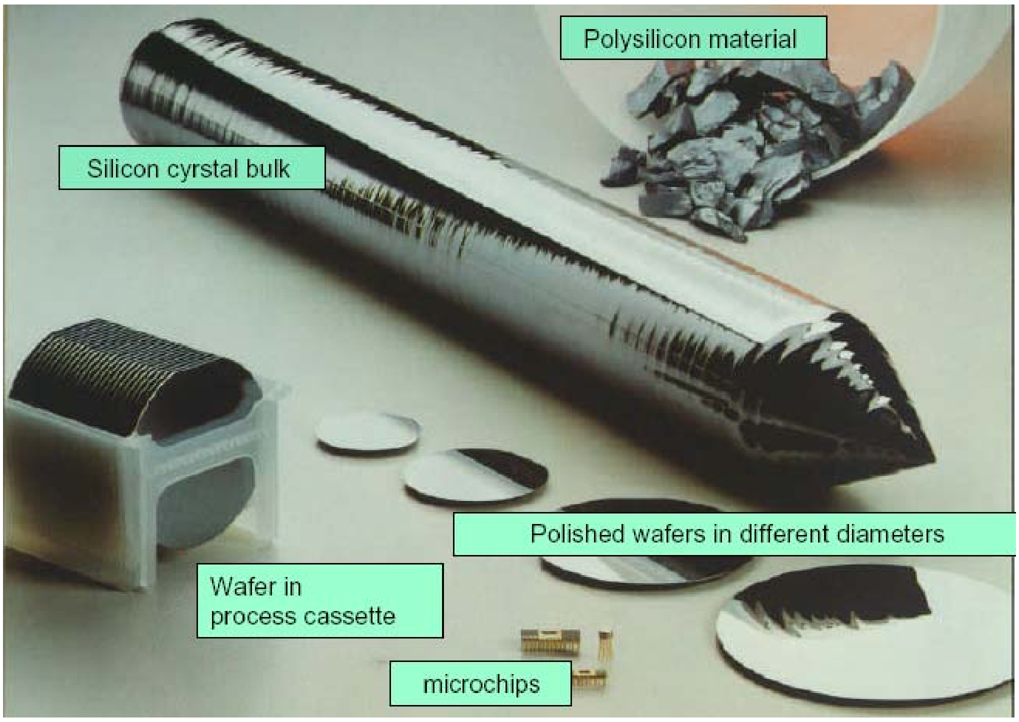
Silicon for Wafer production

Introduction

Production of Silicon

Silicon is used in the semiconductor industry as raw material for the production of integrated circuits and solar cells. Integrated circuits are fabricated on single-crystal silicon substrates with near-perfect crystalline properties: defect free and uniform crystal structure as well as high chemical purity. These substrates are processed in the form of wafers, so the fabrication of circuits on these wafers is known as wafer fabrication. There are several steps in the production process.



Three main production steps:

1.) Refinement of raw material into polycrystalline silicon

2.) Growing of single-crystal silicon ingots by Czochralski or Float Zone process

3.) Production of silicon wafer out of ingots

1.) Refinement of raw material into polycrystalline silicon


Quarzkies 16-60mm

The silicon is produced out of quartzite SiO_2, which consists to 46% out of Silicon (Si), to 53% out of bimolecular Oxygen (O_2) and impurities.

Silicon is obtained commercially by heating sand, charcoal and coke in an electric furnace. Charcoal is required to reduce the silica to silicon (ie. $SiO_2 + 2C = Si + 2CO$) - a process that is sensitive to its quality. The carbon also acts as a conductor in the electric arc furnace and a reaction bed.

At about 1650°C the chemical reaction starts: the SiO_2 is giving away one oxygen Atom. In this case, the chemical combination SiO is generated at greater lots. On the one hand, the gaseous SiO reacts under the creation of CO which results during "combustion" of the carbon by formation to raw silicon or metallurgical grade silicon in the melt. On the other hand, the gaseous SiO reacts with oxygen contained in the stove air in exhaust again to SiO2, however in finest beads.


Lichtbogenofen

Reduction of SiO_2 (Quartzite) :

$SiO_2 + 2\,C \rightarrow Si + 2\,CO$

These beads are reprocessed technically for use as Microsilica and are used as a temperature constant filling material e.g. in ceramic and fireproof products.

The liquefied silicon melt is collected in the bottom of the furnace, and is then drained and cooled. The silicon produced via this process is called metallurgical grade silicon and is at least 99% pure.

The metallurgical grade silicon is purified and treated with chemical processes. The silicon is crushed and reacted with HCl (gas) to make Trichlorosilane, a high vapour pressure liquid that boils at 32°C as in:

Reaction of raw silicon to liquid Trichlorosilane:

$Si + HCl \rightarrow SiHCl_3 + H_2$

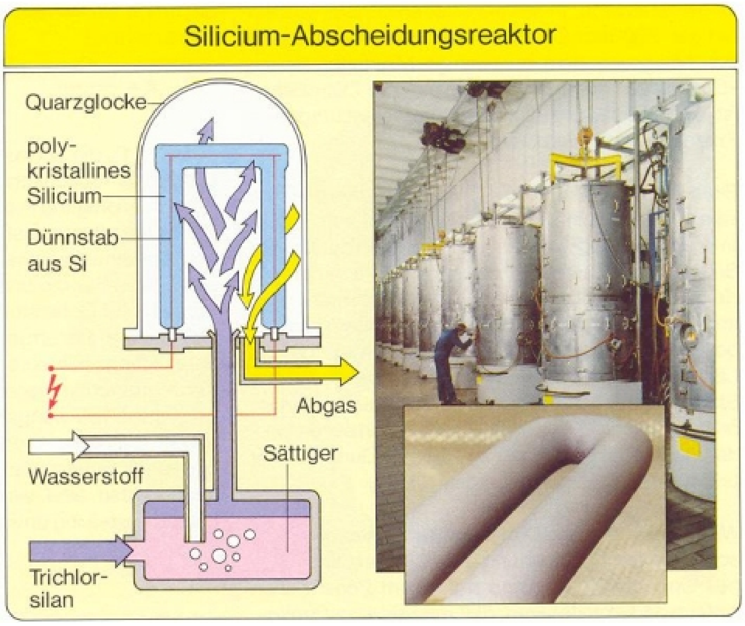
Many of the impurities in the silicon (aluminium, iron, phosphorus, chromium, manganese, titanium, vanadium and carbon) also react with the HCl, forming various chlorides.

One of the nice things about the halogens is that they will react with almost anything. Each of these chlorides has different boiling points, and so, by fractional distillation, it is possible to separate out the $SiHCl_3$ from most of the impurities. The (pure) Trichlorosilane then reacts with hydrogen gas (again at an elevated temperature) to form pure electronic grade silicon (EGS) / polycrystalline silicon.

Reduction of Trichlorosilane to polycrystalline Silicon:

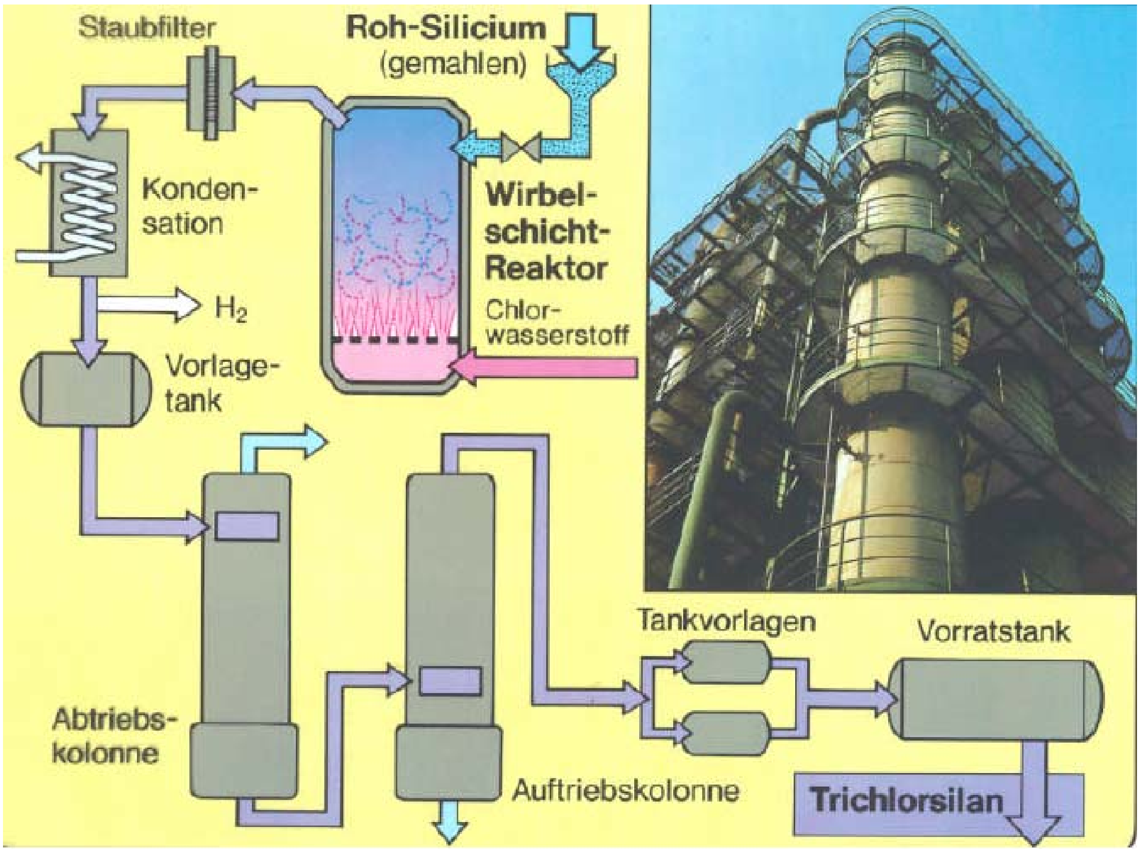
$SiHCl_3 + H_2 \rightarrow Si + HCl$

Scheme of the polycrystalline silicon reactor



In the meantime the silicon has reached a purity of nearly 100%. The impurities conduct only <10^{-9}, that means only 1 impurity comes to 10 billion silicon atoms. Although the EGS is relatively pure, it is in a polycrystalline form which is not suitable for device manufacture.

Scheme of a Trichlorosilane Distillation:



2.) Growing of single-crystal silicon bulks / ingots

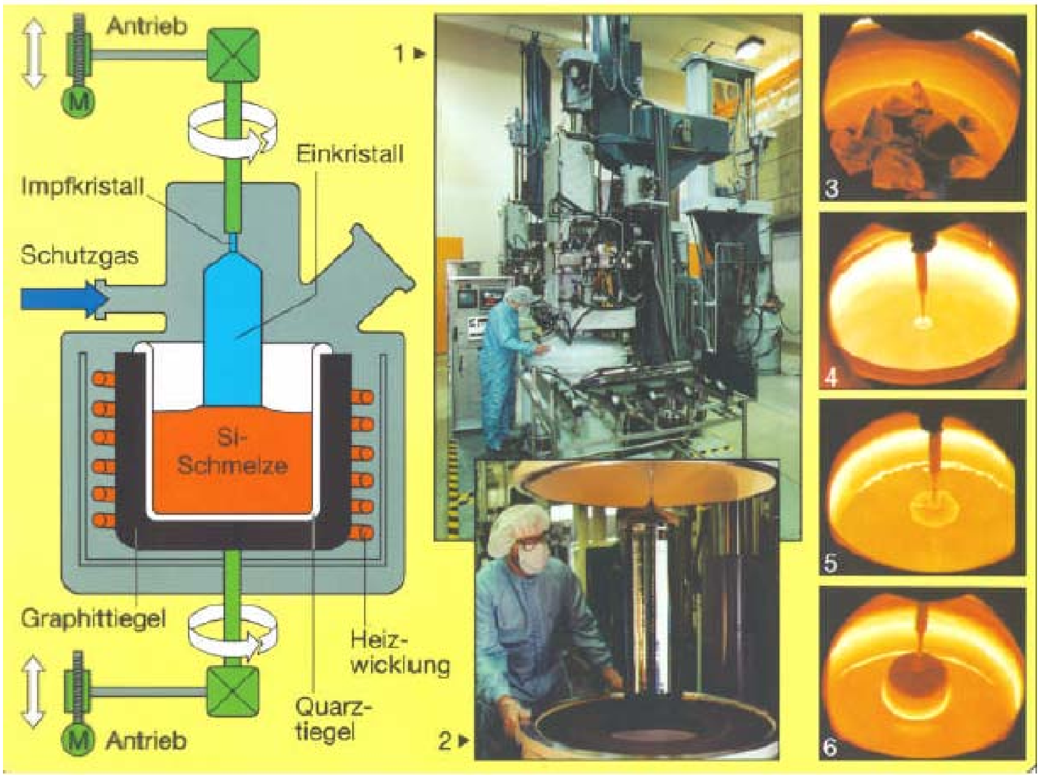
Integrated circuits are built on single-crystal silicon substrates that possess a high level of purity and perfection. Aside from the need to be single-crystalline in nature, silicon substrates must also have a high degree of chemical purity, a high degree of crystalline perfection, and high structure uniformity. The acquisition of such high-grade starting silicon material involves the growing of single-crystal silicon either by Czochralski (CZ) or Float Zone process.

The Czochralski (CZ) crystal growth, so named in honor of its inventor, involves the crystalline solidification of atoms from a liquid phase at an interface. The CZ process is the standard process of the most part of all produced Silicon wafer. Chunks of virgin polycrystalline silicon / electronic grade silicon are placed in a quartz crucible along with small dopants. The added dopants give the desired electrical properties for the grown ingot. The most common dopants are boron, phosphorus, aresenic and antimony. Depending on which dopant is used, the ingot becomes a P or N type ingot (Boron: P type; Phosphorus, Antimony, Arsenic: N type). The gases inside the growth chamber are then evacuated. Then the growth chamber is back-filled with an inert gas like Argon to inhibit the entrance of atmospheric gases into the melt during crystal growing. The materials are then heated to a temperature above the melting point of silicon, 1420 degrees Celsius.

Monokristallines Silicium

Once the polycrystalline and dopant combination has been liquefied, a single silicon crystal, the seed, is positioned on top of the melt, barely touching the surface. The seed has the same crystal orientation required in the finished ingot. To achieve doping uniformity, the seed crystal and the crucible of molten silicon are rotated in opposite directions. Once conditions for the crystal growth have been met, the seed crystal is slowly lifted out of the melt. Growth begins with a rapid pulling of the seed crystal in order to minimize the number of crystal defects within the seed at the beginning of the growing process. The pull speed is then reduced to allow the diameter of the crystal to increase. When the desired diameter is obtained the growth conditions are stabilized to maintain the diameter. As the seed is slowly raised above the melt, the surface tension between the seed and the melt causes a thin film of the silicon to adhere to the seed and then to cool. While cooling, the atoms in the melted silicon orient themselves to the crystal structure of the seed. The now created bar also called as ingot or bulk is up to 2 m long and 30 cm thick.

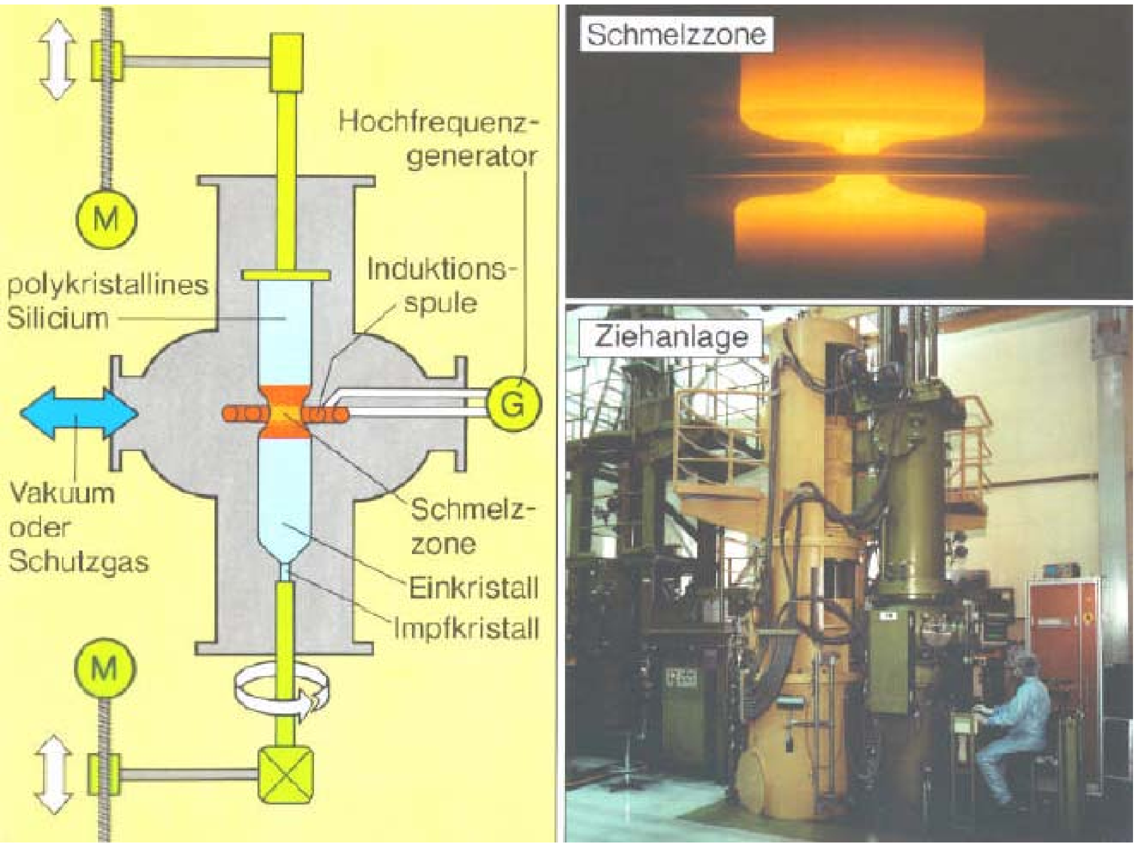
Scheme of the CZ process:



The CZ process has one disadvantage due to the used quartz crucible. The produced silicon ingot has not the highest conductivity.

The float zone (FZ) process is another method for growing single-crystal silicon. It involves the passing of a molten zone through a polysilicon rod that approximately has the same dimensions as the final ingot. The purity of an ingot produced by the FZ process is higher than that of an ingot produced by the CZ process. As such, devices that require ultra pure starting silicon substrates should use wafers produced using the FZ method. The FZ process consists of the following steps. A polysilicon rod is mounted vertically inside a chamber, which may be under vacuum or filled with an inert gas. A needle-eye coil that can run through the rod is activated to provide RF power to the rod, melting a 2-cm long zone in the rod. This molten zone can be maintained in stable liquid form by the coil. The coil is then moved through the rod, and the molten zone moves along with it. The movement of the molten zone through the entire length of the rod purifies the rod and forms the near-perfect single crystal. This can be repeated several times to reach a high purity. The dopants as for example Phosphin PH_3, Diboran B_2H_6 are added to the inert gas.

Scheme of the FZ-process:



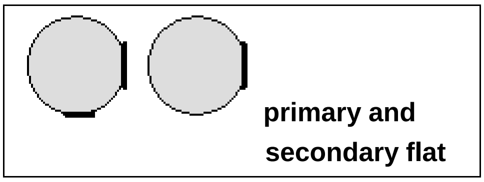
3.) Production of a wafer from a silicon crystal

Main production processes:

1. Silicon ingot pulling with Czochralski - or Float - Zone - process
2. Ingot grinding on precise diameter
3. Grinding a flat
4. Inner diameter slicing of the ingot into thin wafers
5. Edge rounding; prevents break outs during the handling
6. Lapping for defining the wafer macro geometry (thickness, ripple, wedge-shaped)
7. Contact polishing to remove the mechanical imperfections of crystal layers
8. Etching process to remove the mechanical imperfections
9. Semi contact polishing as finishing of the surface (only front surface)
10. Cleaning, testing (Particle, Defects), packing

The above process of silicon growing, grinding, shaping, sawing, etching, and polishing to produce input wafers is known as wafering.

Flat: The largest flat, called the primary flat, is used by automated wafer handling systems for alignment. Flats (primary and secondary) are also used to identify the crystallographic orientation and conductivity of the wafer.

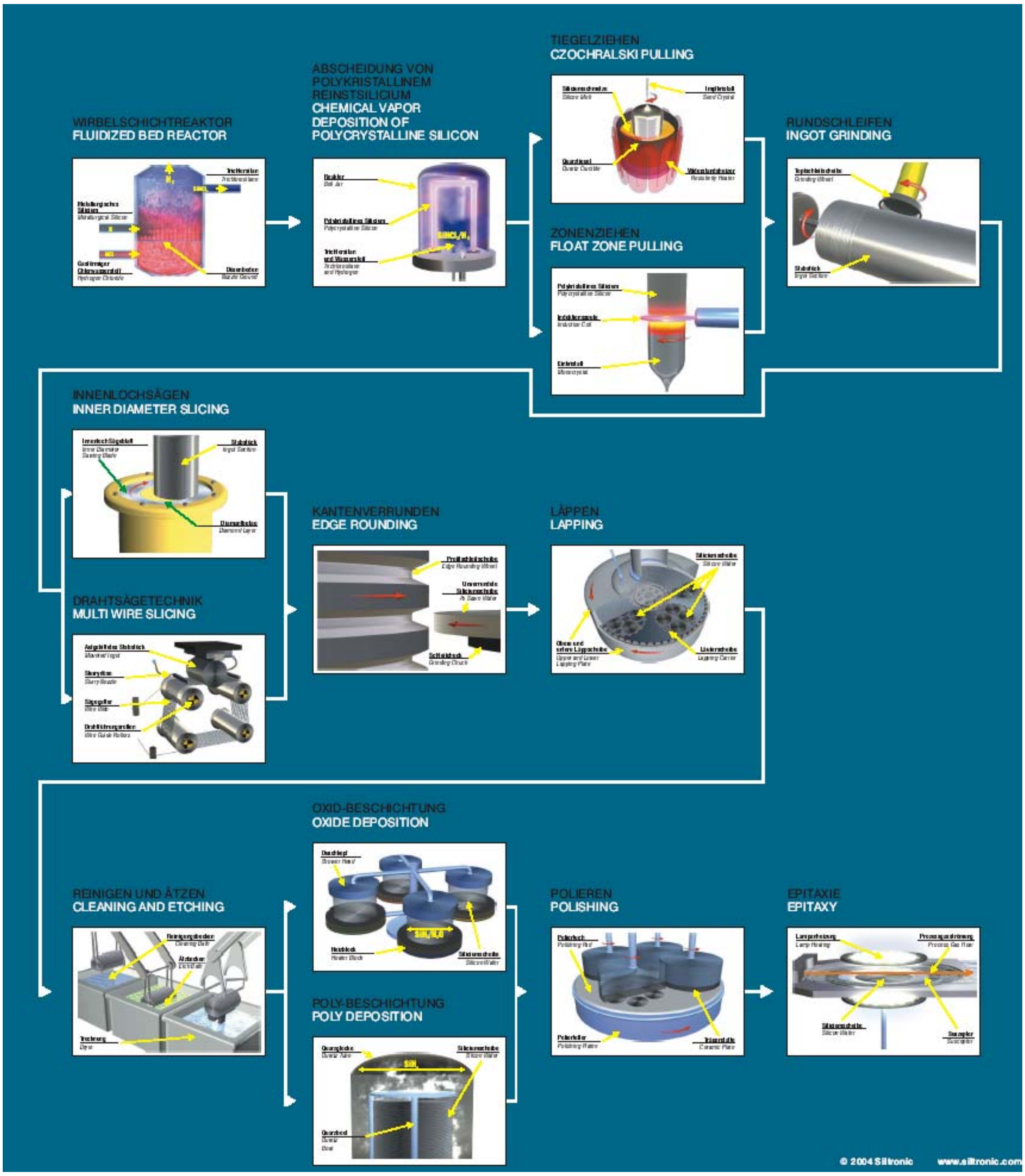


Ingot / bulk: A cylindrical solid made of polycrystalline or single crystal silicon from which wafers are cut.

Dopant: An element that contributes an electron or a hole to the conduction process, thus altering the conductivity. Dopants for silicon wafers are found in Groups III and V of the Periodic Table of the Elements

Doping: The process of the donation of an electron or hole to the conduction process by a dopant

Scheme of the wafer production:



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Market segments

- Producer of raw silicon
- Producer of polycrystalline silicon for the semiconductor industry
- Producer of wafer for the semiconductor industry
- Installation contractors & control manufactures

Description of the challenge

At all process steps of the wafering a leakage at the supplying pipes, gas cabinets or the equipment can not be excluded. It can come to an emission of the used high toxic, inflammable or explosive gases such as Phosphine, Trichlorosilane, Hydrogen chloride or Diborane. Furthermore, pollutants are generated in the processes, which also mean a danger for the people in the environment and/or working place in the plants. There are essentially two danger areas through the construction of the semiconductor factories. The first one is in the field of the storage and of appropriation of the gases in the corresponding cabinets. It can come here for a leakage at the flanges or directly at the utility line. No persons are usually in this field. The second field is the actual clean room with the equipment for the different process steps. In this field it can come to a leakage at that to- and vent pipes of the reactors. The space for the mounting of the transmitter is limited. Because of that in the most cases an extraction system or Remote-Sensor is used.

Persons stay here for the service and check of the processes. In the case of a recognized leakage, the entire field is evacuated and all processes disturbed. Fault alarms must be avoided, because high cost will rise up by the production

Selection of relevant substances

name	Carbon monoxide	Hydrogen chloride	Chlorine	Trichlorosilane	Tetrachlorosilane
formula	CO	HCl	Cl_2	$SiHCl_3$	$SiCl_4$
MAK[1]	30 ppm	5.3 ppm	0.5 ppm	-	-
TWA	25 ppm	1 ppm	0,5 ppm	0,1 ppm	1 ppm
LEL	10.9 Vol %	-		6.9 Vol %	
attributes	- colourless and odourless gas	- colourless, prickly smelling gas - non-flammable	- toxic, yellow-greenish, pungent-smelling gas - corrosive - non combustible - oxidising	- colourless, smoking liquid with a pricking odour - highly inflammable - remote ignition possible - spontaneous inflammation in the case of contact with air - disintegration while heating and formation of toxic and corrosive steam	- colourless, smoking liquid with a pricking odour - non-flammable - disintegration while heating and formation of toxic and corrosive steam

name	Diborane	Phosphine	Dichlorosilane	Boron triflouride	Boron trichloride
formula	B_2H_6	PH_3	SiH_2Cl_2	BF_3	BCL_3
MAK[1]	0.1 ppm	0.1 ppm	5 ppm	1 ppm	5 ppm
TWA	0.1 ppm	0.3 ppm			
LEL	0.8 Vol %	1.0 Vol %	2.5 Vol %	-	
attributes	- colourless, prickly smelling gas - low perception in the case of low concentrations - very toxic - highly inflammable gas - self igniting in air	- colourless, prickly smelling gas - only during impurities after garlic or carbide - highly inflammable gas - Gas-air mixtures are combustible	- Smoking at moist air - prickly smelling gas - highly inflammable gas - heavier then air and can expand itself on the floor - Gas-air mixtures are combustible	- Smoking at moist air - prickly smelling gas - ery toxic - non-flammable	- Smoking at moist air - prickly smelling gas - very toxic - non-flammable

[1] all values are from 2009, subject to change

Solution from Dräger

For application within the semiconductor factories almost all transmitter can be used with the electrochemical sensors. The only exceptions are the Polytron TX and Polytron L, which are based on the technical design, are limited for the detection of some specific gases (s. matrix).

In particular the Dräger Polytron 7000 with integrated pump, Remote-Sensor and relay module fits the requirements for application in clean rooms.

With the wide range of different electrochemical sensors in combination with the long life time and the very good technical qualities Dräger can offer complete solution.

Following DrägerSensor are possible for the detection:

- DrägerSensor HCl for the measurement of HCl, BCl_3, SiH_2Cl_2, $SiCl_4$, $SiHCl_3$
  (Measurement range: 0 – min 5 ppm / max. 20 ppm, Lower detection limit: 1 ppm)
  for HCl (Measurement range: 0 – min 30 ppm / max. 100 ppm, Lower detection limit: 1 ppm)
- DrägerSensor Cl_2 for the measurement of Cl_2
  (Measurement range: 0 – min 1 ppm / max. 50 ppm, Lower detection limit: 0.05 ppm)
- DrägerSensor AC for the measurement of HCl, BCl_3, BF_3, SiH_2Cl_2, $SiCl_4$ und $SiHCl_3$
  (Measurement range: 0 – min 10 ppm / max. 30 ppm, Lower detection limit: 0.5 ppm)
- DrägerSensor Hydride for the measurement of B_2H_6 und PH_3
  (Measurement range: 0 – min 0.5 ppm / max. 1 ppm, Lower detection limit: 0.05 ppm)
  for PH_3
  (Measurement range: 0 – min 0.3 ppm / max. 20 ppm, Lower detection limit: 0.03 ppm)
- DrägerSensor Hydride SC for the measurement of B_2H_6 und PH_3
  (Measurement range: 0 – min 0,3 ppm / max. 5 ppm, Lower detection limit: 0.02 ppm)
  for PH_3 (Measurement range: 0 – min 0.3 ppm / max. 1 ppm, Lower detection limit: 0.01 ppm)

- DrägerSensor PH3/ASH3 for the measurement of PH_3
  (Measurement range: 0 – min 0.3 ppm / max. 20 ppm, Lower detection limit: 0.02 ppm)
- DrägerSensor CO for the measurement of CO
  (Measurement range: 0 – min 50 ppm / max.. 1000 ppm, Lower detection limit: 5 ppm) bzw.
  (Measurement range: 0 – min 200 ppm / max. 5000 ppm, Lower detection limit: 10 ppm)

Application of the different Dräger measuring transmitter

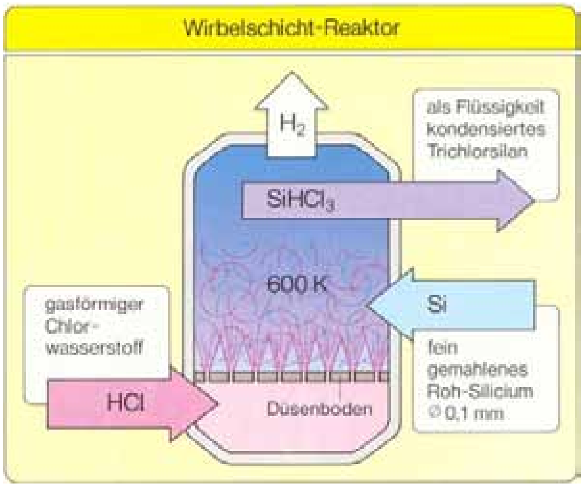
Transmitter	Cl_2	HCl	$SiHCl_3$	SiH_2Cl_2	$SiCl_4$	PH_3	BF_3 /BCL_3	B_2H_6	CO
Polytron 3000*	✓	✓	✗	✓	✓	✓	✓	✓	✓
Polytron 7000	✓	✓	✓	✓	✓	✓	✓	✓	✓
Polytron 2 XP	✓	✓	✓	✓	✓	✓	✓	✓	✓
Polytron TX	✓	✗	✗	✗	✗	✗	✗	✗	✓
Polytron L	✓	✓	✗	✗	✗	✗	✗	✗	✗

* Polytron 3000 has a defined measuring range for each sensor - not configurable (s. datasheet); calibration gas is not always available in the needed concentration

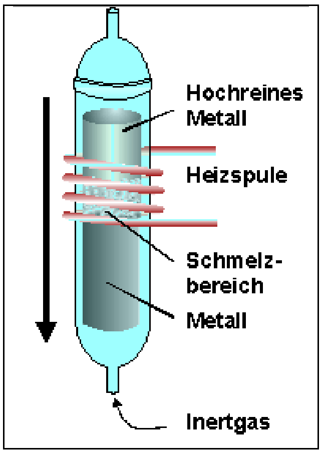
See also:

http://en.wikipedia.org/wiki/Silicon_wafer
http://www.siltronic.com
http://www.semiconfareast.com/crystal.htm
http://www.osha.gov/SLTC/semiconductors/substratemfg/polysiliconprod.html#Hydrogen%20Chloride

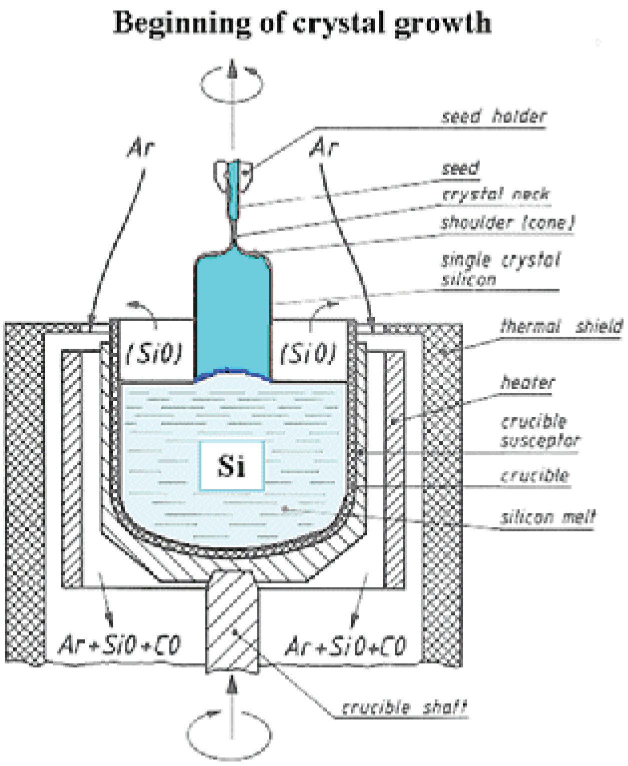
Appendix



Wirbelschicht Reaktor – Trichlorosilane Destillation

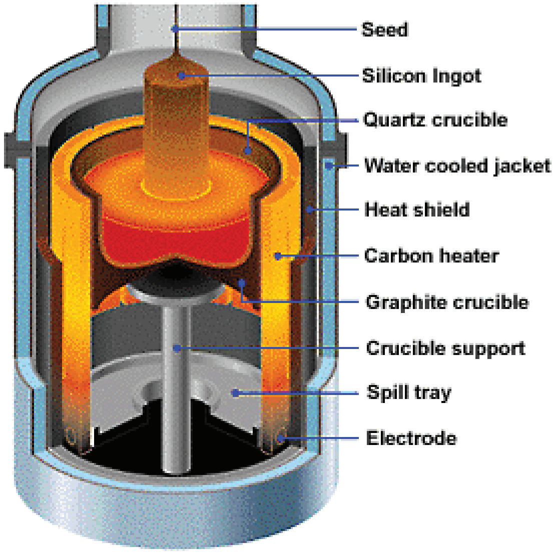


Float Zone (FZ) -Verfahren



Czochralski (CZ) – process

Czochralski puller



Cz crystal pulling furnace