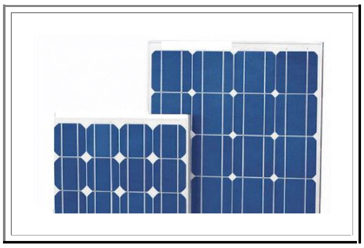
8.2 Making Bulk Si Solar Cells

8.2.1 Production Necessities and Silicon Starting Material

Boundary Conditions for Production

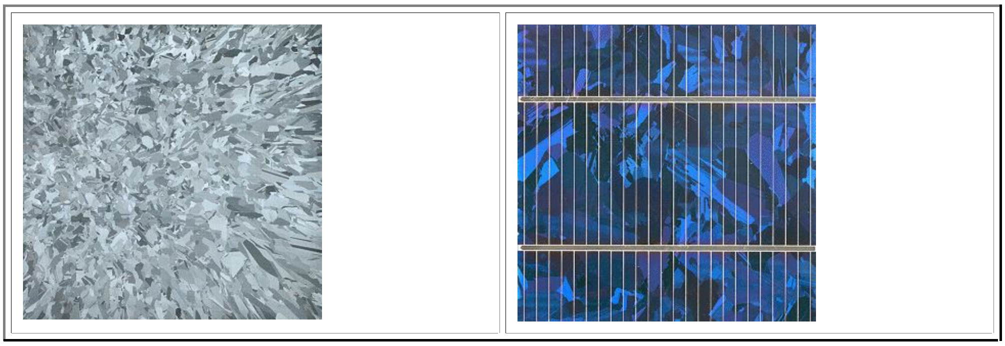
- It seems that a solar cell is just a **pn**-junction with a relatively large area, some defects and and some contacts, following relatively simple junction theory - as described before?
  - No - so far we have only looked at a large real **pn**-junction. A real *solar cell* that will end up on somebodies rooftop is a bit more than that. If it is a standard **2007 Si** bulk solar cell (***SC***), it must meet the following criteria on top of being just a large **pn**-junction:
- ***Processing Time***. A typical **12.5 cm x 12.5 cm** bulk Si solar cell comes off a production line at the rate of about **1 SC/s**.
  - If its size is **$150\ \text{cm}^2 = 1.5 \cdot 10^{-2}\ \text{m}^2$**, the factory produces **$1.5 \cdot 10^{-2} \cdot 3\,600 \cdot 24 \cdot 365 = 4.73 \cdot 10^5\ \text{m}^2$** per year; good for about **$7 \cdot 10^7\ W_p$** or **$70\ MW_p$**.
  - At at thickness of **300 µm** you used up **$45\ \text{m}^3$** of **Si** or about **105 t**. At a **kg** price around **(10 - 40) €/kg**, this costs around **(1 - 4) Mio €**
  - Nevertheless, you still have a very small factory according to **2007** standards. Presently, the first **1 GW_p** factories are being built. Whichever way you look at it, is simply means that process time is even less than **1s** per cell, that you process in large batches, i.e. many cells in parallel like in a furnace, or you just have several factories in parallel. However way you look at a **1 GW_p/a** factory - this is tough, man!
- ***Cost Decrease*** The productions costs of a solar cell must go down about **5 % - 7 % /year** for the next **10 - 15** years.
  - If you can't meet this goal this, you close your factory and go bankrupt. There is no market for solar cells per se, there is only a market for power plants on roof tops (or other easily available cheap areas) with a well-defined price for the **kWh** produced.
  - The price in most countries is defined by politics and decreases with **5 % - 7 %** per year (in Germany it is the "**Energieeinspeisegesetz**" (***EEG***); presently emulated by many other countries). If there is such a well-defined price decrease for energy, people are only willing to pay for a solar module if its price decreases at the same rate. I you can't meet this goal, chances are that your competitors can - and that will be the end of *your* business while *they* will roll in money.
- ***Efficiency Increase*** The efficiency of your solar cells must go up by about **1 %** (absolute) every **12 - 18** month before it might level out around η **= 20 %**.
  - There are $\eta \approx$ **20 %** solar cells on the market right now (Sunpower Corp.), proving that you can get efficiencies that high even in a (presently limited) mass production. If you competitor manages to get his efficiencies up and you don't - see above.
  - All serious companies therefore are working very hard on improving efficiencies -while still lowering costs.
- ***Key Material Supply*** Your solar cell will use up less of the key materials, especially **Si**, meaning it becomes thinner.
  - Not only does this save costs - there is simply not enough **Si** around at present (**2007**), to make all the solar cells the market would buy. Saving on **Si** thus makes a lot of sense.
  - If you can make your cell thinner, you can go farther with the **Si** you managed to buy. However, you cells are mechanically less stable and tend to break more easily.
- ***Business Growth Rates*** The solar cell you make is just one of many solar cell made world-wide per year - and their number increases with about **30 % - 40 %**.
  - You have exponential growth at an extremely high growth rate and what that means has been described very briefly in the context of microelectronics in chapter 5.3 and in somewhat more detail in the link. In fact, much of what has been stated (and meanwhile observed) in the microelectronic business will repeat itself with solar energy, just more so (there will be far more money involved as soon as solar energy can be measure in **%** of the total energy needs of the world).
- ***Summing Up*** Be prepared for some turbulent times in solar cell **R&D** and production! Watch some companies grow from nothing to Microsoft proportion and watch some people getting rich very fast
  - Maybe on of those winners will be *you*?

Silicon Starting Material



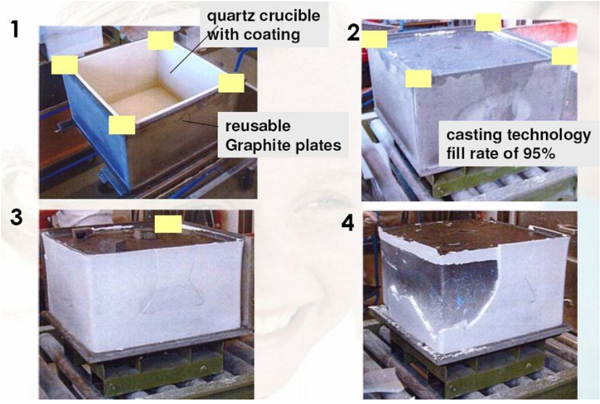
- You either start with single crystalline **Si**, i.e., more or less regular wafers, or with what is called **multi-crystalline Si**
  - If you go for single crystalline **Si**, you do everything pretty much as already described except for the following points.
    - You cut your crystal into an almost square shape because you loose to much area in your module if you "fill" it with round solar cells as made from regular wafers. So you must find the best compromise between wasting expensive single crystal **Si** or module area. The picture shows somewhat different solutions obviously because of different wafer size.
    - You try to stay cheap. You might use slightly dirtier **Si** for growing your crystal and you might grow them somewhat faster allowing a few dislocations or other defects not acceptable for microelectronics.
    - You cut your crystal into very thin wafers, as this as you can make it, say **250 µm** (instead of **(600 - 800) µm** used for microelectronics).
    - You do not produce wafers with a highly perfect and flat surface. You may just etch off the saw damage and leave it that.
  - There is nothing really new, so we will not go into any more detail here but take a slightly closer look at multi-crystalline **Si**.

- Multi-crystalline **Si** is simply coarse-grained poly-**Si** but since the name poly-**Si** is already taken, multi-crystalline **Si** is what it is called.
  - The picture below shows an example.



- Multi-crystalline **Si** is produce by **casting** and cutting. As raw **Si** you must use rather clean electronic grade **Si** coming straight from the Siemens process. Now melt this poly-**Si** it and cast it into a mold. That sounds easy but their are a few catches:
- **1. Melting point density anomaly**. **Si** belongs to the few material that do not contract upon crystallization but **expands** - by a whopping **10 %**!
  - Producing a sizeable lump of **Si** by simple casting would be equivalent of casting ice (solid $\mathbf{H_2O}$) at very low temperatures, say **80 K**. Pour you molten ice (= water) in a bucket kept at **80 K** and watch what will happen. A major explosion will happen!
  - If you just leave your bucket around at low temperature, the surfaces will cool down first and start to crystallize. Liquid water then is trapped inside a solid and tremendous forces will develop as soon as it crystallizes an tries to expand.
  - What we have to do is to keep the surface of the **Si** liquid and crystallize slowly from the bottom only. The crystal forming then can expand upwards and everything will be well behaved. The catch, of course, is that we need to control the temperature *and* the temperature gradients closely, taking into account that a lot of crystallization energy is released that needs to be taken out of the system. No is not a serious technical problem - except that solving it takes money and that you have to wait longer for your **Si** melt to crystallize and cool down (more money).
- **2. Reactivity of Si**. We have poured some liquid Si into a mold, cooled it down properly without encountering problems, and now want to take it out of the mold and reuse the mold for the next batch.
  - The problem now is that your **Si** is firmly bounded to the walls of your mold if didn't take proper precautions. In chemistry circles, **Si** is known as an **universal solvent** because everything dissolves in liquid **Si** and thus sticks to the solidified **Si** in a major way.
  - Of course, you can cut your **Si** ingot free, destroying the mold; all that takes is a lot money for molds. this is obviously not a good idea.

- A good idea is to use some "grease" that squeezes between the **Si** and the old (and covers the **Si** surface) because it lowers the surface tensions of the system.
- In other words, use a **liquid encapsulation technique** - we already encountered this trick when we looked at the growth of III-V single crystals.
- Now we encounter a new twist to an old technique: As far as casting **Si** is concerned, everything from now on is top secret. Exactly how is to done has never been fully disclosed, so we will not belabor this point anymore. The picture below shows how it is done in reality

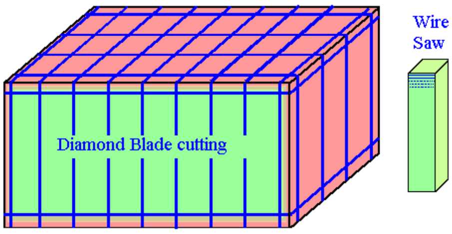


- The yellow patches hiding something have been placed by the source. What you see is the solidified white "grease" and a sizeable chunk of **Si** in the **4th** picture. Now we can cast *and* reuse the mold, but we are still left with a problem.

- **3. Cleanliness and Structure**. We don't just want any big chunk of **Si**, we want it to be *multi-crystalline* , meaning coarse- grained, and we certainly don't want it any dirtier that the raw **Si** we poured into the mold.
  - So we have to make damned sure that the liquid **Si** - which, after all, is an universal solvent - doesn't pick up some dirt from its surrounding.
  - We also have to make sure that crystallization produces big grains in some **columnar** arrangement (why we need this we will see right below). This brings us back to an optimized temperature control and some secret issues I can't tell you concerning casting **Si**.
- Now we are done. If you actually could obaibn some poly-**Si**, that is. The solar energy business right now (**2007 /08**) is having a supply-side crisis; there just isn't enough electronic grade **Si** around for everybody. You should have some vague idea by now, why it took **>10** years and a lot of work and money to come up with an industrial casting process that meets all requirements (including costs).
  - All that's left to do is to cut the big block of **Si** into very thin, standard-sized, square, multi-crystalline **Si** wafers, taking care that grain boundaries are always at right angles to the surface.

Cutting Silicon Ingots into Wafers

- Why is it important to have no grain boundaries running parallel to the wafer surface?
  - Because grain boundaries are always efficient recombination centers and thus screen minorities "below" from making to the the front side side contacts and take out minority carriers from above that happen to come by.
  - If the grain boundaries are at more or less right angles to the surface of the wafer, they are still bad but far less so then at **90^{o}**.
- So we first cut our huge **300 kg** ingot into square columns as indicated, taking care to cut off the "dirty" (= reddish) surface-near regions; especially the bottom regions, where grain nucleation started and we have fine-crystalline **Si**, and the top region, where all the dirt with low segregation coefficient will be found. This we do with a big diamond-blade saw.



  - The columns left have the right wafer size and the grain boundaries inside all are more or less at right angles to the major axis if our casting process was OK.

- All we need to do now is to cut the column into very thin wafers (about **250 µm** at present (**2008**)), making sure that the cutting grooves are very thin in order to minimize cutting losses.
    - Easy? **-** No, very difficult. In fact, a new process tool needed to be invented, the industrial-scale, extremely precise wire saw. A very fine but very strong closed wire loop runs around the **Si** column many times, moving fast, under high mechanical tension, and in an abrasive slurry.
    - In essence, its like a gigantic egg cutter with moving wires, just a bit more expensive. Cutting off the joke: the **Si** multi-wire saw, cutting fast, in parallel, and with very high precision, is an essential piece of equipment for multi-crystalline **Si** solar cells and you will thus not find much information about process details floating around.
- Just in case you didn't notice: We now have two *special* semiconductor technologies here that originated from solar cell technology: casting and wire-saw cutting.
    - In fact, cutting **Si** with wire saws is now moving into the wafer business for microelectronics, too.
- What we have no are square slices or wafers of multi-crystalline **Si**, about **250 µm - 300 µm** thick and up to **(150 × 150) mm^2** in lateral size;.. And, yes, you're right - they fracture very easily.
    - Right after cutting, the surface of the multi-crystalline wafers is "destroyed"; or more precisely, on both sides are layers full of "saw-damage" that are electronically "dead". The thickness of these layers scales with the size of the hard grains in the abrasive slurry and thus will be in the range of several **µm**.
    - This surface damage must be removed before we can start to make a solar cell. Fortunately this is easy if, once more, something of a black art: Certain chemicals attack and dissolve "damaged **Si**" far faster than perfect **Si** (CMP relies on this!). So all we have to do is to put a batch of wafers in a chemical tank for a while.
    - Since we have a **batch process** with, say, **100** wafers, we can allow a process time of ≈ **100 s** and still meet our goal of **1** Solar cell per second.
- With the "over-etched" wafers we can now start solar cell production