

## 6. Materials and Processes for Silicon Technology

### 6.1 Silicon

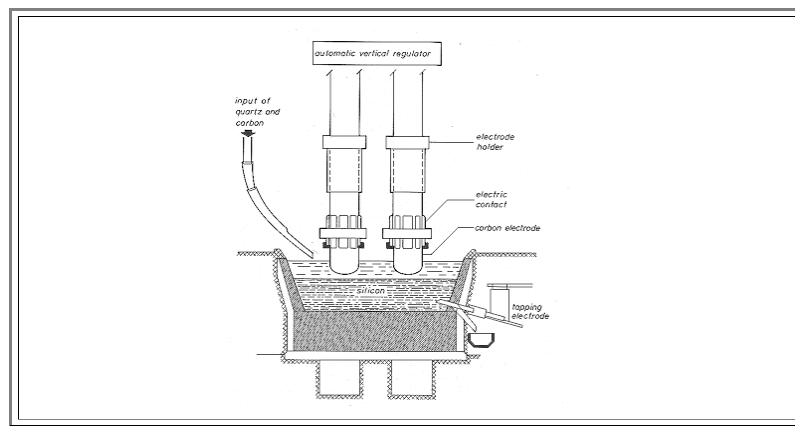
#### 6.1.1 Producing Semiconductor-Grade Silicon

##### Introductory Remarks

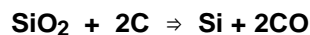
- It is written somewhere that in the beginning God created heaven and the earth. It is not written from what.
  - We do not know for sure what the heaven is made of but we do know what the earth is made of, at least as far as the upper crust is concerned. Interestingly enough, he (or she) created mostly **Silicon** and Oxygen with some 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 **SiO<sub>2</sub>** 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.
  - 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 **SiO<sub>2</sub>** - 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 **SiO<sub>2</sub>** 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**, **SiO<sub>2</sub>**, fairly clean, if obtained from the right source. Since there is no other material with properties so precisely matched to the needs of the semiconductor industry, and therefore of the utmost importance for our modern society, the production process of **Si** wafers shall be covered in a cursory way.

##### Producing "Raw" Silicon

- Fortunately, the **steel** industry needs **Si**, too. And **Si** 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? More or less like most of the other metals: Reduce the oxide of the material in a furnace by providing some reducing agent and sufficient energy to achieve the necessary high temperatures..
- Like for most metals, the reducing agent is **carbon** (in the form of coal or **coke** (= very clean coal)). The necessary energy is supplied electrically.
  - Essentially, you have a huge furnace (lined with **C** which will turn into very hard and inert **SiC** anyway) with three big graphite electrodes inside (carrying a few **10.000 A** of current) that is continuously filled with **SiO<sub>2</sub>** (= quartz sand) and carbon (= coal) in the right weight relation plus a few added secret ingredients to avoid producing **SiC**. This looks like this



- The chemical reaction that you want to take place at about **2000 °C** is



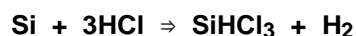
- But there are plenty of other reactions that may occur simultaneously, e.g.  $\text{Si} + \text{C} \Rightarrow \text{SiC}$ . This will not only reduce your yield of **Si**, but **clog up** your furnace because **SiC** is not liquid at the reaction temperature and extremely hard - your reactor ends up as a piece of junk if you make **SiC**.

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 do is to **purify** the **MG-Si** - about **10<sup>9</sup>** fold!

This is essentially done in three steps:

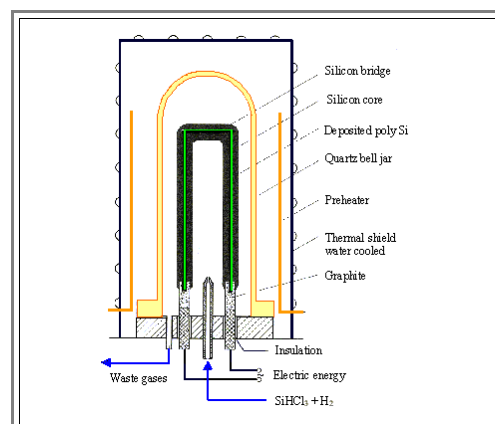
- First**, **Si** is converted to **SiHCl<sub>3</sub>** in a "fluid bed" reactor via the reaction



- This reaction (helped by a catalyst) takes place at around **300 °C**. The resulting **Trichlorosilane** is already much purer than the raw **Si**; it is a liquid with a boiling point of **31.8 °C**.
- Second**, the **SiHCl<sub>3</sub>** 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 - a process which we will encounter more often in the following chapters.

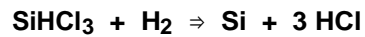
## Producing Doped Poly-Silicon

The doped **poly-Si** (not to be confused with the poly-**Si** layers on chips) used for the growth of single **Si** crystals is made in a principally simple way which we will discuss by looking at a poly-**Si** CVD reactor



- In principle, we have a vessel which can be evacuated and that contains an "U" shaped arrangements of slim **Si** rods which can be heated from an outside heating source and, as soon as the temperature is high enough (roughly **1000 °C**) to provide sufficient conductivity, by passing an electrical current through it.
- After the vessel has been evacuated and the **Si** rods are at the reaction temperature, an optimized mix of **SiHCl<sub>3</sub>** (**Trichlorosilane**), **H<sub>2</sub>** and doping gases like **AsH<sub>3</sub>** or **PH<sub>3</sub>** 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 place.

- On **hot** surfaces - if everything is right this will only be the **Si** - a chemical reaction takes place, reducing the **SiHCl<sub>3</sub>** to **Si** and forming **HCl** (hydrochloric acid) as a new compound:



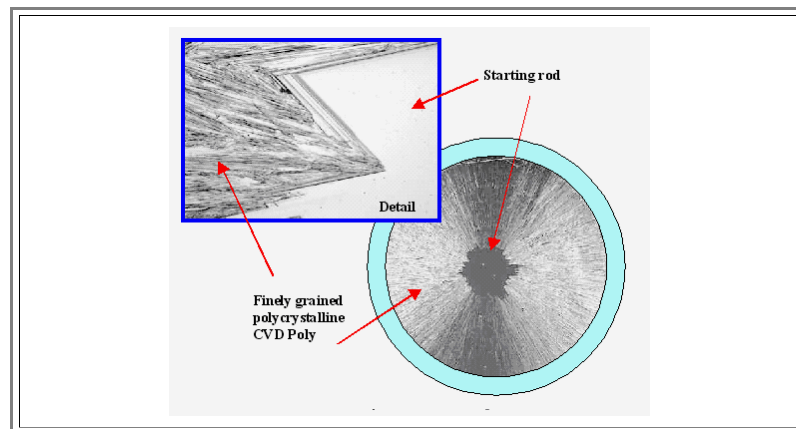
- Similar reactions provide very small but precisely measured amounts of **As**, **P** or **B** that will be incorporated into the growing polysilicon
- The **Si** formed will adhere to the **Si** already present - the thin rods will grow as fresh **Si** is produced. The incorporation of the dopants will produce **doped polysilicon**.

In principle this is a simple process, like all **CVD** processes - but not in reality. Consider the complications:

- You have to keep the **Si** ultrapure - all materials (including the gases) must be specially selected.
- The chemistry is extremely dangerous: **AsH<sub>3</sub>** and **PH<sub>3</sub>** are among the most poisonous substances known to mankind; **PH<sub>3</sub>** was actually used as a toxic gas in world war II with disastrous effects. **H<sub>2</sub>** and **SiHCl<sub>3</sub>** are easily combustible if not outright explosive, and **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 **H<sub>2</sub>** 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 **10.000 tons** of poly-**Si** are produced at present (**2000**) with this technology, which was pioneered by **Siemens AG** in the sixties for the microelectronic industry. (in **2007** it is more like **21.000 to** plus another **30.000** tons for the solar industry).

- Electronic grade Si** is not cheap, however, and has no obvious potential to become very cheap either. The link provides [today's specifications](#) and some more information for the product. Here is an example for the polycrystalline rods produced in the Siemens process:



- While this is not extremely important for the microelectronics industry (where the added value of the chip by far surpasses the costs of the **Si**), it prevents other **Si** products, especially **cheap solar cells** (in connection with all the other expensive processes before and after the poly-**Si** process). Starting with the first oil crisis in **1976**, many projects in the USA and Europe tried to come up with a cheaper source of high purity poly-**Si**, so far without much success.
- By now, i.e. in **2007**, demand for electronic grade **Si** is surging because of a booming solar cell industry. A short overview of the current [Si crisis](#) can be found in the link.