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Lecture – 03 Substrate (Continued)

Welcome back. This is a course on Fundamentals of Micro and Nanofabrication. This is a follow-up lecture that discusses the details of substrates. In the previous lecture, we looked at what sort of materials are available in the market, what are its characteristics and specifications. I very briefly and very generally introduced the concept of crystal growth, specifically the Czochralski method of growth. In this lecture, we will go into little more details of the concepts such as supersaturation, zone refining, distribution coefficient, etcetera.

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In order to understand crystal growth, the most relatable example is probably to understand something that we are all familiar with; the solution of glucose or sugar in water. If you take water and try to dissolve glucose in it, at some point (say at 91 g), no more glucose gets dissolved, and you get a saturated solution. That is the solubility of glucose in water. Now, if you take the same amount of water at 25°C and put 100 g glucose in it, not all of the glucose will dissolve, because the system is not under equilibrium. It starts slowly dissolving. At a point in time when you have 5 g glucose

dissolved, it is an unsaturated solution. If you give it long enough time, the glucose - water system will reach equilibrium which is when the solubility limit of glucose in water is reached (91 g). At that point, the 9 g that is left over is just going to sit at the bottom of the cup because it cannot go into the solution anymore. This solution is at equilibrium and is called a saturated solution in this case.

Now, if you heat this solution up to 50°C, the solubility actually goes up (say more than 100 g) and the 9 g that was sitting at the bottom would also dissolve away. What you now have is an unsaturated solution because the solubility of glucose at 50°C is even more than 100 g. This system is also at equilibrium. Now, if you cool the system down to 25°C (remember the equilibrium solubility limit at 25°C is 91 g) but, right now you have a system that has 100 g glucose in the water. This is a supersaturated solution and it needs to make a transition into its equilibrium saturation state, but that transition may not happen instantaneously.

The system is not under equilibrium and if you allow it a nucleation event, then the excess glucose will precipitate out. As it is slowly precipitating out from a solution, you can, through some tricks get a crystalline glucose precipitate. Now the solution again has 91 g glucose in the water and 9 g as a precipitate. Here, you are going from a supersaturated solution to a saturated solution. Through some trick, you have made the system go beyond its equilibrium capacity to carry that material, and then slowly and controllably precipitated that extra material in crystalline form.

This is how we make misri or rock candy. You can create these very fancy looking candies which are essentially crystals of sugar, with some color in it in this case. What you are essentially doing, is crystal growth: you start with polycrystalline sugar that you can buy in the market, dissolve it in water and by this process of supersaturation to saturation extract larger grains. Here is a QR code of the process of making rock candy at home for those of you who are experimentally inclined.

These are not a single crystal, but they are still larger sized. If you were to do this process very precisely, maybe you can even get a single crystal of sugar. Fundamentally, that is what we are trying to achieve with silicon using the Czochralski method.

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Unlike glucose, we are not dissolving silicon in a solution, instead, we are melting it. The fundamental concept remains the same. How do we achieve supersaturation in a melt? By cooling it to below its melting point. We take a melt and start cooling it down, below the melting point of silicon. So, the liquid silicon or the melt that is below its melting point is now in supersaturation.

This unstable system wants to become solid. By controlling that process, (in this case by incorporating a seed), we are hoping to grow a single crystal of silicon. For example, here is a gif where the water has been supercooled, and then you introduce a seed of ice and that seed of ice suddenly creates a nucleation event, which makes the whole of the water crystallize into a solid. This is what the Czochralski method is trying to do.

The only difference is that in the case of water-ice, the seed is polycrystalline and the crystallization is uncontrolled, causing the formed crystal of ice to be polycrystalline and uncontrolled. Whereas in the Czochralski method, this whole process is much more precisely controlled and because the seed is single crystalline, you grow a single crystalline ingot.

This is how we use supersaturation to form single crystalline ingots. An added advantage of this method is we get zone refining. The solid that we make is purer than the liquid that we started with. So, there is a purification that comes for free while we are doing crystal growth. Why that happens is the subject of the next few slides.

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In order to understand zone refining, you need to know what binary phase diagrams are. The concept of the phase diagram is not part of the course curricula but is necessary to understand the crystal growth. Here is a video, and a QR code to access it. The things to focus on in that video are unitary and binary phase diagrams, the lever rule and binary phase diagrams with limited and unlimited solubility. This is an optional reading.

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A quick primer on what is a eutectic binary phase diagram. You are looking at a plot of temperature versus concentration. This is a binary phase diagram between material A and

B. We have 100 % pure material B on the right, 100 % pure material A on the left and alloy compositions between 100% A and B in the middle. In our case, this could be silicon. We want pure silicon, but it has certain impurity, so, we have an alloy of impurity and silicon. Suppose that impurity is iron. What you would then be looking at is the binary phase diagram between silicon and iron where, on the left is pure silicon, on the right is pure iron and all the transition alloys in the middle. If you have 99.99 % pure silicon, you are very close to the origin, but not exactly at 0.

We are going from melt to solid by reducing the temperature. We start with liquid somewhere from the L region and come down to below the liquidus line, where we form a two-phase system. The system does not instantly cool but forms a mixture of a liquid and a solid. If we cool down even further, we reach the solidus line, below which you form a homogeneous solid.

When you are growing crystals from a melt to solid using the Czochralski method, the area of interest in a phase diagram is the portion where you are starting from a moderately pure liquid and going to a solid through the transition region L+ α . From the next slide, we will just focus on this rectangle. In this region, the melt will phase segregate into a solid α (relatively pure silicon, in this case) and a liquid L (the remaining silicon melt, relatively more impure), with the concentrations of those phases given by the solidus and the liquidus lines at that temperature.



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If you zoom into that region, you see the liquidus line, the solidus line, and the yellow region where the system segregates into two phases. Above this $L+\alpha$ region, you form a single liquid phase and a single solid phase below it.

Let's start with the material that has one impurity of concentration C_o . As you start reducing the temperature of the melt, in the yellow $(L+\alpha)$ region, it phase-segregates into two materials; one at the liquidus line, one at the solidus line. The concentration of impurities in this frozen (solidified) material (α phase) is lower than the melt you started with. The presence of this yellow region ensures that when you freeze a material with an impurity concentration C_o , the solid that you form will have concentration $k \cdot C_o$, where k < 1; k is the **distribution coefficient**.

As you take this impure melt (L, concentration given by the liquidus line) and reduce the temperature further, once again it will enter the yellow region and phase segregate into solid α and melt L. Now, the impurity cannot be created or destroyed. So, where do the impurities go? They into the liquid phase. The liquid that you form has a higher impurity concentration than the solid that you form. The average impurity remains the same, but when you solidify from a melt, the impurity concentration in the solid < liquid. So, the impurity wants to remain in the melt more than it wants to remains in the solid, and that tendency of the impurity is what allows us to form a purer solid. This process is called **zone refining**. You can continue to do this ad nauseam and every time you would get a purer version of the solid then what you started. And more impure liquid.

Notice that as we progress, the initial solid that you formed is the purest solid that you can form, but the subsequent solids would be slightly more impure than the solid formed at the start. Why does this happen? Because all the impurities get more and more concentrated into the liquid. As the impurity concentration is liquid keeps increasing, the solid that you form from that liquid also is slightly more impure. This causes a gradient in the impurities in the solid that you have formed.

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We can define a constant called the distribution coefficient, which tells us that if you were to freeze a solid from a liquid, how many impurities will remain in the solid and in the liquid. The concentration in the solid Cs and the concentration in the liquid CL. This $k = C_S/C_L$ is different for each impurity.

Here is an example of different impurities and their 'k's. The things that are extremely bad for electronics as iron typically have a distribution coefficient of 10^{-6} which means that the probability of an impurity staying in the melt is 10^{6} times higher than the probability of it going into the solid. By just melting and refreezing, you can purify your silicon of iron impurities by 10^{6} times. That is the purification ratio.

Another extremely bad defect is gold, and gold also has an extremely low distribution coefficient of 10⁻⁵, which is extremely good as it allows you to remove gold impurities by melting and refreezing. This is not the case for all the impurities. Impurities like arsenic, phosphorus, boron, that tend to have relatively high distribution coefficients. So, they can still be removed, but not as much as iron and gold. Thankfully, these impurities are also dopants. This allows you to dope the material. Solidifying silicon retains the dopants while still being able to remove the bad metal impurities such as gold and iron.

Note that the metallic impurities' distribution coefficient being very low and the dopant concentration being high is a stroke of complete luck. We got lucky with silicon. One of the reasons why silicon is so popular is that we can create doped silicon with relative ease while at the same time getting extremely pure silicon. For a different material, this may not have been true.

The k does not always have to remain < 1. If the impurity-silicon phase diagram is not eutectic but peritectic, you can actually get a situation where the impurity wants to remain in the solid and not in the liquid. In that case, the distribution coefficient will be >1, for example, oxygen in silicon. This is the reason why the oxygen concentration in the silicon ingot is 10^{17} to 10^{18} cm⁻³ even though the dopant and the impurity concentrations are much lower.

ce Consequence of k<1? 0 Seed 0 Seed Solidified region Flow of impurity More impure melt After $C_{1}(0) = C_{0}$ $C_{L}(0+) > C_{0}$ $C_{s}(0) = k^{*}C_{t}(0) < C_{o}$ $C_{S}(0+) = k^{*}C_{L}(0+) > C_{0}$ Solid is purer than Liquid becomes more impure solution Subsequent solid will also be more impure

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Now, here is a slide to help you visualize this process as a function of distance. Imagine you have a melt and a seed. You are rotating the seed and slowly pulling it out. At t=0, the liquid has an impurity concentration of C_0 . The very first dx length of the solid that forms will have a concentration of k·C_L. If k < 1, this value is < C_0 , which is the fundamental of zone refining. The solid that you have formed is purer than the melt that you started with.

All the impurities from the freezing solid get ejected into the melt. If the melt remains homogeneous (by mixing), you have a melt that is slightly more impure than what it was at t = 0. The next dx length of the solid would see a slightly higher concentration of impurities causing it to be slightly more impure than the solid that was formed at t = 0.

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If this process continues, as you solidify more and more of the material, the concentration of impurities in the solid would also increase. (which can be seen in the plot). This formula (don't need to remember it) of the impurity concentration in the solid as s function of the fraction of the melt solidified can be derived by solving a 1D differential equation as an optional exercise. Note that the concentration changes as you go from x = 0 to x = 1. This is a reason why you cannot specify a single or specific value of the impurity concentration but a range because the concentration will change as you start from the top of the ingot and go to the bottom.

This concentration change also depends on the distribution coefficient. Impurities that have high distribution coefficients, for example, dopants (~0.1) show a relatively shallow change, but for low k (k < 10^{-2} for example), show a very sharp profile. For low k, there is a very little impurity in the initial part and very high impurity in the final part of the ingot, which is the fundamental of zone refining. Very little of the gold and iron will be in the first half. Most of the gold and iron will be in the last half.

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When the impurity is ejected from the solid and enters the melt, we have assumed that the melt would become homogeneous instantly. This does not realistically happen. The impurities that get ejected accumulate near the solid. So, the concentration of impurities near the solid will be higher than deep in the melt. Because of this piling up kinetic effect, the effective distribution coefficient that you would observe will be a little higher than what the theory (assuming equilibrium) tells you.

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Finally, you get an ingot that will have a pure end and an impure end. The starting point will have very few impurities and will tend to be less doped. The ending point will have more impurities and will tend to be highly doped.

Where will you get your wafer from? Whether you get it from the starting point or from the other end is what determines the grade of the wafer. The prime grade wafers come from the first half where impurity concentrations are much lower and mechanical or test grade wafers come from the other end, where the wafer impurity concentrations are higher. So, for electronics, you always want to get wafer from the pure edge.

Dopant concentration is never constant in an ingot but it varies. The doping is lower in the first half, higher in the second half which is why you can never give a precise value of doping.

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Here is some optional reading on nanowire growth for those of you who are interested. Using the same concepts of the eutectic phase diagram and the crystal growth, you can grow silicon nanowires. There is a whole field where people grow single-crystalline nanowires using gold or silver. You can read up this reference to understand how they do that.

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Reality is a little more complicated than the simple 1D model that we just discussed. Here is what an actual crystal growth system looks like. I will just highlight some of the important features. Notice the seed and the shaft lift and rotation. The area of the wafer is decided by the speed at which you pull the seed and the thermal management. If you want to get a certain diameter of an ingot, this needs to be very precisely controlled; these days, it is often done by computers.

Then a sensor, so that the computer can actively get feedback on the diameter and change the rate of pulling depending on it. The second thing you see is the upper housing isolation valves that allow you to make sure the system is sealed and the oxygen from the atmosphere does not get in and the heat does not leave out. If the heat leaves out, your area becomes smaller. And then there is a control power supply that measures the temperature of the melt which is very important to maintain the area uniformity, etcetera.

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If you try to use the same CZ process to make gallium arsenide, which is the most common III-V material, you may not get as lucky as in silicon. It is a remarkably hard, and the major reason is: when you have a melted gallium arsenide, arsenic tends to leave the gallium arsenide, to evaporate out because of the lower boiling point (higher vapor pressure). In order to prevent the escape of arsenic, typically you need to add a capping agent, which often is boron oxide or something like that.

Now, this solves the problem of arsenic leaving, so the stoichiometry of the melt remains the same; however, it makes the thermal management remarkably hard. Heat is lost at this boron oxide interface, making the area very hard to control the area, so you end up making ingots that look like the one shown in the slide. Because of this capping layer, there is a thermal instability and the thermal instability leads to instability in the area. So, the area of the ingot keeps changing.

So, you form these wavy sorts of ingots and that too not of extremely high quality. This is the reason why gallium arsenide often is not made using Czochralski silicon. There is a competing method that we will discuss later.

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The other way of making ingots is called the float zone method. The idea of a float zone method fundamentally is the same; just that the hardware is a little different. A key point is that the melt never touches another solid as it is not inside a crucible. You start with a polycrystalline ingot. This could be a piece of the polysilicon, or it could also be a piece of CZ silicon that you have already made.

Then you introduce an RF coil around this that will cause localized heating. You are not melting the full ingot but causing localized heating. This localized heating will melt a small portion that will fall under the gravity, through the RF coil and then fall down, where it will re-solidified. Because the heating is localized, as soon as it passes the heated zone it re-solidifies.

If you slowly move this RF coil from top to bottom, you would crystallize the material from top to bottom. An actual system and a cartoon of this process are shown in the slide. You can see that this RF coil is going from bottom to top, and as it is going, it is melting and refreezing the silicon. The difference between this and CZ is because of the localized heating, only a zone melts, not the entire feedthrough. This is one great advantage of float zone over the CZ method and it allows you to achieve much lower resistivities, as it is a much more effective method at removing impurities. Why? We will see that later.

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In the slide, you are looking at the concentration as a function of distance. Just like in CZ, there is a variation in the concentration. You typically get purer material at the front end, impure material at the back end and how much more impure will also depend upon the distribution coefficient. A smaller distribution coefficient causes a larger gradient; a larger distribution coefficient causes a smaller gradient.

More interestingly, this process can be done again and again, and every single time you get purer and purer material. You can do multiple passes of zone refining. A single-pass material will, for example, form this blue line, but if you do a second pass it will be purer than the blue line, if you do a third pass it will be even purer. You can arbitrarily increase the amount of purity of the material that you are forming. The impurities keep shifting towards the dirty end. This is how FZ can achieve much more purity than CZ, however, this method is much slower and hence, much more expensive. You would only do this where you really want very high-quality silicon.

For the niche application, where you want extremely pure silicon, the float zone is much more interesting. If you use the CZ method, it would not work because you are melting the whole bulk.

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The third is the gradient freeze method. The concept remains the same, but the hardware is slightly different. You create a melt in a sealed ampule and the ampule is lowered in an oven whose temperature changes from bottom to top. Going from bottom to top, the temperature is different. As this ampule is lowered in the furnace, it starts crystallizing at the lower end and this crystallization front progresses until the whole melt is crystallized. This is called the Bridgman Stockbarger technique.

Without going into details I will just let inform you that this gives lower dislocation density than the CZ method and this gives you a much better quality gallium arsenide wafer. So, for gallium arsenide, this is the method of choice, not the CZ or float zone method.

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10 ¹⁴ cm ⁻³	10^{14} cm ⁻³ \rightarrow 1 in 10 ⁸ or 10 ppb or 99.999999% pure				
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Residual Impurity	Poly Si feedstock (cm ⁻³)	CZ Si (cm ⁻³)	FZ Si (cm ⁻³)		
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Group III Group V	< 10 ¹¹ < 10 ¹³	<10.	2x10 ¹²		
Group III Group V Heavy metals	< 10 ¹³ < 0.5x10 ¹³	(10.	2x10 ¹² < 10 ¹²		
Group III Group V Heavy metals Oxygen	< 10 ¹³ < 0.5x10 ¹³ < 10 ¹⁵	1018	2x10 ¹² < 10 ¹² < 10 ¹⁵		
Group III Group V Heavy metals Oxygen Carbon	< 10 ¹² < 10 ¹³ < 0.5x10 ¹³ < 10 ¹⁵ < 10 ¹⁵	10 ¹⁸ < 10 ¹⁶	2x10 ¹² < 10 ¹² < 10 ¹⁵ < 10 ¹⁵		

Overall, what is the impact of impurities? Bulk silicon has an atomic density of around 10^{22} /cm³. An impurity of 10^{14} /cm³ implies that the material is 1 in 10^{8} or 10 ppb or 99.999999 % pure. Through these processes of crystal growth (CZ, FZ and gradient freeze) methods, you can get silicon that is 10^{14} to 10^{12} /cm³ pure. Group 3 impurities are less than 10^{14} to 10^{12} /cm³ pure. Heavy metals < 10^{12} /cm³. Oxygen is a little higher because the distribution coefficient of oxygen is > 1. The carbon is < 10^{15} /cm³.

Through this process of crystal growth, you are achieving a reduction in impurities by an order or two orders of magnitude and that is a side effect of crystal growth and that is because of zone refining.

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Finally, you have this pure ingot, but this has these wavy patterns on the top that you can grind out. After grinding, you can cut them into wafers and finally, you also grind out flats. Flats are these flat regions that are made in the cylinder for identifying the wafer type. For example, a typical {111} p-type wafer has one major flat. If you see this major flat, it is a p-type {111} wafer.

If it is a p-type $\{100\}$ wafer, it will have two flats. An n-type $\{100\}$ wafer will have two flats that are 180° to each other. Depending upon where the flat is, you can tell the doping type and the orientation of the wafer. So, this is a standard.

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Next, the ingot is sawed into wafers, but during the sawing process, you always create damage at the surface. So, in order to remove that damage typically you etch around 20 microns of the surface of the wafer. This is typically done chemically, using a variety of baths; some of them are acidic in nature, some of them are basing in nature.

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You still have a relatively rough surface. So, in order to smooth it to an optical finish, you then do chemical mechanical polishing. This is very similar equipment to what is used in lens making or in the optical component making where they get smooth surface

through polishing. You take your wafer, put some weight on top, and that silicon wafer is rotated on a bed that is made of some hard material. There is a slurry that is also made of particles of very hard material that functions as an abrasive. By very slow etching and very slow grinding, you smoothen out the surface.

The slide details a typical recipe (which you don't need to remember). The slurry can be aluminum oxide-based or cerium oxide-based. We remove around 25-30 μ m from the top and what is left is a very smooth surface whose flatness is around 5-10 μ m and RMS roughness < 1 nm. You can do this on one side or on both sides, depending upon whether you want a single side or double side polished wafer.

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Not all wafers need to be single crystalline. In solar photovoltaics, there is a market for multi-crystalline silicon where you do not care about single crystallinity. Here the system becomes more simple, you simply take a melt and you do a vertical freeze and there is no seed. So, you do not form a single crystal, but you form multiple multi-crystalline wafers, that have several grains. They have grain boundaries that make them electronically inferior, but cheaper. So, in some cases, for example, solar cells, this is commonly done.

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Specification	Applications	
Float Zone Si	High efficiency solar cell, highly resistive substrates, power electronics, detectors	
Si (111) Prime	Bipolar junction transistor	
Si (100) Prime	General purpose, field-effect transistors	
Si (110) Prime	Perpendicular trenches in microfluidics, higher mobility p- channel FET	
Test/Mechanical grade Si	MEMS, NEMS, dummy samples, substrate for characterization experiments	
Micro-crystalline/solar-grade	For low-cost solar cells	
Double side polished (DSP) wafer	Structures with back alignment, devices on both front and back, etc.	

Finally, we come back to the specifications we started with. Now, some of those specifications will make a lot more sense to you. For example, float zone silicon typically would mean it can be very highly resistive, have a very low concentration of impurities. So, if that is what you need you should get float zone silicon. What does prime mean? Prime simply means that we are getting the wafer from the front end of the ingot where the impurities tend to be the lowest. Whether you should use {100} or {111} or {110} really depends upon the application you want. It is easier to make {110}. So, you pay for the extra effort if your application requires it.

Now, what are the test and mechanical grades? This is the wafer that you get from the other end of the ingot that probably has more impurities. So, if you do not care about the electronic properties but just the mechanical properties of silicon, maybe this is good enough for you. For even lower grade you can buy a microcrystalline wafer. In certain applications you want both the sides to be smooth, you get double side polished wafers.

With that, we come to the end of this series on substrates. In the next lecture, we will discuss cleaning technologies. You may have noticed that so much effort is put into creating a material with very low impurity. That would be of no use if we do not maintain that purity. How you maintain that purity is the subject of the next lecture.

Join you back then. Thank you.