Crystal Growth-I

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Advantages of Si over Ge

- Si has a larger bandgap (1.1 eV for Si versus 0.66 eV for Ge)
- Si devices can operate at a higher temperature (150^oC vs 100^oC)
- Intrinsic resistivity is higher (2.3×10^5 Ω-cm vs 47 Ω-cm)
- SiO_2 is more stable than GeO_2 which is also water soluble
- Si is less costly

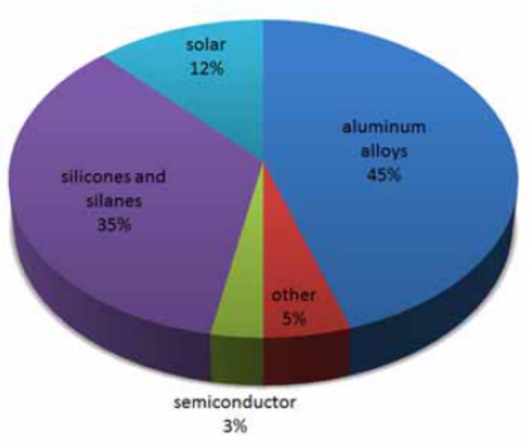
The processing characteristics and some material properties of silicon wafers depend on its orientation.

The <111> planes have the highest density of atoms on the surface, so crystals grow most easily on these planes and oxidation occurs at a higher pace when compared to other crystal planes.

Traditionally, bipolar devices are fabricated in <111> oriented crystals whereas <100> materials are preferred for MOS devices.

Silicon as an Industrial Material

Silicon Metal			
			
Composition	99% Silicon		
Main Market	Aluminum	Silicones	Semiconductors
Usage	Silicon source	Feedstock	Bulk Material



CRU Market Data, 2017

- Out of the 2.5 million of tons of silicon metal produced, about 300k tons goes into producing wafers for solar and microelectronics
- Metallurgical and chemical applications consume over 80% of Si produced

From Quartz to Silicon Wafers

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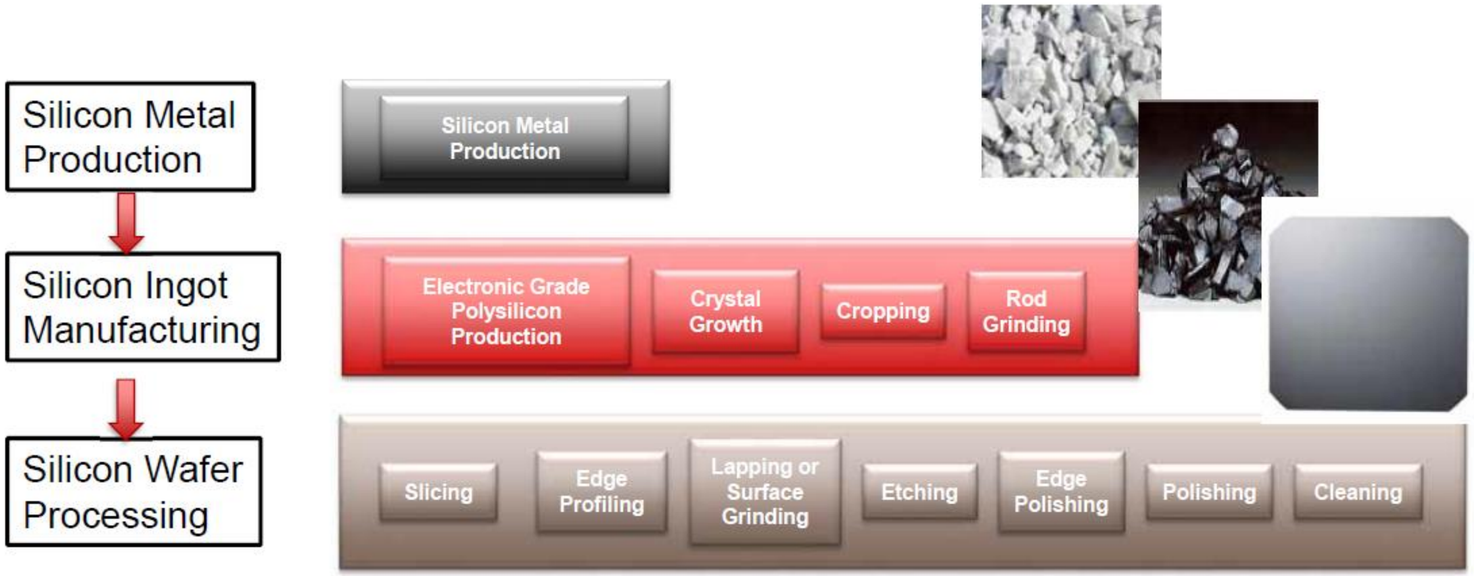

How Do We Make Silicon?

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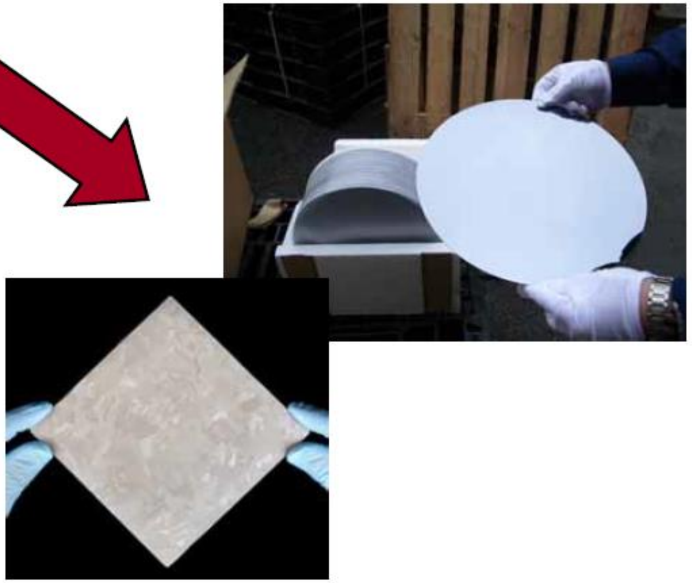
How do we go from quartz …

…to make silicon?



MGS

- The starting material for Si wafer manufacture is called Electronic grade Si (EGS). This is an ingot of Si that can be shaped and cut into the nal wafers. EGS should have impurity levels of the order of ppb, with the desired doping levels, so that it matches the chemical composition of the nal Si wafers.
- To get EGS, the starting material is called Metallurgical grade Si (MGS). The rst step is the synthesis of MGS from the ore.The starting material for Si manufacture is quartzite (SiO_2) or sand. The ore is reduced to Si by mixing with coke and heating in a submerged elec-trode arc furnace. The SiO_2 reacts with excess C to first form SiC. At high temperature, the SiC reduces SiO_2 to form Si. The overall reaction is given by
- SiC (s) + SiO_2 (s) ! Si (l) + SiO (g) + CO (g) (1)
- The Si(l) formed is removed from the bottom of the furnace. This is the MGS and is around 98% pure. The schematic of the reducing process is shown in Fig1. MGS is used for making alloys. The main metallic impurities are Al and Fe.

MGS

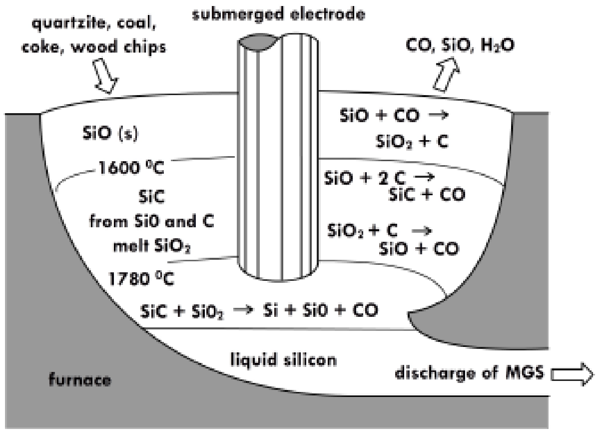


Figure 1: Schematic of the submerged arc electrode process. SiO_2 is mixed with coke and heated. It first forms SiC, which further reacts with the remaining SiO_2 forming silicon. The temperature is maintained above the melting point of silicon so that the molten semiconductor is removed from the bottom. Adapted from *Synthesis and purification of bulk semiconductors - Barron and Smith*

How is Metallurgical Si Made?

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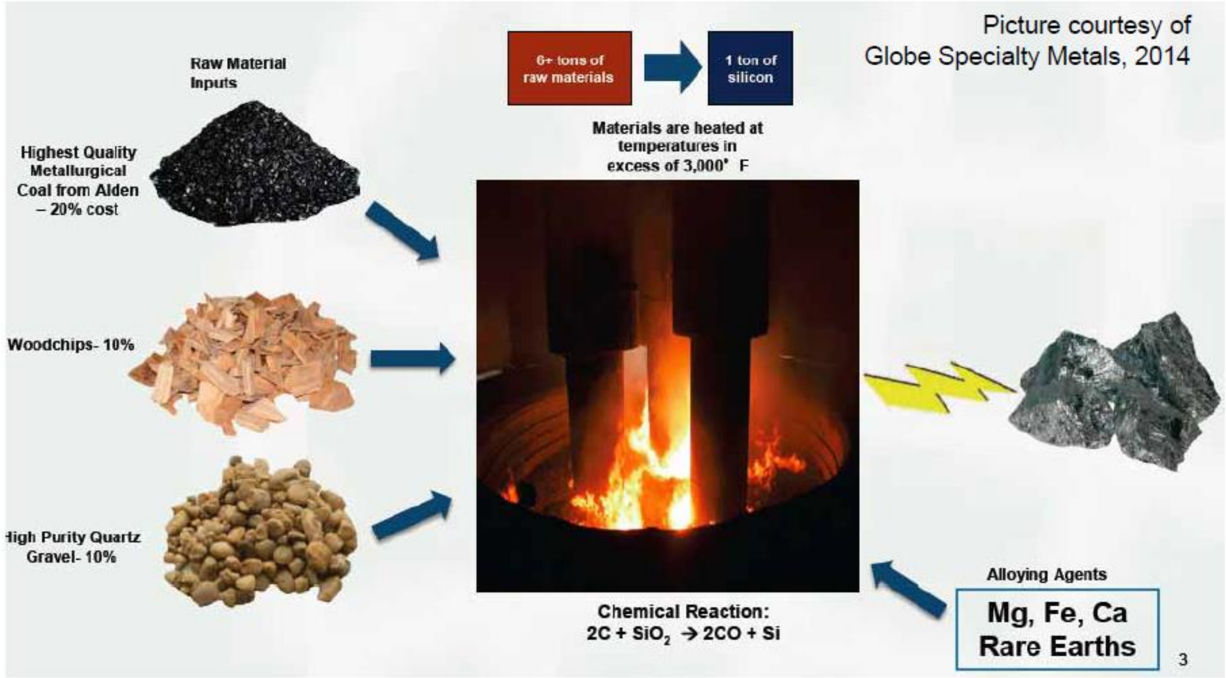

Reduction of quartz in a submerged electric arc furnace. Highly energy intensive process. Large plants. A medium sized EAF has a crucible diameter of 7 m, graphite electrodes each 15 m tall, weighing 20 tons each.

How is Metallurgical Grade Silicon Made #2

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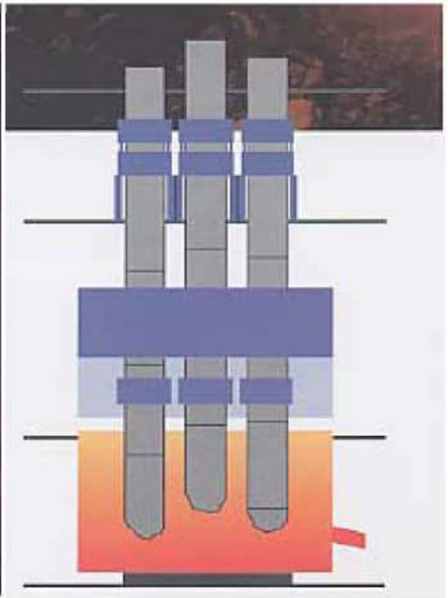
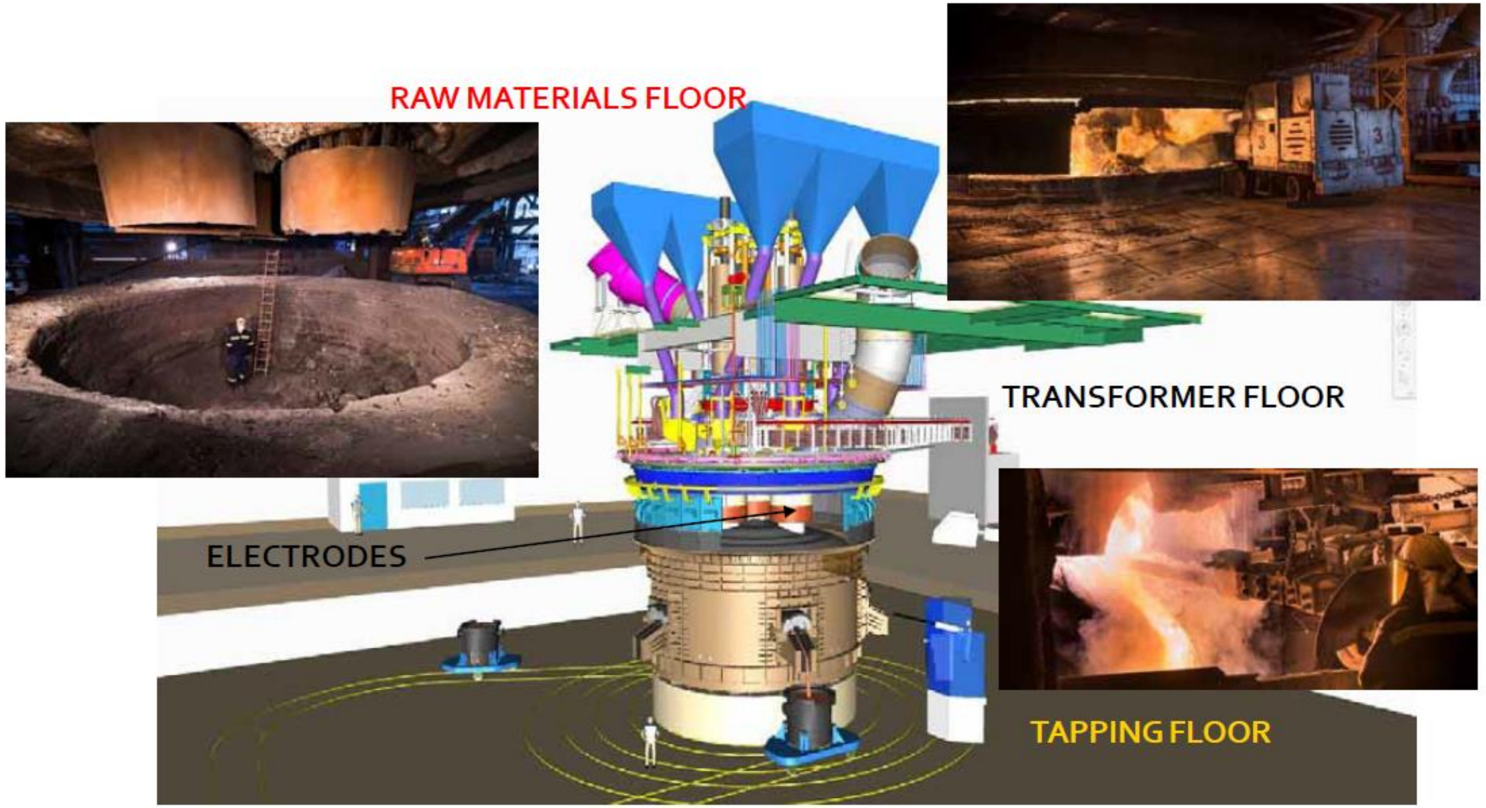


A medium sized submerged arc furnace has a crucible diameter of about 7 metres. It is fed by three carbon electrode columns about 15 metres high and weighing about 20 tons each.

Source: http://www.carbonandgraphite.org/pdf/silicon_production.pdf

Si Smelting in a Submerged EAF



Graphics: Ferroglobe, 2017

Facility layout – Ferroglobe, Polokwane, South Africa

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Graphics: Ferroglobe, 2017

For Si Metal Plants – Low Cost Electricity is Critical

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For every 1 ton of Si production
12 MWh of Electricity consumed

GSM Alloy Plant

Electric Arc Furnace in Operation

Hawk's Nest Hydroelectric Plant

Source: Globe Specialty Metals

Si metal to Semiconductor grade Polysilicon

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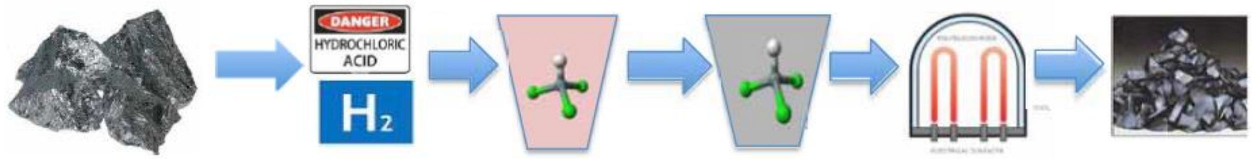

MG Silicon Metal
98.0% to 99.5% Si

MG Silicon Metal Is Dissolved In Hydrochloric Acid To Form Trichlorosilane (HSiCl3)

Trichlorosilane (HSiCl3) is Further Refined

Siemens or FBR Poly Silicon Process

Semiconductor Si
99.999+% Si

Polysilicon

70 MWh - 120 MWh
to produce 1 ton of polysilicon

Impurities in Silicon

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Metallurgical grade	Chemical grade	PolySilicon grade	Solar grade	High Purity
%Fe<0.5	%Fe<0.4	%Fe<0.3	%Fe<0.001	%Fe<0.001
%Ca<0.03	%Ca<0.03	%Ca<0.03	%Ca<0.0001	%Ca<0.0001
%Al<0.1	Min<%Al<Max	Min<%Al<Max	%Al<0.0001	%Al<0.0001
ppmP<limit	ppmP<limit	ppmP<limit	ppmP<1	ppmP : tailormade
	Trace elements <limit	ppmB<limit	ppmB<1	ppmB : tailormade
		Trace elements <limit	ppm others <10	ppm others : tailormade

Semiconductor Grade Si

Typical Impurity Level	
Boron	< 0.1 ppba
Phosphorous	< 0.1 ppba
Other Donors	< 0.03 ppba
Carbon	< 0.15 ppma
Transition Metals (Total Cu, Ni, Fe)	< 1 ppba

Purification of Metallurgical Grade Silicon

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Metallurgical silicon costs about $2 per kg

MG Si contains too many impurities for use in semiconductors or solar cells

In order to purify it we do this:

1) Convert it to a liquid compound containing silicon
2) Distillation of the liquid to purify it
3) Extract silicon from the high purity liquid

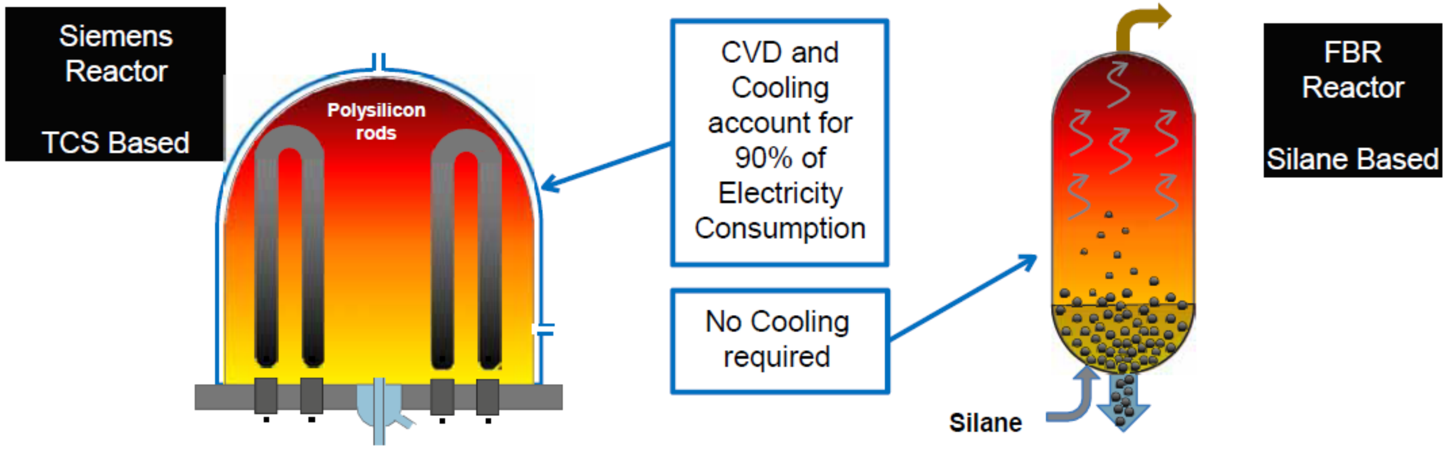
Step 1 is achieved through the following reaction

Silicon	+ Hydrochloric acid	→ Trichlorosilane	+ Hydrogen
Solid	Liquid	Liquid	Gas

$$Si + 3HCl \rightarrow SiHCl_3 + H_2$$

TriChloroSilane is often referred to as TCS

Polysilicon Production



Siemens Process

- Mature 40 year technology
- Batch process
- Requires post processing
- High cash cost

FBR Process

- Energy efficient
- Continuous production
- Lower cash cost

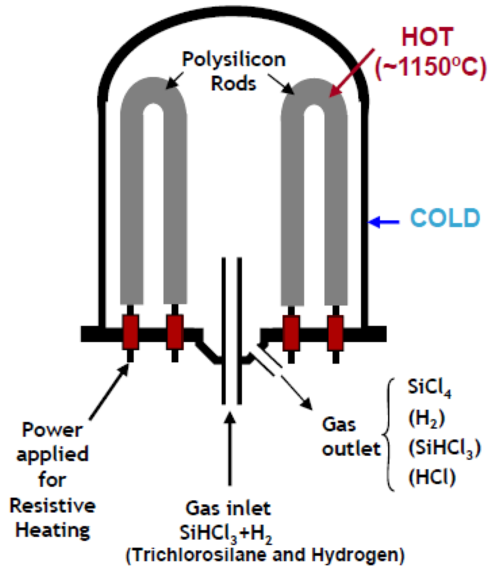
Siemens Process

- Convert metallurgical Silicon into Trichlorosilanes (TCS)

$$Si + 3HCl \rightarrow SiHCl_3 + H_2$$

- Purify TCS in distillation columns
- Recover pure Si using Chemical Vapor Deposition (CVD)

$$H_2 + SiHCl_3 \rightarrow 3HCl + Si$$



Cold wall reactor, high energy consumption. TCS conversion per pass is around 15%, recycling and lower productivity

Siemens Process

The Siemens process is commonly used to produce semiconductor grade silicon

We used this reaction to make TCS:

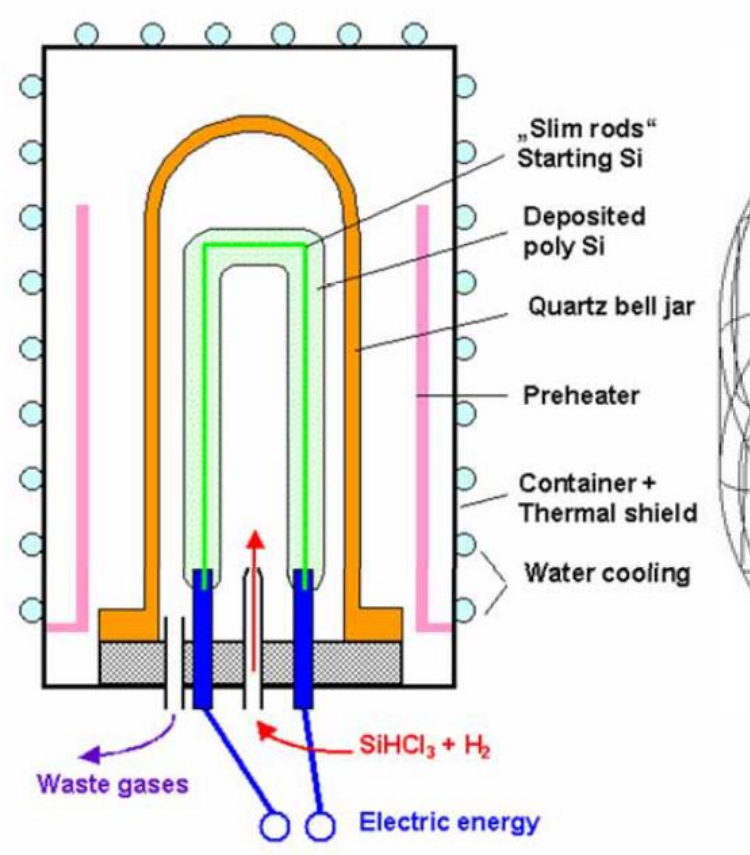
$$Si + 3HCl \rightarrow SiHCl_3 + H_2$$

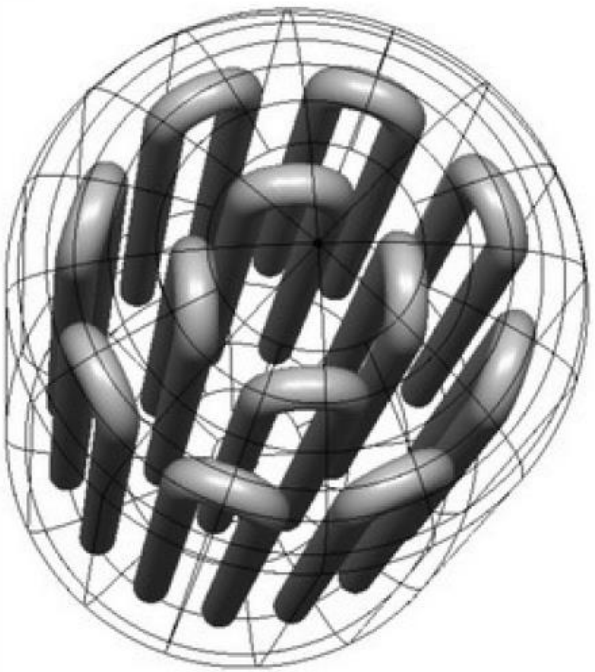
To go back to silicon we just run the same reaction backwards!

$$H_2 + SiHCl_3 \rightarrow 3HCl + Si$$

The reaction is run in a Siemens reactor that looks like this.

Inside the Siemens Reactor





Siemens Polysilicon

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Siemen's reactor

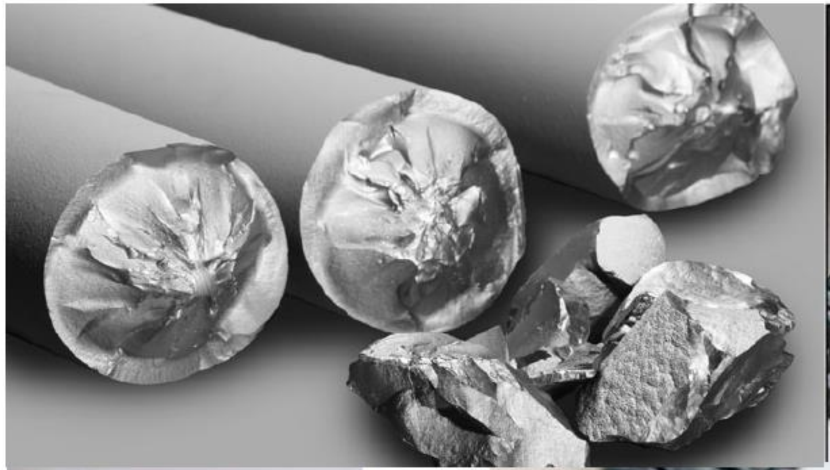
Before polysilicon growth – slim rods

As grown polysilicon rods after a reactor run

Source: GR Fisher, Proc. IEEE, vol. 100, pp. 1454 – 1474, April 2012

80% of the worlds polysilicon is produced using the Siemen's process developed in the 1950's.

Si from Siemens Process – Chunk poly




Graphics: Graham Fisher
MEMC Electronic Materials