Segregation and Striations in CZ Silicon

General Remarks, Macrosegregation, and Controlling Crystal Growth

Segregation in Silicon, a ultra-high purity material, seems to be an oxymoron. What, exactly, is there to segregate?

- A lot of atoms other than silicon, And a lot of vacancies and self-interstitials! Most prominently are the dopant atoms, specified by the customer, usually either arsenic (As), boron (B) or phosphorous (P), in concentrations between 10^{14} cm^{-3} to 10^{19} cm^{-3}, which translates to about 0.5 ppb to 20 ppm. One ppm (= 1/1000 ppb) translates to 0.0001at %, far below anything interesting in iron and steel.
  Then we have 1 ppm oxygen (O) and roughly 0.1 ppm carbon (C) around, plus the rest of the periodic table at concentrations below ppt or ppqt (look it up).
  Not to forget, close to the melting point we have the equilibrium concentration of vacancies and self-interstitials. We don't know exactly how large those concentrations are - but they must be around or just below ppm.

- The customer of silicon wafers specifies the allowed bandwidth of the average doping concentration per wafer (e.g. ± 5 %) *and* the maximum local deviations he can tolerate within one wafer. Same thing for the oxygen concentration. It should be, for example 6.5 · 10^{-17} cm^{-3} ±10 %.

The message is clear: With respect to segregation it is not just the absolute concentration that counts, but the deviations from some specified value, however small.
The steps for making a Si crystal are covered in this link. Here we assume the role of the crystal grower. We need to worry about:

1. *Macro* segregation along the length of the crystal. It determines the average values for all point defect concentrations along the length of the crystal. Typically these average concentrations increase from the top (first part to crystallize) to the bottom of the crystal.
   If we want to make money, we need to keep these concentrations within the accepted bandwidth in as large a part of the crystal as possible.
2. *Micro* segregation; it determines the distribution within one wafer. Typically the maxima and minima of the concentrations are found on concentric rings caused by a general striated distribution of the concentration maxima and minima.
3. *Precipitates* of vacancies (typically small voids), interstitials (typically dislocation loops) and oxygen precipitates (SiO_2). These point defects will get supersaturated during cooling and thus have a strong tendency to cluster. They interact in many ways and are likely to get heterogeneously nucleated by segregated impurities like carbon. The trick is to produce many very small and harmless clusters instead of a few big and deadly ones.

- The question we must ask ourselves is: What can we crystal growers do about this? What kind of "buttons" do we have that we can play with to produce an optimal crystal? I'm not talking science and theory here. I'm talking about standing in front of a big machine and setting the controls to get started, and adjusting the controls while the process is running (for many hours, by the way).
  Well, before we talk about fixes to a problem, we first need to understand the problem. We are serious technicians and not politicians, after all.

As far as *macro*segregation is concerned, we only need to look at the effective segregation coefficients to see that we are in serious trouble. Here is the figure from the "Nirvana Si" module once more:

Effective segregation coefficients as function of the growth velocity
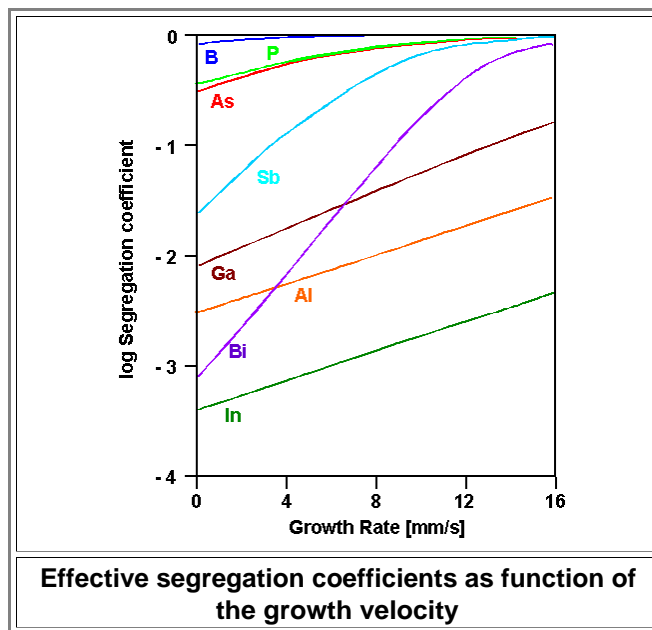
- Oxygen is not included because its concentration is not constant. The melt slowly dissolves the SiO_2 lined crucible and thus gradually increases the oxygen concentration, precluding analysis by the usual theories. Nevertheless, oxygen does show strong segregation effects.

The problem is clear: Some effective segregation coefficients are extremely small, and some change a lot with increasing growth speed. The first property will lead to strong *macro*segregation because in the beginning of solidification the concentration is the crystal is far lower then the nominal one, whereas towards the end it must be far larger.

The second property leads to large concentration changes with fluctuations in the growth velocity, i.e. to strong *micro* segregation effects.

- Not so good! So what can be done to ameliorate those unwanted segregation effects? What's in the crystal growers tool box? Let's look at the schematic drawing of a **Czochralski** crystal-puller again , this time with adjustable parameters shown in **red**.

Parameters during CZ silicon crystal pulling
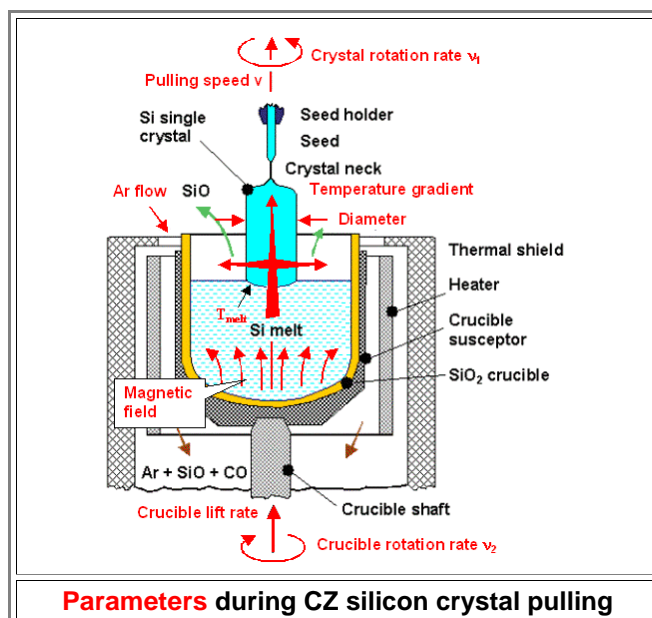
- Let's start to look at the parameters, in particular the "easy " ones that actually do have a button on the control panel. What we have are:

  - *Temperature T*. Of course there is a button for the temperature. Unfortunately it must be firmly set and actively controlled to assure that at the solid liquid interface we have *always exactly* the melting temperature T_{melt} .
  - *Temperature gradients*. Both, the longitudinal one along the crystal axis (G_{lo}) and the radial ones (G_{ra}), are of prime importance and given to some extent by the fixed general geometry of the assembly and the adjustable parameters like argon flow rate, crucible lift rate, and those secret ingredients not shown here. Essentially the temperature gradients must stay relatively constant and do not lend themselves to control segregation.

- *Growth rate* or *pulling speed* **v**. Here we have an "easy" button that simply adjusts the speed of moving seed holder plus growing crystal upwards. We thus have an extremely well-defined macroscopic growth speed **v$_{mac}$** at the solid-liquid interface. Note that in contrat to casting the interface itself does not move!
- *Crystal diameter* **d$_{cryst}$**. While it is certainly important to keep the diameter constant and the cross-section nicely circular, there is no direct button for this. The diameter is a function of growth speed **v** and the temperature gradients *G*. It needs to be actively controlled by a feed-back circuit that relies on an (optical) sensor for measuring the actual diameter, and that changes **v** a little bit to keep it constant. The diameter is changed a lot only at the beginning and the end, to produce the typical cones by (mostly) changing **v**.
- *Crystal rotation rate* ν_1. The crystal rotates with roughly 15 rotations/minute, and the rotation rate is adjustable by an "easy" button. This ensures that differences in the radial symmetry are averaged out and the crystal is perfectly round. Rotating the crystal also stirs the melt to some extent.
- *Crucible rotation rate* ν_2. Now we have a parameter with an "easy" button that we can use to control segregation. Rotating the crucible (either in the same "handiness" as the crystal or (more common) the other way around) with roughly 5 rotations/minute will produce some flow in the melt (in addition to the convective flow) and thus changes the atomic concentrations close to the interface. Moreover, it will also change the way oxygen is incorporated into the crystal because liquid slowly dissolves the crucible walls (always quartz; SiO_2) and the flow pattern influences how it is transported to the solid-liquid interface. Here we have a parameter that interferes mightily with segregation.
- *Crucible lift rate*. You want to keep the solid-liquid interface at about the same position inside the puller to ensure a constant thermal environment. You must then move up the crucible. There could be an easy button but there is little leeway for manipulation.
- *Argon flow rate*. Blowing harder tends to make things cooler. Must be used with care because its primary purpose is to control the CO and SiO "smoke" coming off the hot melt.
- *Magnetic fields* in the melt; pointing hither or thither with all kinds of field strength. Not so easily done (you need rather large electromagnets) but definitely standard. There are a lot of possible arrangements for magnetic fields; we have a large parameter space to fool around with. What happens? Since liquid silicon is partially ionized and a good electrical conductor, flow patterns in the liquid are actually always electrical current patterns too, that interact with magnetic fields.
  Things get rather complicated at that point. In essence, one can use magnetic fields to either induce liquid flow or to hamper it. If you know what you do, you can actually control the flow to some extent. In particular, you can reduce *fluctuations* in the flow pattern that are responsible for parts of microsegregation.
  There are quite a number of eays buttons for the magneiic fields, needed for controlling direction and strength of the magnetic field.

You guessed it! The first law of applied science asserts itself once more: *There is nothing more practical than a good theory!* Fiddling with *any* button changes *everything* - not just some segregation property. You need a good model or theory that can be cast in software and then "automatically" adjusts all parameters all the time to values that are "just right". We have the Goldilock principle at work here, and you, the operator, are not even allowed to touch the machine as soon as it has been started up and runs on some pre-selected routine.
The major parameters to work with are the rotation rates and the magnetic field - and this are the difficult parameters, where it is far from obvious what some changes in the settings will produce.

- The industry does have good working theories and models (that are not much talked about) and can do amazing things with respect to the homogeneity of its huge crystals. There are limits, however. The article in the link will go into details
  For example, the segregation coefficients of gallium (Ga), aluminum (Al), or antimony (Sb) are much smaller (and thus worse) than those of arsenic (As), boron (B) and phosphorous (P). That is one of the reasons why these elements are (almost) never used for doping a crystal.

Link
CZ Si Article

- All you can do is to go for the best compromise. Rotating crystal and crucible is essential for almost everything concerning the uniformity of the crystal at large - but that also produces the *striations* and thus specific microsegregation as we shall see in the next section.

Microsegregation and Limits

This part is heavily connected to the "Segregation Science" module cluster. You should at least browse through these modules before reading on. I cannot dwell at length at all the special words and topics that come up here but have their roots in the segregation science modules.

Link
Segregation science

What we always find in silicon crystals is a striated distribution of everything we care to analyze. In other words, the maxima and minima of the concentrations found on a planes that follow the shape of the solid-liquid interfaces. Illustrative pictures and more explanations to the geometry can be found here.

- In a *simple* model the loci of extreme concentrations form a system of nested bowls that have about the shape of the solid-liquid interface at that point in time when the respective "bowl" solidified.
  In a less simple but more *accurate* model, the loci of extreme concentrations are on a tightly wound spiral akin to long drill chips, looking roughly like this (excuse my limited drawing skills):

Loci of highest (or lowest) impurity concentration
inside the crystal
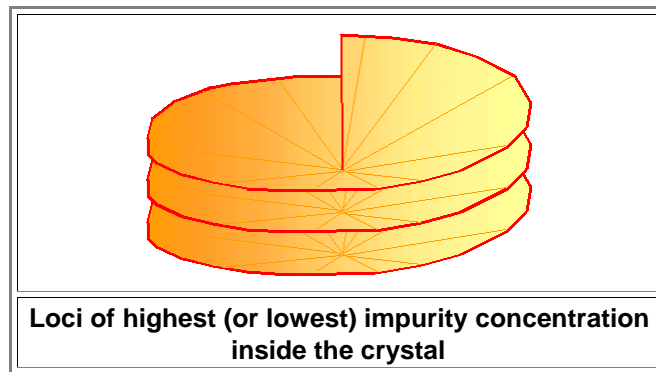
- Nested bowls or spiral - it maks hardly a difference when you look at a <u>cut in radial direction</u>. Structures like that can only be caused by a rhythmic, quasi-periodic modulation of the average growth speed **<v>**!
- Did you realize the conundrum I just posed? No! Then let's quickly recall what we know about *casting*; we'll need it:

  - The <u>decisive quantity</u> controlling the solid-liquid interface geometry (planar, cellular, dendritic) for *all* solidification processes is the ratio of the temperature gradient *G* and the growth velocity **v**, *G*/**v**. Both parameters change a lot during casting and subsequent cooling. It is obvious that they *cannot be controlled* directly and independently - no dials for that on your casting machine. You do get macro- and microsegregation in cast objects, and microsegregation may appear in the form of striations.
    In <u>this module</u> I discussed striations in some detail and posited that rhythmic fluctuations of the growth speed occur either due to external disturbances of a periodic kind, or because some kind of self-organization of local "stochastic oscillators" at the more or less chaotically moving solid-liquid interface occurs
    In stark contrast to casting, when we grow a silicon crystal (or any other crystal) with the Czochralski method we have:

    - A definite and externally controllable constant macroscopic <u>growth speed</u> v_{mac}.
    - Definite and relatively constant <u>temperature gradients</u> *G* that are (within limits, of course) independent of the growth speed.
    - A solid-liquid interface that actually doesn't move at all but is always at the same place and thus should be rather well-defined and non-chaotic.

  - In short: we have ideal conditions for testing all <u>those theories</u>. I'm not aware that this has been done, however. Part of the reason for this is that big silicon crystals are just far to valuable for sacrificing them to test some theories that are not all that important for the silicon business.

- Anyway, the conundrum is: How can the growth speed fluctuate in a quasi-periodic "rhythmic" fashion if it and everything else is solidly fixed?

  - The answer is: because of the rotation! The macroscopic growth speed v_{mac} is indeed fixed to a precise and constant value but that need not be true for the microscopic growth speed v_{mic}! It could fluctuate around v_{mac} as long as $<v_{mic}> = v_{mac}$. The question is: why should it do that?
    The answer is: We have a well-defined axis of rotation, and we have lateral temperature gradients. The temperature decreases from a maximum value somewhere in the center of the freshly grown crystal to smaller values on the outside. This gradient has a radial symmetry, meaning that the way the temperature goes down from the center to the outside is about the same in all radial directions. That implies that the temperature gradient also has an axis: the loci of the maximum temperatures, running roughly up the center of the crystal.
    The rotation axis and the thermal gradient axis are thus *almost* identical - but never *exactly* so. It's just a bit hotter on one side of the crucible than on the other one for all kinds of possible reason. What the growing crystal then experiences is comparable to this:
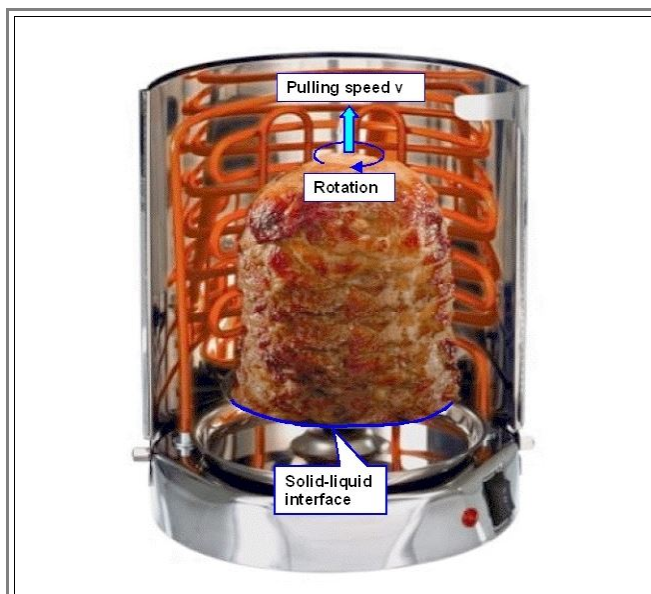
CZ Doener puller for manual operation

The secret of Doener Kebab revealed: You pull it with the Czochralski (CZ) method. I leave it to your (rotten) fantasy to come up with the kind of liquid needed for this.

When we "pull" the meat for a doener kebab, the radial thermal gradients, as shown above, are far more asymmetric than during pulling of a Si crystal. It's just much hotter in the back compared to the front. That means that any point on the doener meat surface experiences a rhythmic up-and-down in temperature.
And so does any point on the *solid-liquid interface* ! All the points on the interface that experience the maximum temperature at the same time are found on a line from the center straight to the outside (a radius in other words). When we pull the crystal up, the "hot line" screws up into the crystal, forming the kind of spiral shaped surface that I tried to picture above. The distance between subsequent striations is constant and given by the ratio of growth rate and rotation rate.

Serefe! We have microsegregation in silicon crystals covered!

Or do we? Not really. On occasion people grow crystals in some CZ set-up without rotating anything - and find striations! The NASA plus the German Space Agency and probably other lunatics too, grow crystals up there in the spacelab to figure out exactly what causes these nonrotational striations [2]. Obviously, looking into this is worth some 50 million $ or more to somebody. In essence, these non-rotational striations are blamed on peculiars of the melt flow, even in small liquid droplets that crystallize. Experimental evidence for that comes from the fact that magnetic fields, that interferes in some tricky but well.understood way with the flow in the liquid, can wipe out striations, induce them, or make irregular once quite regular - depending on what you do with it.

Nevertheless, the doener model goes a long way in explaining the main features of striations in CZ-pulled Si crystals correctly. Here are two pictures of striations in silicon single crystals:

Colors encode an electrical parameter of a solar cell that was made from the silicon. Details can be found here.	The white spots are etch pits delineating "swirl defects"

Striations in single crystalline silicon (Si)

- In the right-hand picture we probably see the effects of atomically dissolved impurities including the intentionally introduced doping element and the still present impurities.
  The right hand picture shows "big" defects, mostly agglomerates of self-interstitials that nucleated at some segregated impurity (possibly carbon in this case).

We have, it appears, a relatively clear idea of how striations in (some kinds of) single crystals come about. They exist because their is some rhythmic "distortion" impressed on the system. We do not need really self-organization.

- Well, yes - but I have a strong feeling that we would get self-organized striations, too, if we were to stop all that rotation business and just grow (somewhat warped and crooked, to be sure) crystals straight from the melt.
  I can't prove that, however, so I stop here and must point out that there is a somewhat involved advanced module that gives an example of exactly how self-organization can lead to rhythmic pulsing of an electrochemical system, and what we might be able to learn from that for striations in solidified objects like wootz steel.

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1) That's how you toast to your Turkish friends, drinking beer and eating a doener kebab (the S should actually have a little hook called cedille on the bottom). Alternatively your can say: Prost, Cheers, Kampai, Skål, or just shut up and enjoy your beer.

2) Helmut Kölker: The Behavior of Nonrotational Striations in Silicon; Journal of Crystal Growth **50** (1980) 852-858

Link Hub: Segregation Science

Special Modules in Segregations Science:

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