Semiconductor Technology from A to Z

Wafer Fabrication

Production of raw silicon

Starting Material: Silicon Dioxide

The silicon used in semiconductor manufacturing is obtained from quartz. In this process, oxygen — which combines with silicon extremely readily even at room temperature, and which in quartz is likewise present in combination with silicon as silicon dioxide — must be removed. This is done in an arc furnace using carbon, at temperatures that reach up to about 2000 °C in the hottest zone of the furnace. The oxygen separates from the silicon and reacts with the carbon (C) to form carbon monoxide (CO):

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

This equation summarizes what actually takes place in the furnace over several stages. In the cooler zone, silicon carbide initially forms; this then reacts with additional silicon dioxide in the hotter zone to produce silicon. Silicon carbide is therefore not an unwanted by-product but a necessary intermediate product; the ratio of carbon to quartz is set so that it is fully consumed again by the end of the process. At these temperatures, the carbon monoxide is gaseous and can easily be separated from the liquid silicon.

The raw silicon obtained in this way (metallurgical-grade silicon) is approximately 98 to 99 % pure. The remainder consists of impurities such as iron, aluminium, calcium, phosphorus, and boron. For use in semiconductor devices, this is far too impure by many orders of magnitude — these substances must be removed in further processes.

Purification of the Raw Silicon

Purification is carried out indirectly via a gaseous compound: the silicon is converted into trichlorosilane, which is purified by distillation, and solid silicon is then deposited from it again. The process is known as the Siemens process, named after its developer, and to this day still supplies the majority of the world's ultra-pure silicon.

Using the trichlorosilane process, many impurities are removed by distillation. The raw silicon reacts with hydrogen chloride (HCl) at around 300 °C to form gaseous trichlorosilane ($SiHCl_3$) and hydrogen (H_2):

$Si + 3HCl \rightarrow SiHCl_3 + H_2$

The impurities, which also combine with the chlorine present, only pass into the gaseous state at higher temperatures. This allows the trichlorosilane to be separated out. Only carbon, phosphorus, and boron, which have similar condensation temperatures, cannot be filtered out by this process.

The trichlorosilane process can be reversed, so that the purified silicon is subsequently obtained in polycrystalline form. This takes place with the addition of hydrogen in a quartz vessel containing heated, thin silicon rods (silicon seed rods), at around 1100 °C:

$SiHCl_3 + H_2 \rightarrow Si + 3HCl$
and
$4SiHCl_3 \rightarrow Si + 3SiCl_4 + 2H_2$

The silicon deposits onto the silicon seed rods, which grow over several days into rods roughly 150 to 200 mm thick. These are subsequently broken up and processed further as chunks.

The process is extremely energy-intensive, since the rods must be kept at temperature the entire time while the chamber wall is cooled. As an alternative, fluidized-bed deposition has become established: here, small silicon granules grow within a bed through which gas flows, which requires significantly less energy and operates continuously rather than in batches. However, its purity does not match that of the Siemens process, which is why this material is used primarily in the solar industry.

This is precisely where an important distinction lies: silicon suitable for solar applications must reach roughly six nines of purity (99.9999 %), whereas silicon suitable for electronics must reach nine to eleven nines. Using the Czochralski process, this polysilicon could already be converted into a single crystal; however, its degree of purity is still not high enough for the fabrication of semiconductor devices.

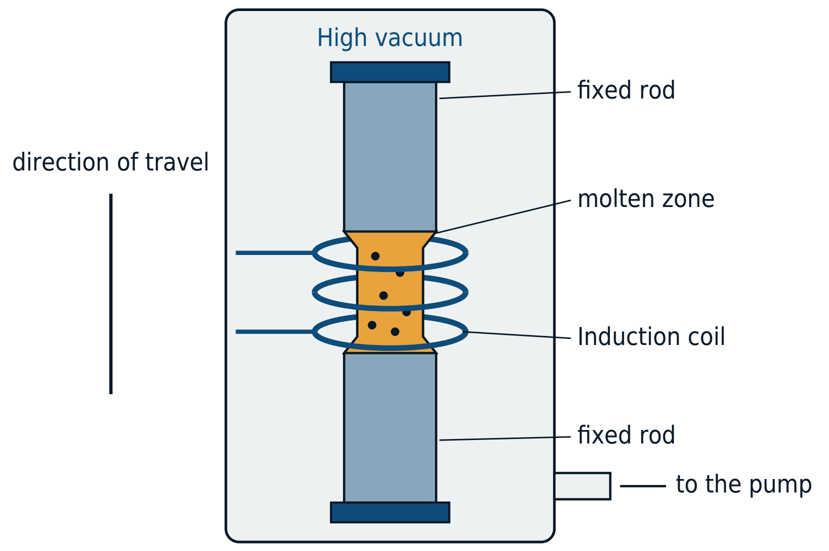
Zone Refining

To further increase purity, zone refining is used. A coil carrying a high-frequency alternating current is placed around the silicon rods. This melts the silicon inside the rods, and the impurities sink downward due to their high solubility in the melt (the surface tension of the silicon prevents the melt from flowing out). By repeating this process multiple times, the level of impurities in the silicon is reduced to the point where it can be further processed into a single crystal.

Illustration of zone refining

Zone Refining of a Silicon Rod

Surface tension holds the melt between the fixed ends



Impurities remain in the melt and travel along with the zone.

All processes are carried out under vacuum to prevent further contamination.

At the end of these processes, the silicon prepared for semiconductor manufacturing has a purity of more than 99.9999999 %, corresponding to less than one foreign atom per 1 billion silicon atoms.