



Produção de silício metálico para aplicações fotovoltaicas

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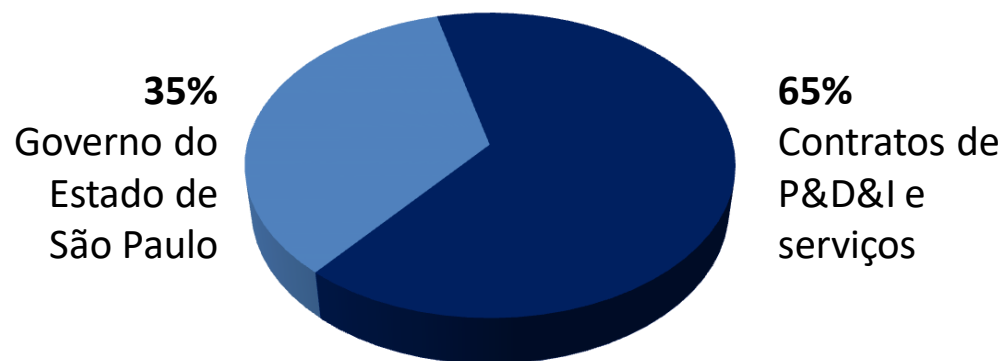
O IPT

- Uma das primeiras instituições de P&D&I aplicados no Brasil
- Sociedade Anônima, cujo sócio controlador é o Governo do Estado de São Paulo, por meio da Secretaria da Fazenda



Números 2015

- Orçamento anual: **R\$ 175,8 milhões**



Indicadores de Produção Técnica

- Documentos técnicos: **22.661** relatórios técnicos
- Empresas atendidas: **3794** CNPJs diferentes
- Projetos em andamento: **145**
- Patentes e softwares: **10**
- Publicações de artigos: **302**

Recursos Humanos em dez. 2015

Pesquisadores	381
Técnicos	196
Apoio administrativo	250
Estagiários	80
Total	907

Estrutura Física

- Unidades em
 - São Paulo
 - Franca
(EPIs, couros e calçados)
 - São José dos Campos
(materiais compósitos)
- 12 unidades de negócio
- 36 laboratórios e seções



Centros Técnicos

■ CTGeo
Tecnologias
Geoambientais

■ CT-Floresta
Tecnologia de Recursos
Florestais

■ CTMM
Centro de Tecnologia em
Metalurgia e Materiais

■ CETAC
Tecnologia do
Ambiente
Construído

■ CQuiM
Centro de Química e
Manufaturados

■ CTMetro
Centro de Metrologia
Mecânica, Elétrica e de
Fluidos

■ CT-Obras
Tecnologia de Obras
de Infra-estrutura

■ CIAM
Tecnologia da
Informação, Automação e
Mobilidade

■ CTMNE
Centro de Tecnologia
Mecânica, Naval e
Elétrica

■ NT – MPE
Suporte às PMEs

■ NT BIONANO
Bionanomanufatura

■ LEL
Laboratório de Estruturas
Leves

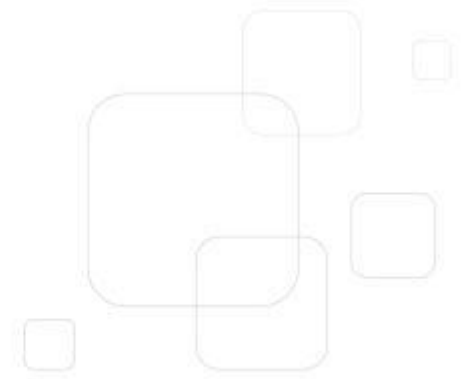
Some customers



Mining and Metals Companies



Silício



- Material abundante:
 - ~ 25% da crosta terrestre (silicatos, sílica)

- Material Versátil - Aplicações:

- Metalurgia (Ligas de Al e Siderurgia)
- Química (Silicones)
- Energia (células fotovoltaicas)
- Eletrônica (Chips)

Pureza

Silício Grau Metalúrgico

Silício Grau Químico

Silício Grau Solar

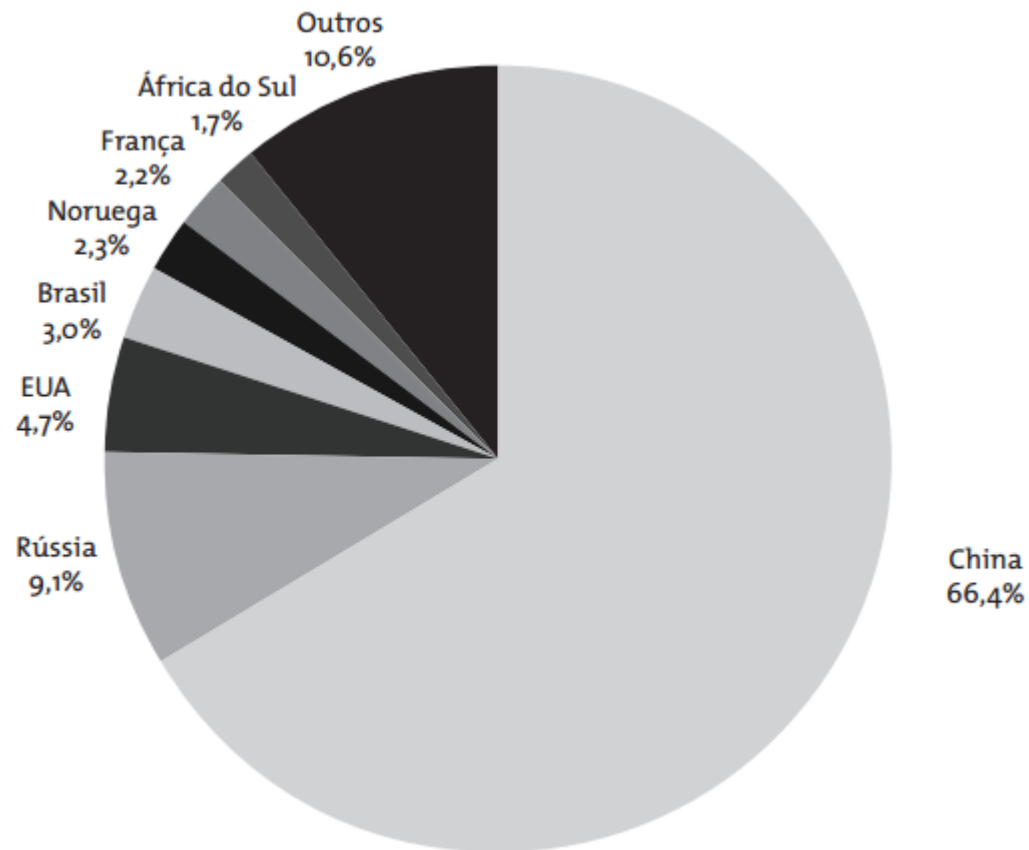
Silício Grau Eletrônico

Mercado de Si

Tipos	Preço (US\$/kg)	Nível impurezas (ppm)
Metalúrgico (SiGM) Químico	1,5	10.000
Solar (SiGS)	16-25	0,5 - 1 Obj: boa eficiência
Eletrônico (SiGE)	45-55	0,0001

Mercado de Si

Produção mundial de silício metálico em 2013 = 7700 mil toneladas

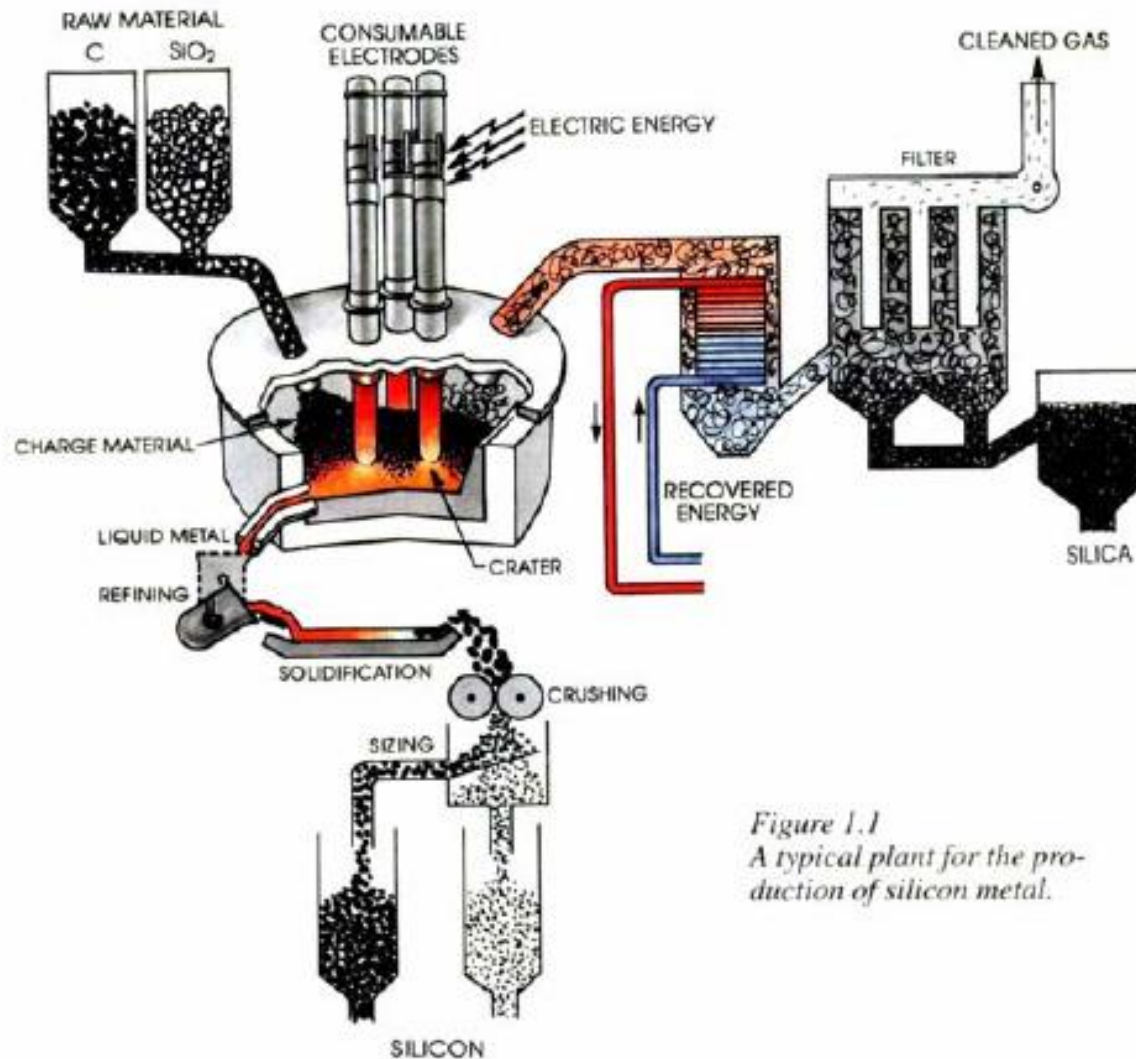


Si metálico e Si contido em FeSi

Silício Grau Metalúrgico - Aplicações

- Ligas de Al (leves e resistentes)
 - Exemplo: Pistões, cabeçotes para motores de automóveis e componentes aviões
 - Silício é usado em teores de até 12 ou 13 %
 - A presença de silício promove o aumento da resistência ao desgaste destas ligas
 - O Si aumenta a fluidez da liga (preenchimento de moldes complexos), melhora soldabilidade, reduz porosidade
 - Qdo tratada termicamente (com Mg) favorece propriedades mecânicas
- Fabricação de aços e ferros fundidos - Ferro ligas de Silício (FeSi e FeSiMn)
 - Desoxidantes e elementos de liga de aços e Fofos

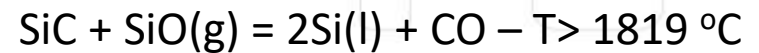
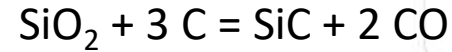
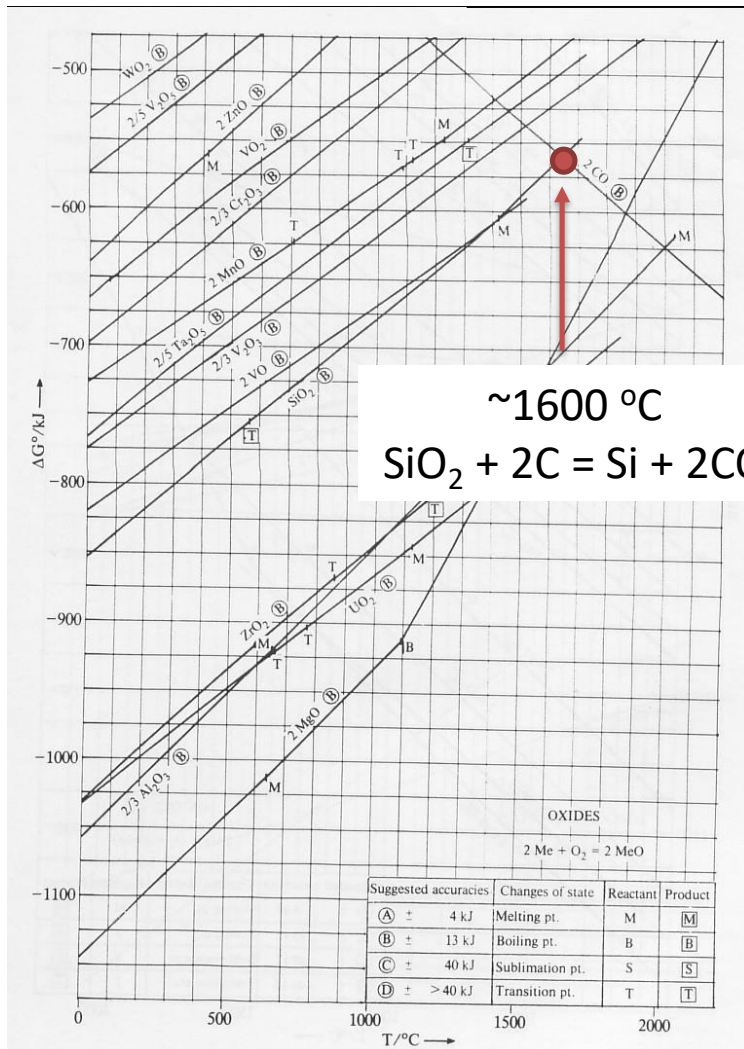
Silício Grau Metalúrgico - Produção



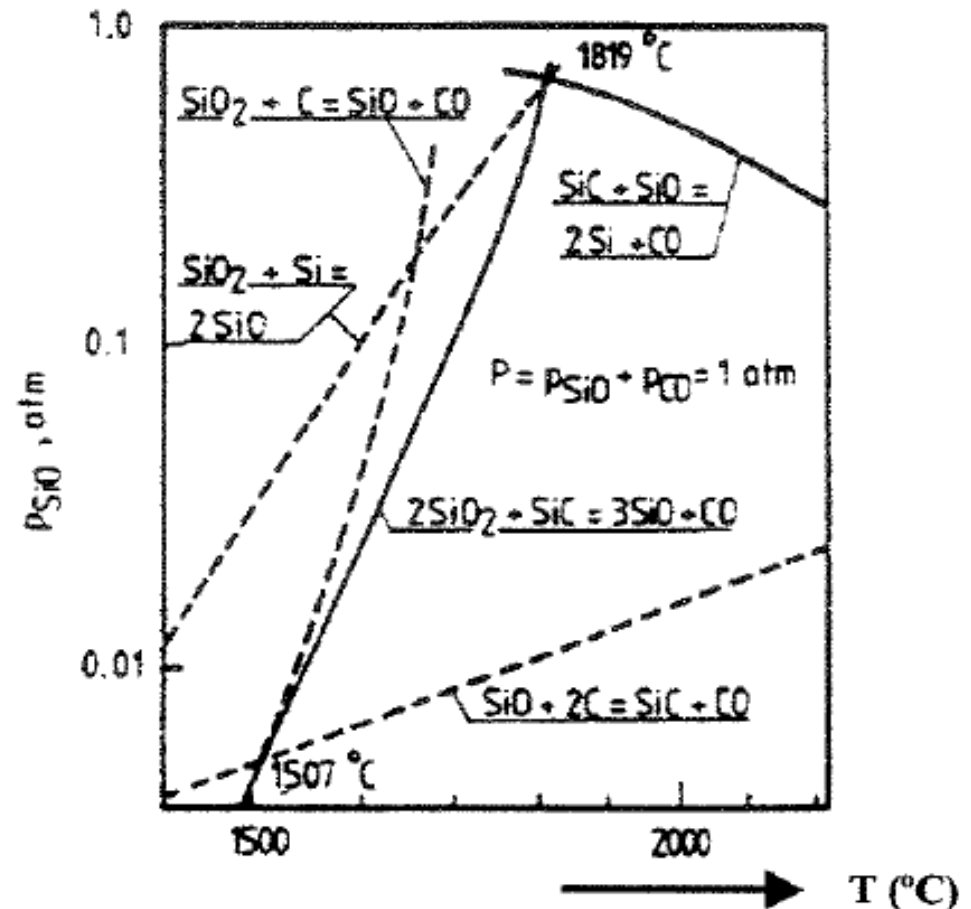
*Figure 1.1
A typical plant for the pro-
duction of silicon metal.*

Silício Grau Metalúrgico - Produção

Diagrama de Ellingham



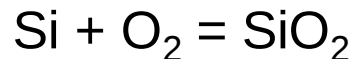
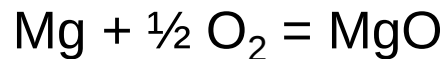
Resultado → 11-13 MWh/t Si



Silício Grau Metalúrgico - Refino

Injeção de O_2 ou ar enriquecido em O_2

Oxidação parcial de:



Refino com escória – remoção de Al, Ca e outros

Fe, Ni, Cr, V, Ti, etc não podem ser removidos por oxidação (SiO_2 mais estável que os óxidos destes elementos) – controle matéria prima

Produto:

SiGM Alta Pureza (HP)

Silício Grau Químico - controle de impurezas e resfriamento

Silício Grau Químico - Aplicações

■ Fabricação de Silicones

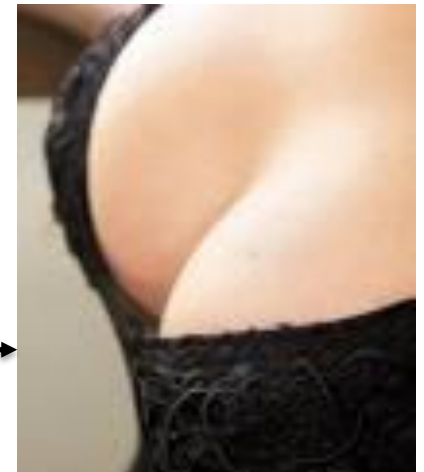
■ Aplicação em diversas áreas:

- Tintas
- Graxas lubrificantes
- Recobrimentos
- Cosméticos
- Biomateriais e Farmacêutica

■ Outra importante aplicação



Aqui tem Silício!



Silício Grau Solar - Aplicação

- Fabricação de Células solares fotovoltaicas
 - Geração de energia
 - Satélites
 - Irrigação
 - Telefonia em locais isolados



*Importante diferenciar o
coletor térmico de painéis
solares fotovoltaicos*

Silício Grau Solar – Célula Solar

Funcionamento da Célula Solar:

- Si é um semicondutor: 4 elétrons em sua última camada compartilhados por ligações covalentes sem liberdade de movimentação. Si não é um bom condutor de eletricidade.
- Quando o Si é dopado com P (grupo V da tabela periódica), por exemplo, que tem 5 elétrons na última camada, restará um elétron livre (não compartilhado). Uma pequena energia é capaz de movimentar este elétron. Este tipo de Si dopado com P é chamado tipo N (N de carga negativa)
- Quando o Si é dopado com B (grupo III da tabela periódica), que tem 3 elétrons na última camada, restará uma lacuna ausência elétrons) para ser ocupada por um elétron. Constitui-se um Si tipo P (positivo).
- Na junção P/N ocorre um desequilíbrio de cargas (campo elétrico formado) – formado um diodo

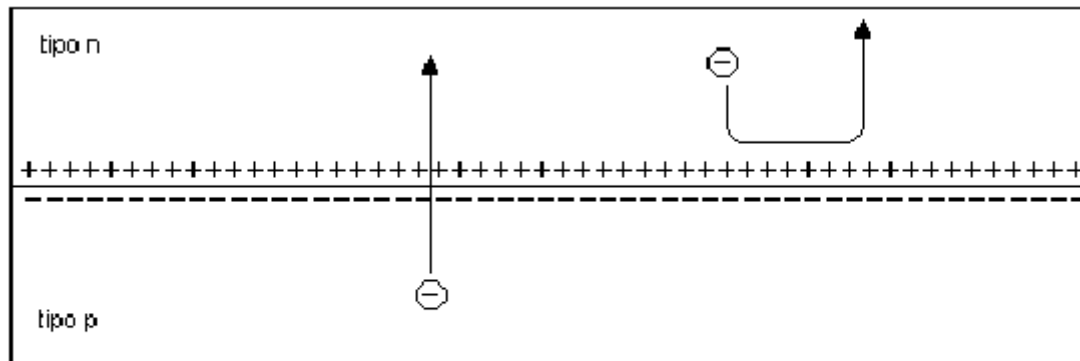


FIG 2.1.1: Esquema do equilíbrio alcançado na conexão tipo p – n.

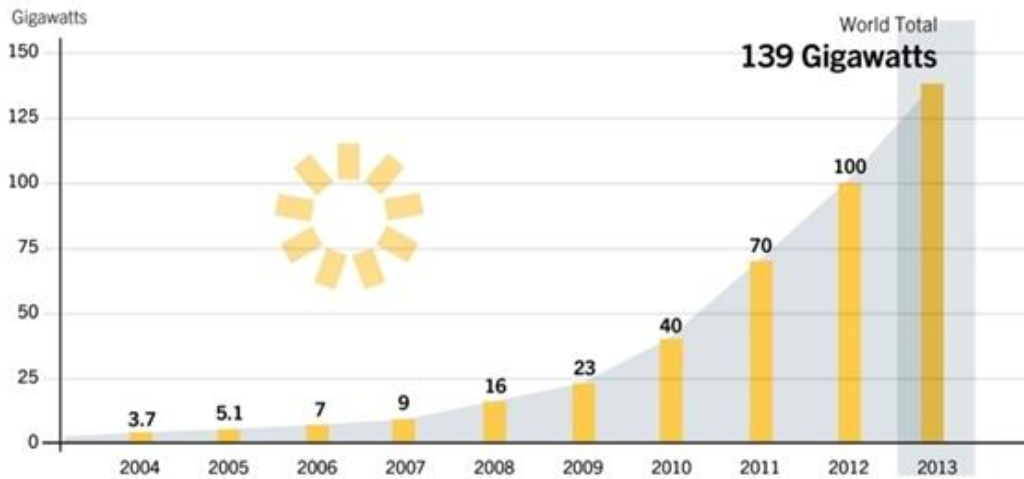
Silício Grau Solar – Paineis Solar

- Painel 36 células de 125 mm (redondas) – pot max 70 W (painel 1242 x 487 mm). Rend ~16% sob radiação solar 1000w/m².



Silício Grau Solar – Energia Solar

Solar PV Total Global Capacity, 2004–2013

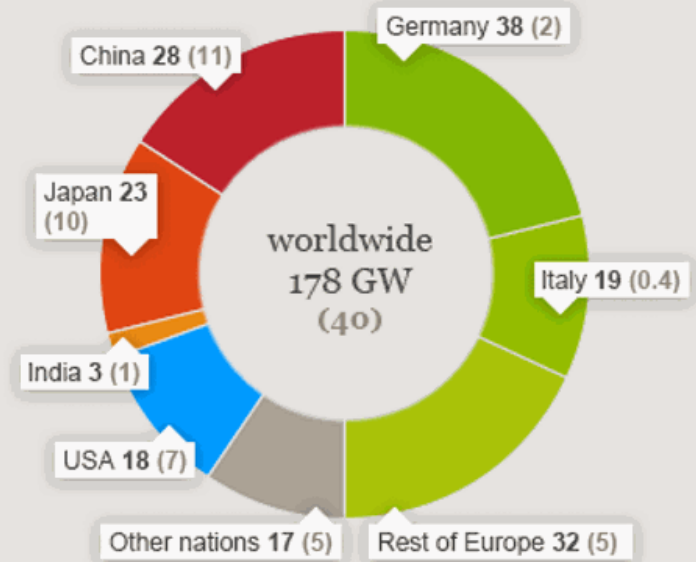


REN21. 2014. *Renewables 2014 Global Status Report* (Paris: REN21 Secretariat).



Global solar photovoltaic

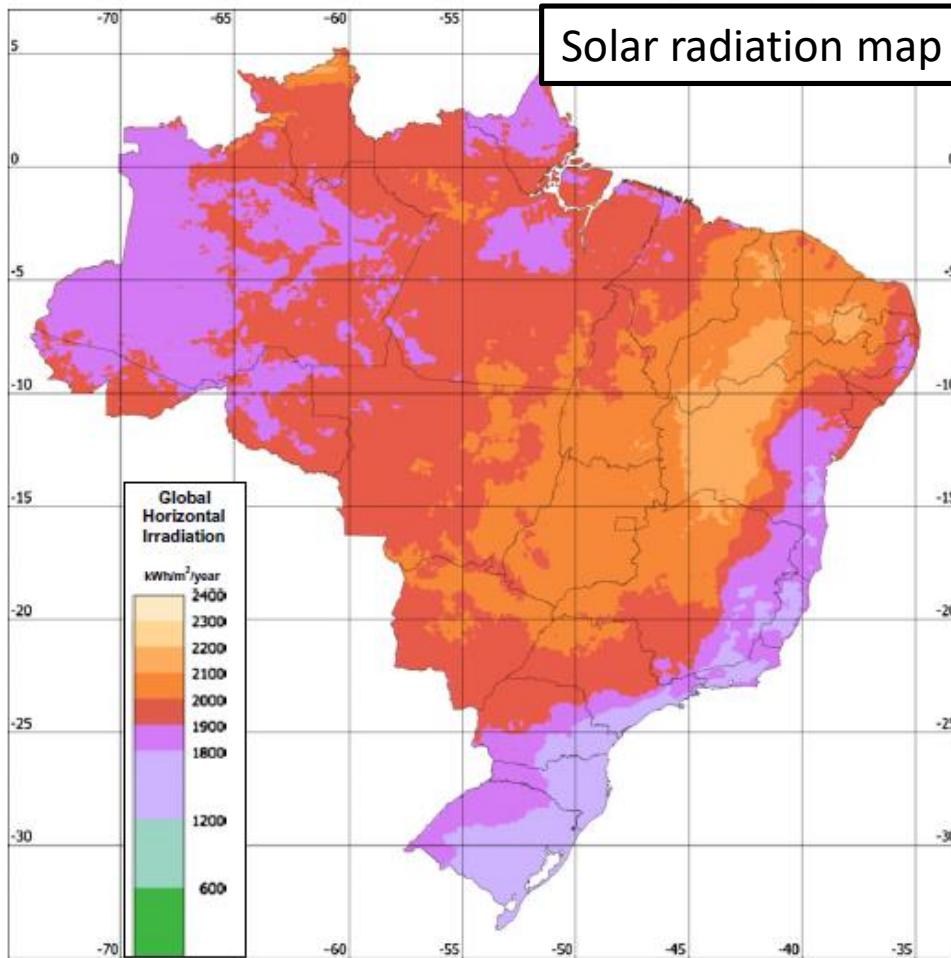
Cumulative capacity in Gigawatt (GW) by end of 2014 (added in 2014)



Source: SolarPower Europe

Para comparação: potência instalada de Itaipu = 14 GW

Solar (PV) energy in Brazil



Brazil (red and orange) – 2 to 2.4 MWh/m²/year

Only 35 MW installed - most as isolated systems (not grid connected)

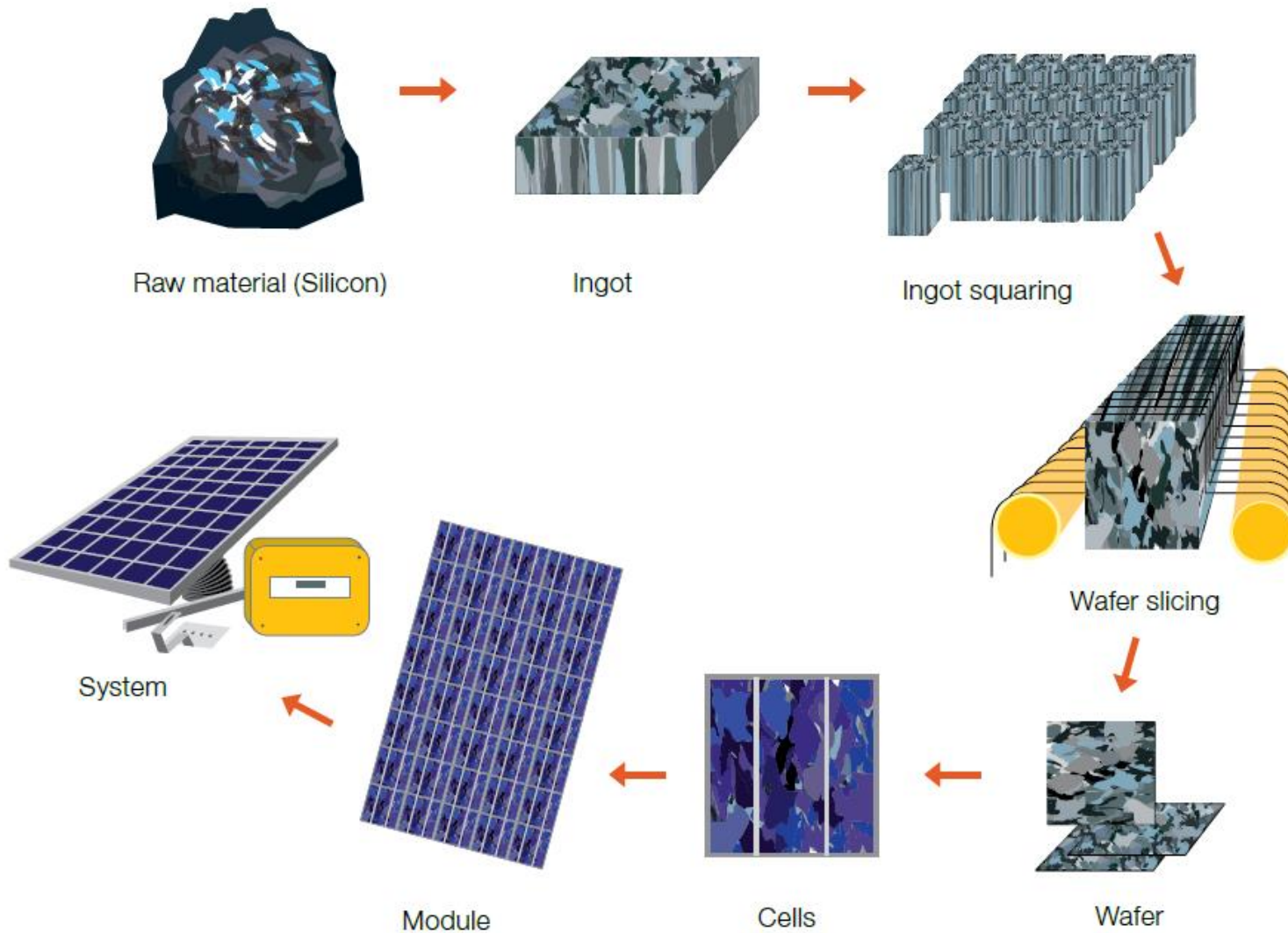
Definition of regulatory aspects for PV implementation in Brazil by Brazilian Electricity Regulatory Agency

- Micro systems (up to 100 kW)
- Mini systems (up to 1 MW)
- Can be connected to the grid

Government energy auction in 2015:

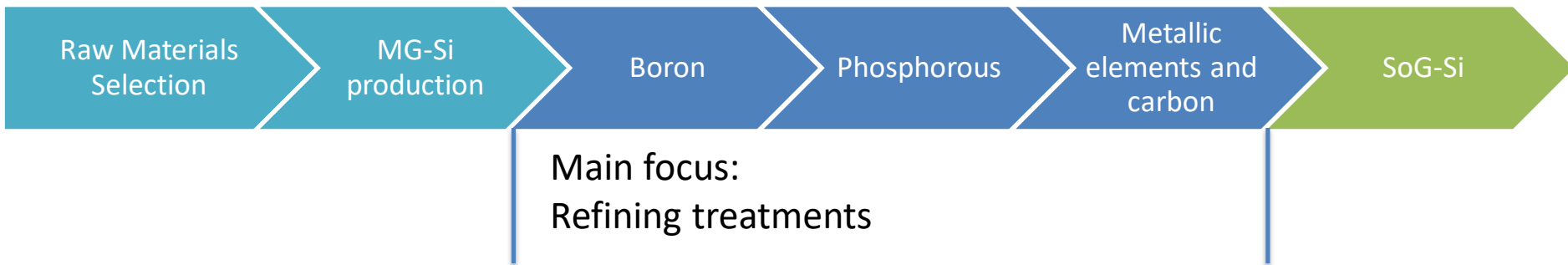
- A capacity of 1 GW for photovoltaic was contracted
- Two new auctions are planned for 2016.

Rota de Produção do Módulo Solar



Metallurgical route to produce solar grade silicon

Project for development of a process to produce solar grade silicon by refining of MG-Si.



Technical partners and funding



Raw Materials
Selection

MG-Si
production

Boron

Phosphorous

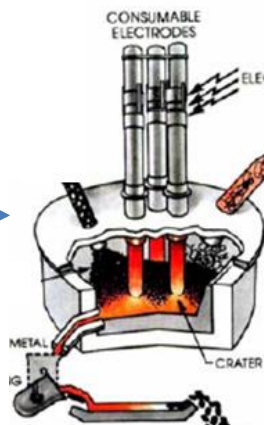
Metallic
elements and
carbon

SoG-Si

Quartz



Reducing agent

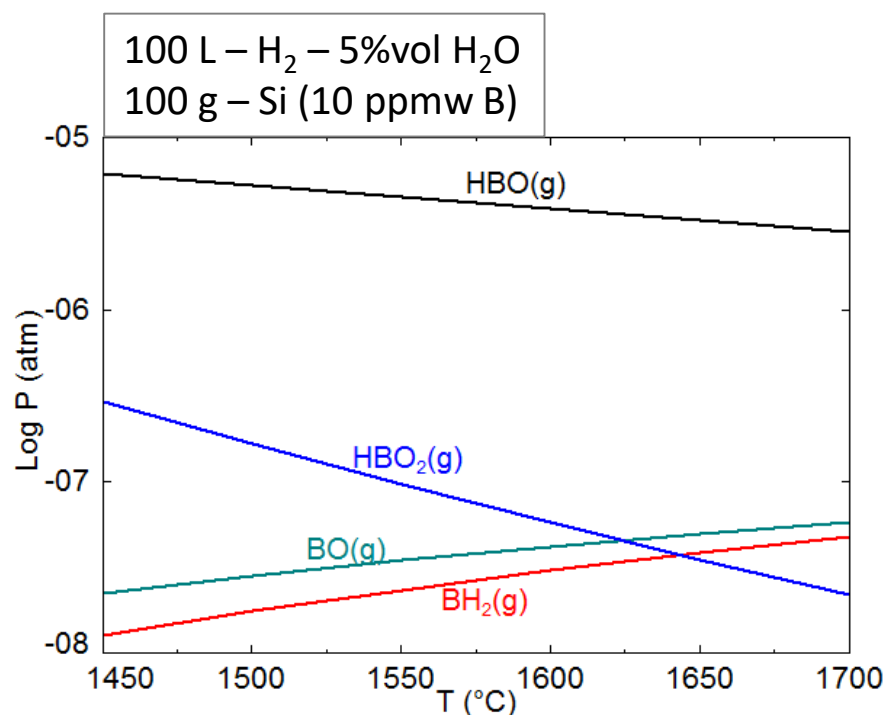
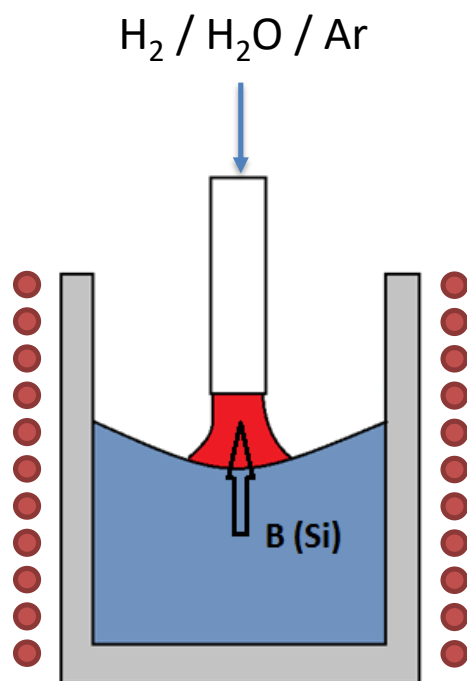


MG-Si with controlled
impurities

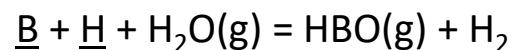


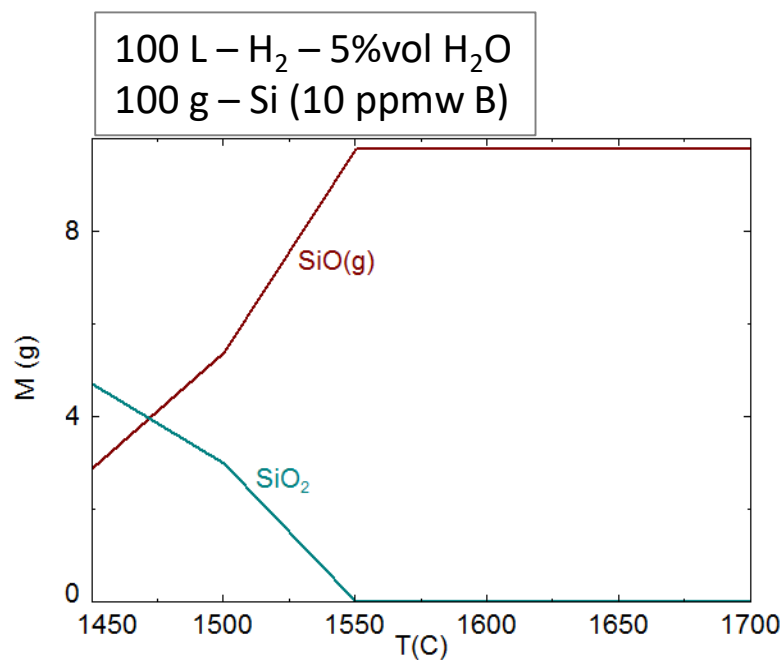
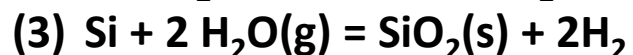
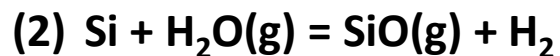


Boron removal by injection of humidified gases

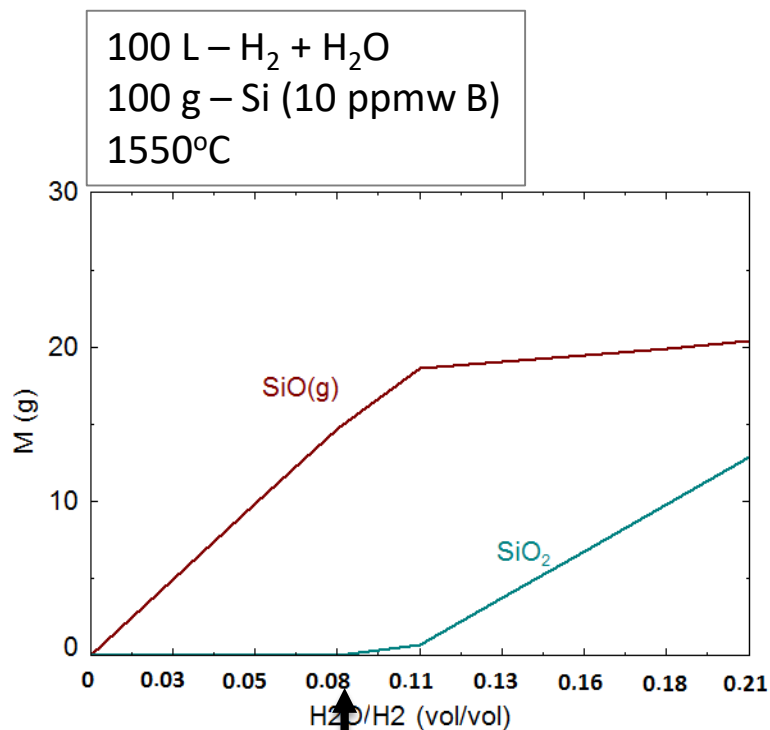


Safarian et. al. - 2014

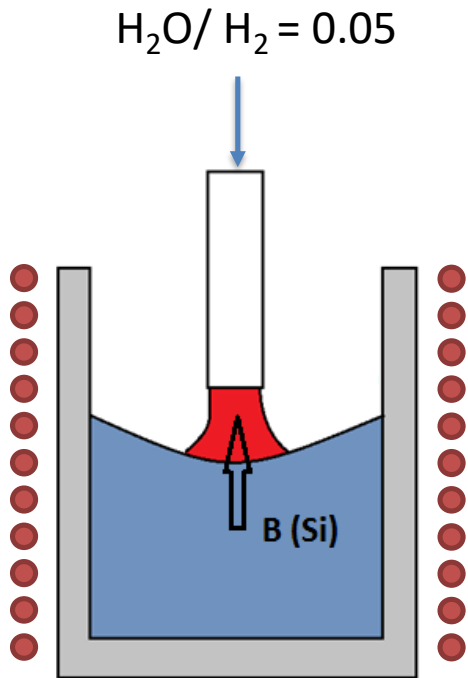




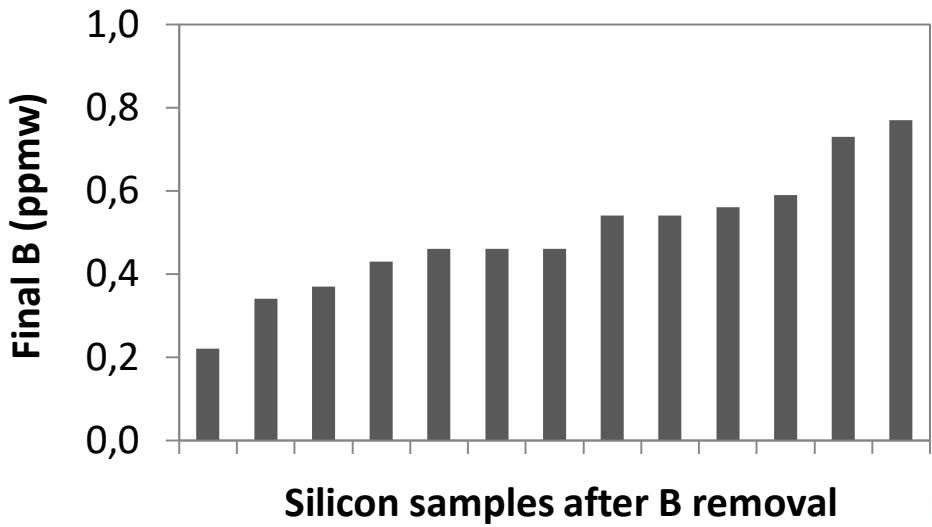
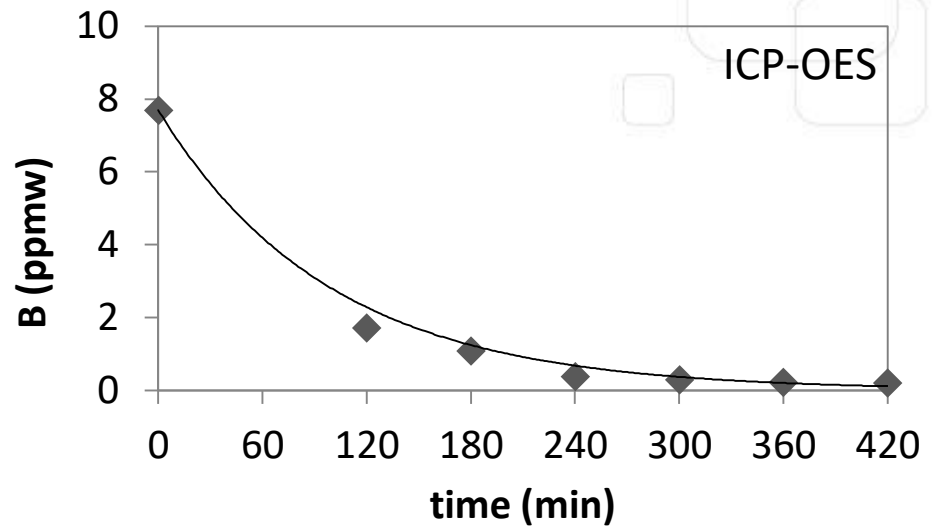
(a)



$\text{H}_2 = 92,6 \text{ \% vol}$
 $\text{H}_2\text{O} = 7,4 \text{ \% vol}$



Induction furnace
Graphite crucible
3 kg of Si
1550°C



Raw Materials
Selection

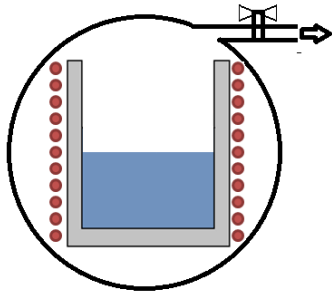
MG-Si
production

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Phosphorous

Metallic
elements and
carbon

SoG-Si



Vacuum Induction furnace
Graphite crucible



Electron Beam furnace
Refrigerated Copper crucible



Phosphorous removal by evaporation

Thermodynamics:

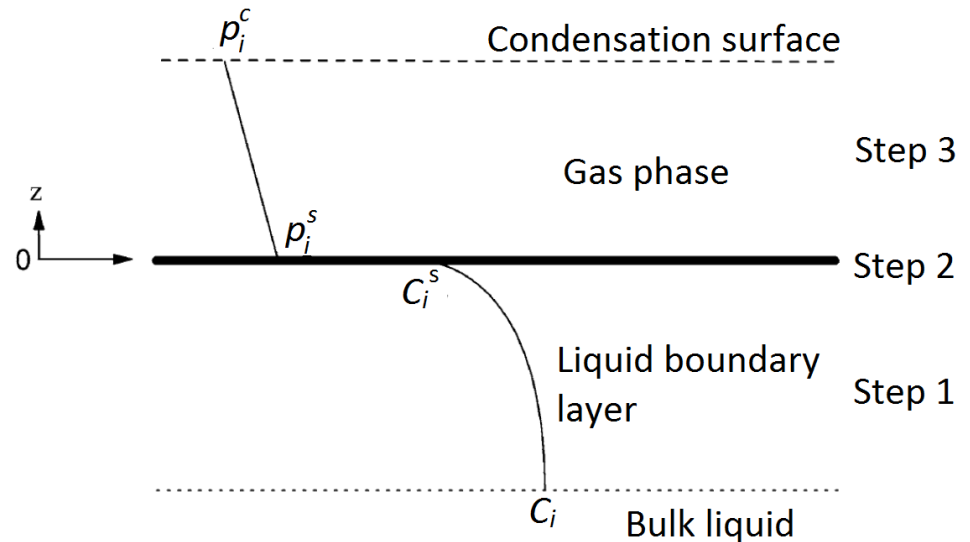
$$\beta = \gamma^0 \cdot \frac{p_i^0}{p_{Si}^0} \cdot \left(\frac{M_{Si}}{M_i} \right)^{\frac{1}{2}}$$

Phosphorous in Si:

$\beta = 485 (>> 1) \rightarrow$ thermodynamically possible to remove by evaporation

Kinetics

3 step model



$$\frac{1}{k_p} = \frac{1}{k_l} + \frac{1}{k_e} + \frac{1}{k_g}$$

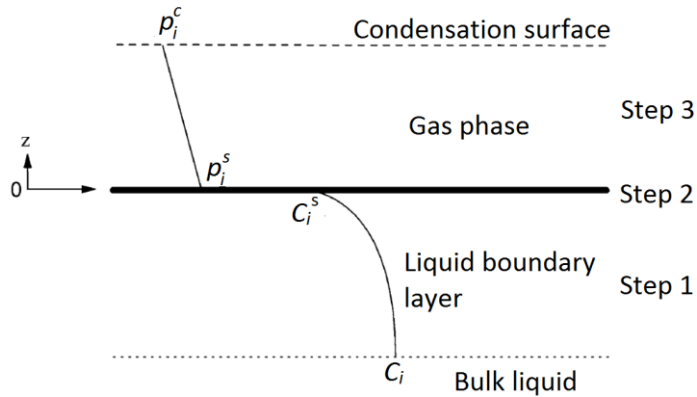
liquid ← k_l ↓ k_e → gas

vaporization



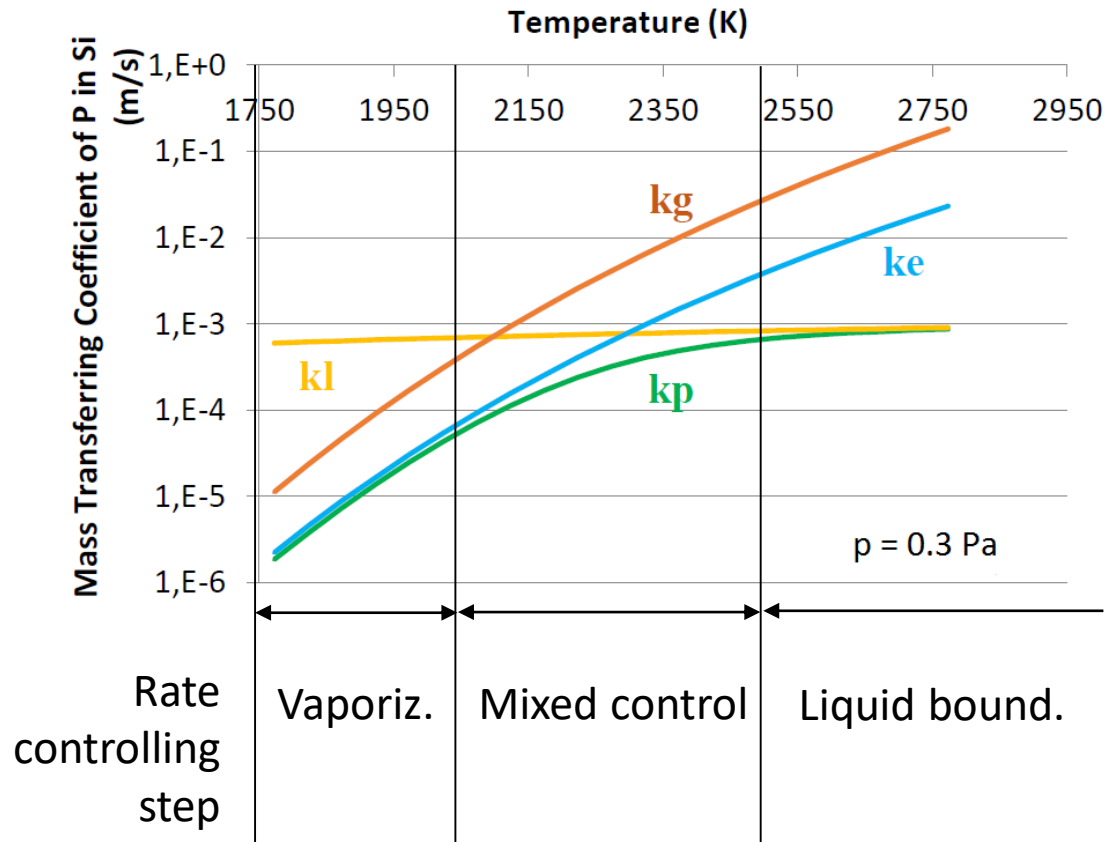
Kinetics

3 step model



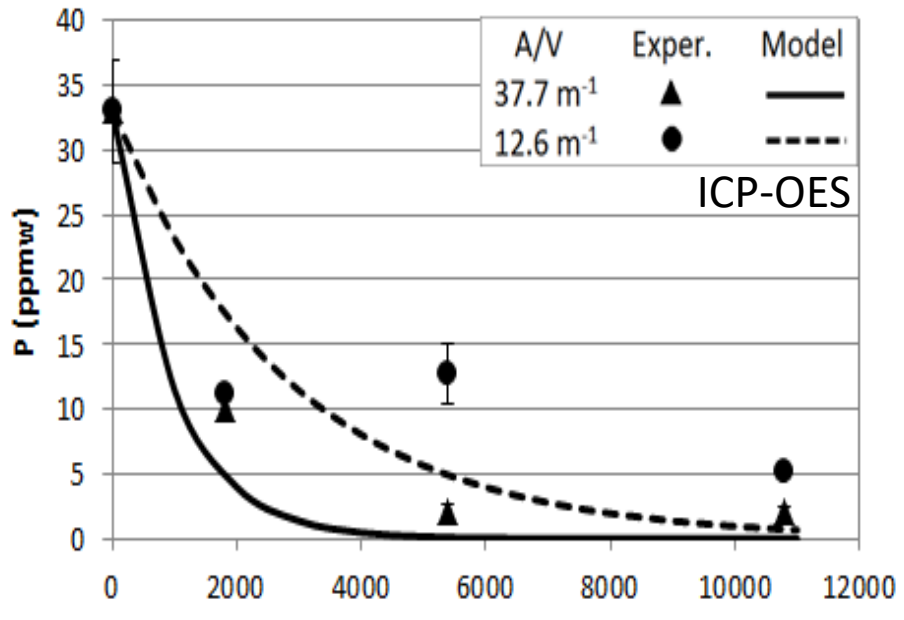
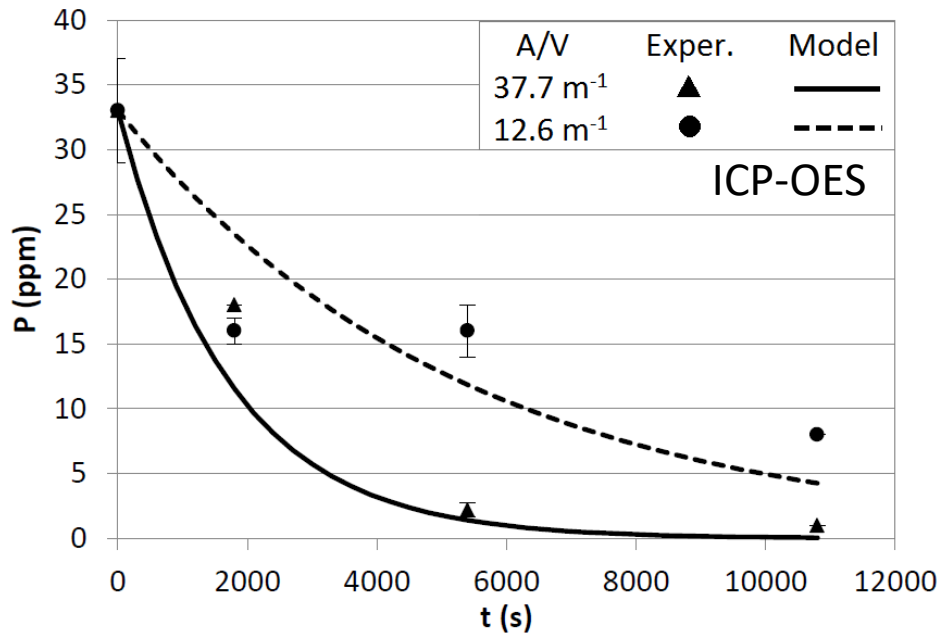
$$\frac{1}{k_p} = \frac{1}{k_l} + \frac{1}{k_e} + \frac{1}{k_g}$$

liquid ← vaporization → gas





Vacuum induction furnace



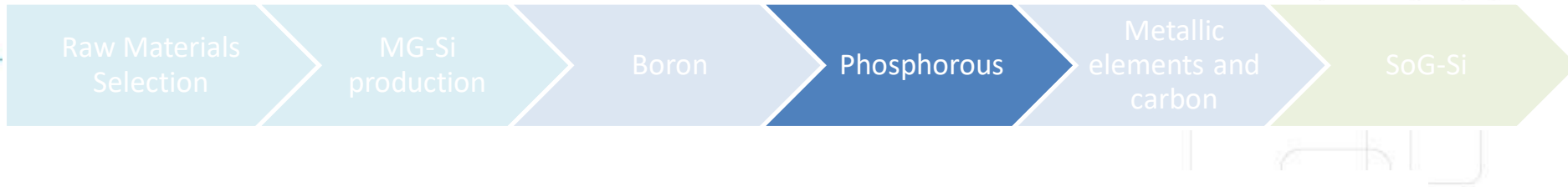
1650°C – 0.3 Pa

1750°C – 0.3 Pa

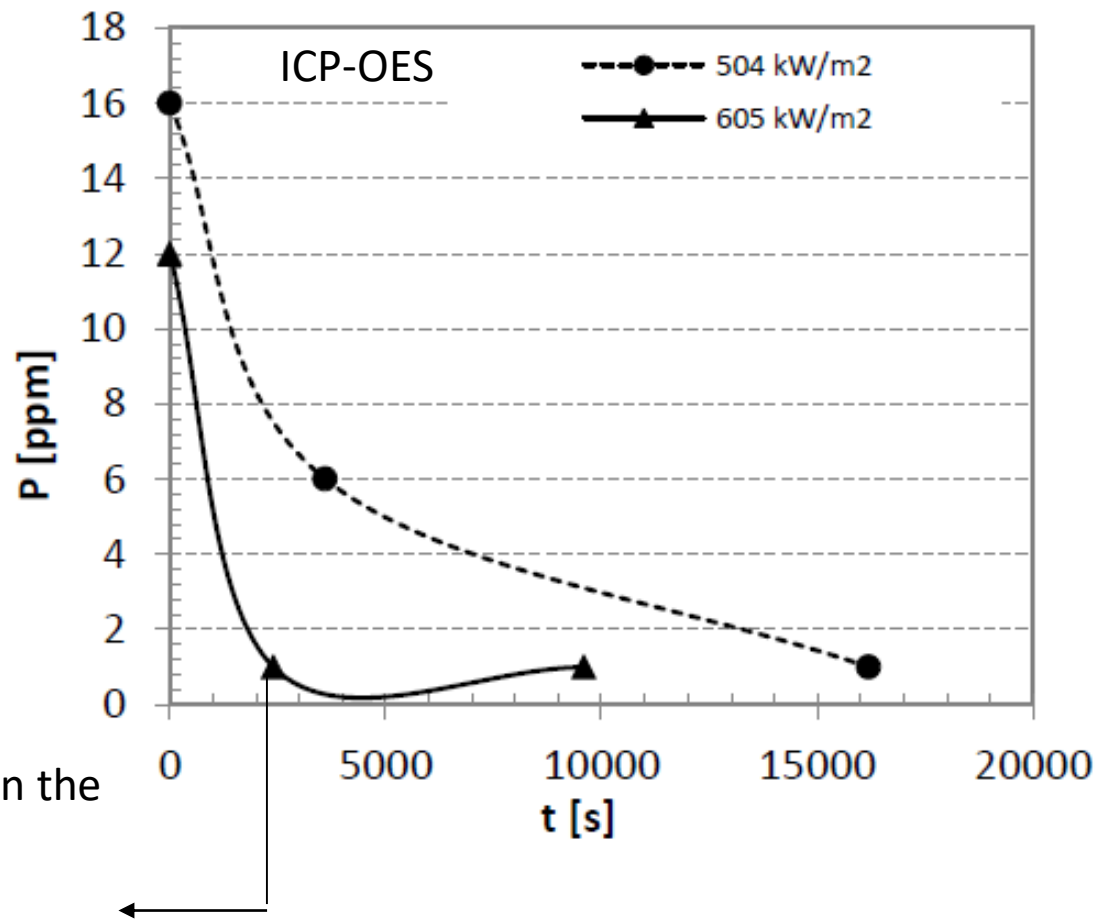
k_p – total mass transfer coefficient (m/s)

Temperature	1650°C	1750°C
Experimental	$7.0 \cdot 10^{-6}$	$4.0 \cdot 10^{-6}$
Model	$1.3 \cdot 10^{-5}$	$2.8 \cdot 10^{-5}$

Safarian and Tangstad, 2012
 $k_p = 4.9 \cdot 10^{-6}$ (1600°C and 0.5 Pa)



Electron Beam furnace

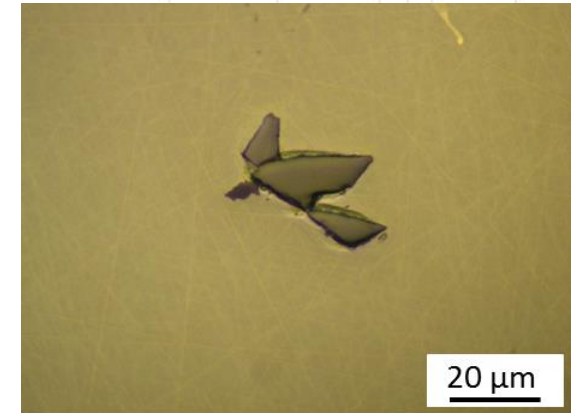


~ ½ of the time required in the induction furnace:

- Higher temperatures
- Lower pressures



- Carbon in Si is mostly presented as SiC particles
- Problems related with carbon in SoG-Si:
 - Shunts in p-n junction → SiC
 - Wire breakage during wafering → SiC
- Removal of C → removal of SiC particles



- Alternatives: Settling and directional solidification

Settling

Results showed low efficiency

Directional solidification

S/L interface may push ahead SiC particles by controlling velocity

Raw Materials
Selection

MG-Si
production

Boron

Phosphorous

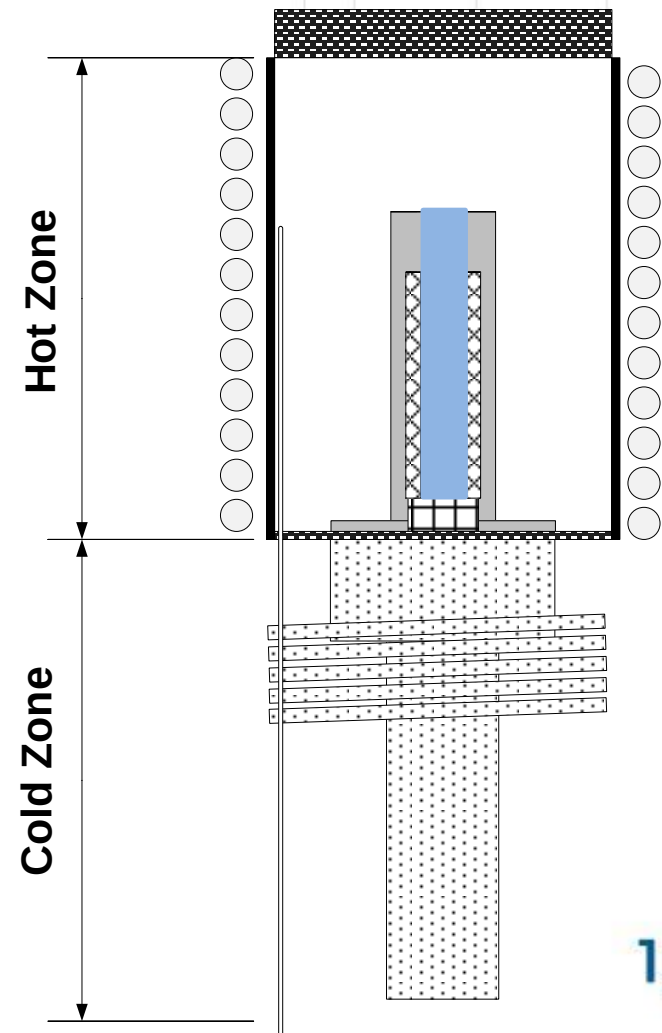
Metallic
elements and
carbon

SoG-Si

Removal of C(SiC) by directional solidification

SiC macrosegregation:

- Quartz crucible - Si_3N_4 coating
- Extraction velocities: 5 to 80 $\mu\text{m/s}$
- Initial C = 1200 ppmw



Raw Materials
Selection

MG-Si
production

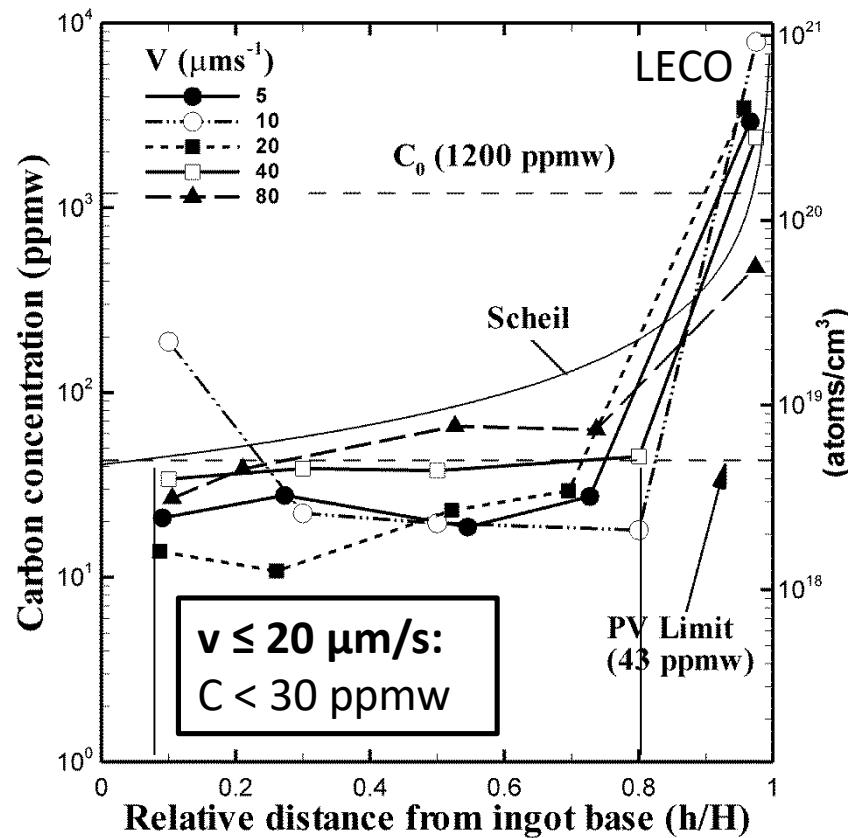
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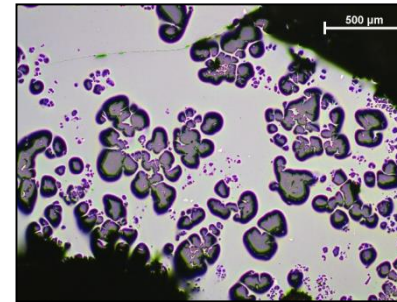
Metallic
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SoG-Si

Removal of C(SiC) by direction solidification

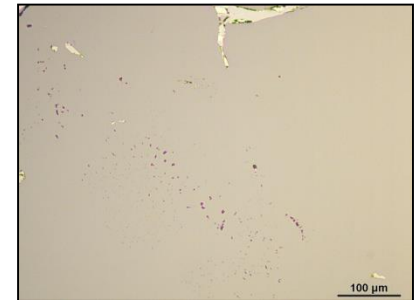


10 $\mu\text{m/s}$

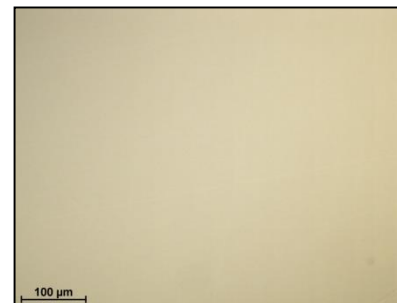


Top - 100 mm

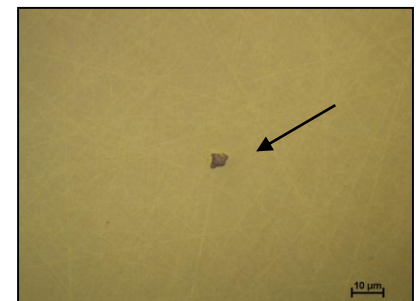
80 $\mu\text{m/s}$



Top - 95 mm



20 mm



5 mm

Raw Materials
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MG-Si
production

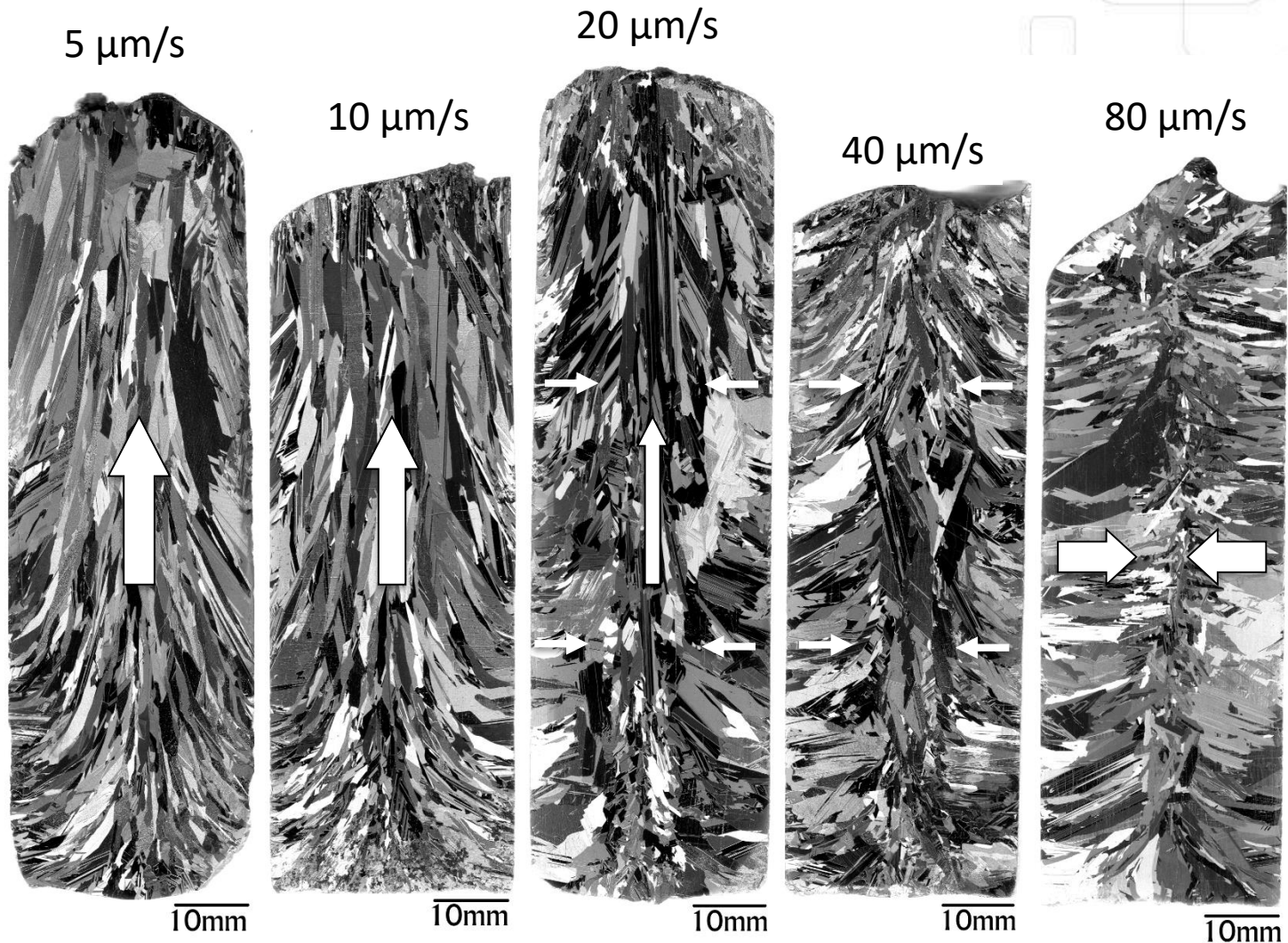
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Removal of C(SiC) by directional solidification





- Metallic elements segregate during solidification of Si

Element	Fe	Al	Ti	V	Mn	B	P
k_0	$8 \cdot 10^{-6}$	$2 \cdot 10^{-3}$	$3.6 \cdot 10^{-6}$	$4 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	0.7-0.8	0.35

k_0 - Equilibrium partition coefficient = C_s/C_l

- By controlling solidification conditions it is possible to macrosegregate impurities.
 - Directional solidification with planar S/L interface is required
 - Criteria for planar interface:
$$\frac{G}{V} \geq - \sum_i \left[\frac{m_{li} C_{si} (1 - k_{0i})}{D_{li} k_{0i}} \right]$$
 - High thermal gradients (G) and low interface velocities (v)
→ planar S/L interface

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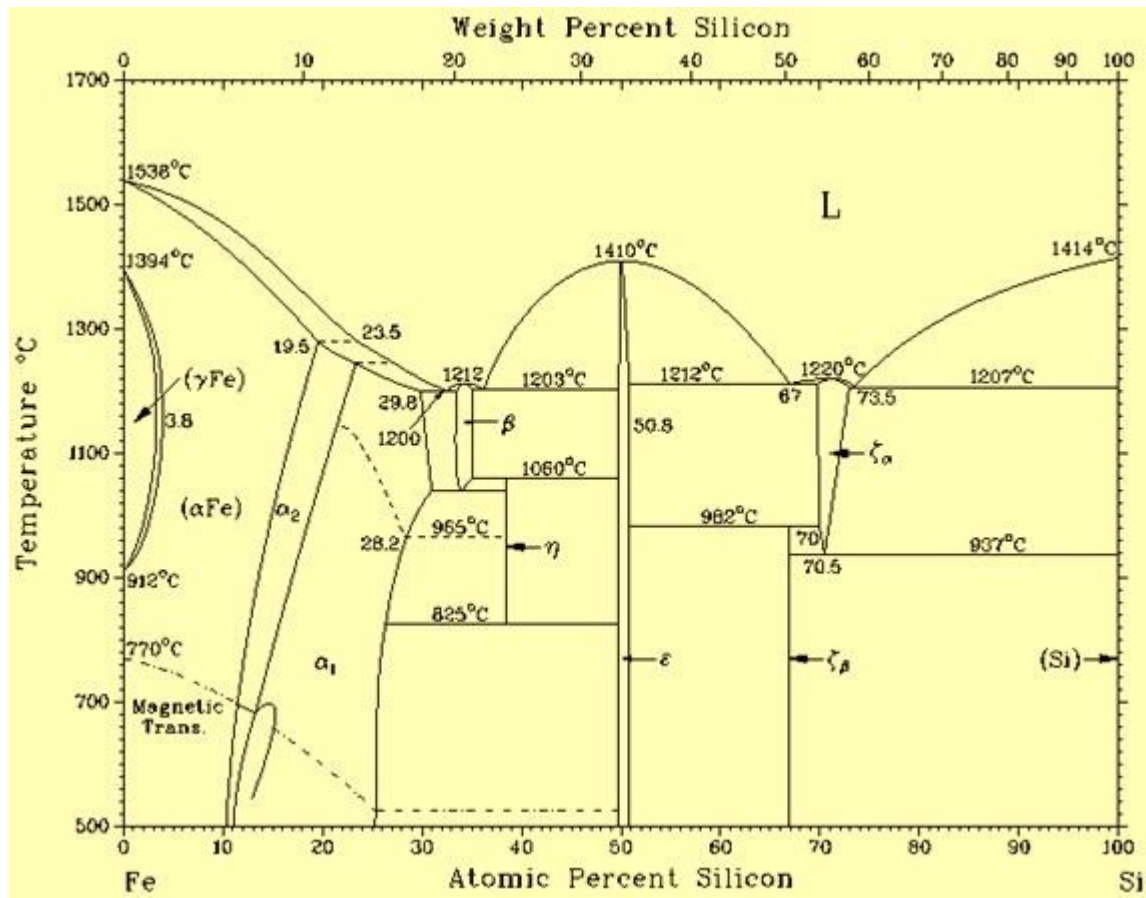
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k_0 - Equilibrium partition coefficient = C_s/C_l



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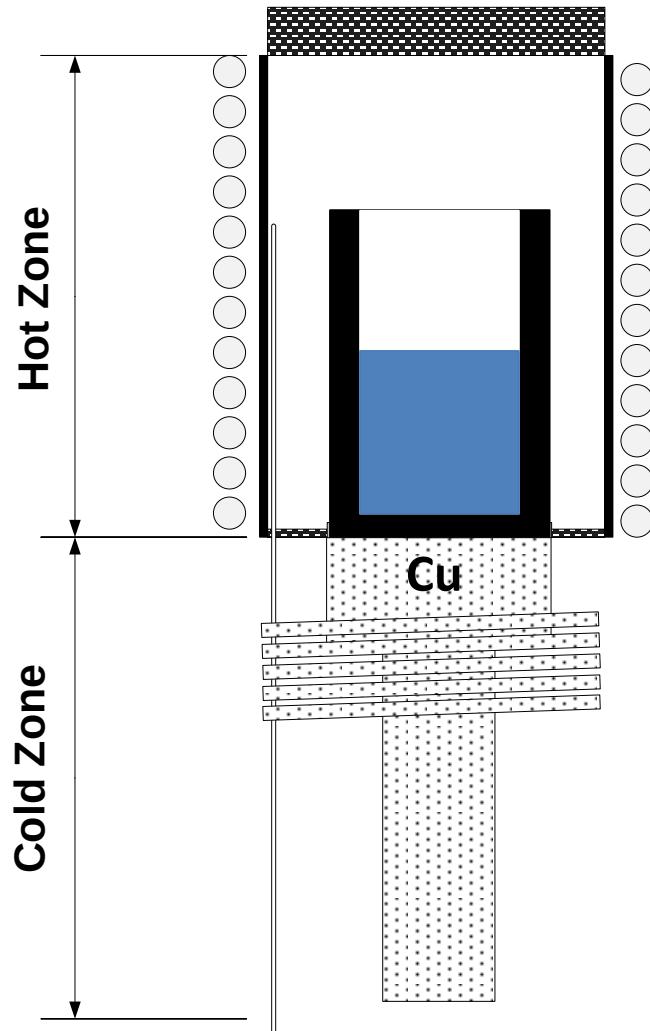
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Metallic elements removal by directional solidification



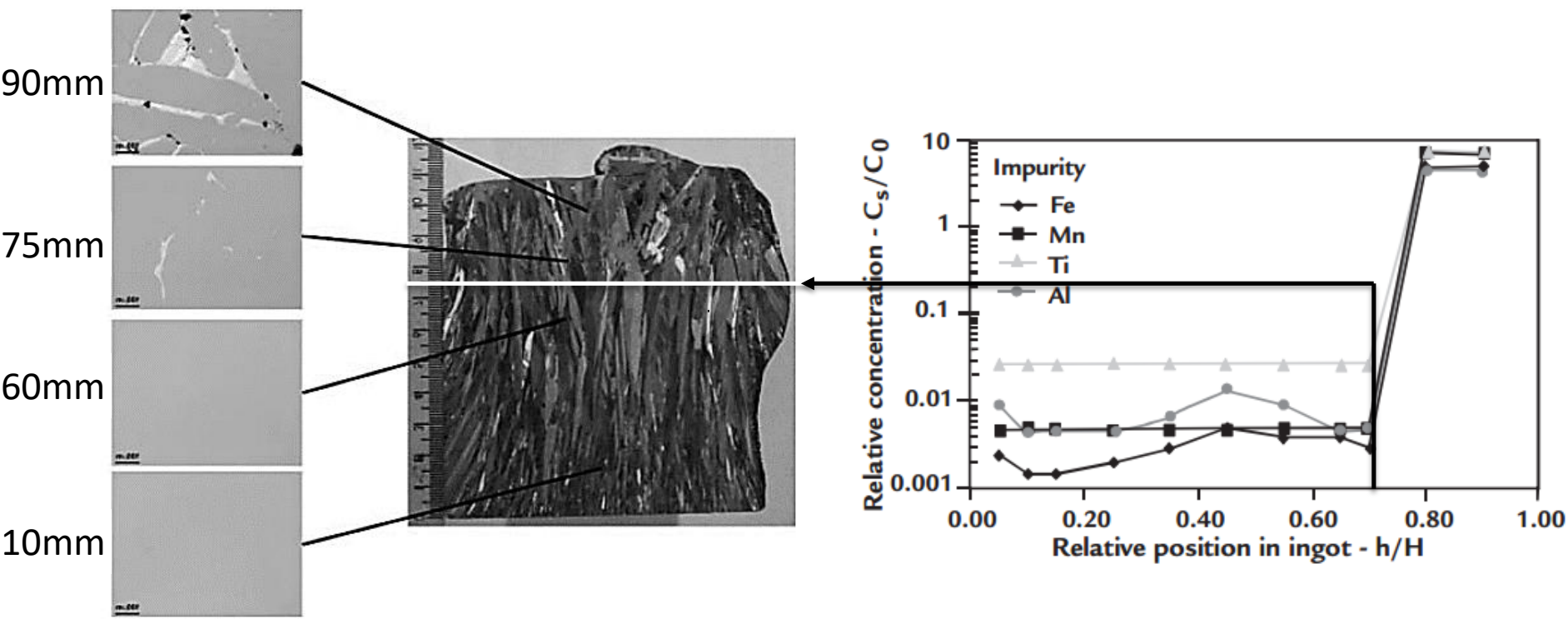
Metallic elements macrosegregation

- Graphite crucible on top of Cu refrigerated base (**high G**)
- Static mold
- Controlled cooling from 1500°C to 1000°C at 0,5°C/min (**low v**)

MG-Si	Fe	Al	Ti	Mn
Initial content (ppmw)	1363	445	117	216



Metallic elements removal by directional solidification





Combination of refining treatments into a process

- Main challenge → contamination
 - To avoid contamination with impurities already removed
 - Sources of contamination: Crucibles, refractories, sensors, lances, etc.
- SoG-Si produced at Lab Scale in IPT
 - GDMS analysis showed that metallic elements contents are lower than 0.1 ppmw

B	P	Fe	Al	Ni	Cu	Ti	Co
0.62	0.49	0.28	0.27	0.12	< 0.1	< 0.1	< 0.1
Cr	Mn	Zn	Mg	Ba	Zr	V	Total
< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 2

ICP-OES – Values in ppmw