Producing "Nirvana" Silicon or Nearly Perfect Silicon Single Crystals

Producing Semiconductor-Grade "Raw" Silicon

Introductory Remarks

It is written somewhere that in the beginning God created heaven and the earth. It is not written what from.

- We do not know for sure what the heaven is made of but we do know what the the earth is made of - at least as far as the upper crust is concerned. Interestingly enough, he (or she) created mostly **Silicon** (Si) and Oxygen (O), with a bit of dirt (in the form of the other **90** elements) thrown in for added value.

- Indeed, the outer crust of this planet (lets say the first **100 km** or so) consists of all kinds of silicates - **Si + O +** something else - so there is no lack of **Si** as a raw material. **Si**, in fact, accounts for about **26 %** of the crust, while **O** weighs in at about **49 %**.

However, it took a while to discover the element **Si**. **Berzellius** came up with some form of it in **1824** (probably amorphous), but it was **Deville** in **1854** who first obtained regular crystalline **Si**.

- This is simply due to the very high chemical reactivity of **Si**. Pure **Si** (not protected by a thin layer of very stable silicon dioxide (**SiO₂**) as all **Si** crystals and wafers are) will react with *anything*, and that creates one of the problems in making it and keeping it clean.
  It also holds on to its oxygen so fiercely that carbon cannot steal it, even at high temperatures. Silicon thus could only be discovered in what I called the "electro-smelting of very difficult metals age".

- *Liquid* **Si** indeed does react with all substances known to man - it is an universal solvent. This makes crystal growth from liquid **Si** somewhat tricky, because how do you contain your liquid **Si**? Fortunately, some materials - especially **SiO₂** - dissolve only very slowly, so if you don't take too long in growing a crystal, they will do as a vessel for the liquid **Si**.

- But there will always be some dissolved **SiO₂** and therefore oxygen in your liquid **Si**, and that makes it hard to produce **Si** crystals with very low oxygen concentrations.

What we *need*, of course, are **Si crystals** - in the form of **wafers** - with extreme degrees of perfection.

- What we *have* are ***inexhaustible*** resources of **Silicondioxide**, **SiO₂** that is fairly clean if obtained from the right sources. Since there is no other material with properties so precisely matched to the needs of the semiconductor industry, the production process of **Si** wafers shall be covered here in a *cursory* way.

It's *cursory* for my students. To you it might look at bit involved. That's because the making of one of the most important "raw" materials of today, the **silicon** wafer, is an extremely involved process. Only a few highly specialized companies are able to do it. In case you wonder: Si wafers (to use the term a bit loosely) are the starting material for almost everything that has to do with electronics or solar cells. If something runs on electricity (or makes electricity), it has almost certainly (processed) Si wafer parts inside.
That's why I thought I will give you a cursory glance of what the making of Si wafers involves.

- And not to forget: What comes *after* that, what is done with a Si wafer called "silicon technology", is a hell of lot more complicated than the "simple" making of the wafer!

Producing "Raw" Silicon

Fortunately, the steel industry needs **Si**, too. Silicon was already used as a crucial alloying component of steel before it started its career as the paradigmatic material of our times.

- Most of the world production of **raw Si** still goes to the steel industry and only a small part is ***diverted*** for the semiconductor trade. This is why this stuff is commonly called "**metallurgical grade**" **Si** or *MG-Si* for short. The world production in **2006** was around **4** Mio tons per year.

- How is **MG- Si** (meaning poly crystalline material with a purity of about **99%**) made? Silicon belongs to the "electro-smelting of very difficult metals" category in my terminology. You must reduce the oxide in a furnace by providing some reducing agent (usually carbon but aluminum also works), sufficient energy *and* some electrical potential at rather high temperatures.

Like for most metals, the reducing agent is *carbon* (in the form of coke (= very clean coal)). The necessary energy is directly supplied by electricity.

- Essentially, you have a huge furnace lined with graphite, which will turn into very hard and inert silicon carbide (SiC) and with three big graphite electrodes inside (carrying a few **10.000 A** of current). The furnace is continuously filled with **SiO₂** (**=** quartz sand) and carbon (= coke) in the right weight relation plus a few added secret ingredients like certain wood chips to avoid producing **SiC**. Schematically it looks like this:

Smelting silicon

Extremely simplified. The human gives an idea about size.
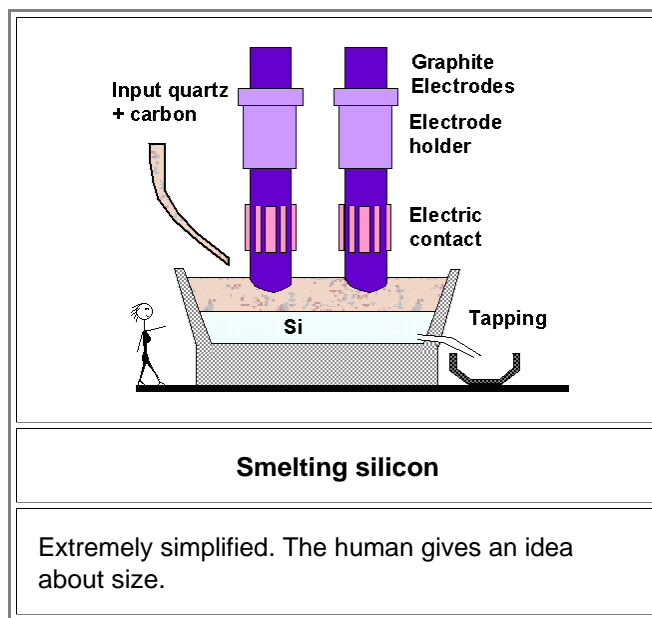
⬤ The chemical reaction that you want to take place happens at about **2000 ºC** and is simple in principle:

$$SiO_2 \ + \ C \ + \ \text{"electricity"} \ \Rightarrow \ Si + CO_2$$

⬤ But there are plenty of other reactions that may occur simultaneously, e.g. **Si + C ⇒ SiC**. This will not only reduce your yield of **Si**, but **clog up** your furnace because **SiC**, short for silicon carbide, is not liquid at the reaction temperature and extremely hard. If you make **SiC**, your reactor ends up as a piece of junk!

� Still, we do not have to worry about **MG-Si** - a little bit of what is made for the steel industry will suffice for all of **Si** electronics applications.

⬤ What we do have to worry about is the *purification* of the **MG-Si**. We must make it at least a billion times (**10^9** fold) cleaner.

� Making clean, "electronic grade" poly silicon is essentially done in three steps:

⬤ *First* , **Si** is converted to trichlorosilane (**SiHCl₃)** in a "fluid bed" reactor via the reaction:

$$Si \ + \ 3HCl \ \Rightarrow \ SiHCl_3 \ + \ H_2$$
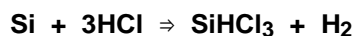
⬤ This reaction (helped by a catalyst) takes place at around **300 ºC**. The resulting **Trichlorosilane** is a liquid with a boiling point of **31.8 ºC**, already much purer than the raw MG Si but still too dirty.

⬤ *Second*, the **SiHCl₃** is distilled (like wodka), resulting in extremely pure Trichlorosilane.

⬤ *Third*, high-purity **Si** is produced by the **Siemens process** or, to use its modern name, by a "**Chemical Vapor Deposition**" (*CVD*) process as detailed below

Producing Doped Poly-Silicon

▶ Typically, we do not produce high-purity **Si** from **SiHCl₃** but "doped" polycrystalline solid silicon. "**Doping**" is the name for putting well-defined small amounts of special impurities into a crystal. We dope the **poly-Si** (not to be confused with the poly-**Si** layers on chips) with either boron (**B**), phosphorous (**P**) or arsenic (**As**), attempting doping atom concentrations of **10^{14} cm⁻³ - 10^{19} cm⁻³**.
The doped *poly*-Si made this way will be used later to grow *single* **Si** crystals. On occasion we do not dope the poly-Si because we want a Si crystal as perfect and clean as possible - the "nirvana" silicon!

⬤ In principle, we have a vessel which can be evacuated and that contains an "U" shaped arrangements of slim **Si** rods that can be heated from an outside heating source. The Si rods become conductive as soon as the temperature is high enough (roughly **1000 ºC**). By passing an electrical current through them, heating can now be done electrically and the outside heating is switched off. That's important because we want *only* the Si rods to be hot, not the rest.

Poly-Silicon reactor ("Siemens process")
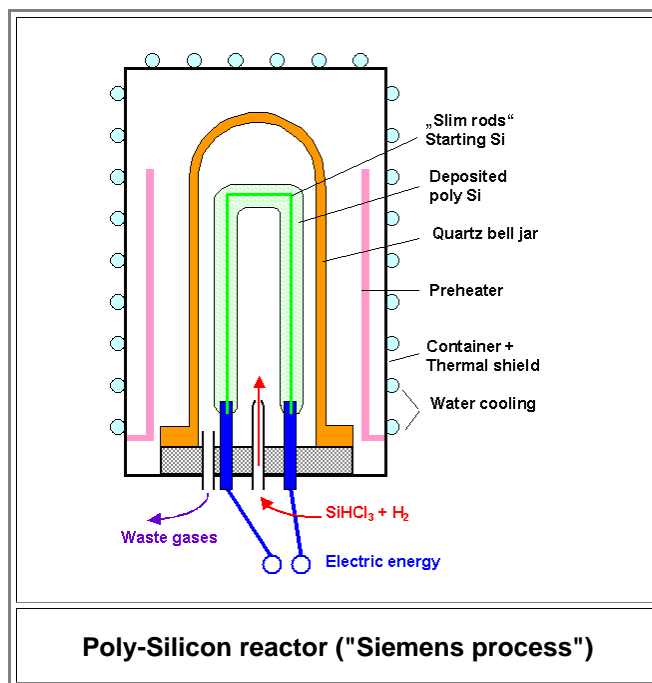
- After the vessel has been evacuated and the **Si** rods are at reaction temperature, an optimized mix of pure *SiHCl₃* (**Trichlorosilane**), **H₂** and doping gases like arsine **AsH₃** or phosphine **PH₃** are admitted into the reactor. In order to keep the pressure constant (at a typical value of some mbar), the reaction products (and unreacted gases) are pumped out at a suitable pace.

- On *hot* surfaces - if everything is right this will *only* be the **Si** - a chemical reaction now takes place, reducing the **SiHCl₃** to **Si** and forming **HCl** (hydrochloric acid) as a new compound:

$$SiHCl_3 \ + \ H_2 + \ "heat" \ \Rightarrow \ Si \ + \ 3 \ HCl$$

- Similar reactions provide very small but precisely measured amounts of **As**, **P** or **B** from the doping gases that will be incorporated into the growing polysilicon

- The **Si** formed will adhere to the **Si** already present - the thin rods will grow as fresh **Si** is produced. The incorporation of the dopants will produce *doped polysilicon*.

As far as Materials Engineers are concerned, this is a simple process. It even has a name: **Siemens process** because the process (and the use of silicon as semiconductor) was pioneered by Siemens company.
Nowadays we call all those processes "**Chemical Vapor Deposition**" (*CVD*) since similar processes are used a lot in microtechnology for depositing some material on a substrate. CVD processes are also used to make titanium (Ti) and other elements.
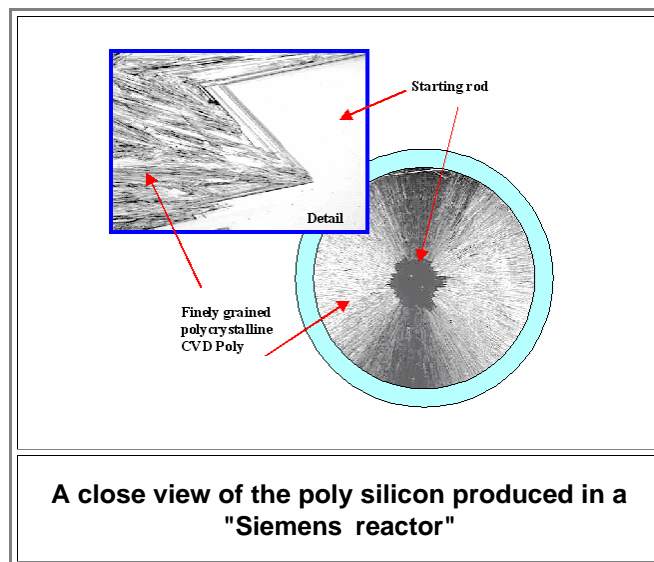It is not all that easy, however, to work with CVD. Consider the complications just for silicon:

- You have to keep the **Si** *ultrapure* - all materials (including the gases) must be specially selected.

- The chemistry is extremely dangerous. **AsH₃** and **PH₃**, a must for doping (no alternative), are among the most poisonous substances known to mankind. **PH₃** was actually used as a toxic gas in world war **II** with disastrous effects. **H₂** and **SiHCl₃** are easily combustible if not outright explosive, and hydrochloric acid **HCl** (in gaseous form) is even more dangerous than the liquid acid and extremely corrosive. Handling these chemicals, including the safe and environmentally sound disposal, is neither easy nor cheap.

- Precise control is not easy either. While the flux of **H₂** may be in the **100 liter/min** range, the dopant gases only require **ml/min**. All flow values must be precisely controlled and, moreover, the mix must be homogeneous at the **Si** where the reaction takes place.

- The process is slow (about **1 kg/hr)** and therefore *expensive*. You want to make sure that your hyperpure (and therefore expensive) gases are completely consumed in the reaction and not wasted in the exhaust - but you also want high throughput and good homogeneity; essentially conflicting requirements. There is a large amount of optimization required!

- And from somewhere you need the slim rods - already with the right doping.

Still, it works and about **50.000 tons** of poly-**Si** are produced at present (**2011**), most of which now goes to the solar cell industry.

- The **electronic grade poly-Si** that results is not cheap, however, and will never become dirt cheap. With somewhat relaxed specifications for solar cell uses, it can be produced relatively cheaply, though.

Here is an example for the poly-crystalline rods produced in the Siemens process:

Detail

Starting rod

Finely grained
polycrystalline
CVD Poly

**A close view of the poly silicon produced in a
"Siemens reactor"**

Silicon Crystal Growth and Wafer Production

Single Crystal Growth

We now have hyperpure poly-**Si**, already doped to the desired level, and the next step must be to convert it to a *single crystal*. There are essentially two methods for crystal growth used in this case:

- **Czochralski** or *crucible* **grown** crystals (*CZ* crystals).

- **Float zone** or *FZ* crystals.

The latter method produces crystals with the highest purity, but is not easily used at large diameters. **150 mm** crystals are already quite difficult to make and nobody so far has made a **300 mm** crystal this way.

- Float zone crystal growth, while the main method at the beginning of the **Si** age, is now only used for some specialities and therefore will not be discussed here. The **Czochralski method**, invented by the Polish scientist **J. Czochralski** in **1916**, is the method of choice for high-volume production of **Si** single crystals of exceptional quality. Below is a schematic drawing of a crystal growth apparatus (about three stories high) employing the Czochralski method. The article gives an idea about the history and the present state of the art of Si crystal growth

Link

CZ Si Article

**The Czochralski method for (silicon) crystal
growth**
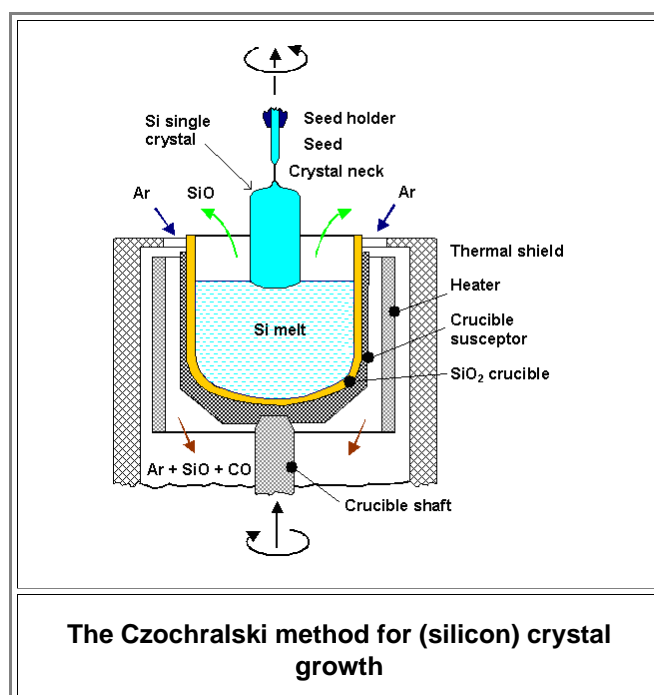
- Essentially, a crystal is "pulled" out of a vessel containing liquid **Si** by dipping a **seed crystal** into the liquid which is subsequently slowly withdrawn at a surface temperature of the melt just above the melting point. A crucial step for making dislocation-free silicon is to produce a "neck", i.e. a very thin region in the seed crystal before enlarging the diameter to the desired value. This can be seen nicely in this module.
  The *pulling rate* (usually a few mm/min) and the *temperature profile* determines the crystal diameter. The basic problem is to get rid of the heat of crystallization.
  Everything else determines the quality and homogeneity - crystal growing is still as much an art as a science!
- Here we only look cursorily at one major point, the **segregation coefficient k_{seg}** of impurity atoms. The full story can be found here. Segregation, by he way, is also the key process for making wootz blades.
 - The segregation coefficient in thermodynamic equilibrium gives the relation between the concentration of impurity atoms in the growing crystal and that of the melt. It is usually much lower than **1** because impurity atoms "prefer" to stay in the melt. This can be seen from the liquidus and solidus lines in the respective phase diagrams.
    In other words, the *solubility* of impurity atoms in the melt is larger than in the solid.
    "Equilibrium" refers to a growth speed of **0 mm/min** or, more practically, very low growth rates. For finite growth rates, k_{seg} becomes a function of the growth rate (called k_{seff}) and approximates **1** for high growth rates (whatever comes to the rapidly moving interface gets incorporated).
- This has a positive and a negative side to it:
  - On the positive side, the upper part of a crystal will be *cleaner* than the liquid, crystal growing is simultaneously a purification method. Always provided that we discard the lower part of the crystal, where all the impurities are now concentrated. After all, what was in the melt must be in the solid after solidification - only the distribution may now be different.
    This defines the negative side: The *distribution of impurities* - and that includes the doping elements and oxygen - *will change along the length of a crystal* - a homogeneous doping etc. is difficult to achieve.
    That segregation can be a large effect with a sensitive dependence on the growth rate is shown below for the possible doping elements; the segregation coefficients of the unwanted impurities is given in a table.

Effective segregation coefficients as function of the growth velocity
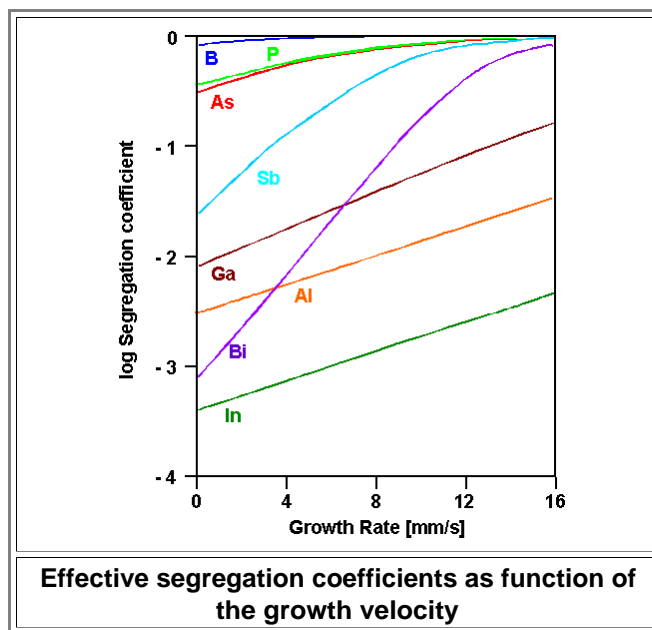
Atom	Cu	Ag	Au	C	Ge
k_{seg}	$4 \cdot 10^{-4}$	$1 \cdot 10^{-6}$	$2,5 \cdot 10^{-5}$	$6 \cdot 10^{-2}$	$3,3 \cdot 10^{-2}$
Atom	O	S	Mn	Fe	Co
k_{seg}	$1,25$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$8 \cdot 10^{-6}$	$8 \cdot 10^{-6}$

- We recognize *one* reason why practically only **As**, **P**, and **B** is used for doping! Their effective segregation coefficient is still close to **1** which assures half-way homogeneous distribution during crystal growth. Achieving homogeneous doping with **Bi**, on the other hand, would be exceedingly difficult or just impossible.

Present day single crystals of silicon are the most perfect objects on this side of Pluto! Remember that perfection can be measured by using the <u>second law of thermodynamics</u>, so this is not an empty statement!

- What the finished crystal looks like can be seen in the <u>link</u> . What we cannot see is that there is no other crystal of a different material that even comes close in size and perfection.
  Our silicon crystal is even rather homogeneous. The concentration of the doping atoms (and possibly interstitial oxygen) is radially and laterally rather constant, a feat not easily achieved.

- Our crystal does *not* contain dislocations - a unique feature that only could be matched by (really expensive) germanium (Ge) crystals at appreciable sizes (which nobody grows or needs).
  It also does not contain many impurity atoms. With the exception of the doping atoms (and possible interstitial oxygen, which often is wanted in a concentration of about **30 ppm**), substitutional and interstitial impurities are well below **ppb** if not **ppt** level (except for relatively harmless carbon at about **1 ppm**) - unmatched by most other "high purity" materials.

- Our crystal is as close to nirvana as a crystal could be. However, it still must contain the point defects that must have been there in thermal equilibrium right after solidification because they had nowhere to go during cooling down.
  The story going with that is found in <u>this link</u>.

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