ET3034TUx - 4.2 - Manufacturing of crystalline silicon

We have various types of silicon wafers such as monocrystalline silicon and polycrystalline silicon.

In this block I will give an answer to the question: how do we make these various types of silicon?

How can we make the silicon material pure?

The lowest quality of silicon is the so-called metallurgical silicon.

The source material of making metallurgical silicon is quartzite.

Quartzite is a rock of pure silicon oxide.

In the next animation the process of making metallurgical silicon out of quartzite is shown.

During the production the silicon is purified by removing the oxide.

This happens in a submerged electrode arc furnace.

The quartzite is moved into the furnace, where it is melted.

Using an electrode the quartzite is heated up to a temperature around 1900 degrees Celsius.

The molten quartzite is mixed with carbon.

The carbon source is a mixture of coal, coke and wood chips.

The carbon reacts with the silicon oxide.

I won't discuss the details of the reaction, which is rather complex, but the result is that the oxygen is leaving the furnace as carbon monoxide.

The molten silicon that is formed is drawn of the furnace and solidified.

The purity of metallurgic silicon is around 98 up to 99%.

70% of the worldwide produced metallurgical silicon is used in the aluminum casting industry to make aluminum silicon alloy parts which are used in automotive engine blocks.

The other 30% is being used to make a variety of chemical products like silicones.

Only around 1% of metallurgical silicon is used to make electronic grade silicon.

The silicon material with the next level of purity is called polysilicon.

In the next animation you see how out of metallurgical silicon, rods of polysilicon are produced.

The source material is powder of metallurgical silicon.

The metallurgical silicon is then exposed in a reactor with hydrogen chloride at elevated temperatures in presence of a catalyst.

The silicon reacts with the hydrogen chloride and starts to form trichlorosilane.

This is a molecule that contains one silicon atom, three chlorine atoms and one hydrogen atom.

The trichlorosilane gas is cooled and liquified.

Impurities with higher or lower boiling points are then removed using distillation.

The purified trichlorosilane is evaporized again in a different reactor and mixed with hydrogen gas.

Trichlorosilane reacts with the hot rods which are at a high temperature of 850 up to 1050 degrees Celsius.

The silicon atoms are deposited on the rod whereas the chlorine and hydrogen atoms are desorbed from the surface of the rod back into the gas phase.

As a result a pure silicon material is grown and this deposition method is called chemical vapor deposition.

As the exhaust gas still contains chlorosilanes and hydrogen, these gasses are recycled and used again.

Chlorosilane is liquified and distilled and reused.

The hydrogen goes through a cleanup process and is recycled back into the reactor.

In the animation we have seen a chemical vapor deposition furnace that leads to polysilicon rods.

This is the so-called Siemens process and consumes a lot of energy.

Another method is the production of polysilicon granules in the so-called fluidized bed reactors (FBR).

This process operates at lower temperatures and consumes much less energy.

Polycrystalline silicon can have an purity as high as 99.9999%, or in other words one out of million atoms is not a silicon atom.

Lastly, I would like to mention an alternative approach, that of upgraded metallurgical silicon.

In this process metallurgical silicon is chemically refined by blowing gasses through the silicon melt removing the impurities.

Although this processing is cheap, the purity of its silicon is not as high as the Siemens or the FBR approach.

The next step is making wafers out of the polysilicon.

But first we consider two methods to make monocrystalline silicon ingots.

Ingots are large blocks of crystalline silicon.

The monocrystalline ingots are solids that consist of one big crystal.

In the next animation you will be introduced to the Czochralski processing method.

Let's start with the Czochralski method, as developed by Polish scientist Jan Czochralski in 1918.

It is a method to grow single crystal silicon.

In this method, highly purified silicon is melted in a crucible at typical temperatures of 1500 degrees Celsius.

Intentionally boron or phosphorous can be added to make p-doped or n-doped silicon, respectively.

A seed crystal that is mounted on rotating shaft is dipped in to the molten silicon.

The orientation of this seed crystal is well defined.

It is either a 100 orientation or an 111 orientation.

The melt solidifies at the seed crystal and adopts the orientation of the crystal.

The crystal is rotating and pulled upwards, allowing the formation of a large, single-crystal cylindrical column from the melt.

This big single crystalline silicon block is called an ingot.

In this process the temperature gradients, rate of pulling up and speed of rotations are precisely controlled.

This process is further developed through years of advances and nowadays crystal ingots of diameters of 200 mm and 300 mm with lengths of 2 meters can be processed.

To prevent the incorporation of impurities this process takes place in an inert atmosphere, like argon gas.

The crucible is made from quartz, which partly dissolves in the melt as well.

Consequently, Czochralski monocrystalline silicon has a relatively high oxygen level.

The second method to make monocrystalline silicon is the so-called float zone process.

This is a process which results in monocrystalline silicon ingots with extreme low densities of impurities like oxygen and carbon.

The process is shown in the next animation.

The source material is a polycrystalline rod as processed in the earlier mentioned Siemens process.

The end of the rod is heated up and melted using a radiofrequent heating coil.

The melted part is put in contact with seed crystals.

Here it solidifies again and adopts the orientation of the seed crystal.

Again both 100 and 111 orientations are being used.

As the molten zone is moved along the polysilicon rod, the single crystal ingot is growing as well.

Many impurities remain in and move along with the molten zone.

During the process nowadays intentionally nitrogen is added which improves the control on microdefects and improves the mechanical strength of the wafers.

The advantage of the float-zone technique is that the molten silicon is not in contact with other materials like quartz as in the Czochralski method.

In the float-zone process the molten silicon is only in contact with the inert gas like argon.

The silicon can be doped by adding doping gasses like diborane and phosphine to the inert gas to get p-doped and n-doped silicon, respectively.

The diameter of float-zone ingot is generally not larger than 150 mm, as the size is limited by the surface tensions during the growth.

Next to monocrystalline silicon ingots, multicrystalline silicon ingots can be processed as well, as you can see in the next animation.

Multicrystalline and polycrystalline silicon consist of many small crystalline grains.

This can be made by melting highly purified silicon in a dedicated crucible and pouring the molten silicon in a cubic shaped growth-crucible.

Here the molten silicon solidifies into multicrystalline ingot.

This process is called silicon casting.

If the melting and solidification occurs in the same crucible it is referred to as directional solidification.

The cross-section of a multicrystalline ingot can go up to 70 by 70 cm and the height is typically 25 cm.

Now we know how to produce monocrystalline and multicrystalline ingots.

How do we make wafers out of them?

The answer is sawing as you can see in the next animation.

A disadvantage of the sawing step is that we waste a significant fraction of the silicon as a kerf loss.

The kerf loss is usually determined by the thickness of the wire or saw used for sawing and is in the order of 100 microns of silicon.

This is a large fraction of the ingot if we consider that typical crystalline silicon wafers used in solar cells nowadays are in the order of 150 up to 200 microns.

Sowing will logically damage the surface of the wafers, so this processing step is followed by a polishing step.

Silicon ribbon is a completely different approach to make wafers as you will see in the next animation.

Silicon ribbon does not face the problem of kerf losses, due to the simple reason that it does not include a sawing step.

Silicon ribbon is the last processing method I would like to discuss.

Silicon ribbon is based on a high temperature resistant string, which is pulled up from a silicon melt.

The silicon solidifies on the string and a sheet of crystalline silicon is pulled out of the melt like this.

The ribbon is then cut into wafers.

The surface is further treated before they are further processed into solar cells.

The electronic quality of ribbon silicon is not as good as that of monocrystalline silicon.

Summarized, we have discussed how out of quartzite we first make metallurgical silicon and then polysilicon.

Monocrystalline ingots are made using either the Czochralski or the float-zone process.

Multicrystalline ingots are made using a casting method.

Wafers are being made by sawing these ingots.

A method which does not have any kerf losses is the so-called ribbon silicon approach.

Now we know how we make the wafers.

Let's make solar cells out of them.

We will discuss the design rules in the next block!