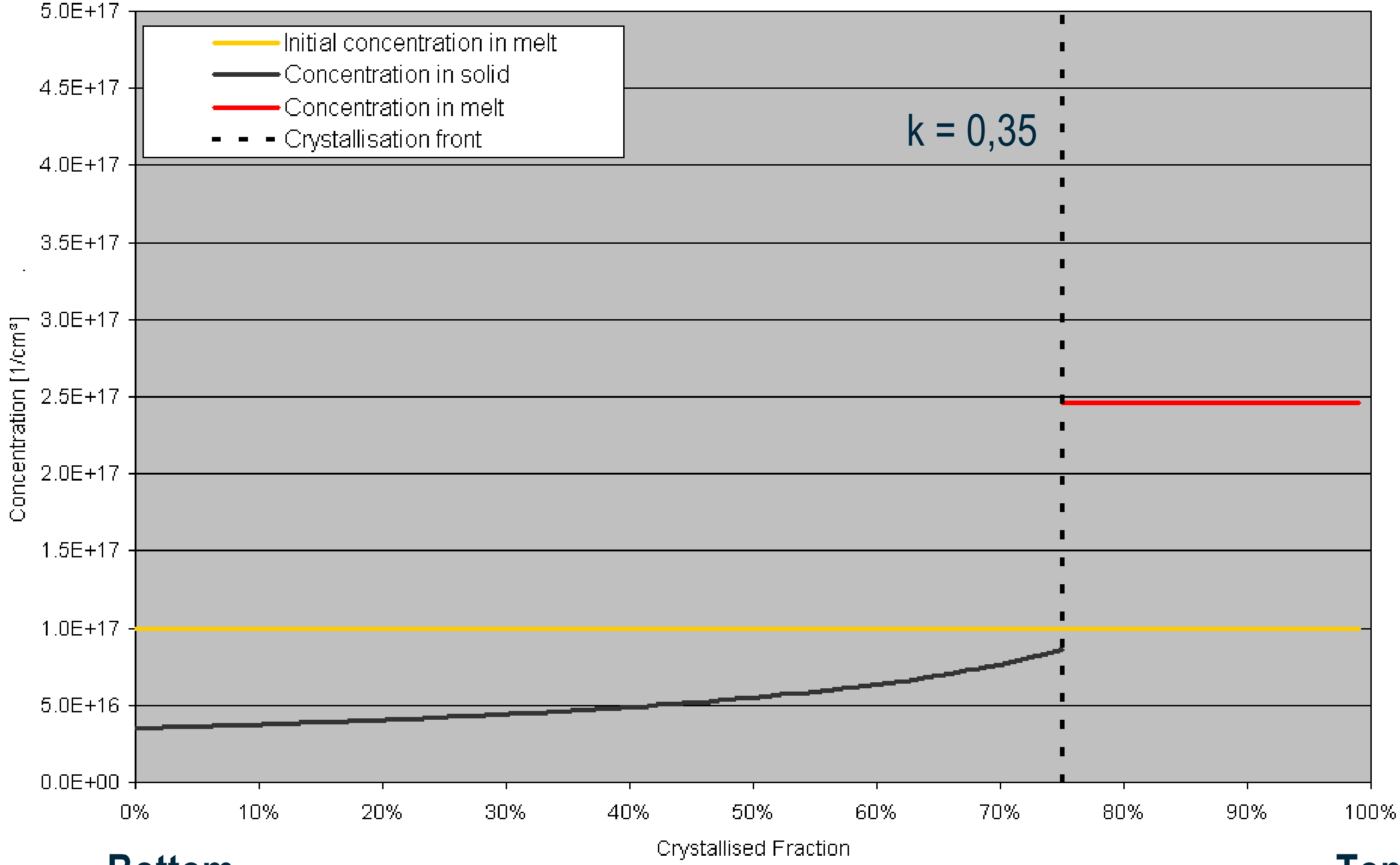


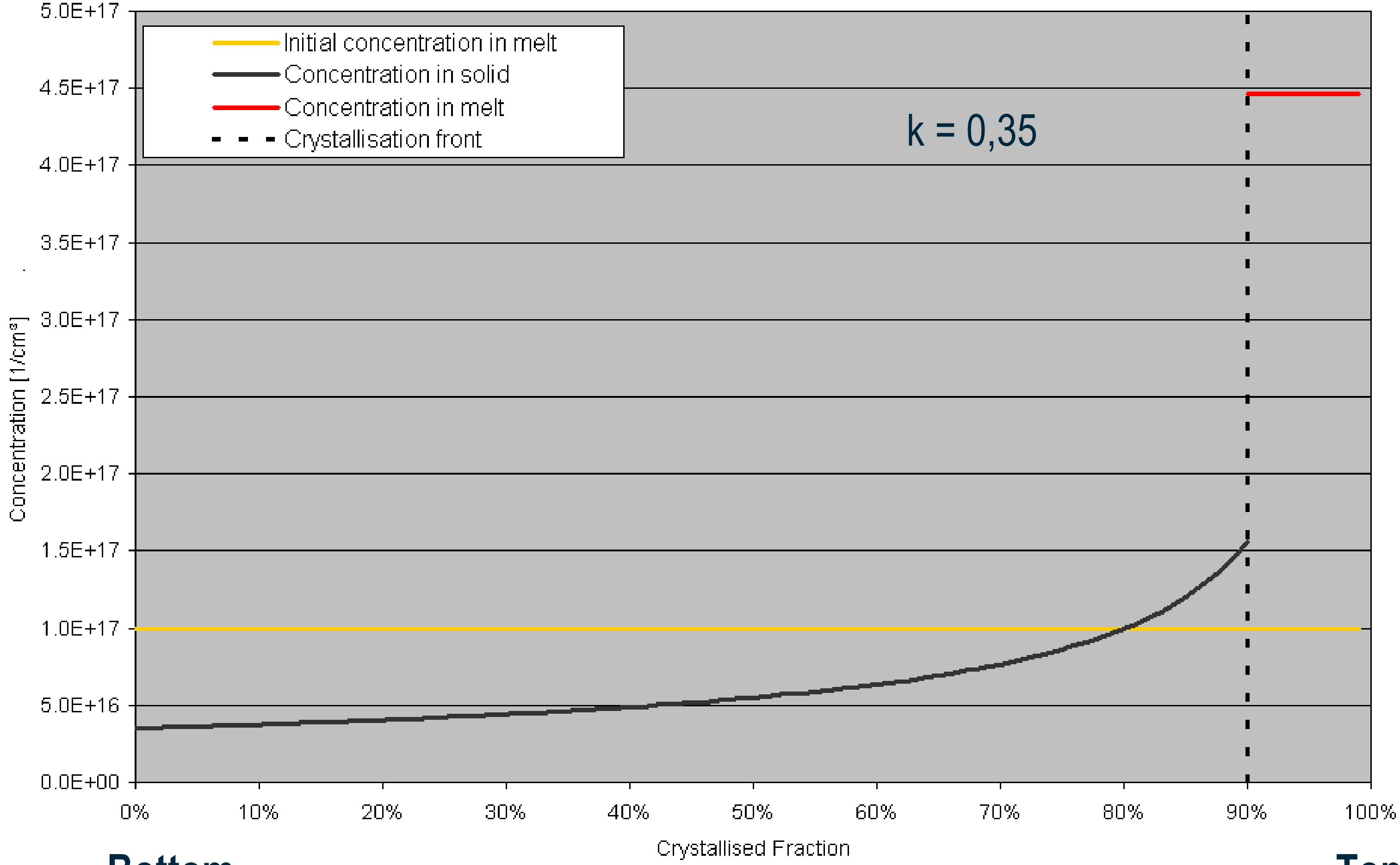
Bottom **Top**

Segregation



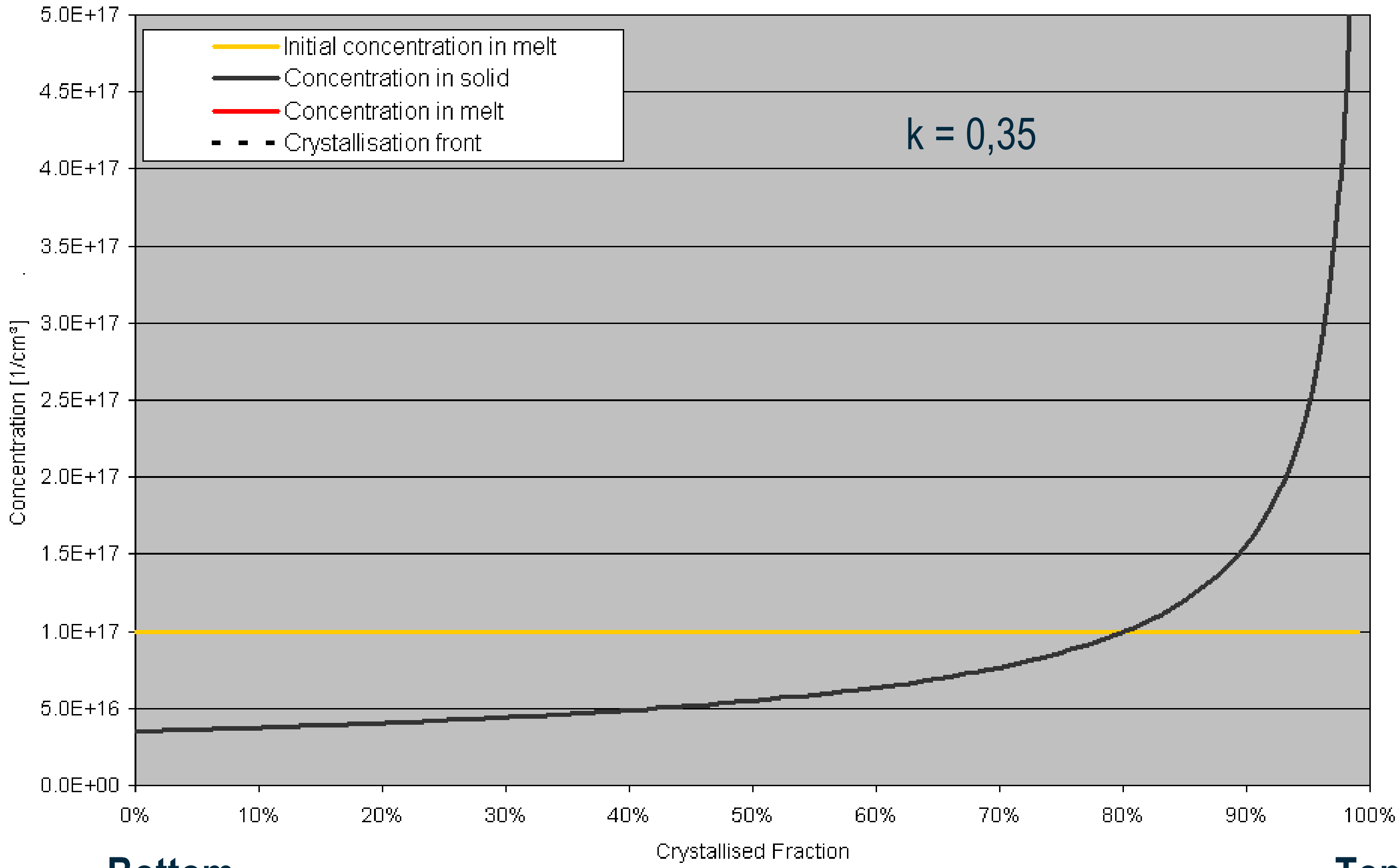
Bottom **Top**

Segregation



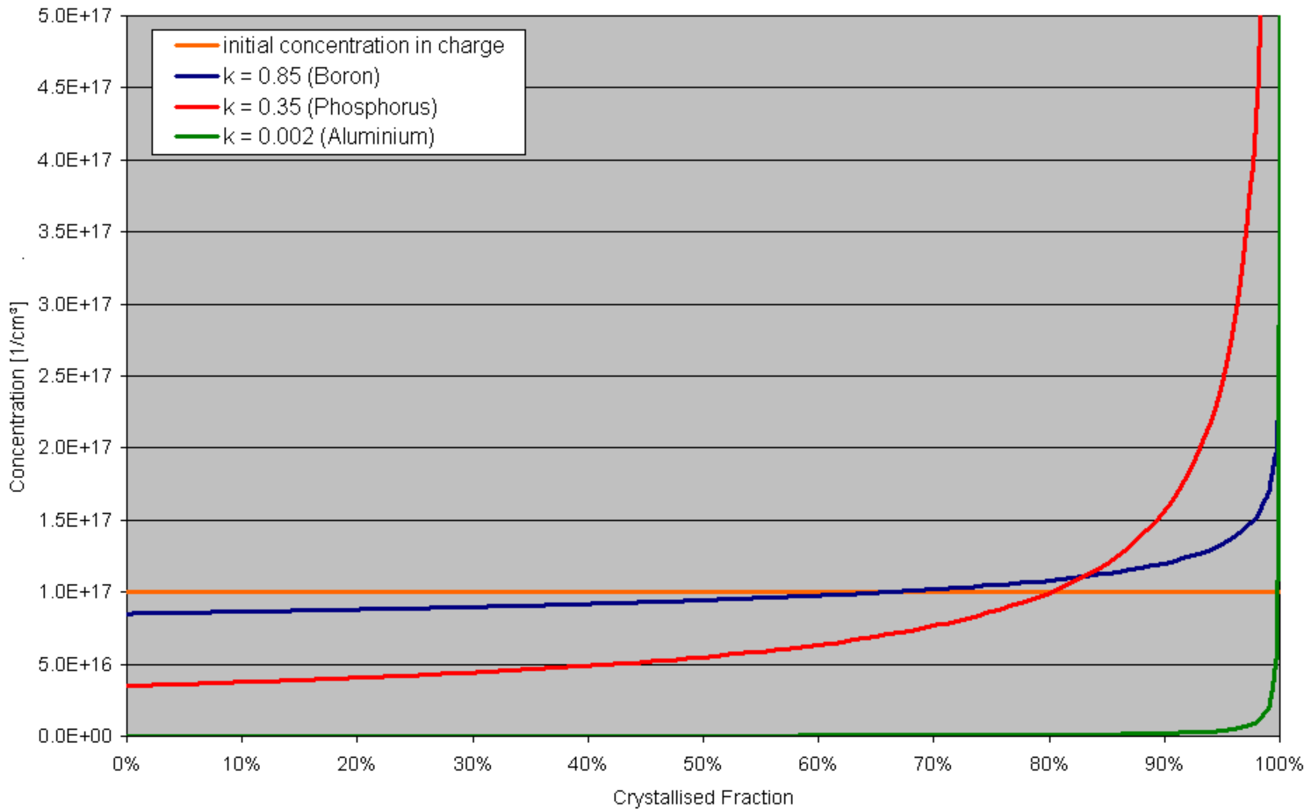
Bottom **Top**

Segregation



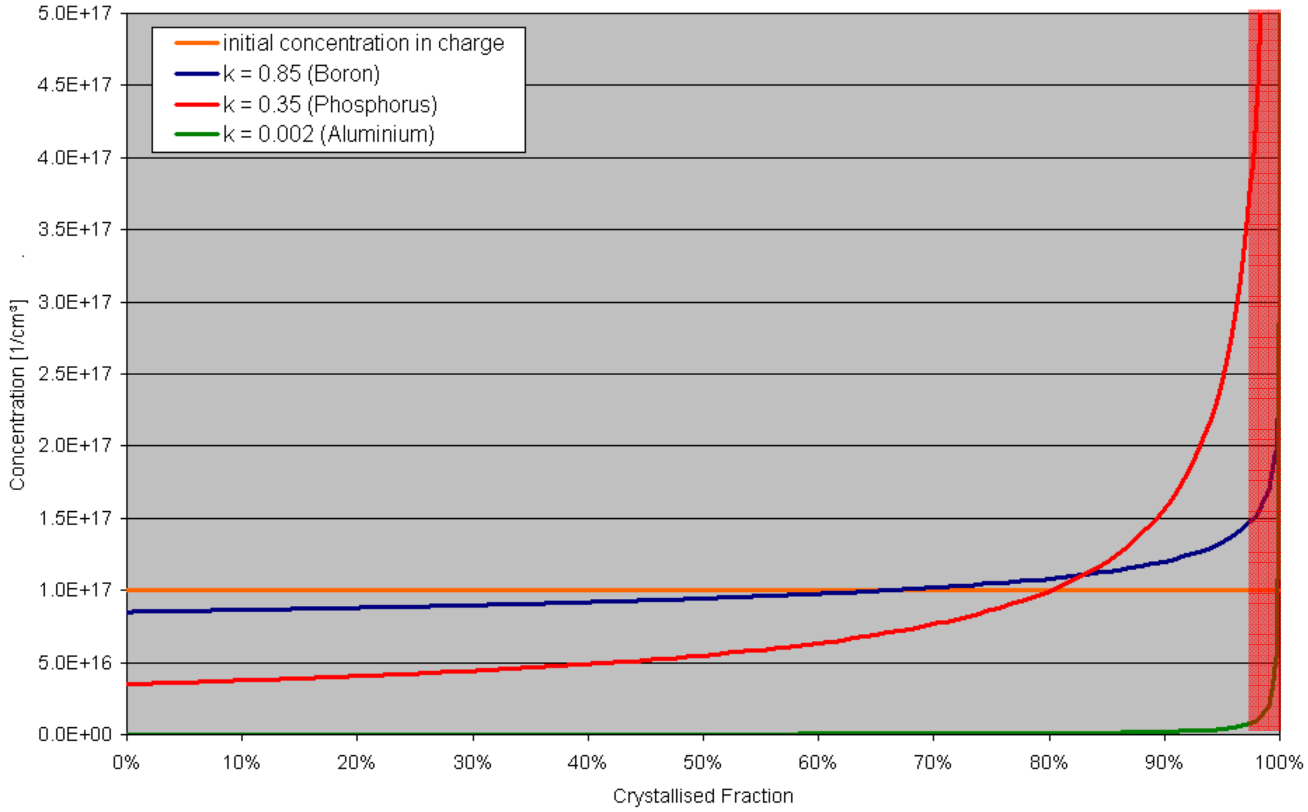
Bottom **Top**

Cleaning by solidification ?



Elements are distributed non uniformly in the crystal.
k ~ 1 → distribution is relatively homogenious
k << 1 → elements segregate towards the top of the ingot

Cleaning by solidification ?



Rejecting a small amount of material from the top

- **k ~ 1 (Dopants like B / P) → no strong cleaning effect**
- **k << 1 (e.g. metals) → efficient cleaning**

→ Biggest task for all umg-Si producers is the reduction of B and P

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Process Elkem Solar

Reduction of dopants

Reduction of metals

Metallurgical silicon → **Slag treatment** → **Leaching** → **Solidification** (segregation) → **Post treatment**

- In-house production only
- Based on Elkem's core competencies

- Three sequential purification steps designed to reduce the level of impurities for critical elements
- Largely based on Elkem's core competencies in high temperature processes, process and equipment design

- Ingots cleaned and sawed into bricks of ~10 kg
- Quality control

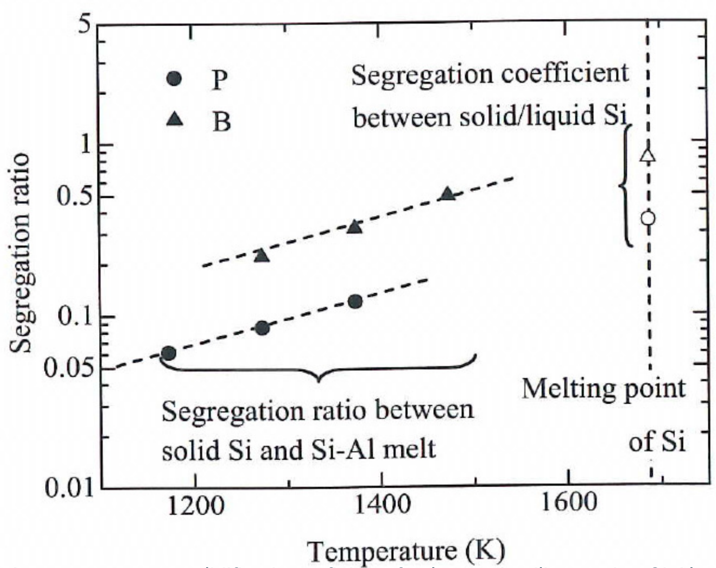
Elkem Solar – status and future outlook, Helge Aasen, 6th Solar Silicon Conference, Munich, 2008

Process 6N Silicon

Aluminum/Silicon Melt

- Lower temperature than molten Silicon
- Safer
- Less expensive, lower energy costs
- Fast, efficient purification

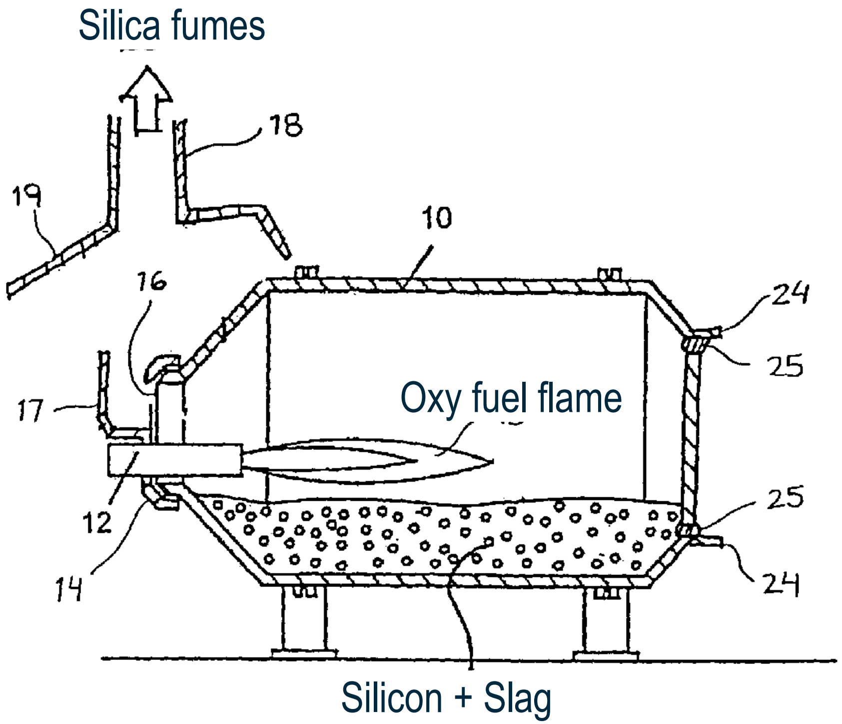
Solar Silicon Solution in a Dynamic Market!, David Dunnison, 7th Solar Silicon Conference, Munich, 2009



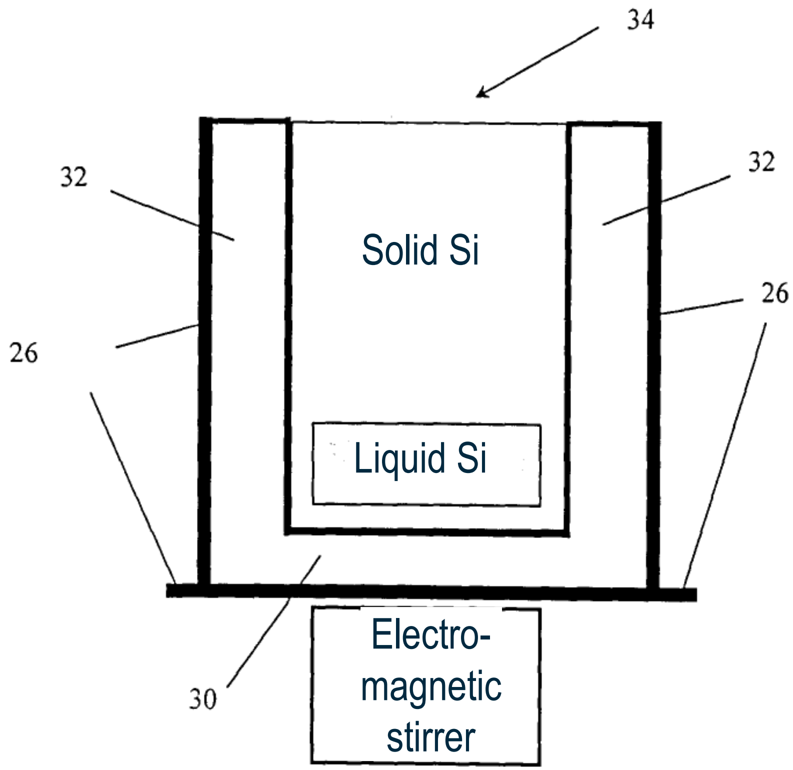
Low temperature solidification refining of solar grade silicon using Si-Al solvent, K. Moriata, Silicon for the Chemical and Solar Industry, Oslo, 2008

Process BSI Becancours / Timminco

Rotary furnace with slag and oxidising flame
→ Boron reduction



low cost solidification
→ reduction of metals



Patent WO08031229_2008_BSI_process and Apparatus for purifying Low-Grade silicon material

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Impurities in Silicon

Typical influences of impurities in Silicon

Impurity	Examples	Influence
Dopants	B, P, Ga	▪ Resistivity, Yield ▪ Light Induced Degradation
Metals	Fe, Co, Ni	▪ Defectlevels in Middle of Bandgap → Recombination
Alkali-Metals	Ka, Na	▪ Crystallisation: Corrosion of Crucible
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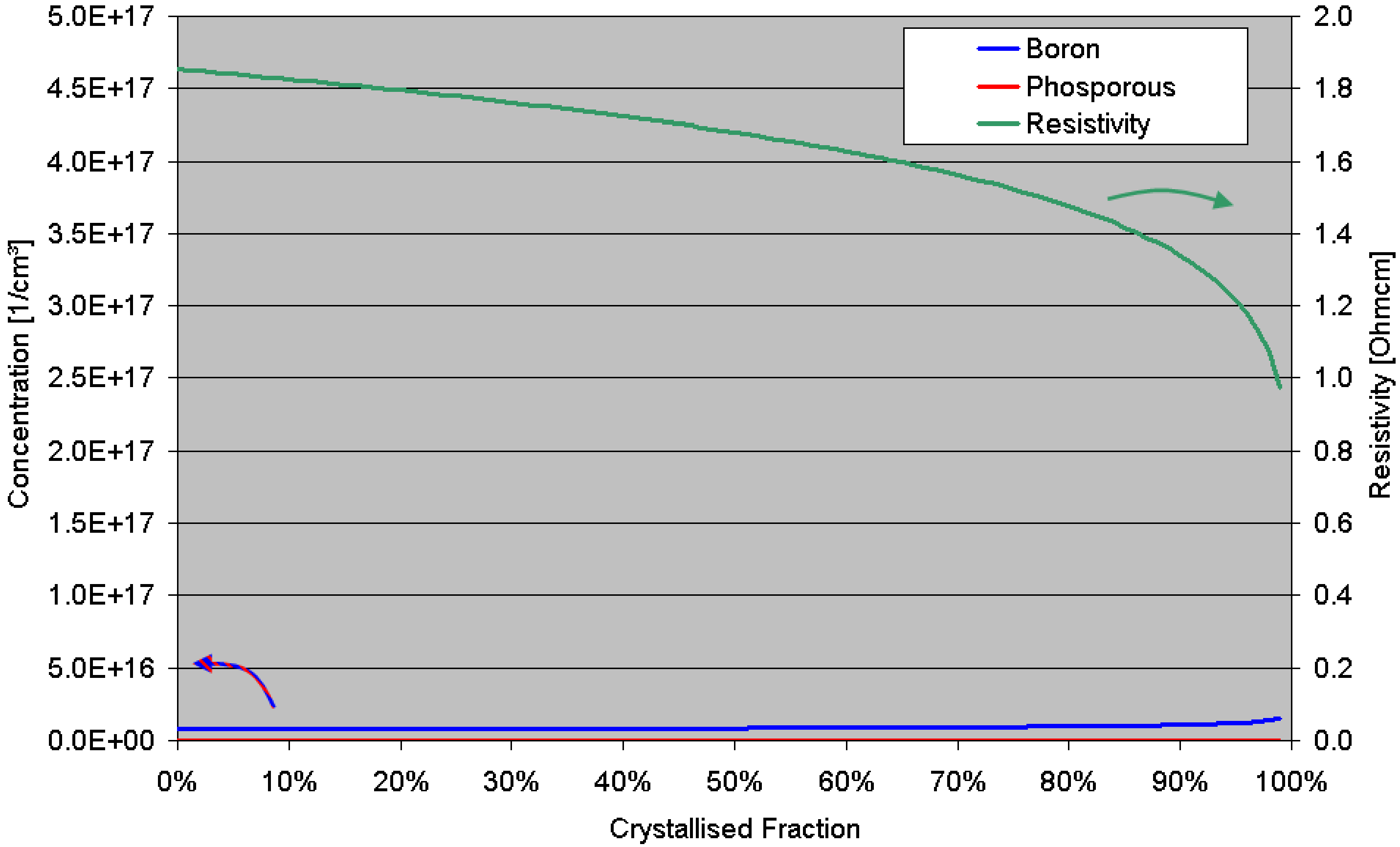
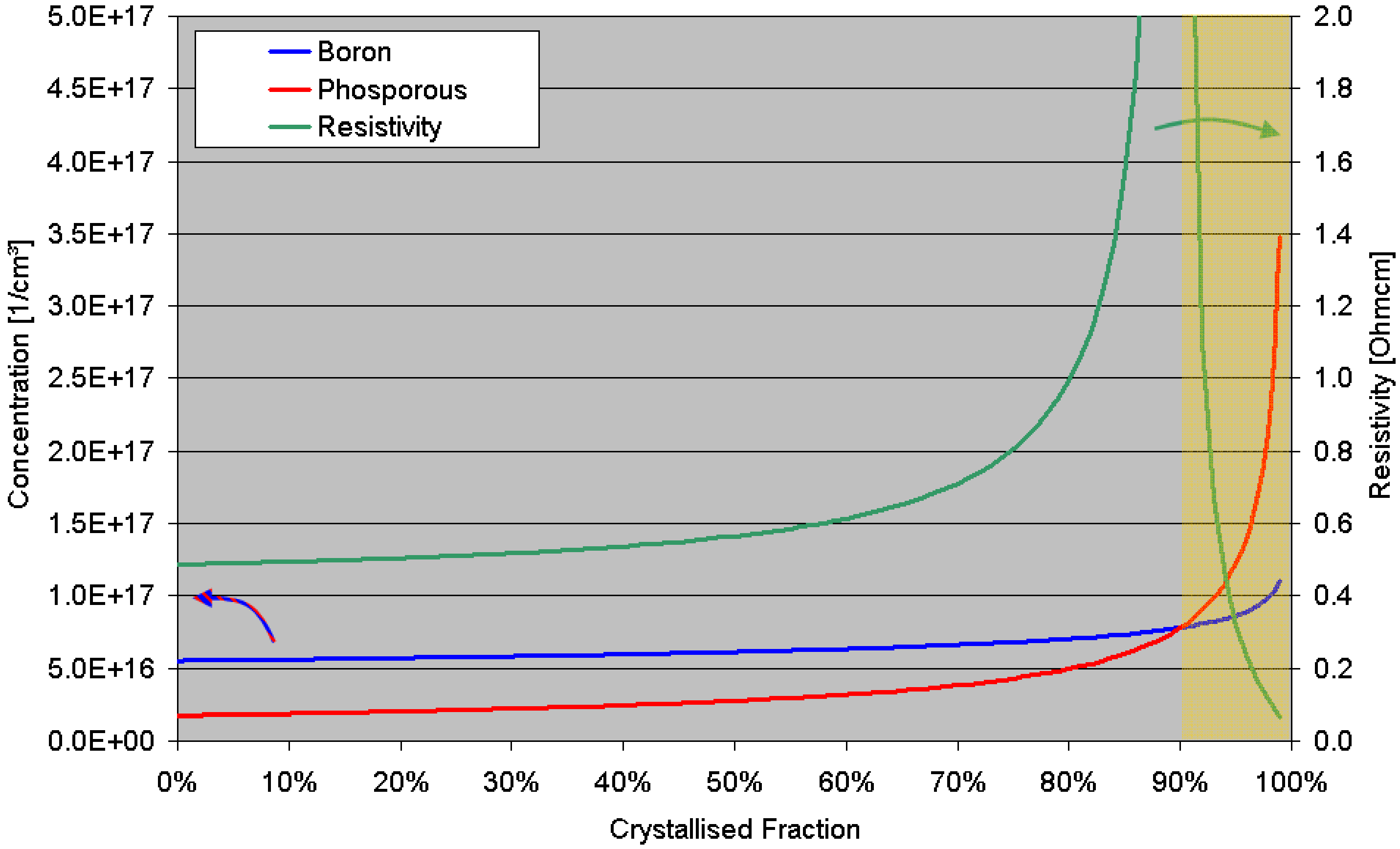
Influence of Dopants - Resistivity



Feedstock: semiconductor grade Silicon
0.07 ppmw B intentionally added to the feedstock → resistivity distribution ~ 1-2 Ωcm, optimal range for standard cell concepts

Influence of Dopants - Resistivity



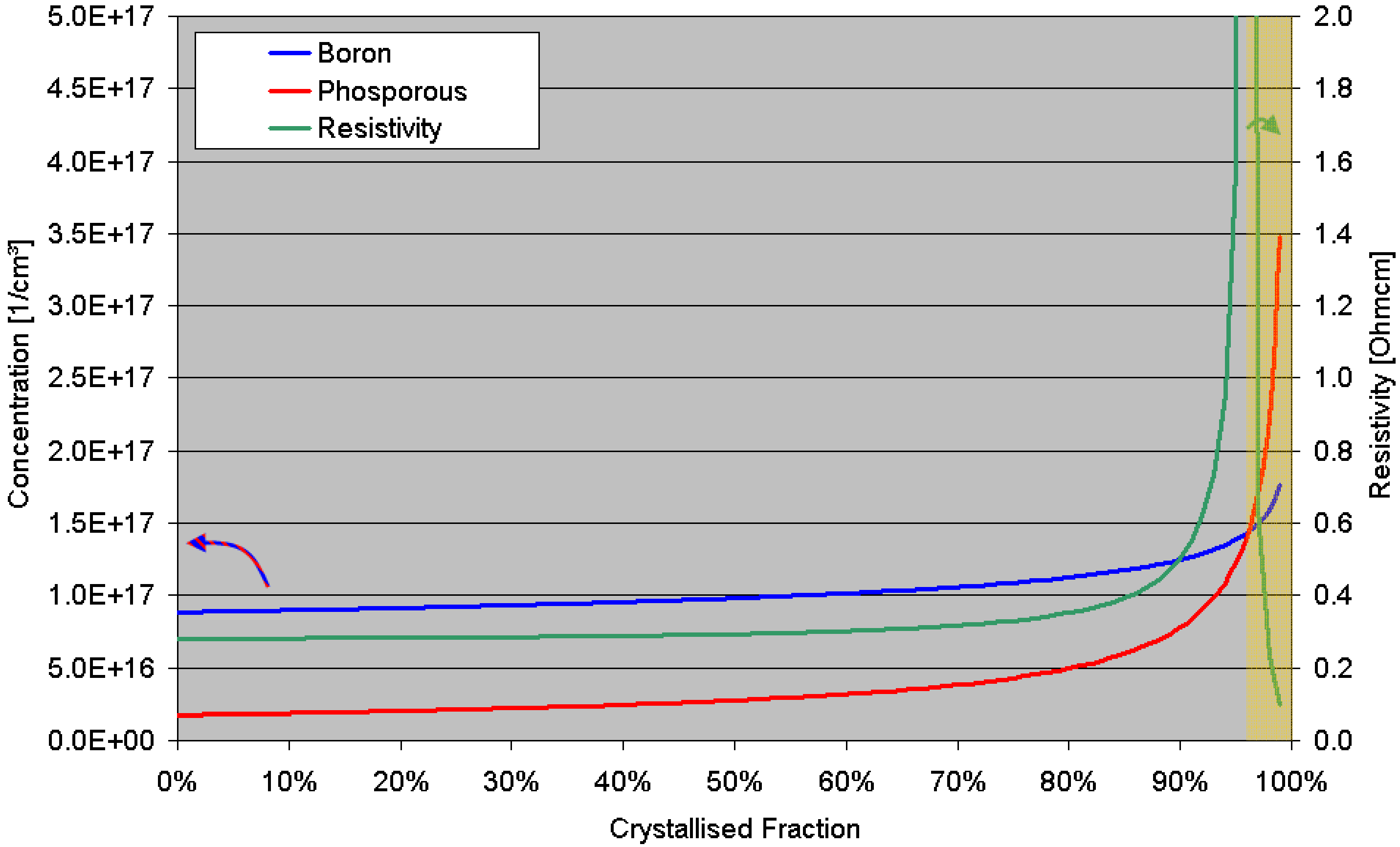
Feedstock: umg-Si

~ 0.5 ppmw of B and 1.1 ppmw of P,

→ resistivity distribution > 0,5 Ohmcm →small efficiency losses

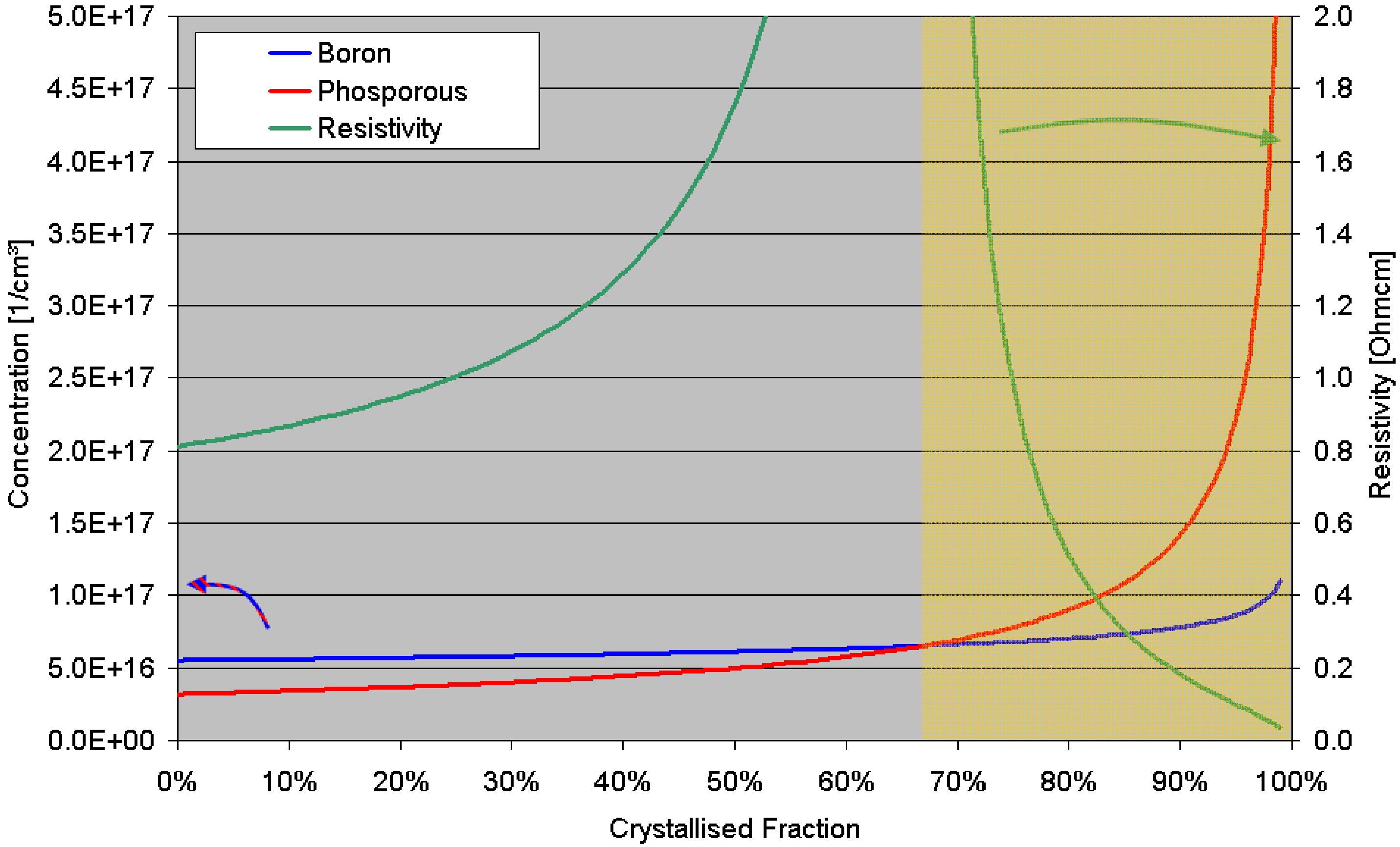
→ Yield loss due to transition to n-type material in top of Ingot

Influence of Dopants - Resistivity



Feedstock: umg-Si + Addition of Boron
~ 0.8 ppmw of B and 1.1 ppmw of P,
→ Yield increases
→ Average Resistivity decreases → effciency decreases

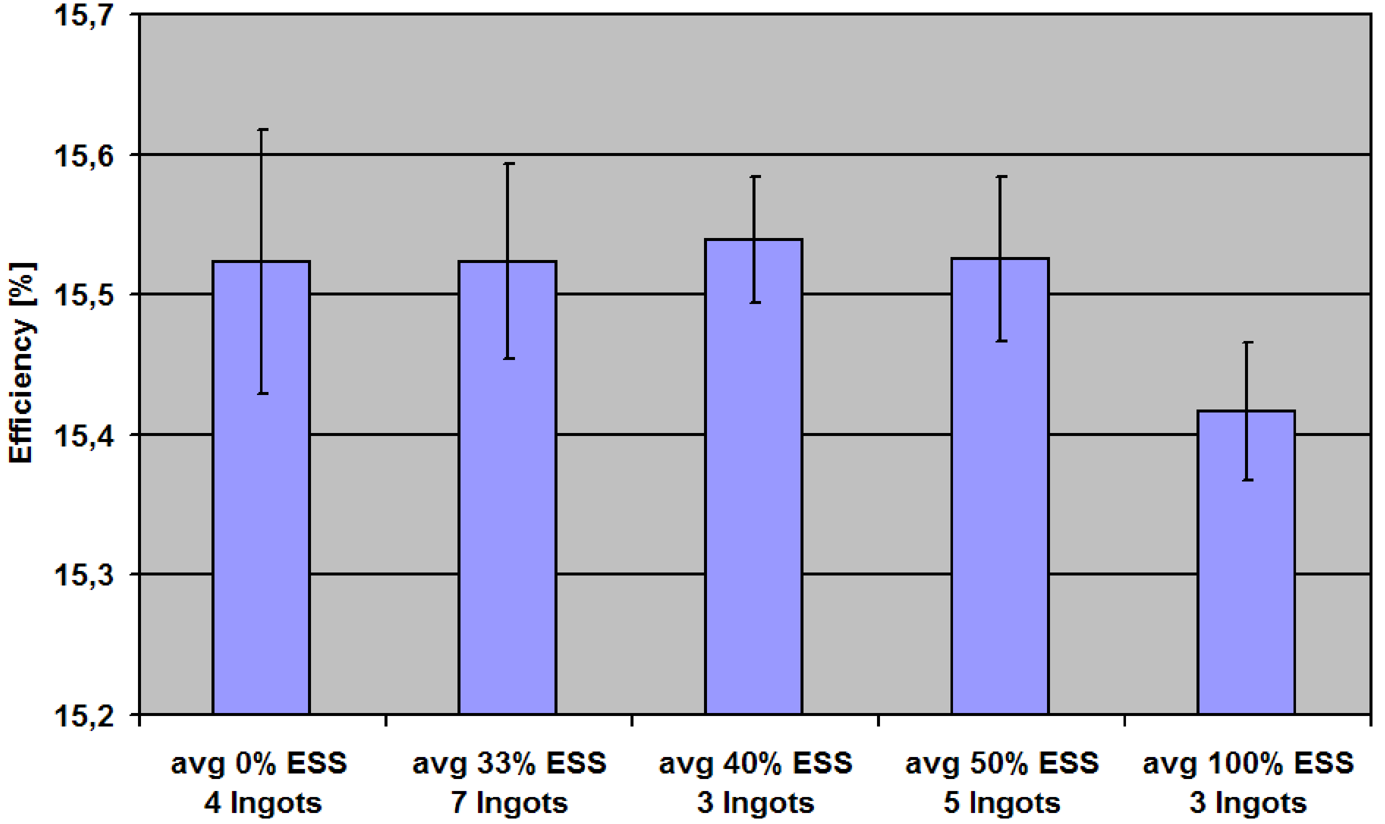
Influence of Dopants - Resistivity



Feedstock: umg-Si + Addition of Phosphorus
~ 0.5 ppmw of B and 2.0 ppmw of P
→ Average Resistivity increases → efficiency rises
→ Yield decreases

Results on cell efficiency with Elkem umg-Si

average cell efficiencies for 18 ESS ingots



FIRST RESULTS ON INDUSTRIALIZATION OF ELKEM SOLAR SILICON AT PILLAR JSC AND Q-CELLS
Volker Hoffmann, PVSEC, Valencia, 2008

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Metallic impurities can limit cell efficiency

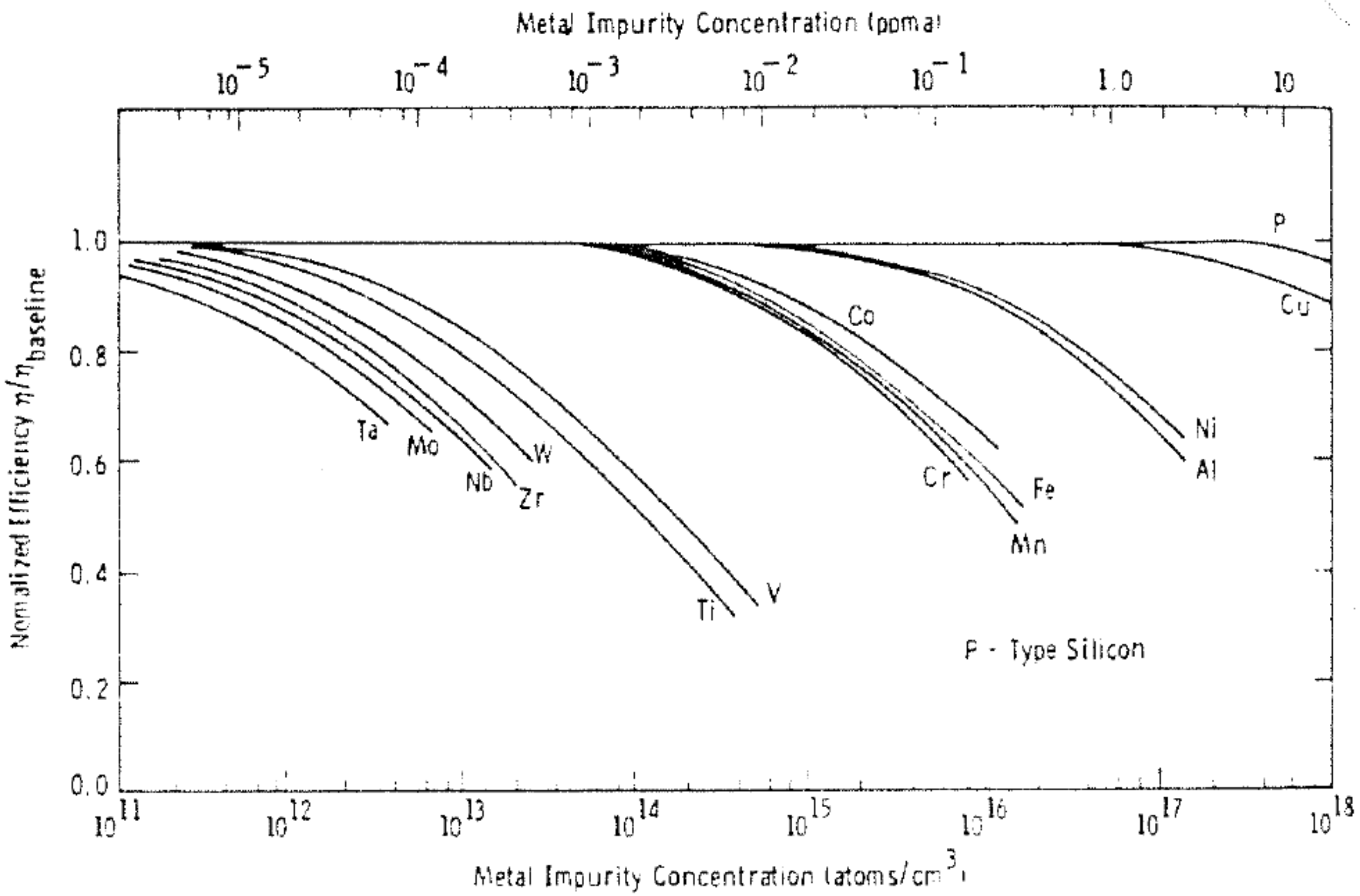
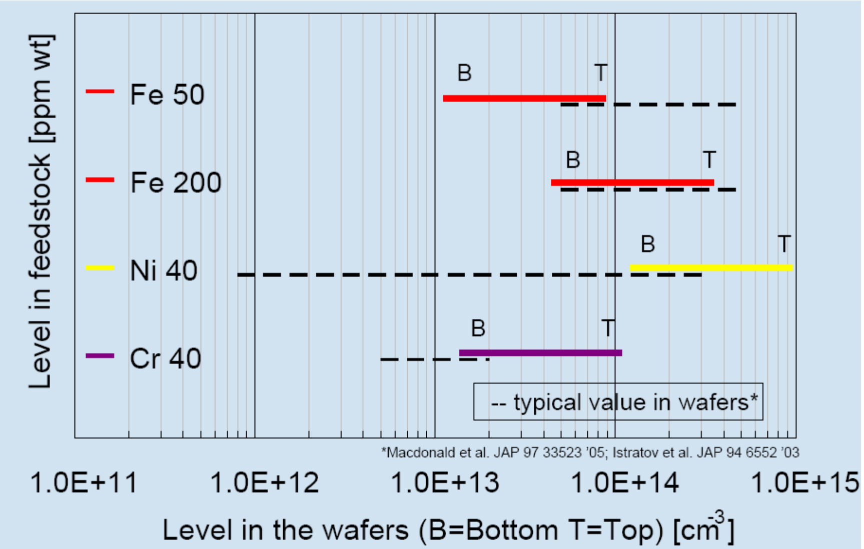


Fig. 4. Solar-cell efficiency versus impurity concentration for 4-Ω · cm p-base devices.

J.R. Davis *et al.*, IEEE Trans. Electron. Dev. ED-27 (1980) 677

Recent studies

Main question: Which concentrations can be allowed in the feedstock with todays crystalisation and cell processes?
Two projects (Crystal Clear and Solarfocus) produced several intentionally contaminated Ingots:

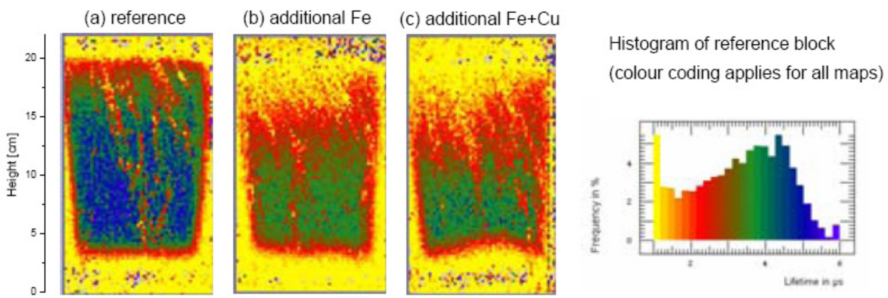


About 10 ppmw of Fe, Cr or Ni will be allowed

Effect of metals in silicon feedstock on multiicrystalliine silicon solar cells
Gianluca Colletti, Crystal Clear Workshop: Arriving at well-founded SoG silicon feedstock specifications, Amsterdam, 2008

Study of impurities in block Silicon by intentional contamination

Crystallization of small mc-Si blocks with addition of impurities to the feedstock:
(a) reference block with high purity feedstock
(b) addition of Fe (target concentration of 2ppma in the melt)
(c) addition of Fe and Cu (target conc. of 2ppma and 20ppma, respectively)

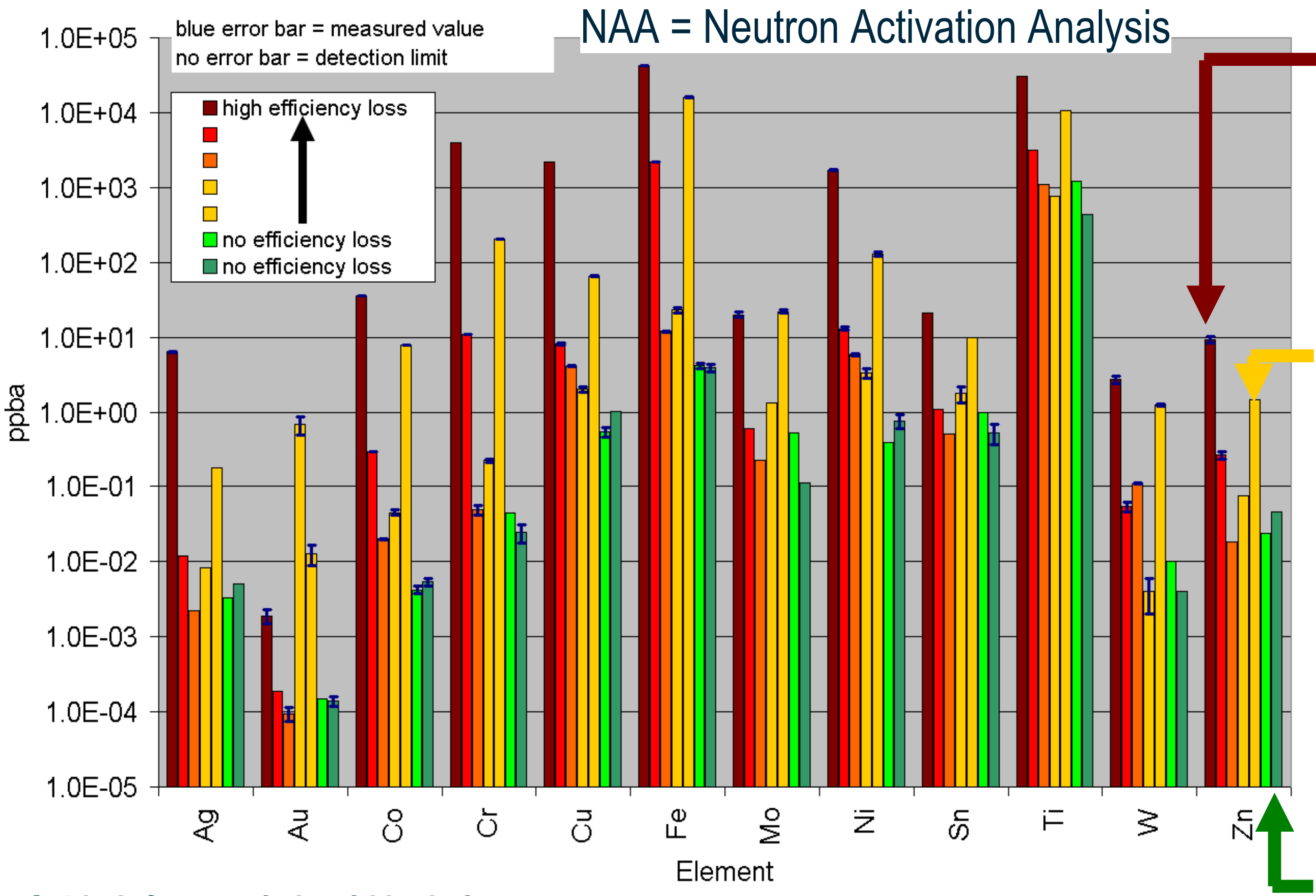


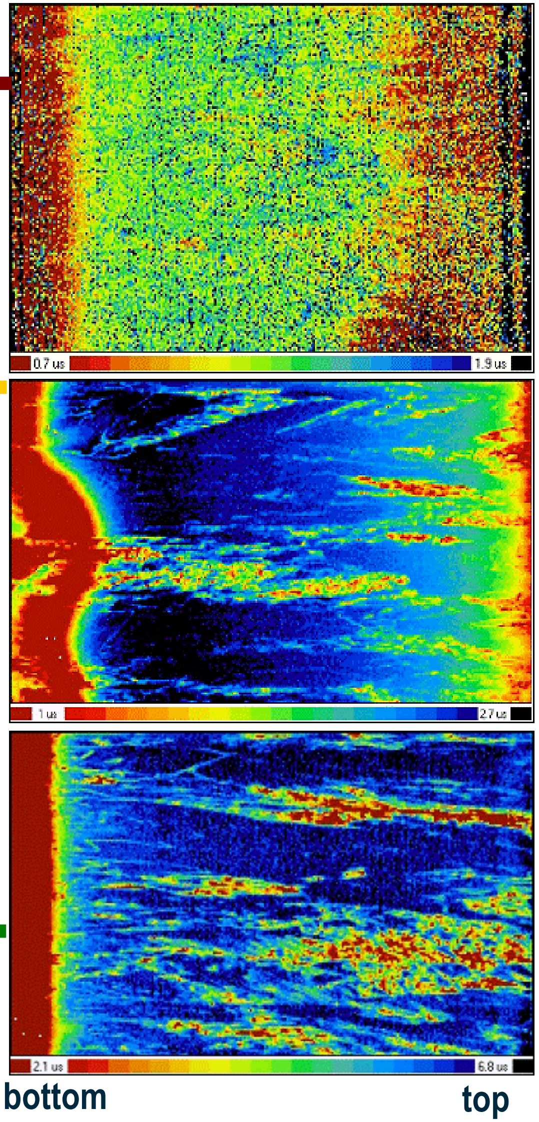
MW-PCD images of transverse section of blocks, measured at unpassivated bricks with 12.5cm width

SOLAR SILICON MATERIAL RESEARCH NETWORK – SOLARFOCUS
Stephan Riepe, PVSEC, Valencia, 2008

Conclusion from Projects:
→The acceptable concentration of metals is in the ppm - range

Results obtained with umg-Si at QC





→ **Limit for metal should be below ppm range**

Todays acceptable umg-Si Qualities have metal concentrations below critical limit

- producers have crystallisation steps in their processes

- metals have low segregation coefficients k

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Alkaline Metals

Figure 2a

Figure 2b

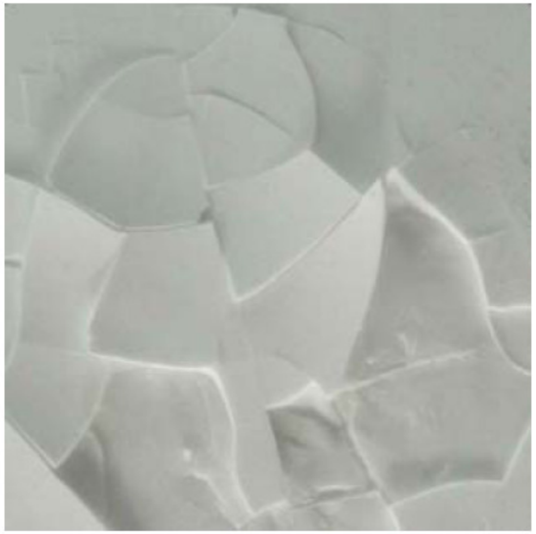


Figure 2c

Figure 2: Pictures of fused silica crucible containing Si feedstock before (a) and after test (b). Crucible cover internal surface exhibiting important flaking (c).

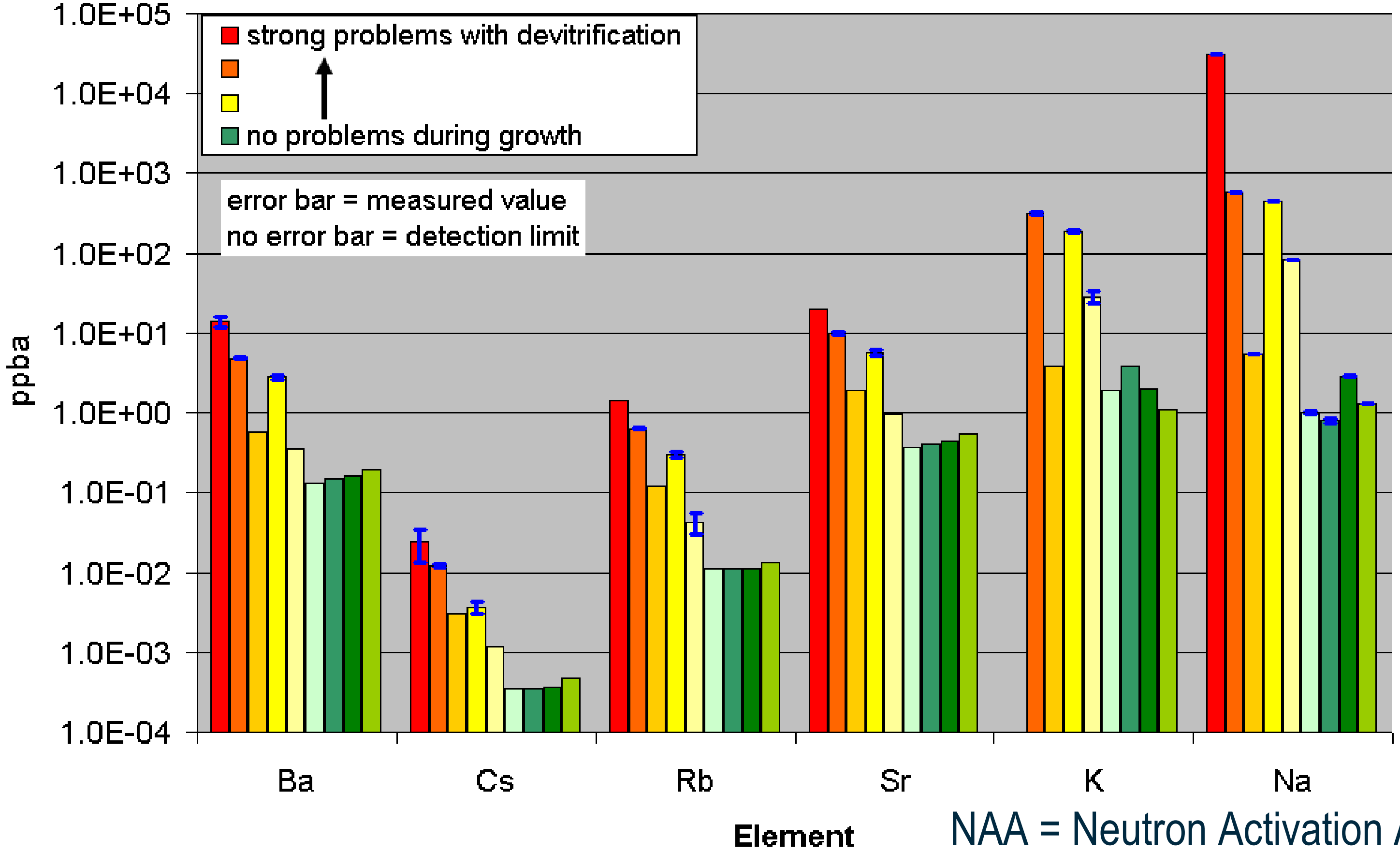
C. Martin, CSSC3, SINTEF/NTNU Trondheim 2009

Table 1: Sodium content by AAS and cristobalite content in XRD analyses of the surface compared to the bulk of the material.

	Bulk	Surface
Na content / ppm	25	480
Cristobalite content / %	10	60

Results obtained with umg-Si at QC

Alkaline metals can lead to a devitrification („Entglasung“ / „crystallisation“) of the Quartz Crucibles → they become brittle and may break



NAA = Neutron Activation Analysis

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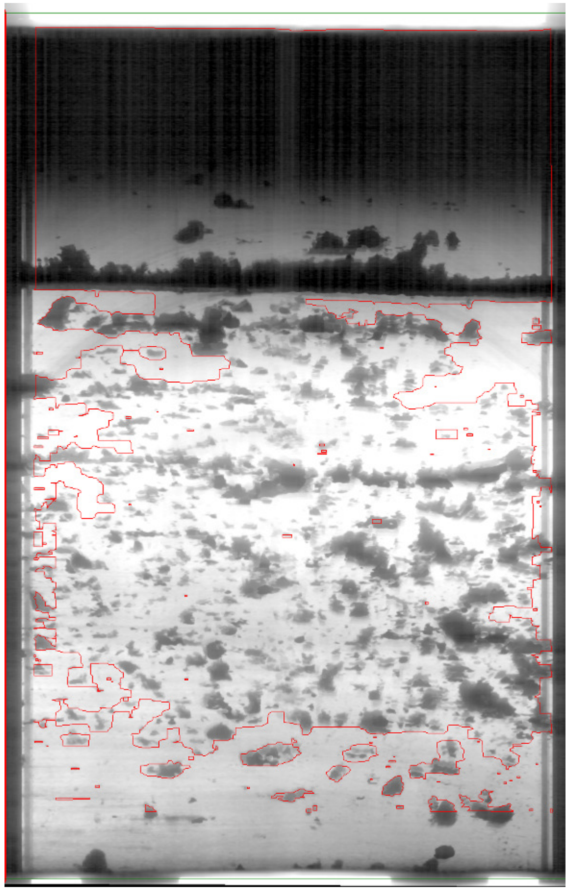
Inclusions in Silicon Feedstock

Too high concentrations of C / N in the feedstock can lead to the formation of SiC / SiN inclusions in the ingot

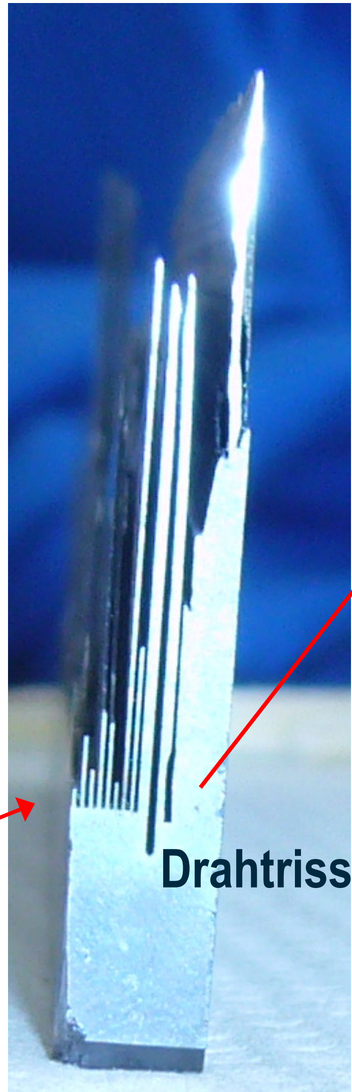
IR transmission images of crystallised blocks:

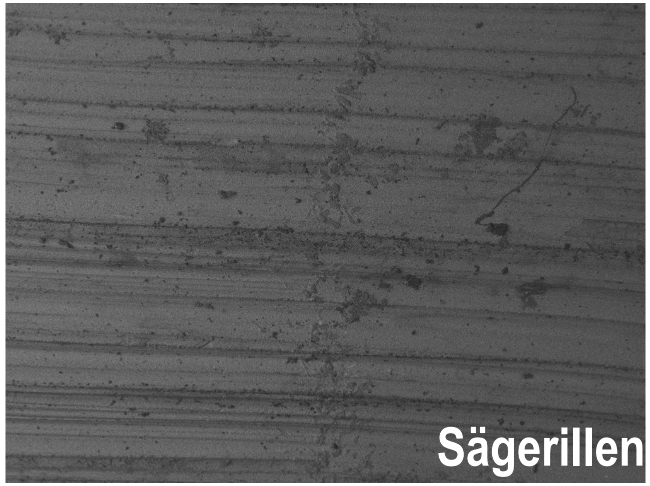


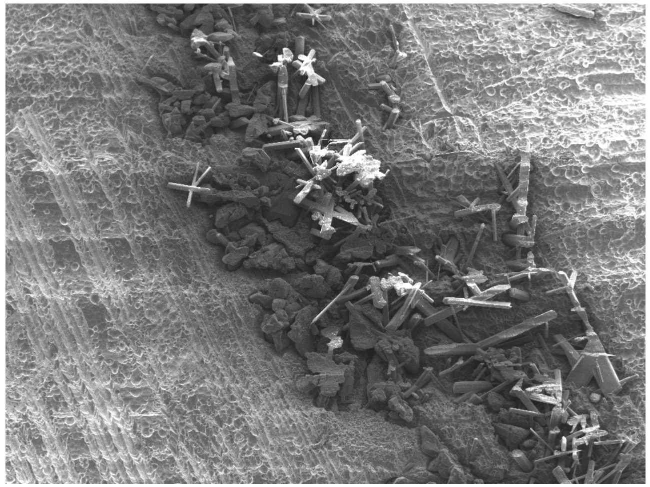
Feedstock with
too much C / N
→ SiC / SiN inclusions

Feedstock with
acceptable concentrations
of C / N
→ Inclusion free block

Wire breakage due to SiC inclusions







REM + EDX: SiC, SiN

Bor-Sauerstoff-Defect → Light Induced Degradation

Boron doped Silicon:

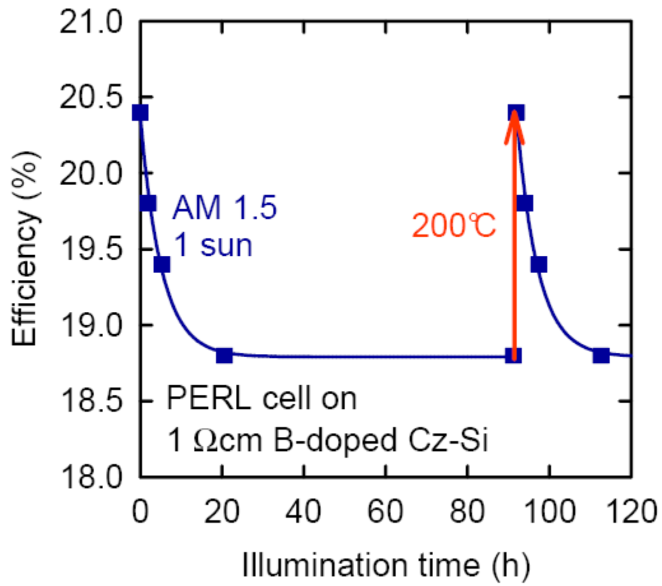
- $[O_i]$ <1x10^{17} cm^{-3} up to > 10^{18} cm^{-3}

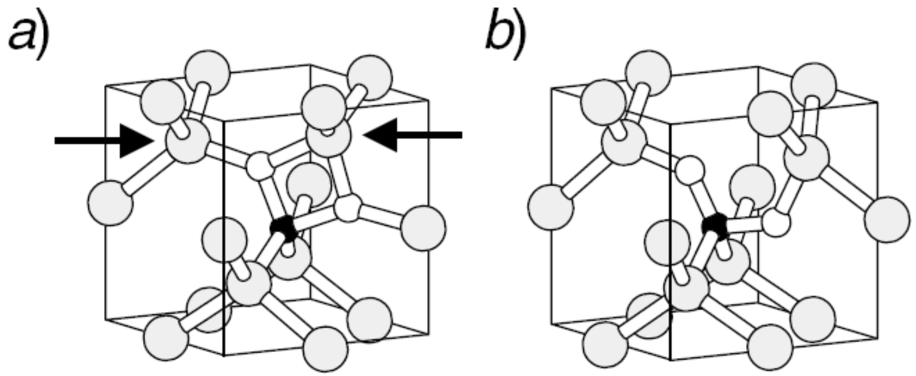
- Light induced Degradation (LID) of Efficiency

Recombination active defect density

- $N_{def} \sim [B]$
- $N_{def} \sim [O]^2$

→ Defect model with one boron and two oxygen atoms

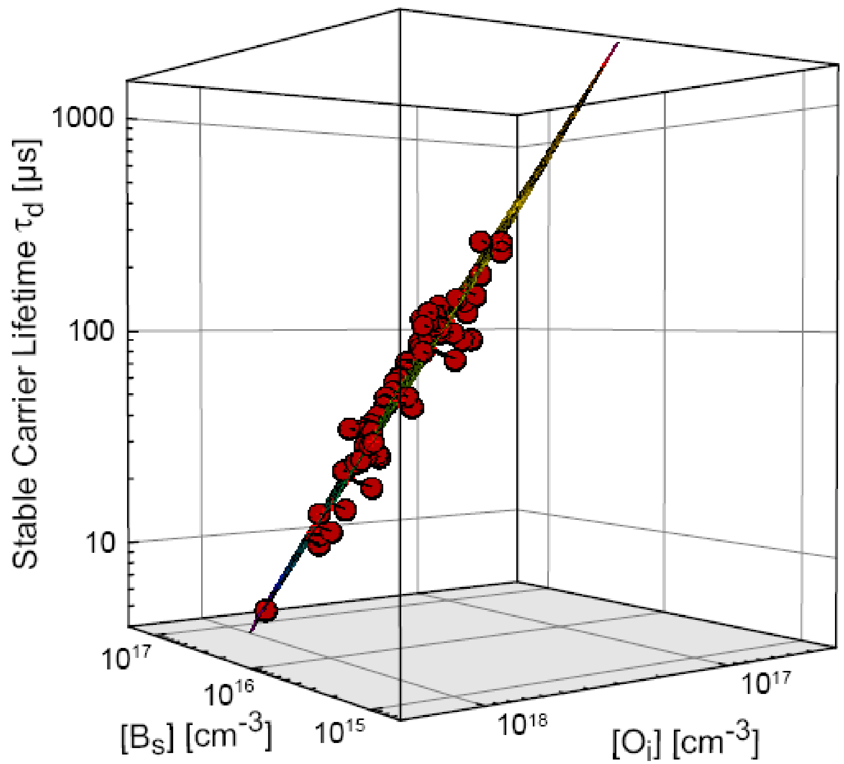




Adey *et al.* , Phys. Rev. Lett., **93** (5), (2004).

Lifetime after LID

Simultaneous fit of τ_d for varying boron and oxygen content



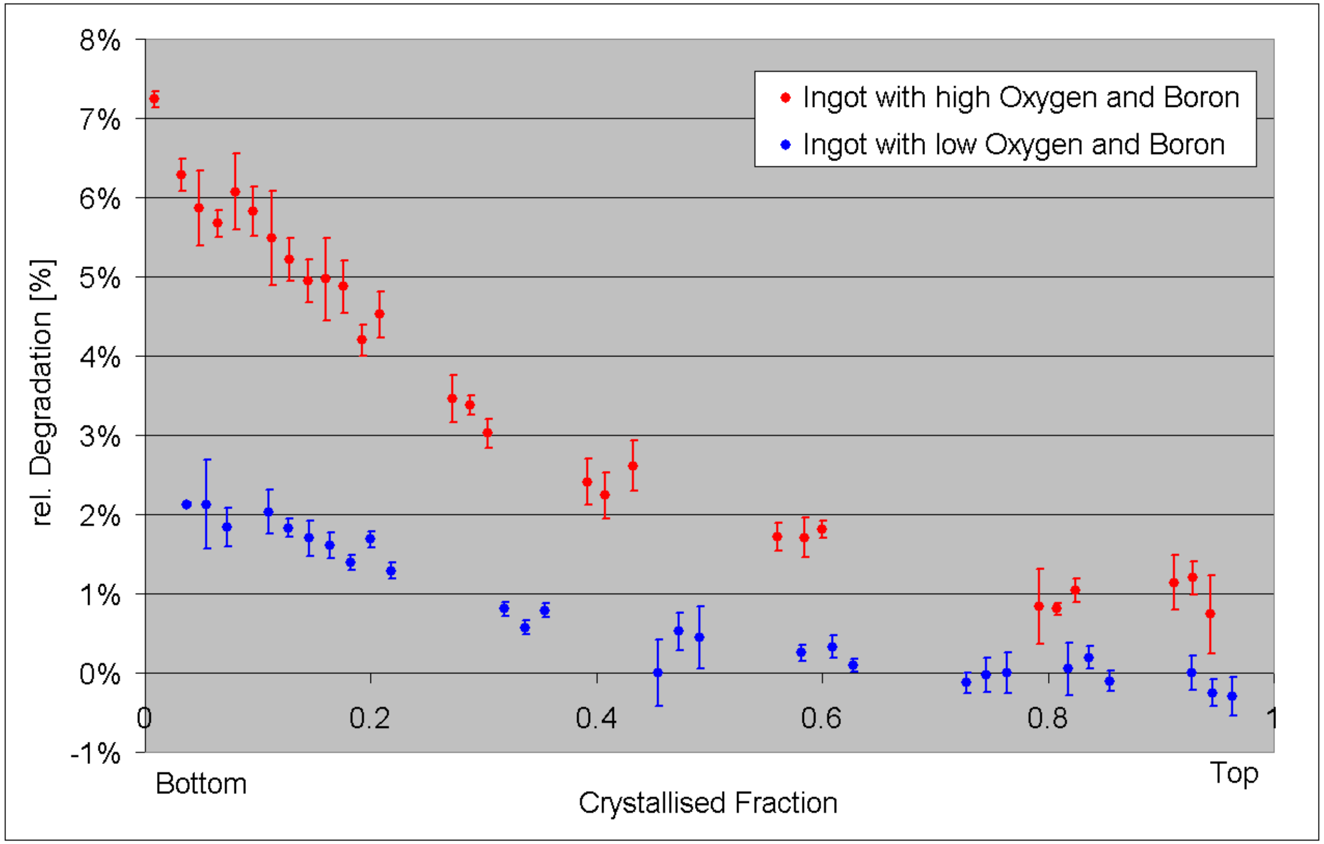
Remarkable small deviation between data points and fit

Boron and oxygen content predicts carrier lifetime !

$$\tau_d = 7.675 \times 10^{45} \cdot [B_s]^{-0.824} \cdot [O_i]^{-1.748}$$

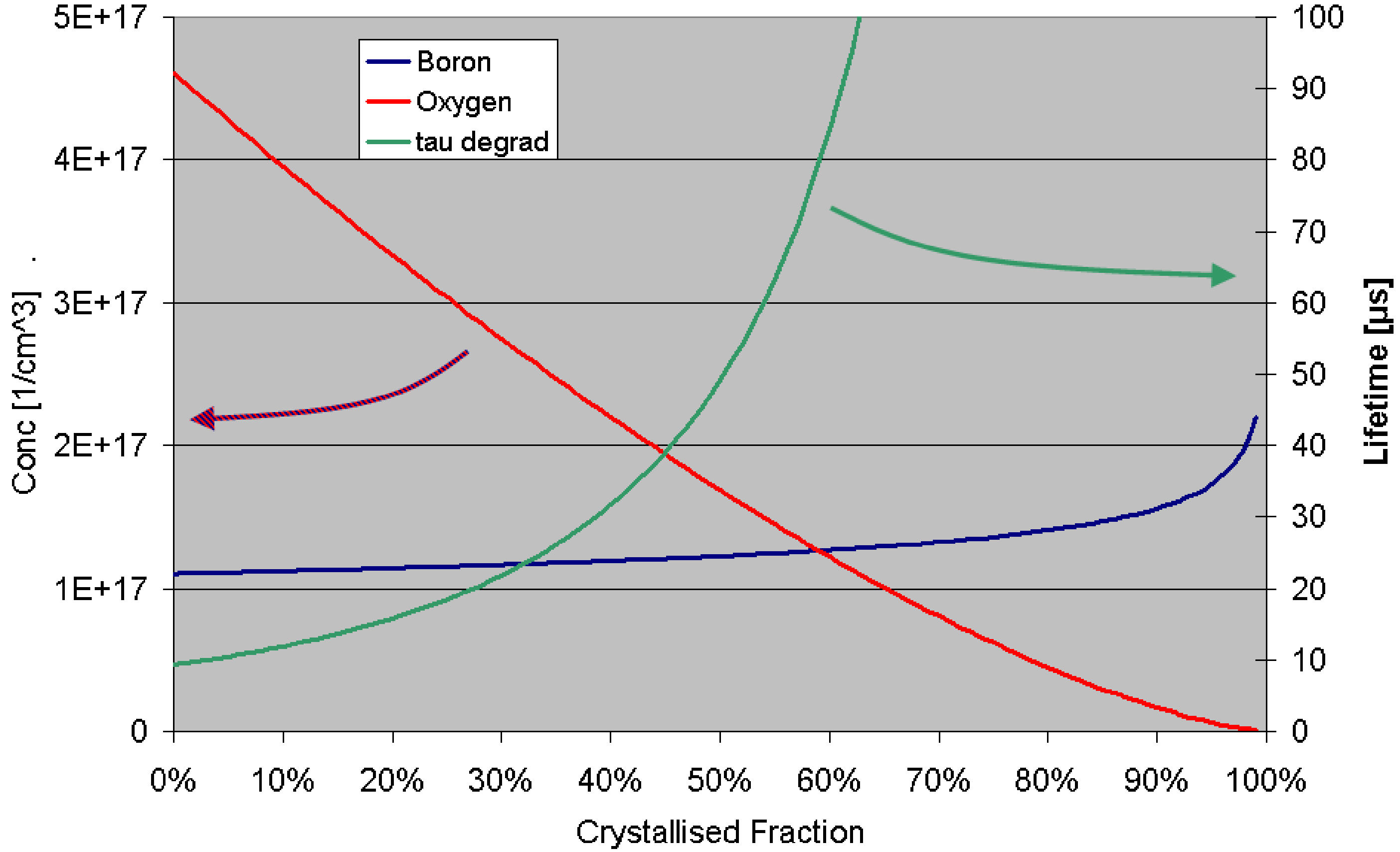
Scource: K. Bothe

Distribution of LID for umg-Si



Using umg-Si with too high oxygen and boron concentrations can lead to very high degradation > 5% relative
Control of B and O can reduce Degradation to below 2%

Distribution of LID for umg-Si



Distribution of Degradation in Ingot can be explained well by distribution of B and O in the Ingot

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Typical influences of impurities in Silicon

Impurity	Examples	Influence
Dopants	B, P, Ga	▪ Resistivity, Yield ▪ Light Induced Degradation
Metals	Fe, Co, Ni	▪ Defectlevels in Middle of Bandgap → Recombination
Alkali-Metals	Ka, Na	▪ Crystallisation: Corrosion of Crucible
Non Metals	C, N, O	▪ Inclusions ▪ Light Induced Degradation ▪ Wire breakage ▪ shunts

Overview

- **Introduction: Impurity concentration in different Silicon Qualities**
- **Production of multicrystalline Ingots and Wafers**
  - Ingot Growth
  - Sawing process
  - Segregation – an important process
- **Companies that produce umg-Si / SOG-Si and their processes**
  - Elkem
  - BSI
  - 6N Silicon
- **Influence of impurities**
  - Dopants
  - Metals
  - Alcaline Metals
  - O / C / N
- **Summary and conclusions**

Summary

- Difference in impurity concentrations between semicond.-grade Si and umg-Si ~ three orders of magnitude (ppb vs. ppm)

- Cleaning process for metals mainly done by crystallisation (segregation)
- Cleaning of B / P main task and special know how of umg-Si producers

- High concentrations of B / P can lead to efficiency and yield losses
- High concentrations of metals can lead to additional losses of efficiency
- High C / N concentrations can lead to the formation of inclusions
- High concentrations of O can lead to strong light induced degradation

Conclusions

▪ **Todays best umg-Si qualities can be used to produce solar cells with acceptable and controllable properties**

- Dopant concentrations are low enough to give reasonable efficiency and yield (still improvements are needed in future)
- Metal concentrations are low enough and lead to no additional efficiency loss
- C/N concentrations are low enough to make processing and sawing unproblematic
- O concentrations low enough to give controllable low degradation (LID)

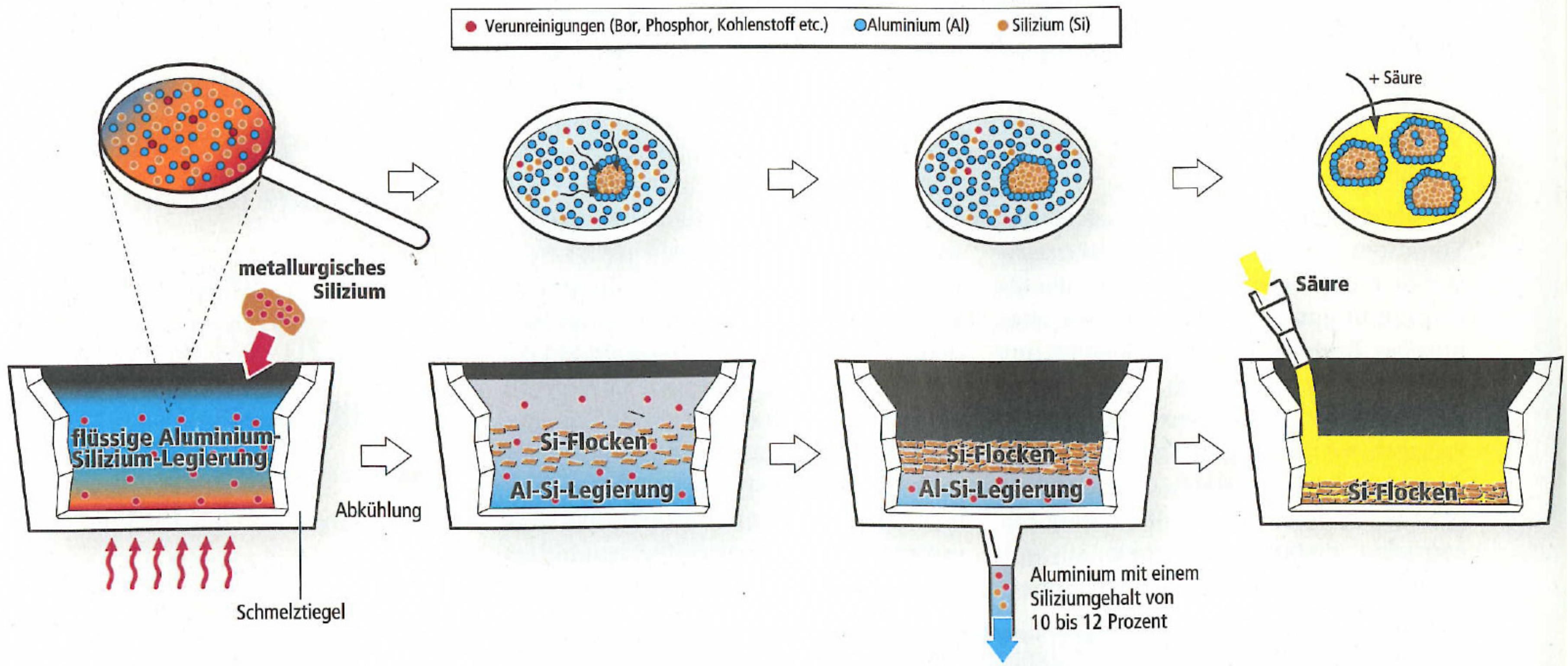
▪ **Still strong quality variations exist between different umg-Si suppliers**

▪ **umg-Si is a very attractive scientific topic with a lot of „low hanging fruits“ → fast progress was made and will probably be made in the near future in all steps of value chain**

→ now: umg-Si is an attractive second scource for wafer and cell manufacturers
→ in the future: umg-Si will be necessary to provide enough Si for Terawatt market

VIELEN DANK

Process 6N Silicon



In einer Aluminiumschmelze mit einer Temperatur von rund 800 Grad Celsius wird metallurgisches Silizium aufgelöst, das mit chemischen Elementen wie Bor oder Phosphor verunreinigt ist. Dieses besitzt eine Reinheit von 97 Prozent oder höher.

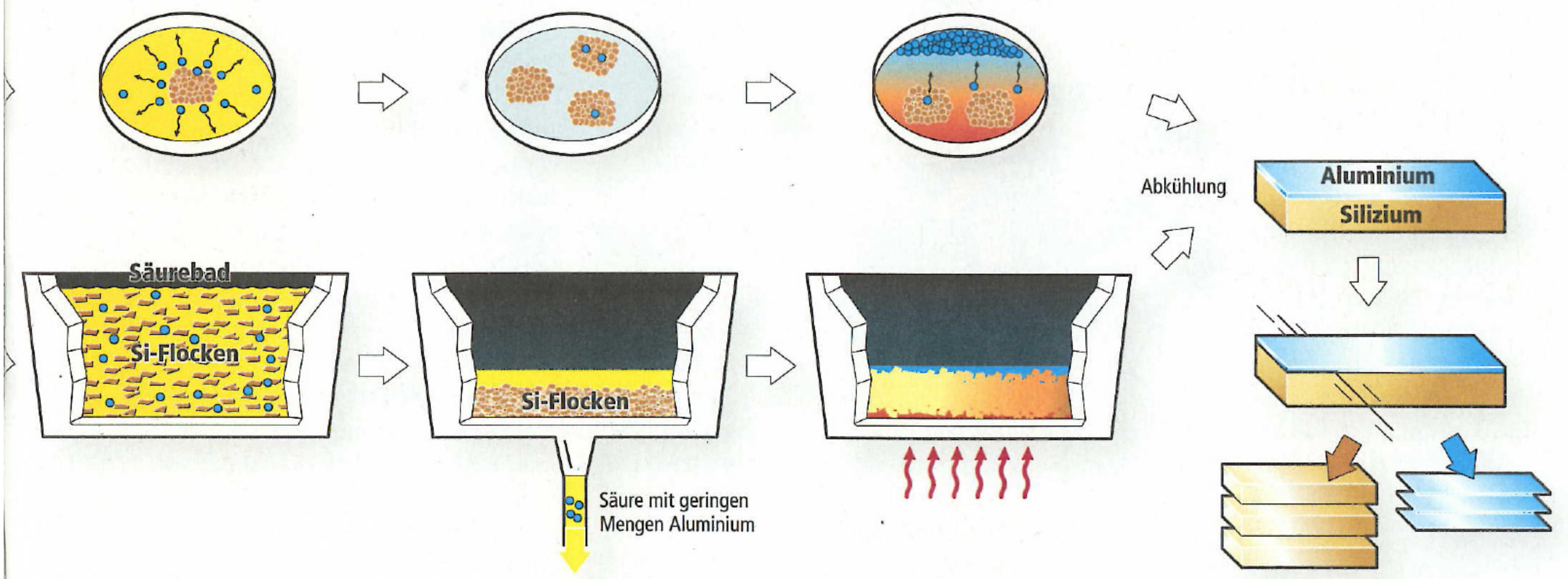
Beim Abkühlen der flüssigen Aluminium-Silizium-Legierung kristallisiert zuerst das Silizium in Form von Flocken aus. Die Verunreinigungen bleiben dabei im Aluminium zurück, was den primären Reinigungsschritt des Verfahrens darstellt. Um die Reinheit der Siliziumflocken zu erhöhen, werden weitere metallurgische Reinigungsschritte wie etwa Ausgasungen vorgenommen.

Ist die Auskristallisierung des Siliziums abgeschlossen, wird das flüssige Aluminium abgegossen. Da es mit 10 bis 12 Prozent Silizium angereichert ist, wodurch seine Stabilität erhöht wird, kann es gewinnbringend verkauft werden.

Die Siliziumflocken sind noch mit einer dünnen Schicht Aluminium überzogen. Um diese zu entfernen, wird das Silizium mit Säure übergossen.

Scource: Photon

Process 6N Silicon



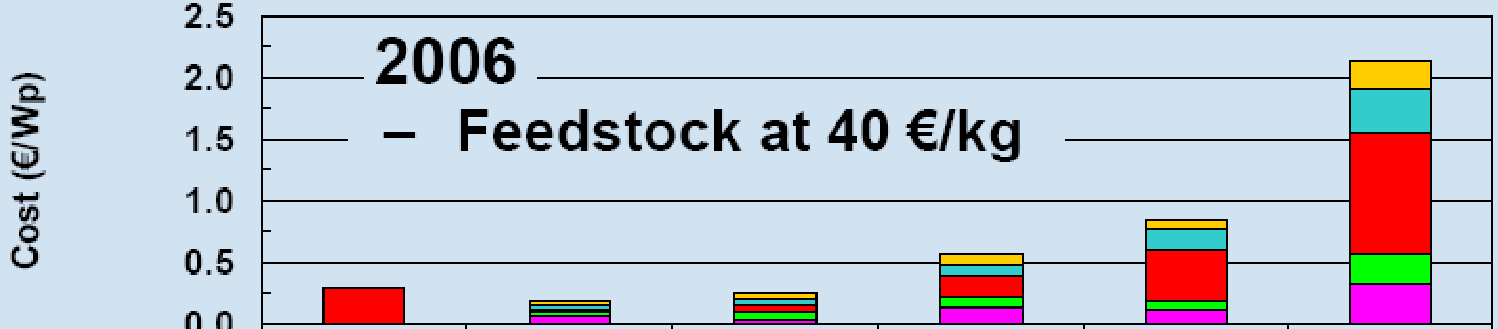
n Säurebad löst sich die Aluminiumschicht on der Oberfläche der Siliziumflocken.

Wenn das Säurebad abgegossen wird, bleiben nahezu reine Siliziumflocken übrig.

Anschließend werden die Flocken eingeschmolzen. Letzte darin eingeschlossene Aluminiumatome lösen sich auf und wandern an die Oberfläche.

Beim Abkühlen bildet sich aus den verbleibenden Aluminiumatomen eine dünne Schicht an der Oberfläche. Diese wird vom Silizium getrennt, das dadurch einen letzten Reinigungsschritt durchläuft.

Scource: Photon



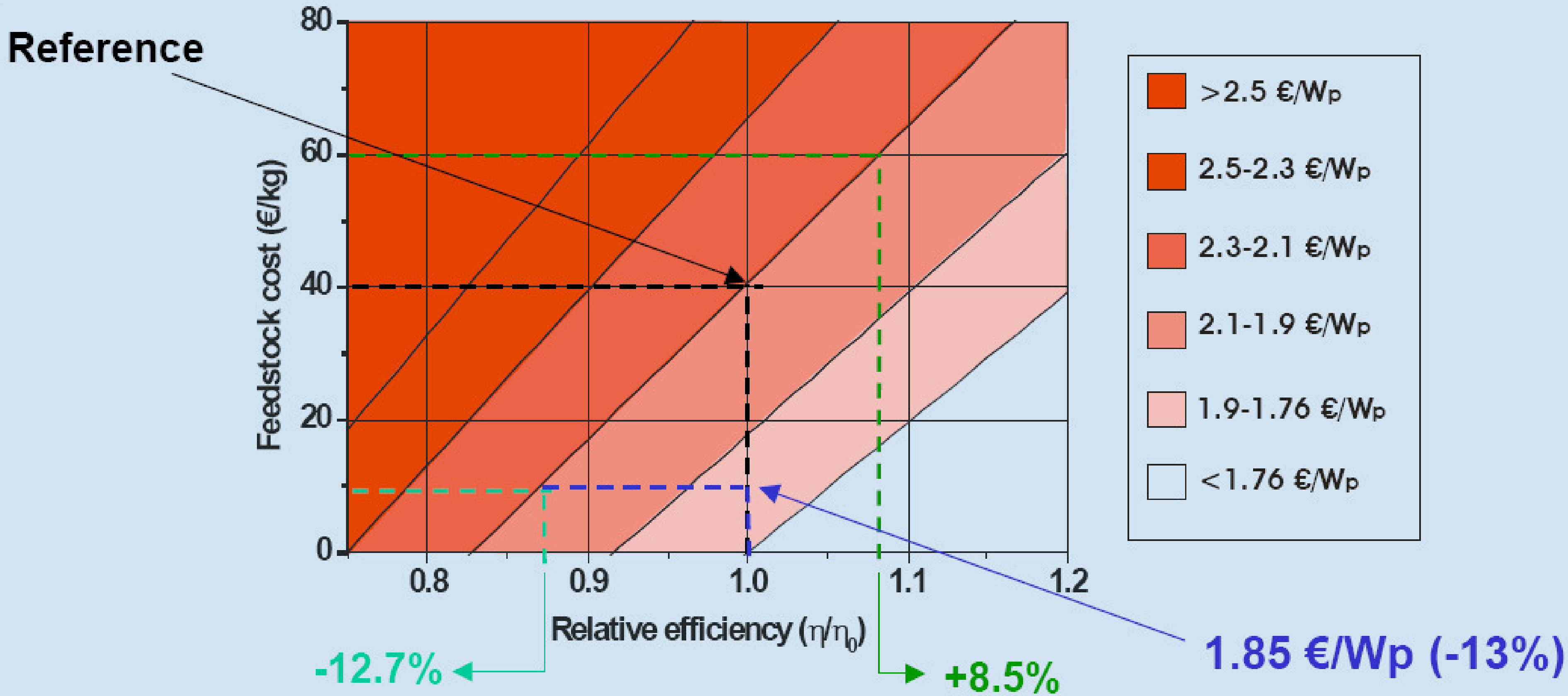
	Feedstock	Ingot Growth	Wafering	Cell processing	Module Assembly	Total
Equipment		0.03	0.03	0.09	0.07	0.22
Labour		0.03	0.05	0.11	0.17	0.36
Material	0.29	0.04	0.08	0.15	0.42	0.99
Yield losses		0.02	0.06	0.09	0.06	0.23
Fixed		0.06	0.02	0.13	0.11	0.33
Total	0.29	0.18	0.24	0.58	0.84	2.13

Impact of Si feedstock features on PV costs, Carlos del Cañizo (UPM – IES), Crystal Clear Workshop: Arriving at well-founded SoG silicon feedstock specifications, Amsterdam, 2008

In 2007 / 2008: Silicon prices on the spot market went up to 400 $ / kg

→ Feedstock costs were up to 50% of module costs

Situation now: Silicon prices have gone down to ~ 40€/kg again



Impact of Si feedstock features on PV costs, Carlos del Cañizo (UPM – IES), Crystal Clear Workshop: Arriving at well-founded SoG silicon feedstock specifications, Amsterdam, 2008

Situation now: Silicon prices have gone down to ~ 40€/kg again
Still umg-Si can be a commercially attractive material if price is significantly lower
But: only very small efficiency losses are allowed !