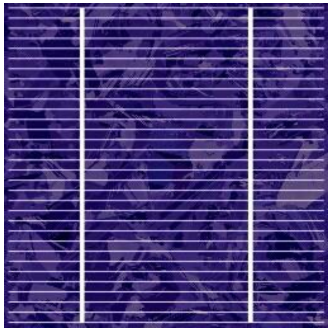
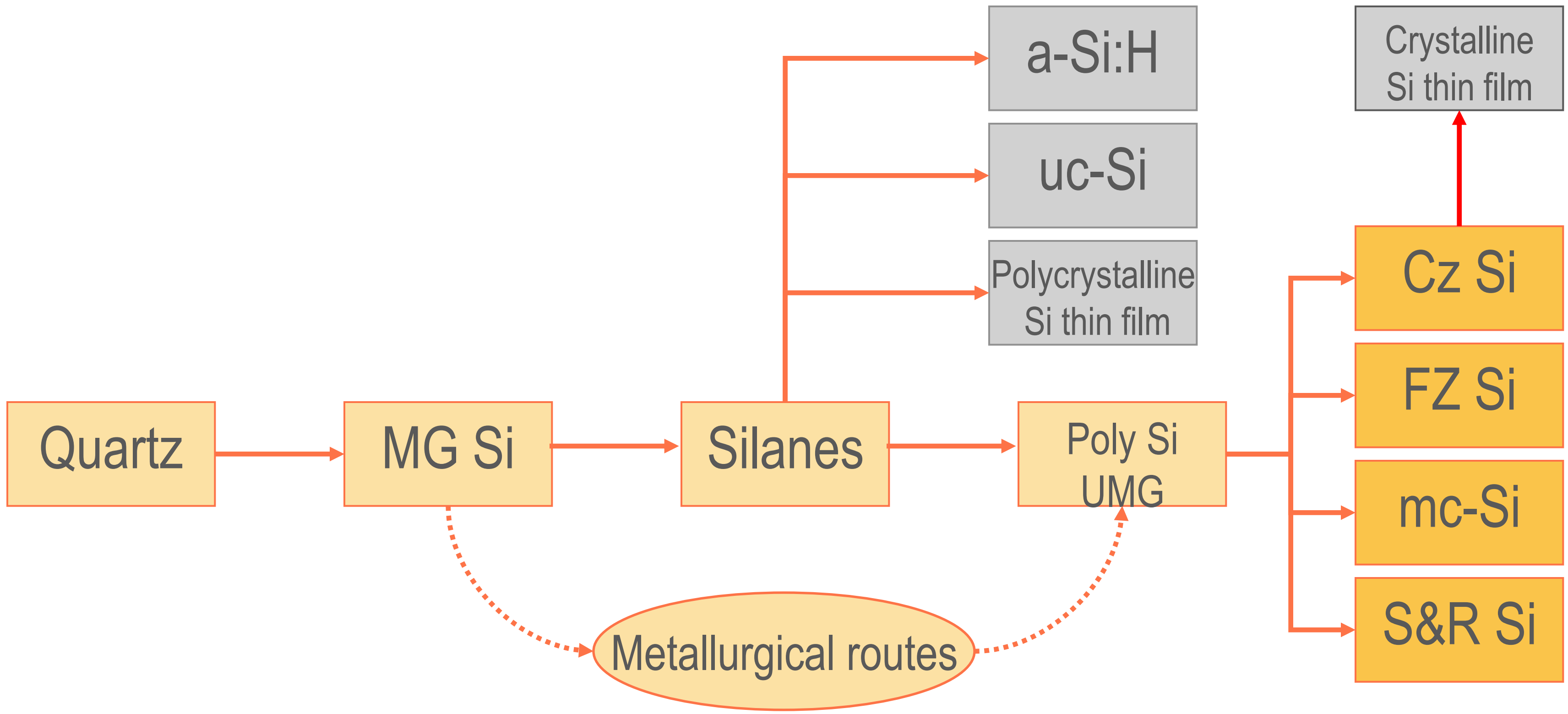
From raw materials to crystalline silicon wafers



Overview

- Segregation
- Metallurgical grade Si (MG Si)
- Silanes
- Polysilicon (poly Si)
- Monocrystalline Si (sc-Si)
  - Cz Si
  - FZ Si
- Multicrystalline Si (mc-Si)
  - mc-Si wafers
  - Silicon sheets and ribbons (S&R Si)
- Defect engineering

Silicon for solar cells



Si for solar cells

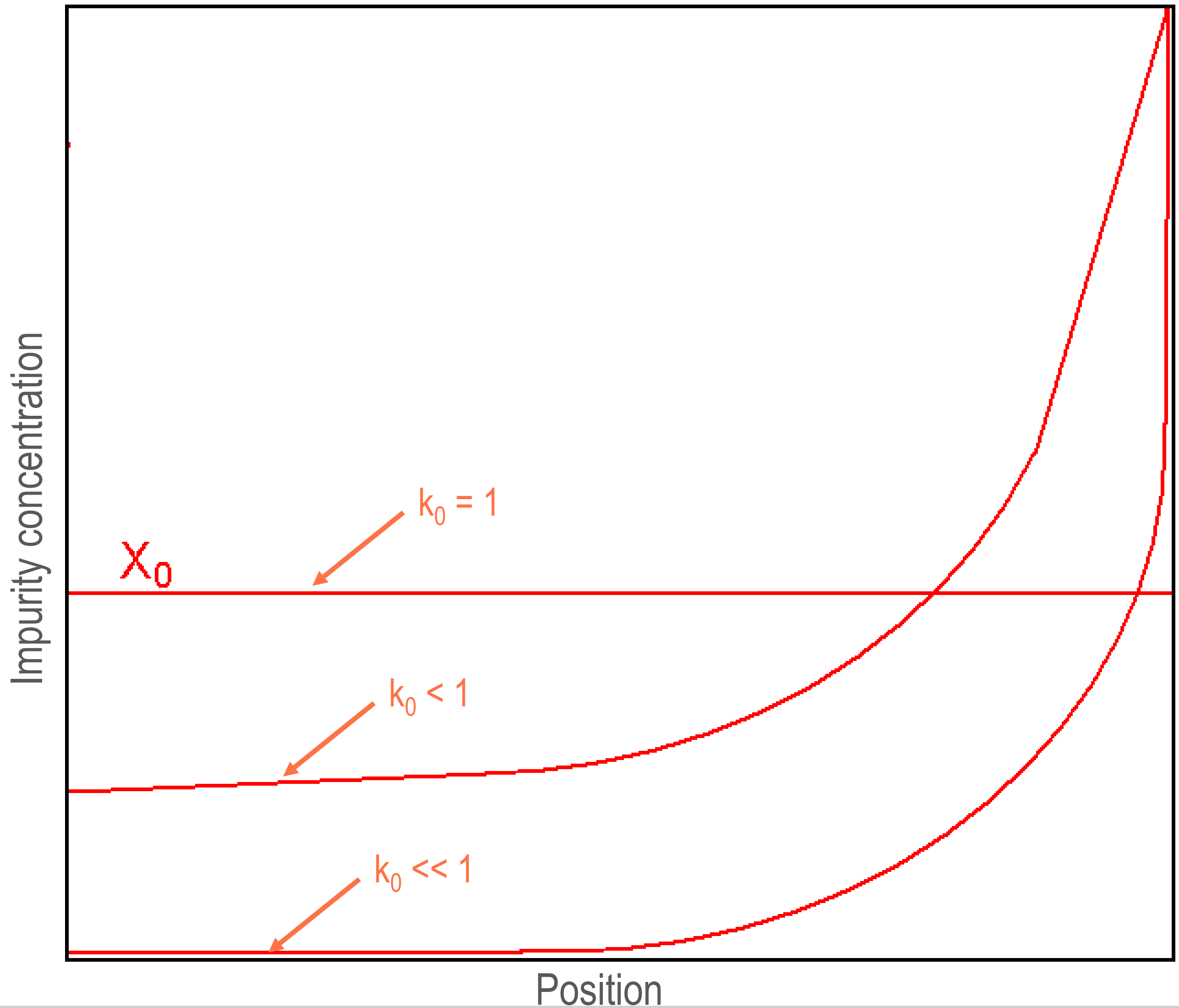
- Solar cells are made up of different types of Si
  - Thin-film Si (amorphous, microcrystalline, crystalline)
    - Requires silanes
    - Quantity and cost are not critical, only very thin films are used
  - Crystalline Si substrates
    - Mono- and multicrystalline Si grown by different processes from melts of poly-Si
    - Quantity and cost are critical, high material consumption
  - Q: *"How pure must Si be if it is to be used in a solar cell?"*

Segregation

- When Si solidifies, a homogenous melt will generally NOT result in a homogenous solid!
  - Different concentration gradients of impurities appear as a result of different segregation coefficients (k_0)

$$k_0 = X_{sol}/X_{liq}$$

  - X_{sol} : equilibrium concentration in a solid
  - X_{liq} : equilibrium concentration in a melt
- During a real solidification process, the effective segregation coefficient k_{eff} will depend on several factors, including the mixing of the melt
  - Poor mixing: $k_{eff} = 1$
  - Good mixing: $k_{eff} = k_0$



$k_0 = 1$
X_0
$k_0 < 1$
$k_0 << 1$
Impurity concentration
Position

Example segregation coefficients

- Elements with k_0>1 accumulate in the bottom of the material
- Elements with k_0~1 remain relatively homogenously distributed
- Elements with k_0<<1 can be effectively removed from the material during solidification
  - Accumulation towards top

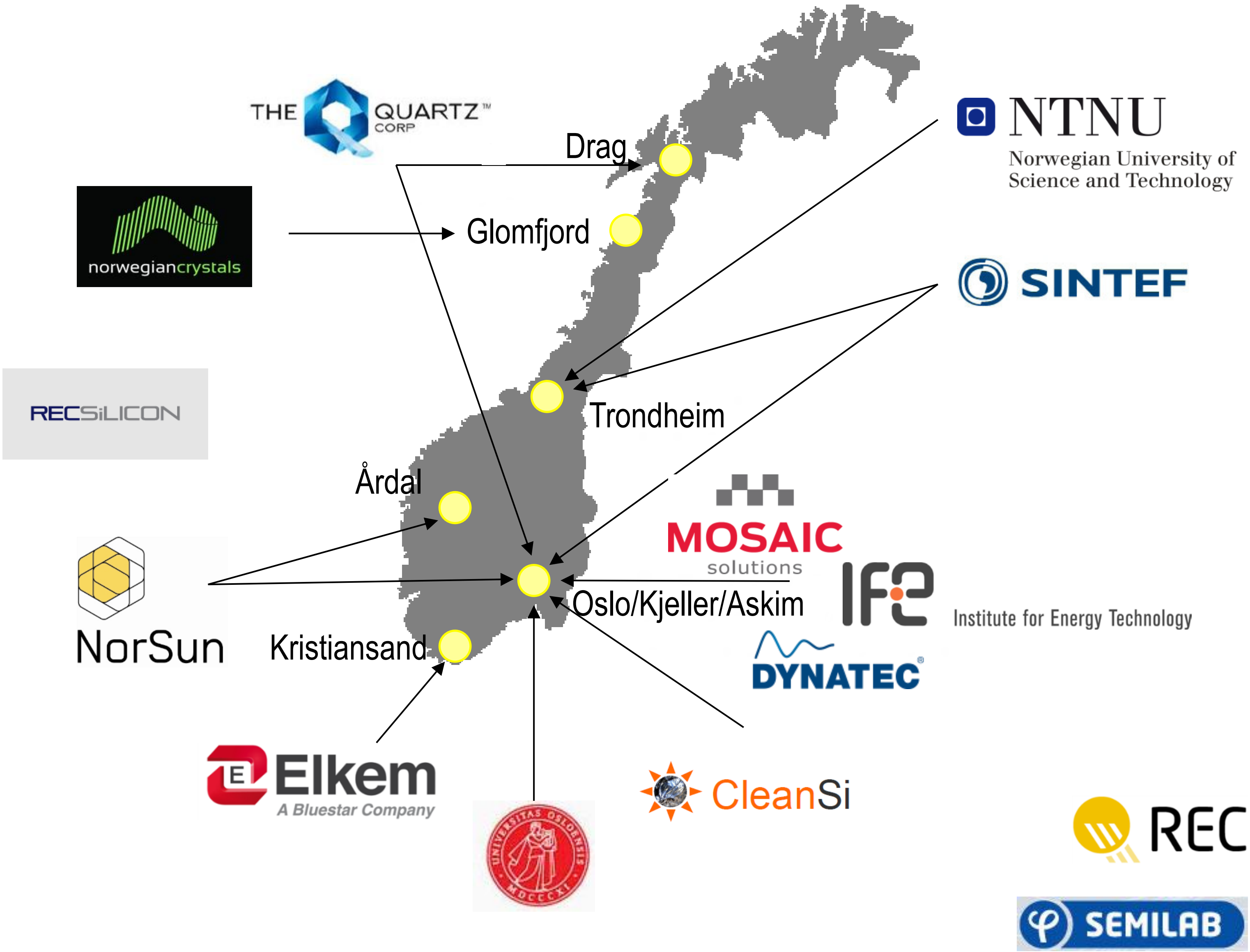
Element	k_0
B	0.8
P	0.35
O	0.25 – 1.25
C	0.07
Al	0.02
Cu	4E-4
Ti	3.6E-4
Fe	8E-6
Ni	8E-6
Co	8E-6

Luque and Hegedus: "PV Handbook"

A silicon-based Norway

Elkem Solar/Google Earth/SINTEF/NTNU

The Norwegian Research Centre for Solar Cell Technology



FORSKNINGS-
SENTER FOR
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Raw materials

Quartz (SiO_2)

Coke/coal (C)

Step 1: metallurgical silicon

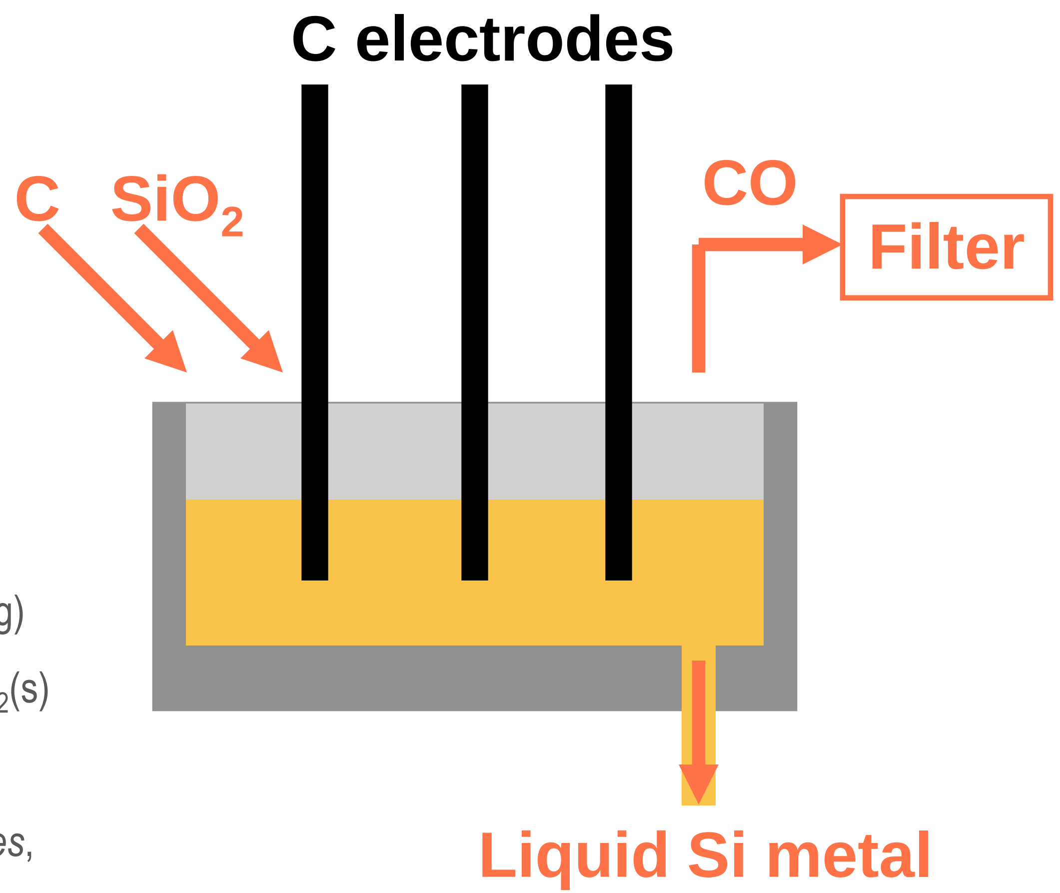
MG Si

- Purity specification
  - Minimum > 96 % Si
  - Typically ~ 98.5 % Si
- Total, global production 2000 about 1 000 000 MT
- Made by carbothermic reduction of silica
  - Overall reaction

$$SiO_2(s) + 2C(s) = Si(l) + 2CO(g)$$

- Raw materials selected for achieving the highest possible purity
  - SiO_2: NOT usually sand, but lumpy quartz (10 – 100 mm)
  - C: MG C, charcoal, coke

MG Si – arc furnace



Important side reaction:

$$2Si(l) + O_2(g) = 2SiO(g)$$

$$2SiO(g) + O_2(g) = 2SiO_2(s)$$

Silica fumes are mostly *fines*, particles with Ø < 1 µm

Elkem Solar

MG Si – arc furnace

- Arc furnace
  - T: 1900 – 2100 ^oC
  - Si yield: 80 – 90 %
  - Much of the remainder is made of silica fumes
- Si(l) is subsequently refined
  - Treated with oxidative gases and slag-forming additives
    - Silica (SiO_2), lime (CaO), limestone ($CaCO_3$)…

      Example: $4Al + 3(SiO_2) = 3Si(l) + 2Al_2O_3$
    - Some elements (Al, Ca, Mg…) are oxidized, form particles (slag) and can be removed from the Si melt by gravity or mechanically
    - T reduced to 1500 – 1700 ^oC

MG-Si – casting

- Refined Si melt is often casted by pouring it into a cast iron mold
- The molten Si solidifies and becomes multicrystalline Si
- Si is subsequently crushed into lumps of useful size
  - Up to 100 mm
  - Additional fines created during crushing removed

MG Si – typical impurities

Element	O	Fe	Al	Ca	C	Mg	Ti	Mn
Low (ppm)	100	300	300	20	50	5	100	10
High (ppm)	5000	25000	5000	2000	1500	200	1000	300
Element	Zr	V	Cu	Cr	Ni	Mo	P	B
Low (ppm)	5	1	5	5	10	1	5	5
High (ppm)	300	300	100	150	100	10	70	100

Luque and Hegedus: "PV Handbook"

Step 2: solar grade silicon / polysilicon

Polysilicon

- Use of Si in semiconductor devices and solar cells require impurity levels in the ppb range
- Main approach:
  1. Form volatile Si hydride (silane)
  2. Purify silane
  3. Decompose silane to ultra-pure Si through pyrolysis or chemical vapour deposition (CVD)
  4. Recycle by-products

Production of polysilicon

- Three main methods
  - Siemens process
    - Thermal decomposition of trichlorosilane on heated Si rod
  - Union Carbide process
    - Thermal decomposition of monosilane on heated Si rod
  - Ethyl corporation process
    - Thermal decomposition of monosilane on fluidized bed of heated Si particles

The Siemens Process

Thermal decomposition of trichlorosilane on heated Si rod

1. $HSiCl_3$ is prepared by hydrochlorination of MG Si at ~ 350 ^oC
   - $Si(s) + 3HCl = HSiCl_3 + H_2$
   - $HSiCl_3$ is easy to purify and has a high deposition rate of Si

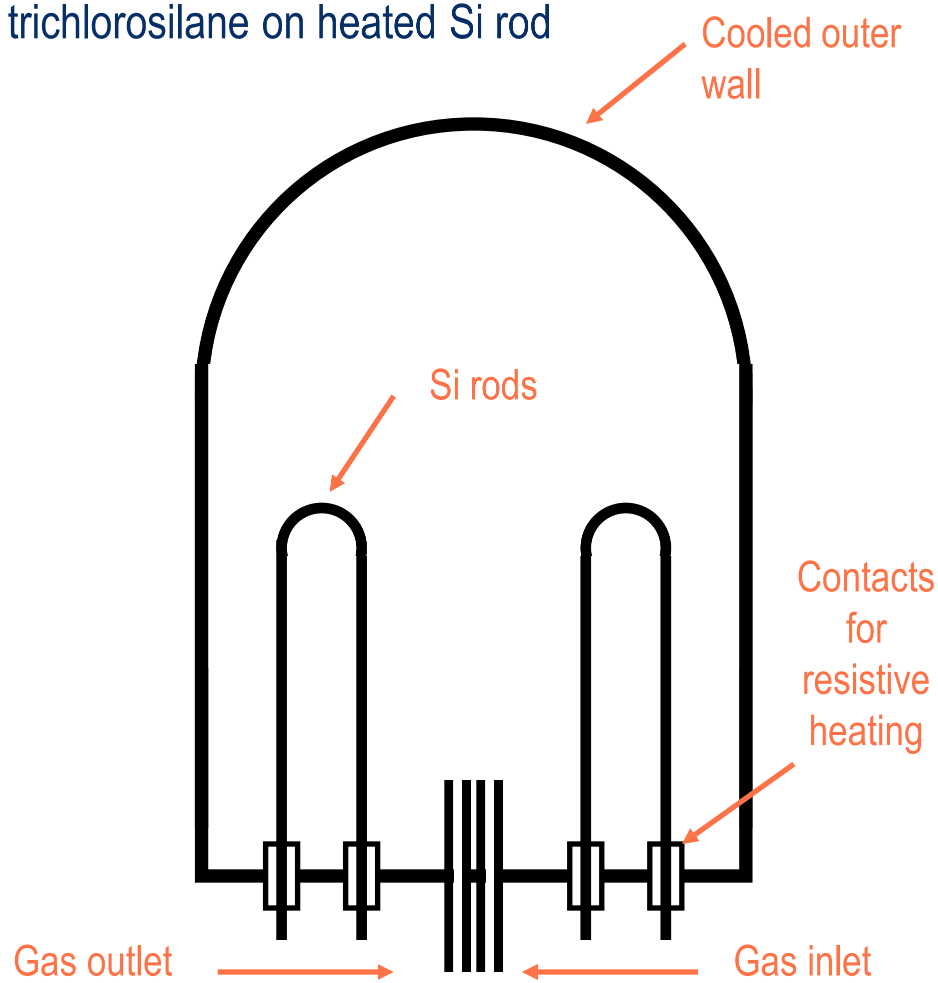
2. A competing, unwanted reaction is
   - $Si(s) + 4HCl = SiCl_4 + 2H2_2$

3. High-purity $HSiCl_3$ is diluted with pure H and introduced into a deposition reactor (”bell jar”)

The Siemens Process

Thermal decomposition of trichlorosilane on heated Si rod

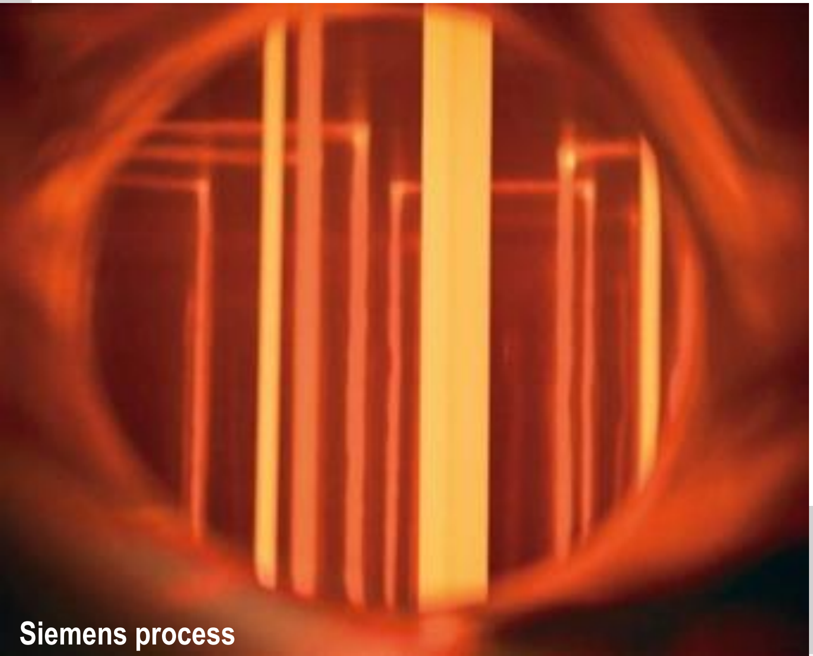
- $HSiCl_3$ is decomposed at ~ 1100 °C
- The main reactions are
  - $2HSiCl_3 = SiH_2Cl_2 + SiCl_4$
  - $SiH_2Cl_2 = \mathbf{Si} + 2HCl$
  - $H_2 + HSiCl_3 = \mathbf{Si} + 3HCl$
  - $HCl + HSiCl_3 = H_2 + SiCl_4$
- Many by-products form
  - 3 – 4 moles of $SiCl_4$ for each mole of Si
  - Before, much of this could be used in the production of silica
  - Recycling back to $SiCl_4$ a solution e.g. $SiCl_4 + H_2 = SiHCl_3 + HCl$



The Siemens Process

Thermal decomposition of trichlorosilane on heated Si rod

- The dominant process in the Si industry
- Several drawbacks including
  - High energy consumption
  - Batch process: aborted runs (e.g. power failure) causes waste
  - Large amount of by-products must be handled

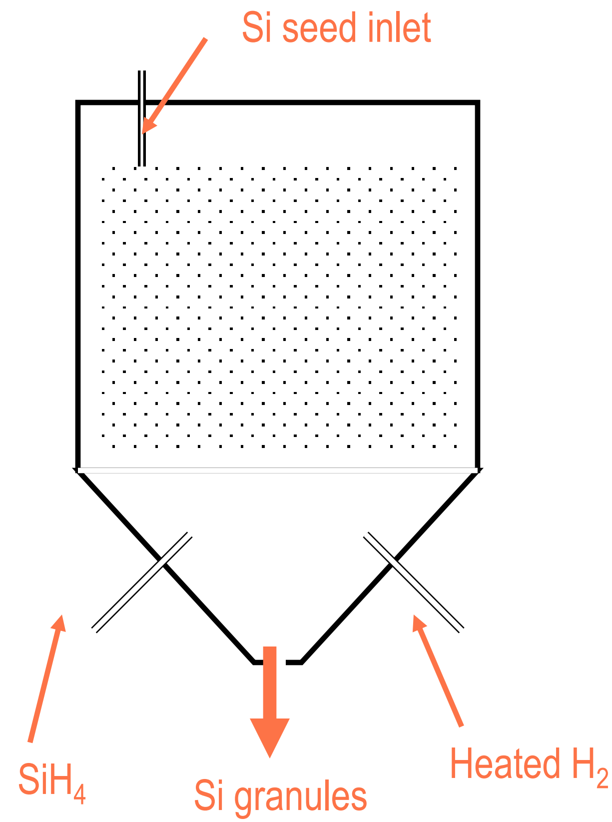


Siemens process

Wikipedia

Fluidized bed reactors

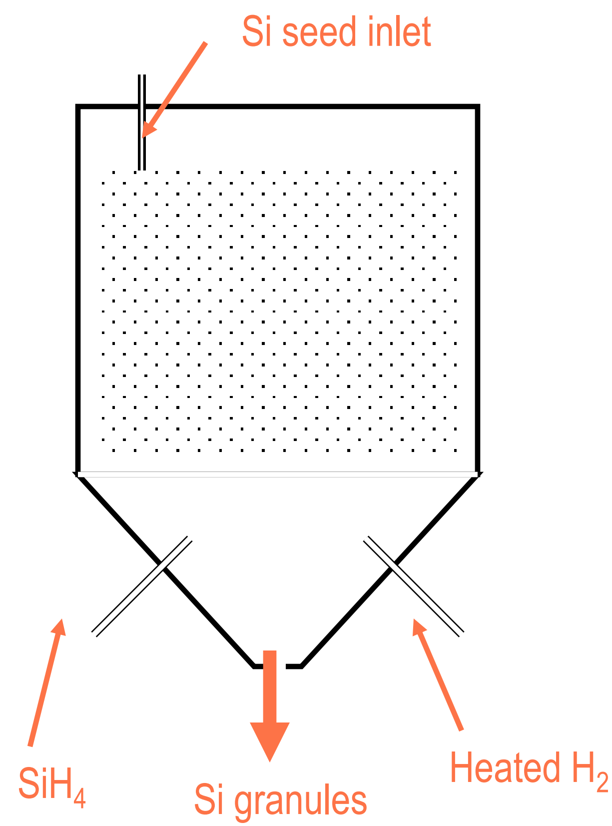
- Fluidized bed reactor
  - Small Si seed grains form a so-called ”fluidized bed” when gas streams of SiH_4 and H_2 flow upwards through the reactor
- End product: granules, not rods
  - Can be used for crystallization processes requiring continuous feeding
  - Can not be straight-forward be used for FZ Si fabrication



Siliken

Fluidized bed reactors

- Benefits
  - Reduced energy consumption
  - Continuous operation
- Drawbacks
  - Si powder forms
  - Much H absorbed in deposited poly-Si



Novel concept: CCVDR

- Concept:
  - Centrifugal CVD reactor

- Benefits
  - Reduced energy consumption
  - High silane utilization


NORGE
ETTER
OLJEN
DYNATEC

Large scale process plants

REC

Metallurgical routes

- Avoid costly silane production and decomposition
- Utilize metallurgical processes
  - Slagging
  - Leaching
  - Directional solidification

The poly Si industry

Ceccaroli & Lohne – 2003

- Historically mostly dedicated to the semiconductor industry
- Capital-intensive industry
  - A 1000 MT unit might cost 100M US$
- High comsumption of energy
  - About 100 kWh/kg
- Only a handful of plants (~ 10) in operation
- Increases value of Si
  - MG Si ~ 1 kg/US$ (1 000 000 MT/y)
  - Poly Si ~ 20 kg/US$ (20 000 MT/y)

Poly Si – typical impurities

Lowest grade Si used to make mc-Si wafers (Ceccaroli & Lohne – 2003)

Element	O	Fe	Al	Ca	C	Mg	Ti	Mn
MG Si (ppm)	100 - 5000	300 - 25000	300 - 5000	20 - 2000	50 - 1500	5 - 200	100 - 1000	10 - 300
Poly Si (ppm)	< 5	< 0.1	< 0.1	< 0.1	< 4	-	< 0.1	-
Element	Zr	V	Cu	Cr	Ni	Mo	P	B
MG Si	5 - 300	1 - 300	5 - 100	5 - 150	10 - 100	1 - 10	5 - 70	5 - 100
Poly Si (ppm)	-	-	-	-	-	-	< 0.1	< 0.3

Luque and Hegedus: "PV Handbook"

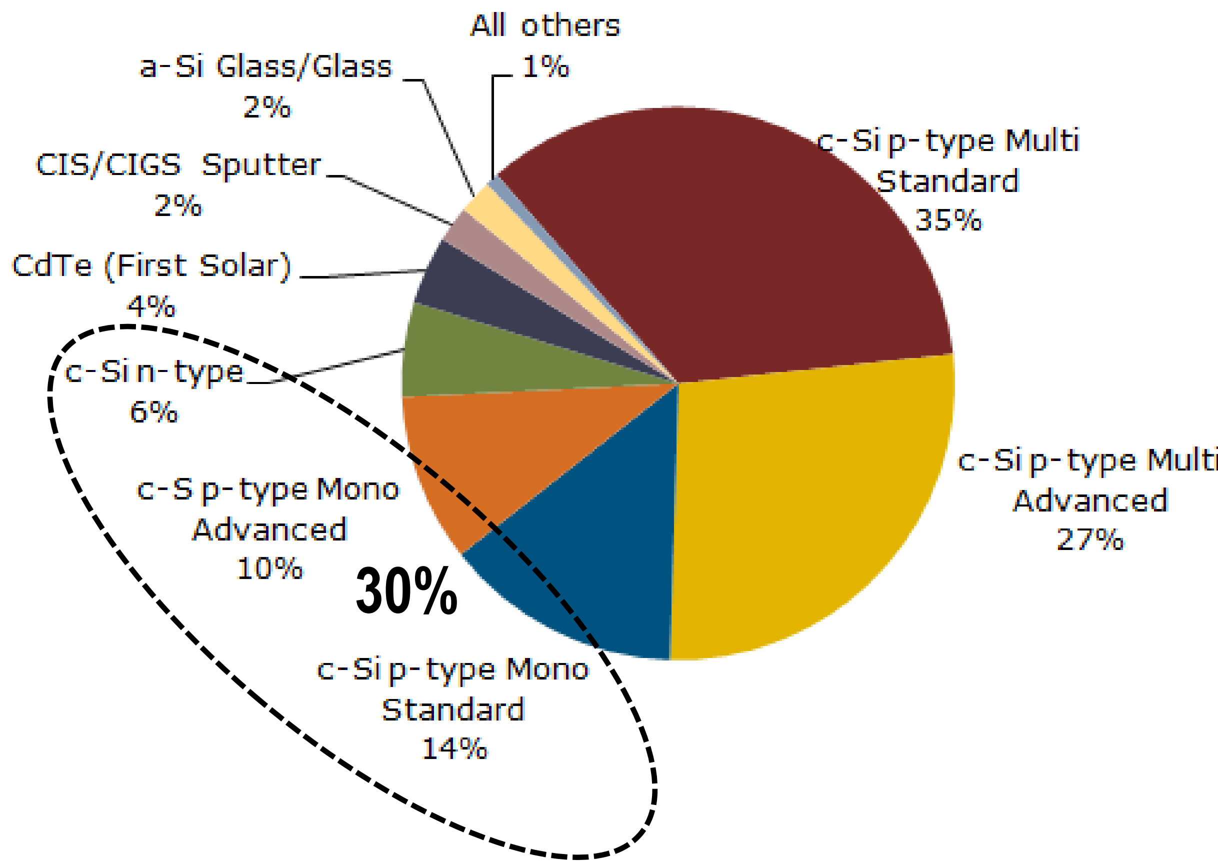
Past feedstock for Si solar cells

- Si selected from less-expensive 2nd grade Si
  - Rejects from crystal growth
    - Heads and tops (Cz) are rejected and re-uesd
    - Ingots from aborted runs
    - Ingots that fail to meet certain criteria
    - Pot scrap
  - Rejects from poly Si production
    - Chunks and rods from aborted runs
    - Broken or imperfect seed rods
    - Rod sections with unacceptable purity
- Expensive semiconductor grade Si hitherto has made up the rest

Designated solar grade Si feedstock

- There is much ongoing effort related to the development of production processes of Si designated for solar cells
- A range of different concepts
  - Further exploit segregation during crystallization
  - Metallurgical routes
    - Raw material choices, leaching, slagging,
  - Modified poly Si processes
    - Fluidized bed

Step 3: silicon crystallization



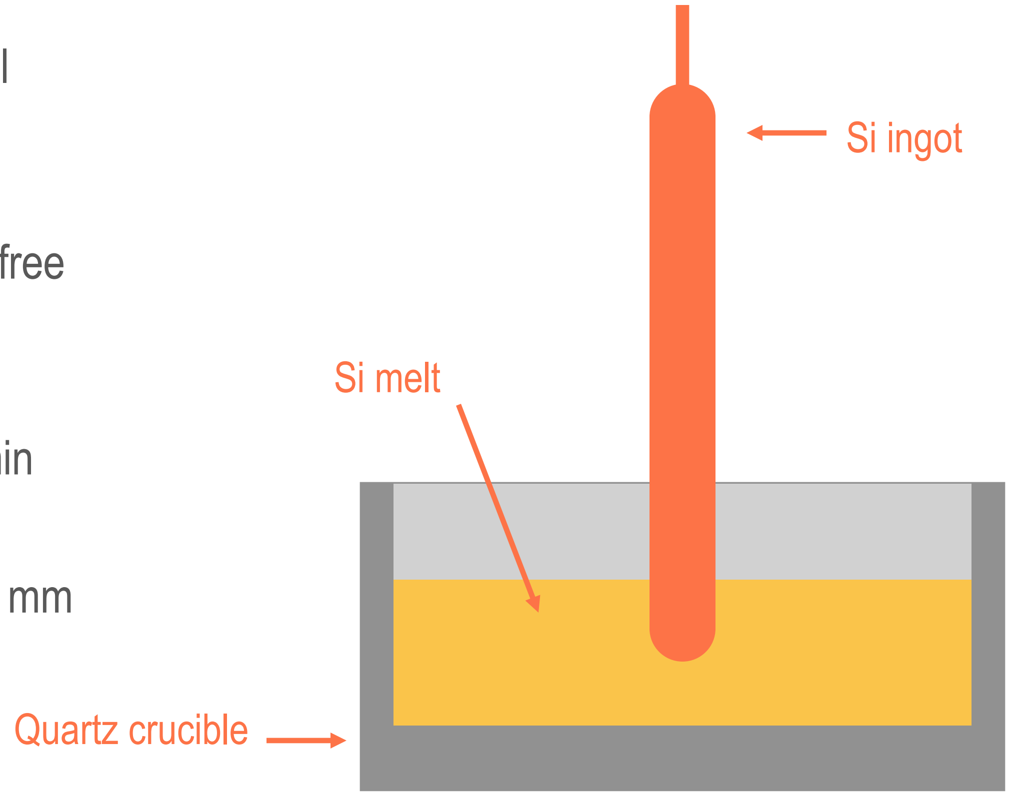
NPD Solarbuzz forecast for 2014

Growth of Si crystals

- Monocrystalline Si
  - Czochralski (Cz) Si
  - Float zone (FZ) Si
- Multicrystalline Si
  - Directional solidification
- Wafering
- Si ribbons, sheets and foils

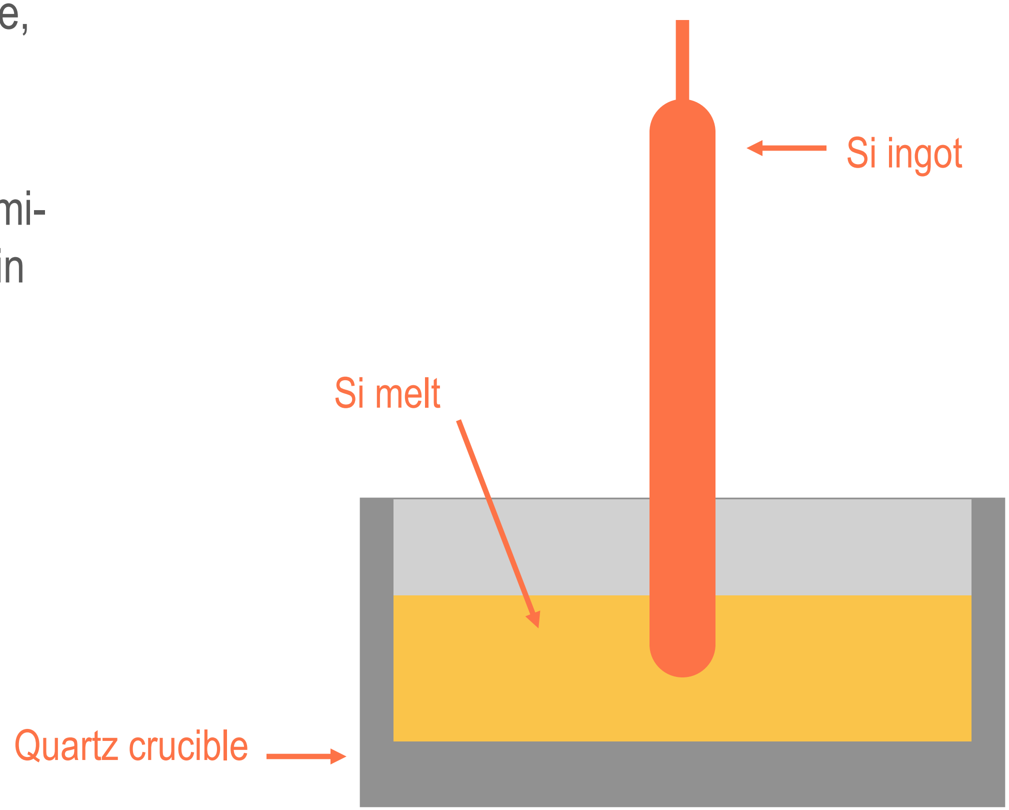
Czochralski (Cz) Si

- Monocrystalline Si
- Puller used to draw growing crystal slowly from melt
- Purified by segregation
- Necking used to make dislocation-free material
- Can pull <100> Si
- Standard pull speed 0.5-1.2 mm/min
- Typical length: 40 – 150 cm
- Diameters for PV often 100 or 150 mm

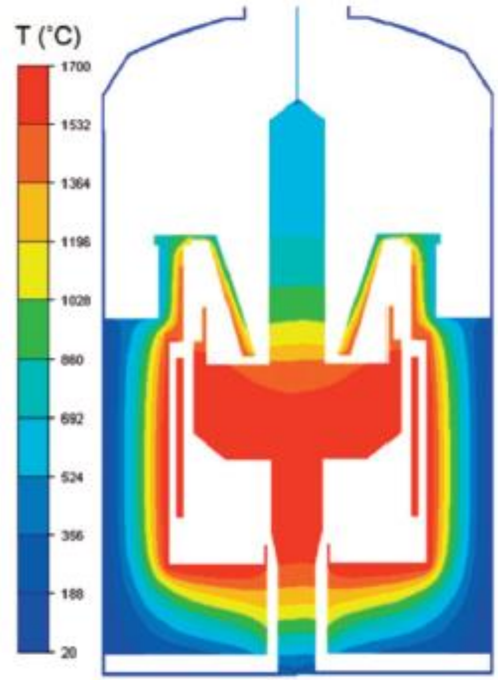


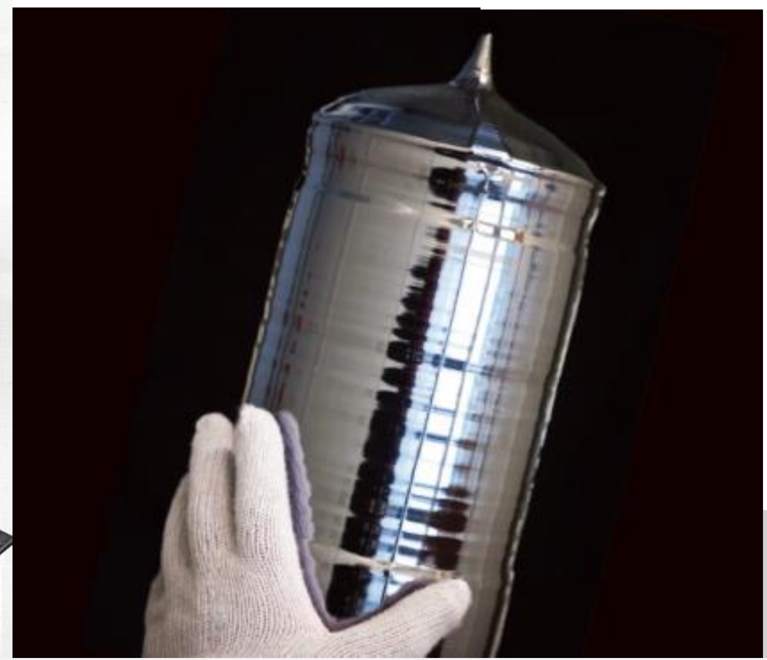
Czochralski (Cz) Si

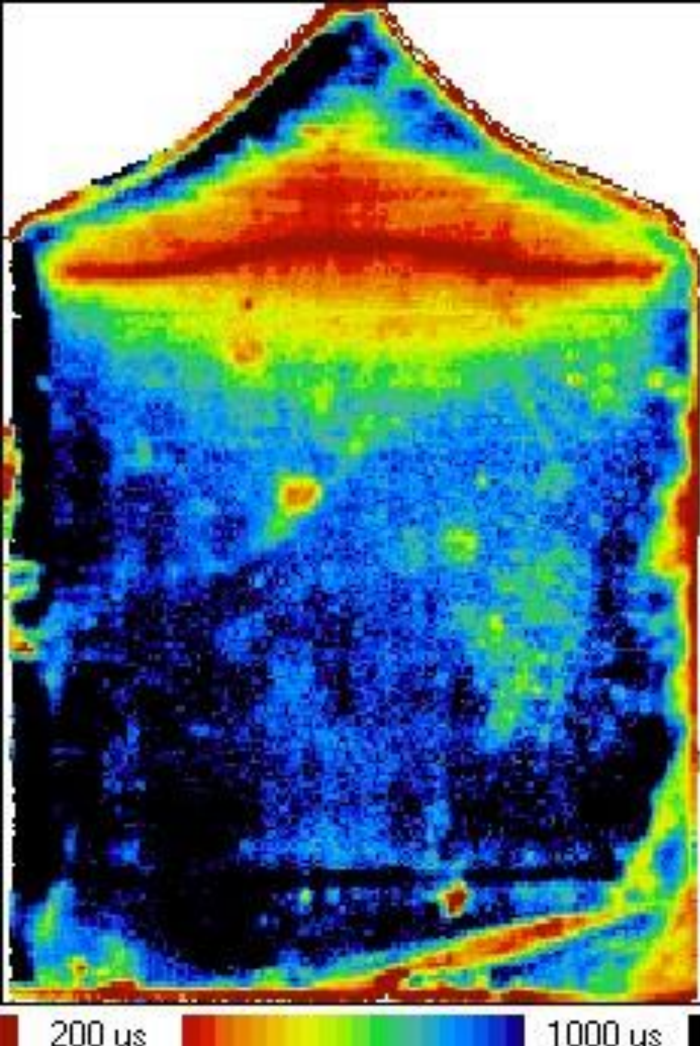
- O contamination from crucible large, typically ~10^{18}/cm^3
- Light-induced degradation
- Circular ingots must be cut into semi-square shape for good area filling in modules

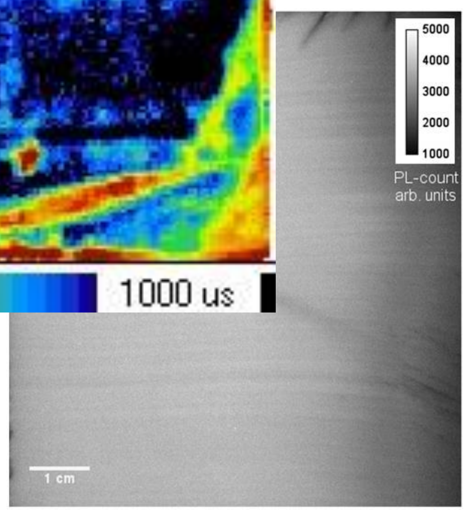


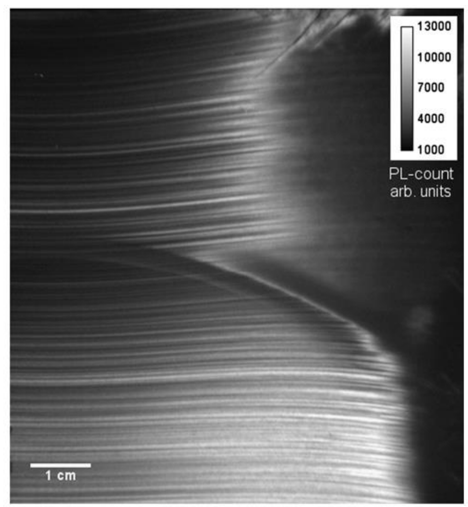

PU 16
PU16

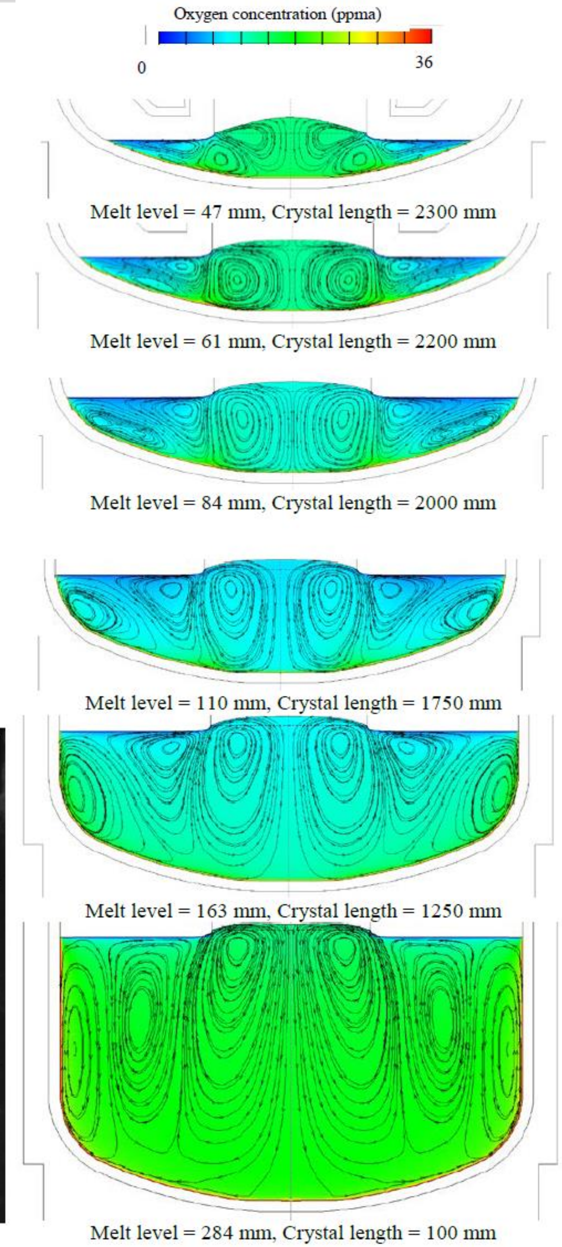

T (°C)
1700
1532
1364
1196
1028
860
692
524
356
188
20




200 us
1000 us

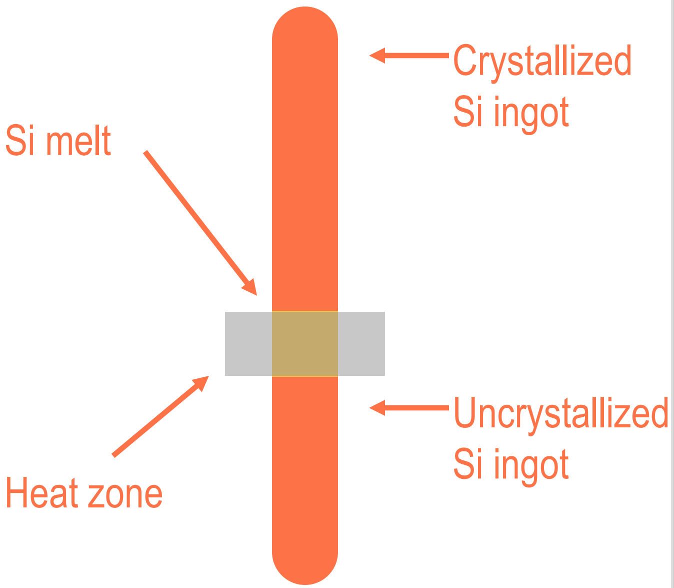

5000
4000
3000
2000
1000
PL-count
arb. units
1 cm


13000
10000
7000
4000
1000
PL-count
arb. units
1 cm


Oxygen concentration (ppma)
0
36
Melt level = 47 mm, Crystal length = 2300 mm
Melt level = 61 mm, Crystal length = 2200 mm
Melt level = 84 mm, Crystal length = 2000 mm
Melt level = 110 mm, Crystal length = 1750 mm
Melt level = 163 mm, Crystal length = 1250 mm
Melt level = 284 mm, Crystal length = 100 mm

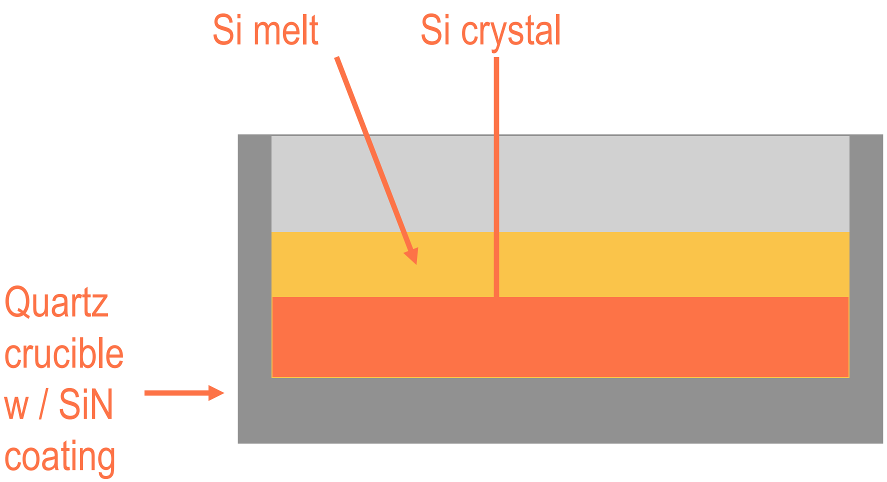
Float zone (FZ) Si

- Monocrystalline Si
- Heated coil creates local melt



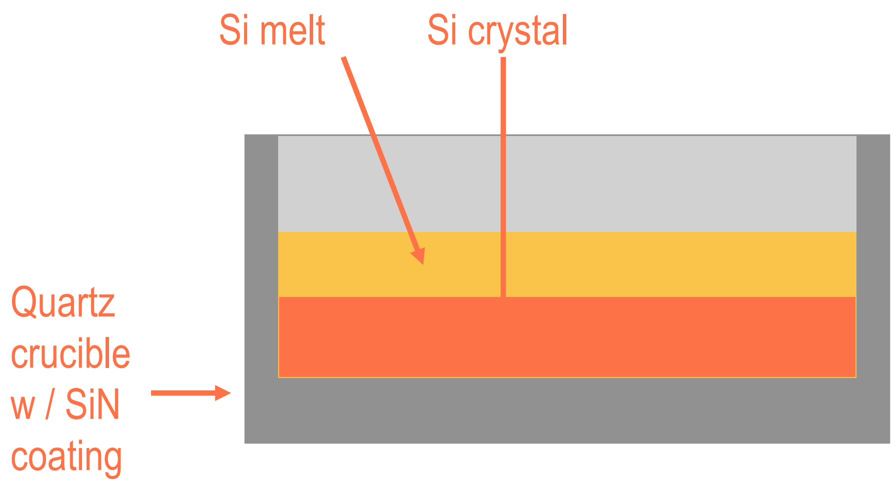
Multicrystalline (mc) Si

- Fabricated using Bridgman technique or block-casting
  - Bridgman: one crucible used both for melting and crystallizaton
  - Block-casting: one crucible for melting, another for crystallization
- Directional solidification of Si
- SiN used for avoiding sticking
- Typical crystallization speeds: 1cm/h

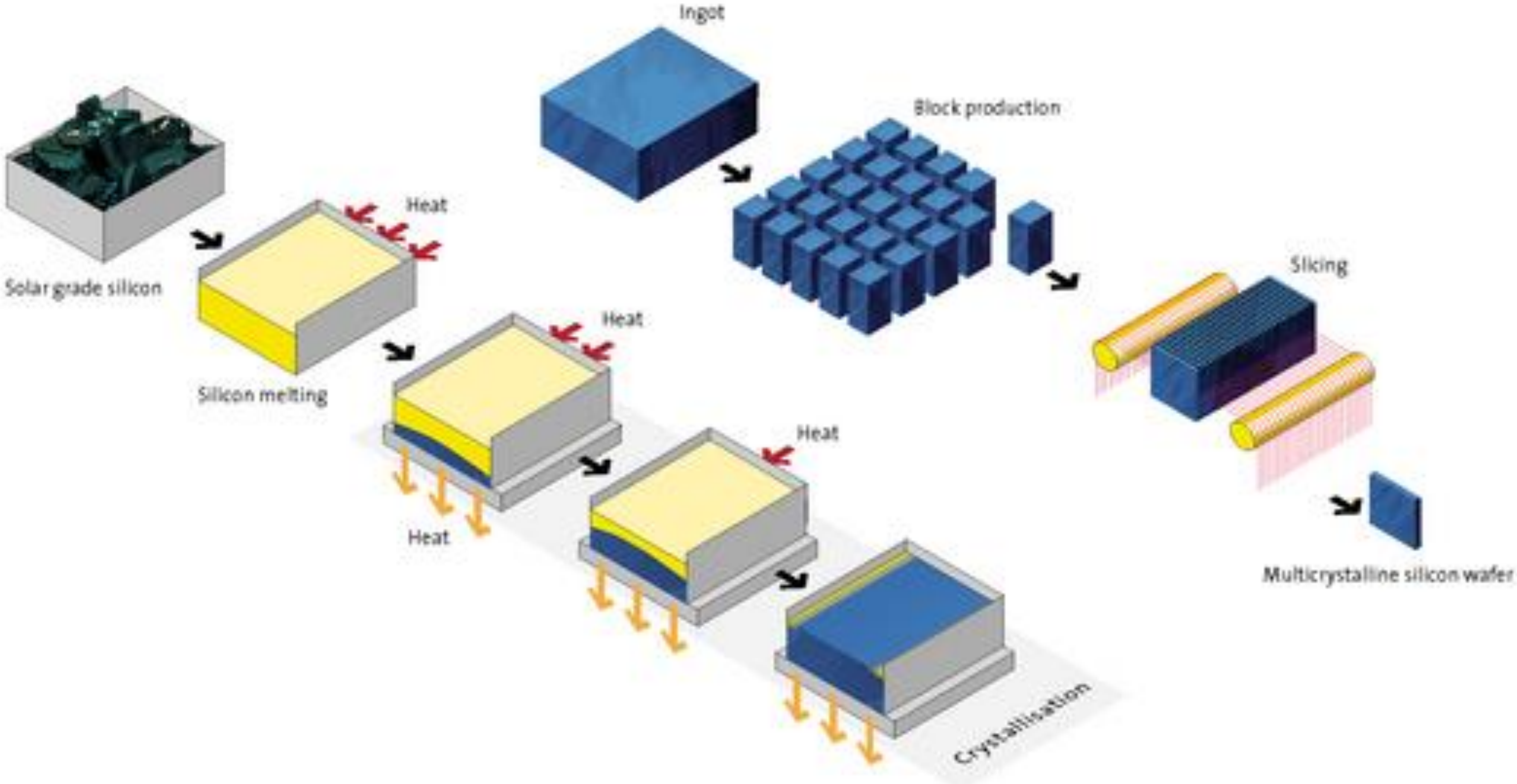


Multicrystalline (mc) Si

- Causes grain boundaries, twinning and dislocations
- O contamination from crucible can be significant, typically
  ~ $1\text{-}5 \cdot 10^{17}/cm^3$
- C can cause formation of SiC particles, mostly towards the ingot top
- SiN particles can also be found
- Transition metals most important with respect to efficiency



Multicrystalline (mc) Si

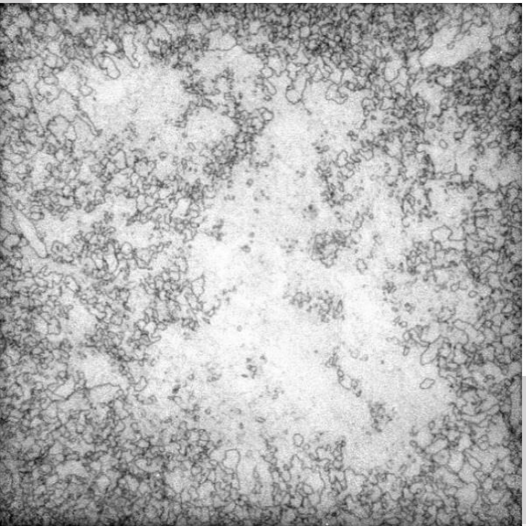


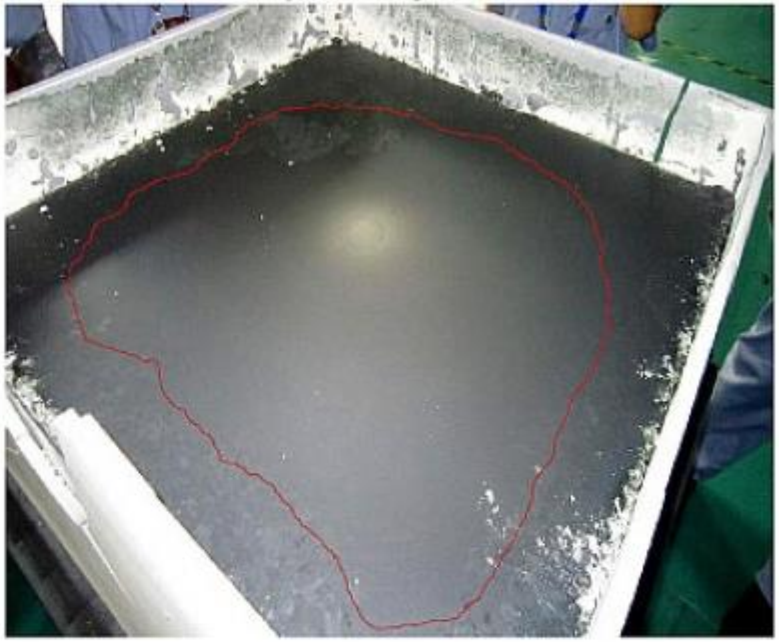
REC ScanWafer

Mono-like Si

- Idea:
  - Use low casting process to obtain high quality, mono-like material

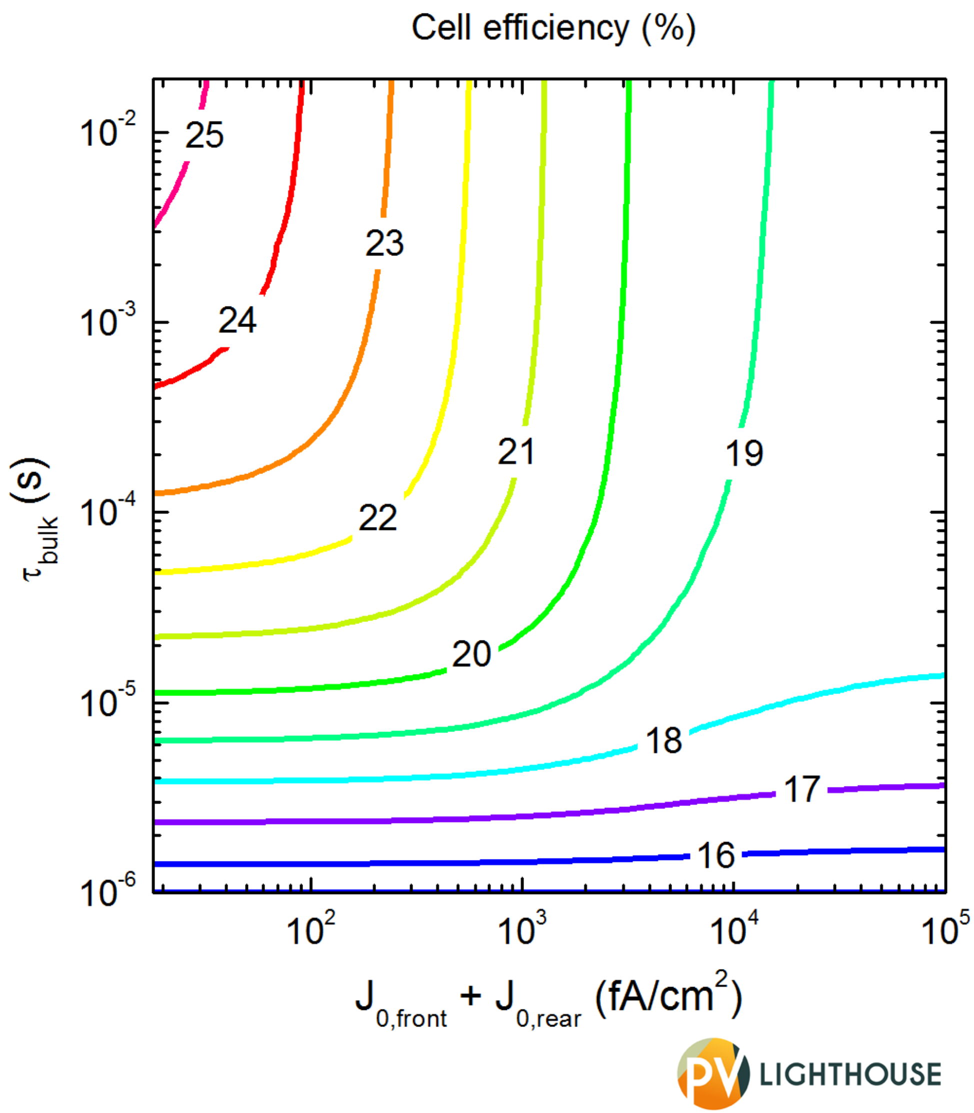
- Principles:
  - Seeding
  - Dendritic growth





High Performance MultiCrystalline Si

- Idea:
  - Control structural properties of material to reduce dislocation-related losses



H. Haug et al (IFE, 2014)

Step 4: wafering

Wire sawing

Meyer Burger

Wire sawing

Wire sawing

Wire sawing

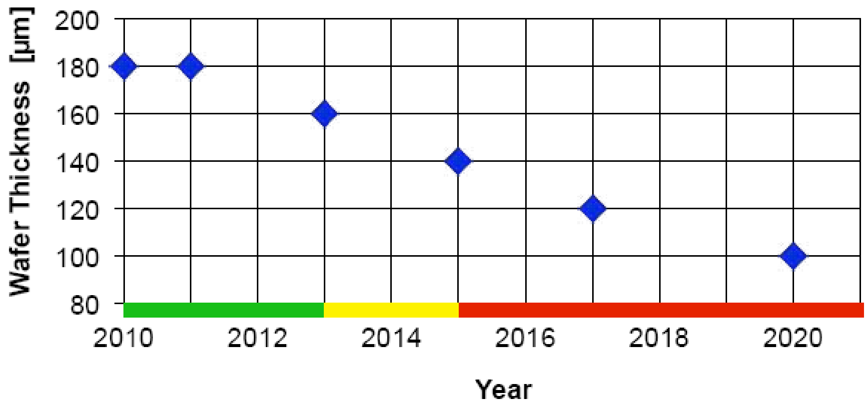


Fig. 5: Trend of minimum wafer thickness processed in mass production of solar cells.

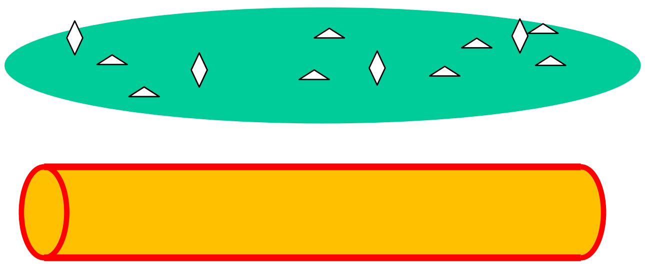
Wafer thickness reduction has the following implications:

1. Cost reduction through reduced wafer pricing by reduction of poly-silicon use.
2. Need for innovative handling concepts for thinner wafers to reduce wafer breakage.
3. Need for new cell concepts suitable for achieving high efficiencies on thin wafers.
4. Need for new interconnection and encapsulation concepts suitable for thin wafers.

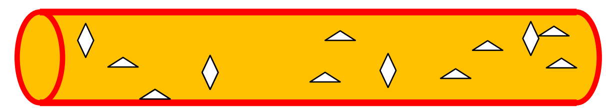
ITRPV

Two competing technologies

Slurry / SiC



Diamond wire



Marstein

Wafering

- Sawing costs substantial part of wafer production costs
- Currently, multi-wire sawing most commonly used
    1. Ingot is cut into suitable blocks
    2. Blocks cut into wafers, all wafers cut simultaneously
- Steel wire used with slurry and SiC abrasive particles
- Typical wafer thicknesses: 250 – 300 µm
- Typical wafer diameters: 5”, 156 med mer
- Large material losses (~50 %?)
- Surface after wafering damaged (”as cut”)

Wafers

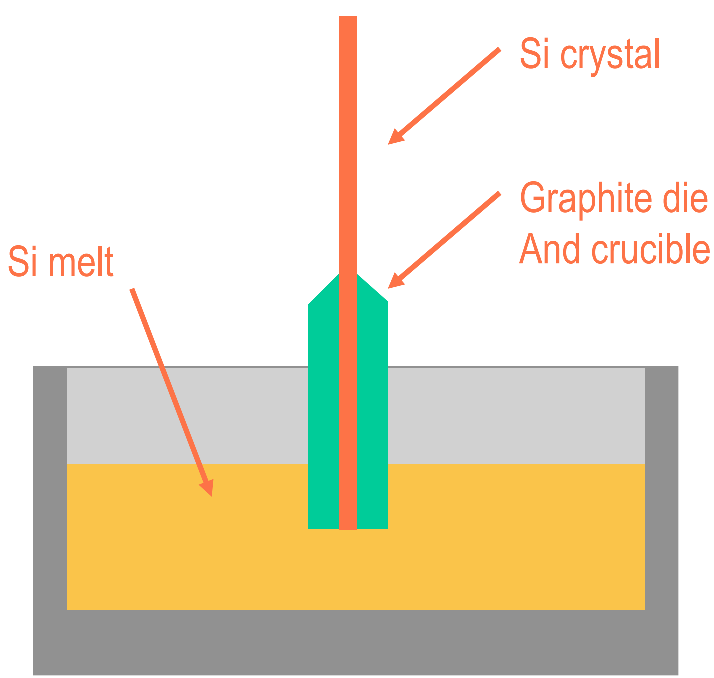
Cool concepts of the week

Ribbons, sheets and foils

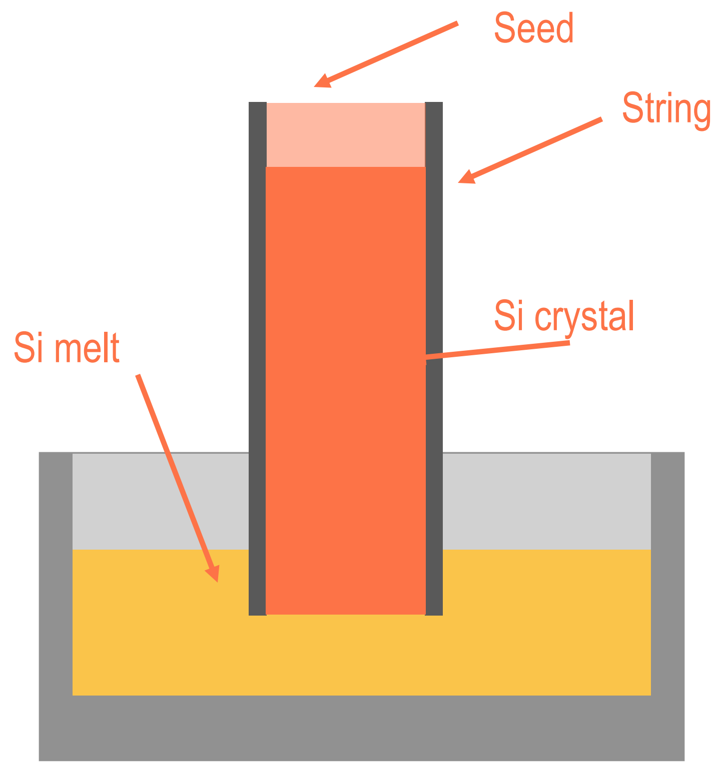
- A range of techniques aim at producing mc-Si wafers without sawing
  - Edge-defined film-fed growth (EFG)
    - ~~Schott Solar~~
  - String ribbon
    - ~~Evergreen~~, Sovello
  - Dendritic web production
  - Ribbon growth on substrate (RGS)
    - ECN

Ribbons, sheets and foils

- Edge-defined film-fed growth (EFG)

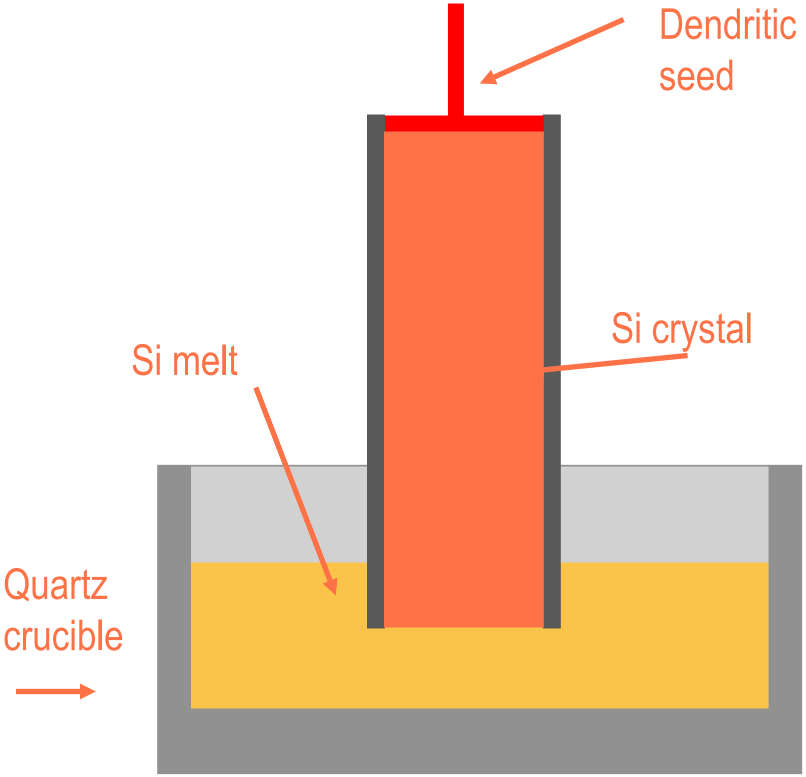


- String ribbon

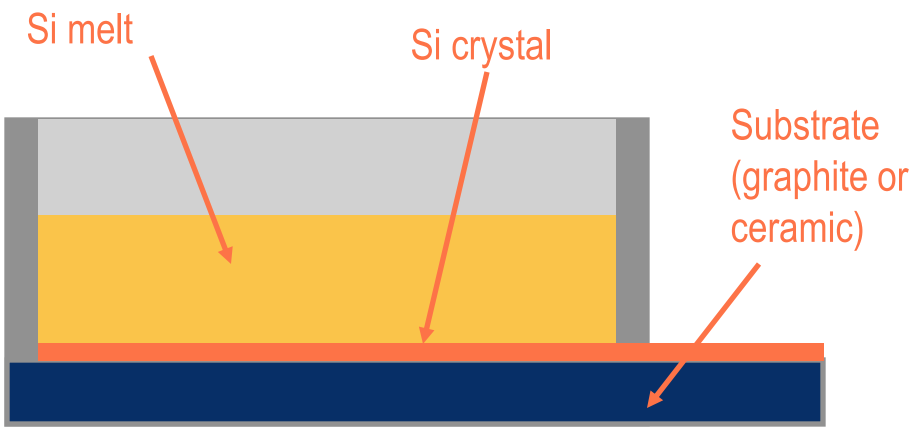


Ribbons, sheets and foils

- Dendritic web



- Ribbon growth on substrate



EFG

RWE

String ribbon

Evergreen

Comparing R&S Si

	Pull speed [cm/min]	Width [cm]	Crystallinity	Defects	Thickness [µm]	Best η [%]
WEB	1 – 3	5 – 8	(111) twin planes, boundary in sheet	O main impurity, dislocations: 10^3–10^4 cm^{-2}	75 – 150	17.3
EFG	1 – 2 (octagonal)	3 – 5"	Columnar grains in growth direction	C main impuriry, dislocations 10^5–10^6 cm^{-2}	250 – 350	15-16
STR	1 – 2	5 – 8	Columnar grains through thickness	C and O, dislocations $5 \cdot 10^5$ cm^{-2}	100 – 300	15-16
RGS	600 – 1000	5"	Columnar grains through thickness	C and O dislocations 10^5–10^7 cm^{-2}	300 - 400	12

G. Hahn