VLSI Technology

Dr. Nandita Dasgupta
Department of Electrical Engineering
Indian Institute of Technology, Madras

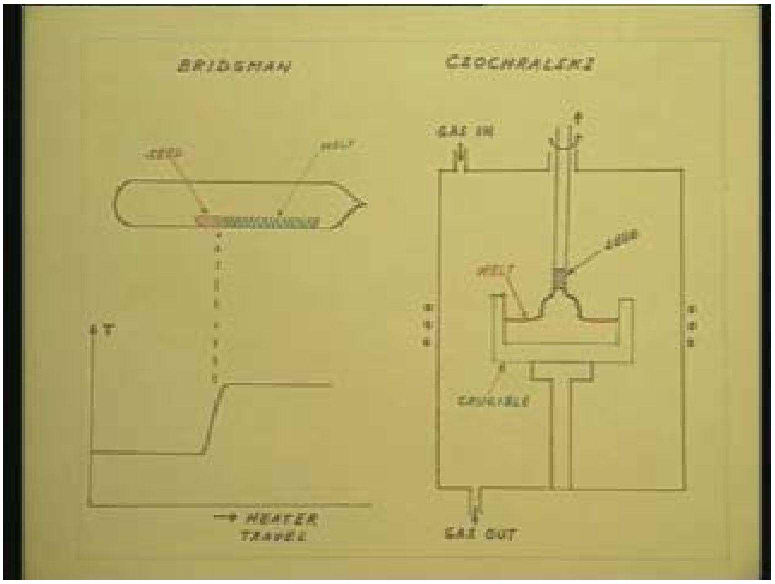
Lecture - 6
Defects in Crystal + Crystal growth

So, now that we are familiar with the crystal structure of silicon and also we have seen what are that common defects which are possible to be in a practical crystal, it is time to see how this single crystal can be grown in practice. Because as you know, the starting point in any integrated circuit fabrication is we must have a silicon wafer, a single crystal silicon wafer. So, we must get the substrate material. In order to get the substrate material, we must grow a single crystal of silicon. As I have already mentioned, silicon is one of the most abundant material in the world. It is formed, it is found in nature as silicon dioxide. So, first the silicon dioxide is reduced in order to obtain silicon. It is purified further in order to get very high purity semiconductor grade silicon that is 6N purity or 99.9999% purity. Once we have obtained this highly pure semiconductor grade silicon, we can use it as the starting material to obtain a single crystal.

(Refer Slide Time: 3:01)

So, that brings us to the unit process step of crystal growth and the crystal growth can be broadly classified as Bridgman technique and Czochralski technique. Let me on the onset tell you that most of the silicon that is grown today, that is available, commercially available today, are grown by Czochralski technique and sometimes further purified. But for historical significance, I would like to discuss the Bridgman technique first and then I will also tell you why the Czochralski technique is preferred for growth of single crystal silicon over Bridgman. So, let us begin our discussion with the Bridgman system of crystal growth. The Bridgman system of crystal growth is a very simple process. It is very simple, can be very easily achieved. But of course, there is a catch; there will be some problems associated with this Bridgman grown crystal.

(Refer Slide Time: 4:12)



Let us look at the system, where a single crystal can be grown by using the Bridgman technique. What we have here, it is a quartz ampoule, a quartz tube. The mouth of the tube is sealed. It is evacuated and sealed. So, first of all a quartz ampoule and inside this ampoule, you have a quartz boat. This is the outline of the boat. In this boat, a seed crystal, a small single crystal is placed and the rest is filled with the charge. What do I mean by charge? I mean the high purity silicon which is poly crystalline or powdered. That is called the silicon charge. So, the charge along with the seed crystal is placed in the quartz boat inside an evacuated quartz ampoule and then the charge is heated. Charge is heated to its melting point, but make sure that the seed crystal is not molten.

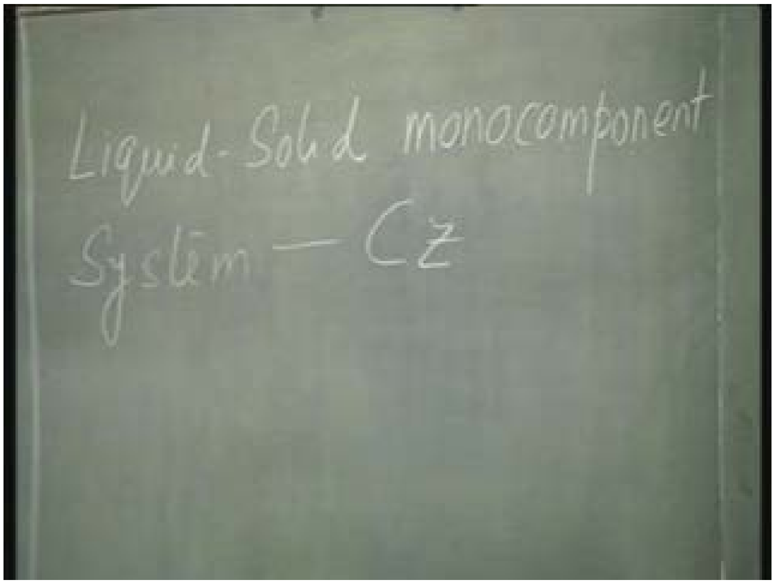
Therefore, the temperature profile of the furnace has to be something like this - temperature versus x. So you see, the seed end is kept at a lower temperature, while the charge, the melt is at high temperature and therefore it is in the molten condition. This has to be very critically maintained. Therefore, the temperature profile in a Bridgman furnace has to be very accurate. Care must be taken, so that the seed crystal is not molten and then, once the charge is in molten condition, the heater can be moved in this direction. What is going to happen when the heater is moving in this direction? That means the end of the melt which is in contact with the seed crystal is now becoming progressively cooler. It is coming in the low temperature zone of the furnace. Therefore, that end is going to solidify and since this is in contact with the seed crystal, it will take the orientation of the seed crystal and the solidification will take place as a single event. That is I am going to realize a single crystal.

So, as progressively the heater is moved in this direction from this end that is from the seed end, the melt is going to get solidified and I am going to realize a single crystal. Alternately, you could also move the quartz ampoule in this direction, same purpose will be served. Instead of moving the heater, you could just move the quartz ampoule in this direction. Even in that case, the seed end of the melt will come into the low temperature zone and therefore, it will get solidified. In contact with the seed crystal it will get solidified as a single event and will realize a single crystal. So you see, essentially this is what the Bridgman crystal growth system is all about. All you need to have is a quartz ampoule and a quartz boat, both of which is readily available and you just have to evacuate the sample before, after placing the charge and the seed crystal in it and have a very good furnace with an accurate temperature profile and maintain a relative motion, either move the heater or move the quartz ampoule and you will have your single crystal.

In principle, this is what Bridgman crystal growth is all about. But, as we have already mentioned, silicon is a material which expands on solidification. So, in a Bridgman crystal growth that is the greatest drawback, because the charge is kept in a quartz boat. The confining boundary of the quartz boat is going to create a lot of stress during the solidification of the charge. Because the charge is in the molten condition, the solidification is taking place at the seed end where the charge is in contact with the boat, so the surface of the boat is going to act as a confining barrier. It is going to create a lot of stress on the crystal and therefore you know, whenever there is a lot of stress, dislocations will be formed. Therefore, Bridgman growth single crystals have a lot of dislocations in them. In fact, that is one of the reasons, a major reason, why, in spite of the inherent simplicity of the Bridgman crystal growth technique, people go for Czochralski system of crystal growth.

Czochralski system of crystal growth is actually a much more complicated system, compared to a Bridgman system. It is a much more sophisticated, much more difficult system to handle. You will have to control a large number of parameters, but you can grow single crystals which have much less dislocations, much less defects. That is the greatest advantage of a Czochralski system. So, a Czochralski system is also known as a liquid solid mono component growth system, liquid solid mono component growth system. What do we have in a Czochralski system?

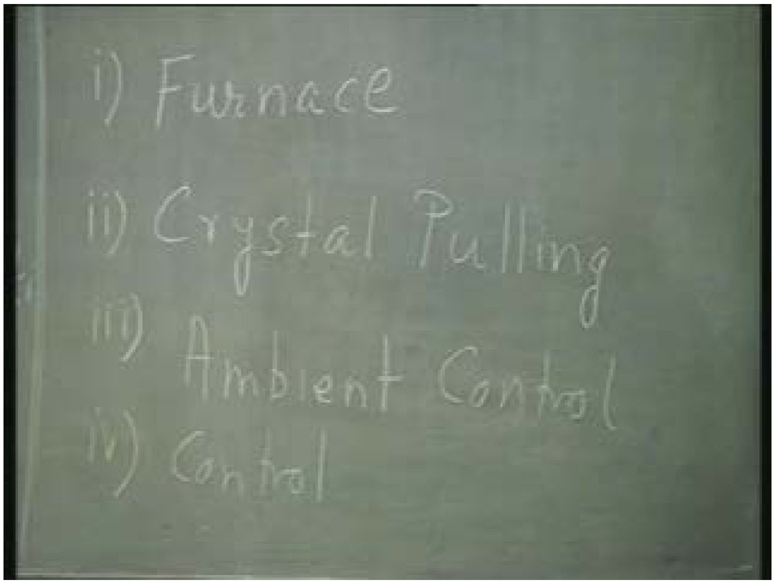
(Refer Slide Time: 10:54)



Liquid-Solid monocomponent
System — Cz

Essentially the Czochralski system on a liquid - solid mono component system that is Czochralski, commonly referred to as the Cz, Cz crystal that is the Czochralski grown crystals. We have basically four subsystems in this Czochralski crystal growth system.

(Refer Slide Time: 11:38)

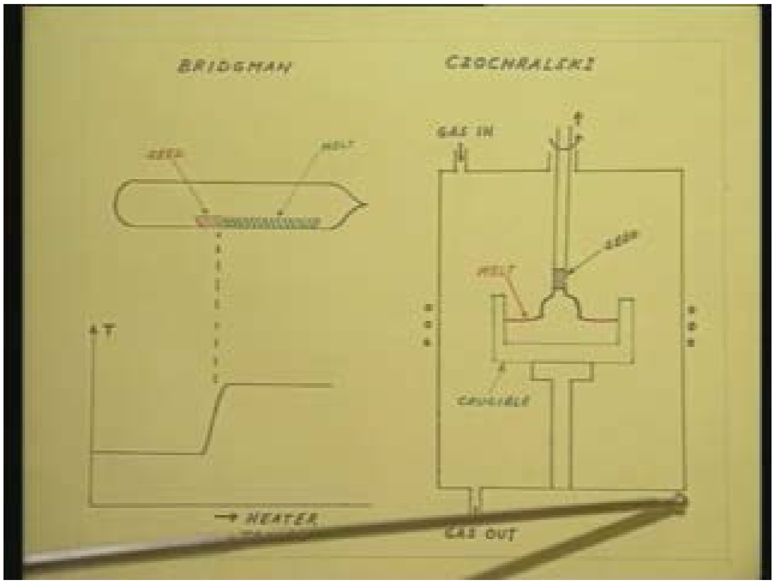


i) Furnace
ii) Crystal Pulling
iii) Ambient Control
iv) Control

First is a furnace, second is known as the crystal pulling mechanism, third is the ambient control and finally we have the control systems. So, these are the four subsystems of a Czochralski crystal growth system - furnace, crystal pulling mechanism, ambient control and a control system.

Now, let us take a look at the Czochralski crystal growth system.

(Refer Slide Time: 12:41)



What I have here is a quartz envelope, big quartz chamber with gas inlets, gas outlets, may be even some pumps, which I have not shown in the figure, some pumps in order to maintain the requisite pressure in it and you have another opening through which a pull rod is passed. This quartz envelope may be water cooled. The most important part in this furnace is the crucible that is a cup in which the charge is going to be placed and this is usually made of quartz. See, quartz is nothing but silicon dioxide. So, there is less chance of contamination through a quartz crucible, because it is also comprised of silicon. But, it is actually silicon dioxide, therefore some oxygen may come from the crucible to the single crystal. We will investigate that later, what happens if oxygen comes into it and usually the crucible is made of quartz and it is actually a single, you can use it only once usually, because after the crystal growth when you are cooling down the system, then because of the thermal mismatch usually the quartz crucible is going to crack. So, you cannot reuse the crucible and this quartz crucible is usually placed inside a graphite susceptor.

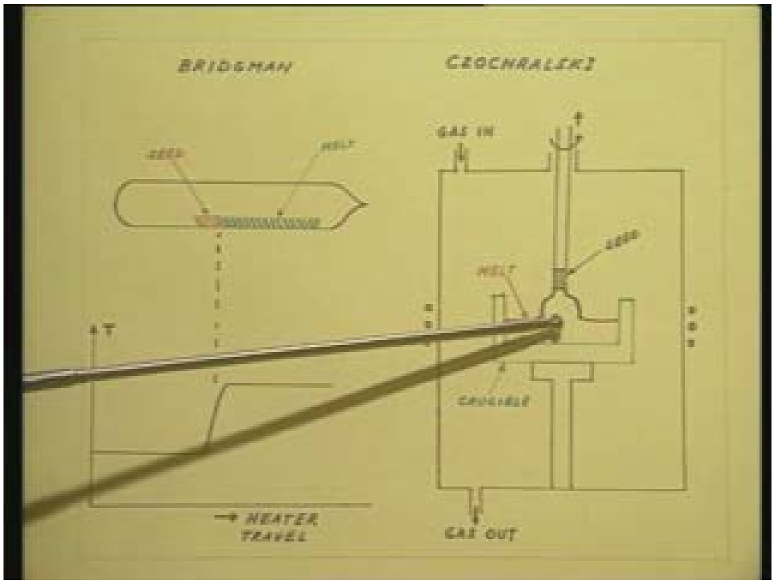
A susceptor is, you can view it as an outer jacket. That is I have a bigger cup of graphite in which I am going to place the quartz cup. The quartz cup is called the crucible, the graphite cup is called the susceptor and the graphite susceptor is placed on a heater, graphite heater usually, very high purity graphite heater and the heating is done by, usually by RF. These signifies the RF heating. Sometimes for large charges, resistance heating is also employed, but mostly it is RF heating. So, these are the things inside the furnace. You have a quartz crucible, a graphite susceptor, a heater and the cooling for the outer quartz chamber, quartz envelope. Then, we have the crystal pulling mechanism. I have already mentioned that through this a pull rod is passed and at the end of the pull rod, a small seed crystal is fixed in a …..

(Refer Slide Time: 16:10)

It is like you have this pull rod and at this end a small seed crystal is fixed, it is held in a …… and as can been seen from the figure, the pull rod is pulled up during the crystal growth and then of course, we have the ambient control. See, the ambient is very important in a crystal growth system. First of all realize that I am using a graphite susceptor and graphite heaters. Therefore, there must not be any oxygen inside the system. The whole thing will just go up in smoke, so to speak. It will just form carbon dioxide and there will be no susceptor, no heater, nothing left. The other thing is of course, it should not react with silicon. I want to have high purity single crystal silicon. If I have oxygen in it, oxygen is going to react with silicon to form silicon dioxide; I cannot allow that. Therefore, beware of oxygen. That is why the usual practice, even though I have not shown it in the figure, is first of all to evacuate the quartz chamber. After you have put the charge in it, first of all evacuate the quartz chamber and then fill it up with an inert ambient - argon or helium or nitrogen, something like that. You can do it in, you can fill it up and maintain atmospheric pressure or sometimes even reduced pressure.

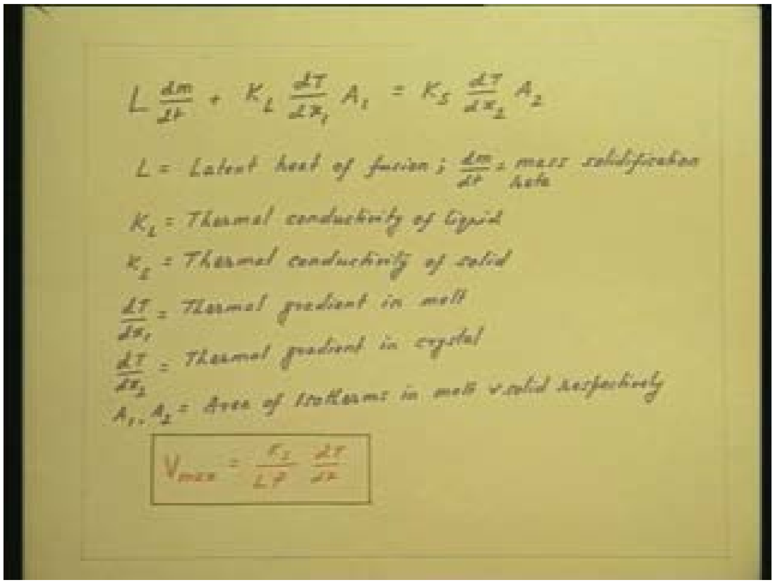
Now, let us see how exactly the crystal growth is achieved? What do you do? So, we have put in the charge, we have created the requisite ambient condition inside and we are heating the assembly. So, what happens? The charge gets molten. I have a melt inside the crucible. Remember, all this while the seed crystal was not, I repeat, not in contact with the melt. It was held somewhere up there, while the charge was below. After the charge is molten, it is uniformly in the liquid state, then the pull rod is gradually lowered till the seed crystal touches the melt surface.

(Refer Slide Time: 18:51)



This is the point till the seed crystal touches the melt surface and then, very slowly the pull rod is pulled up. So, what will happen? The melt that is in contact with the seed crystal will get solidified and as we pull up, we are going to pull up the solid crystal. Care must be taken, very accurate control is necessary, so that instead of growing the crystal you do not melt down the seed crystal itself. The pull rod must be carefully adjusted, so that I get a single crystal. I do not melt down the seed crystal, because you see the seed is in contact with the melt. If the pull rate as well as the thermal conditions are not carefully adjusted, the reverse can also happen. The seed can also, can get melted. Therefore, therefore you can appreciate that the Czochralski crystal growth technique is a much more complicated process, but the quality of crystal would be very good, which brings us to the question of how the pull rate should be adjusted. Pull rate should be adjusted very carefully. If you draw it too fast you may not get a single crystal. If you draw it too slow, you may even get the seed crystal melted. Therefore, the pull rate must be very carefully adjusted which brings me to the second card, where we discuss how the pull rate should be carefully adjusted.

(Refer Slide Time: 20:48)



$$L\frac{dm}{dt} + K_L\frac{dT}{dx_1}A_1 = K_S\frac{dT}{dx_2}A_2$$

L = Latent heat of fusion ; $\frac{dm}{dt}$ = mass solidification rate

K_L = Thermal conductivity of liquid

K_S = Thermal conductivity of solid

$\frac{dT}{dx_1}$ = Thermal gradient in melt

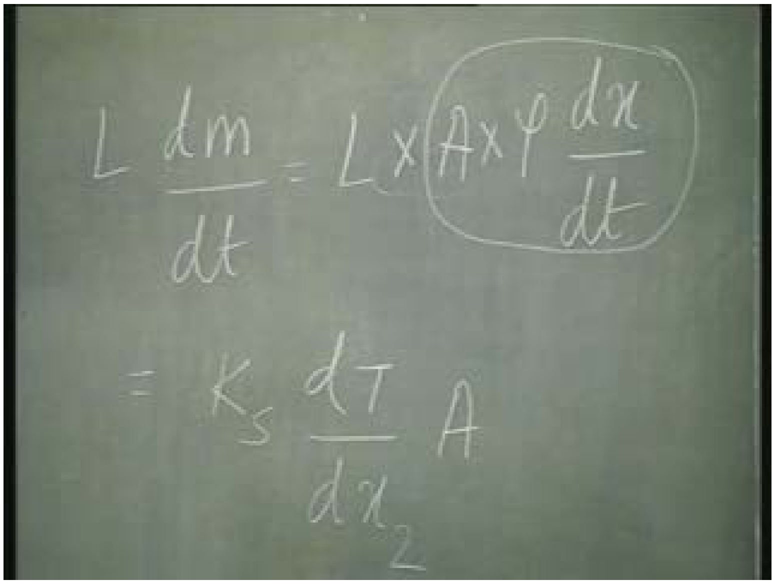
$\frac{dT}{dx_2}$ = Thermal gradient in crystal

A_1, A_2 = Area of isotherms in melt & solid respectively

$$\boxed{V_{max} = \frac{K_S}{L\rho}\frac{dT}{dx}}$$

I have written down an equation there, L dm dt plus K L dT dX 1 A 1 is equal to K S dT dX 2 A 2, where L is the latent heat of solidification, latent heat of fusion or latent heat of solidification, dm dt that is the mass solidification rate. K L is the thermal conductivity of the liquid, K S is the thermal conductivity of the solid, dT dX 1 is the thermal gradient in the melt, dT dX 2 is the thermal gradient in the solid that is in the crystal and A 1 and A 2 are the area of the isotherms in the melt and in the solid. So, basically what I have written is a heat transfer equation. Now, from this equation you can very easily see that if I assume that the thermal gradient in the melt is zero, that is the entire melt is in the constant temperature that is at the melting point, it is maintained at the melting point, so if dT dX 1 can be made equal to zero, then L dm dt is going to be equal to K S dT dX 2 times A.

(Refer Slide Time: 22:46)

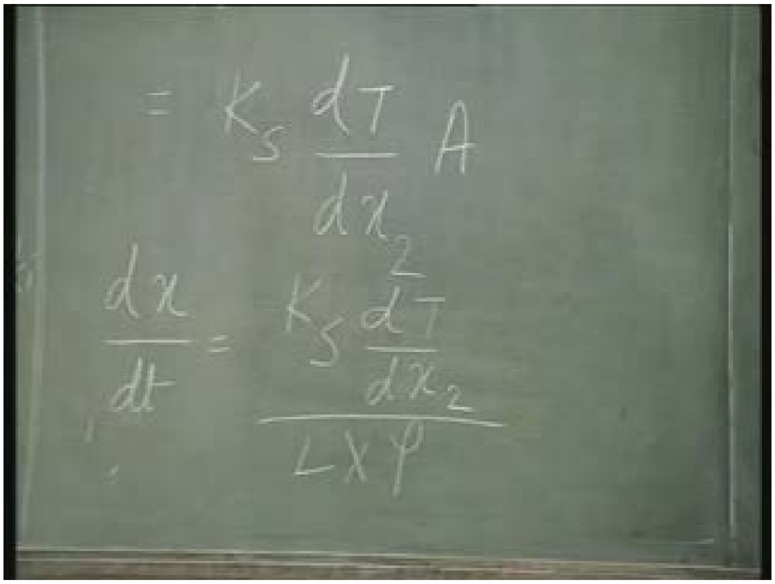


$$L\frac{dm}{dt} = L \times \boxed{A \times \rho \frac{dx}{dt}}$$

$$= K_S \frac{dT}{dx_2} A$$

L, I have already said is the latent heat of solidification, dm dt is the mass solidification rate. So, what is dm dt really? I can write it as L, can I not? L times area into rho, rho that is the density into dx dt. This is actually equal to the dm dt term, rate of change in volume times the density. That is the rate of change in mass. So, if I consider that the thermal gradient in the melt is zero, then this is equal to, this dx dt is nothing but my pull rate. This is the rate at which I am pulling the crystal.

(Refer Slide Time: 24:29)



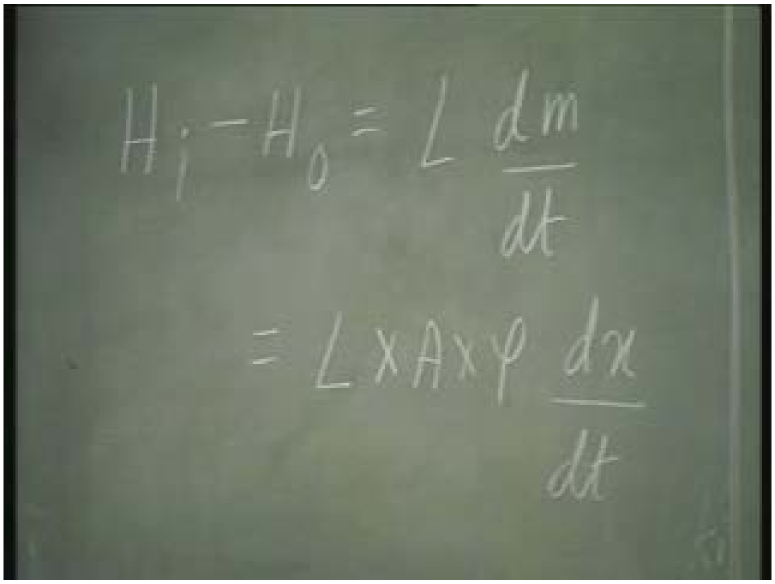
$$= K_S \frac{dT}{dx_2} A$$

$$\frac{dx}{dt} = \frac{K_S \frac{dT}{dx_2}}{L \times \rho}$$

So, from this equation I can say that dx dt K S by L into rho times dT dx, it is dx 2; this we prefer. This is the maximum attainable pull rate, maximum attainable that is when I am assuming that the thermal gradient in the melt is going to be zero.

In practice, the pull rate is kept less than the maximum pull rate. In a practical system what happens is that there will be a small change in the temperature of the melt. Because we are pulling out the crystal, the thermal conditions, they are continuously changing. So, in a practical system actually, a feedback system is used, a feedback control is used. That feedback control is used to supply the heat to the melt, so that the temperature is maintained within plus minus half degree centigrade or so and now you can understand that this heat loss, the heat needed to be supplied in the system, heat input minus heat output, the heat loss is almost entirely taken off by the latent heat of solidification, no other path of heat loss. Almost entirely this thing is going to be taken by the latent heat of solidification, if the temperature gradients are considered to be very small. So you see, in a practical system the difference between the heat input and the heat output will be almost totally taken off by this.

(Refer Slide Time: 26:47)



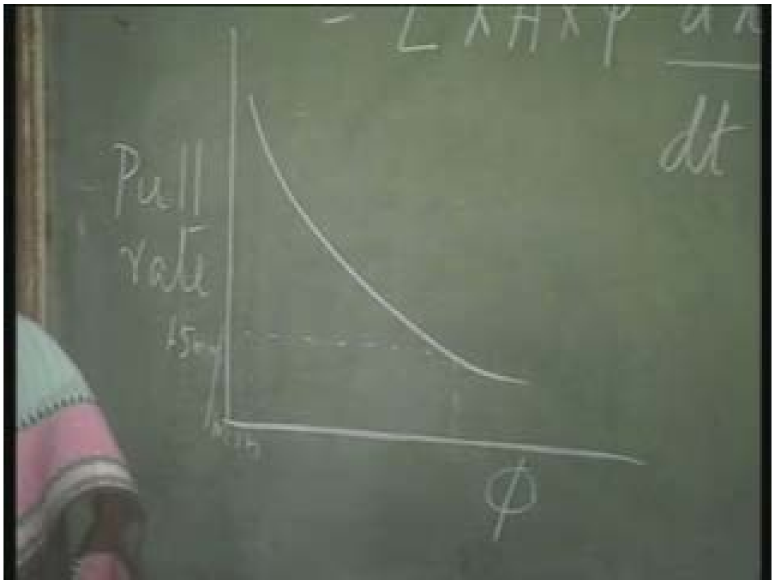
$$H_i - H_0 = L \frac{dm}{dt}$$

$$= L \times A \times \varphi \frac{dx}{dt}$$

This is the heat transfer. This is taken off almost totally by L dm dt or ..... Actually, this H i minus H naught should be small. So you see, in this equation L is a constant. I cannot do anything about L, same is for rho. Latent heat and the density, these are the material properties. So, the only variables are the area and the pull rate. So you see, actually therefore, the pull rate is going to vary inversely with the area for a given H i minus H naught. In other words, the larger your crystal, the smaller should be the pull rate. Now, this pull rate, it has a lot of effect on the defects. The defect finally in the crystal, it is going to depend quite significantly on the pull rate. How? See, as the crystal is cooling, from its mere melting point as it is cooling, the thermal point defects will try to coalesce into dislocation groups. It will try to agglomerate, it will try to, all of them will come together and form a dislocation group and form an array agglomerate. This is seen to happen at a temperature around 950 degree centigrade.

Now, if the pull rate is larger, if the pull rate is say, greater than 2 millimeters per minute, then you can quench this defect formation. That is when you are pulling it very quickly, you are forcing it to cool quickly, so you can quench this defect formation. But again, as I said, if you have large diameter crystal, then you cannot afford to use a very large pull rate. They are inversely proportional.

(Refer Slide Time: 29:48)



In fact, the pull rate you can plot, if this is the diameter of the crystal and if this is the pull rate, it actually varies something like this and this is about 1.5 mm per minute when the diameter is about 75 centimeters or so,75 millimeters or so. 75 millimeter that is about 7.5 centimeter that means about 3 inch diameter wafer. Funnily enough, for measuring silicon wafer diameter we still use inches. That is the common way of referring to the wafer as 2 inch dia or 3 inch dia or 4 inch dia or 6 inch dia. Now you can even get 12 inch diameter wafer.

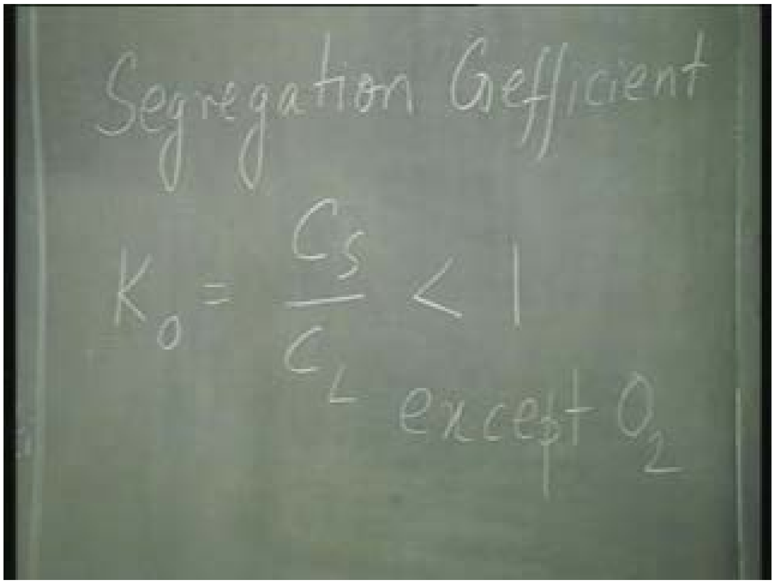
Now, the point I am trying to make is this. Therefore you see, it is relatively easier to grow a smaller diameter single crystal with very low defect density, isn’t it? Because for a smaller diameter crystal, you can afford to use a large pull rate and when you use a large pull rate, the problem of this dislocation forming is less severe. That is the reason why 10 years back, the silicon crystals that were grown were almost exclusively 2 inch or 3 inch diameter; 10 years or 15 years back. At the beginning of the integrated circuit evolution, the silicon wafers available were only of 2 inch or 3 inch diameter. As the system became perfect, more perfect, technologically more advance was made, it was, it became possible to grow large diameter crystal with low defect density.

Obviously, more stringent control is needed on the pull rate, more stringent control on the thermal control system, all that is required if you want to grow larger diameter crystal with low defect density. So, you will appreciate that it is difficult to grow a bigger diameter crystal. That is why they came later in the market. Now, it is even possible to grow a 12 inch diameter crystal like a big plate. It was not possible 10 years back, because of the technological limitations. So, this is about the pull rate.

Now, the next interesting point is, of course, how about the dopant, dopant incorporation in the crystal. Suppose I want to grow a p-type crystal or an n-type crystal, how can I do that? More importantly, suppose I want crystals of a particular doping concentration, how do I maintain that? That is inadvertently if something else comes inside, suppose I wanted to grow an n-type crystal, but I find that it is p-type because of some unintentional dopants, how do I control that? How are the dopants incorporated during the crystal growth process itself?

The dopant incorporation during crystal growth is actually a very interesting thing. You see, any impurity it will have a solid solubility in the crystal and it will also have an equilibrium solubility in the melt and these two are not necessarily same. There is a different solubility in the crystal and in the melt.

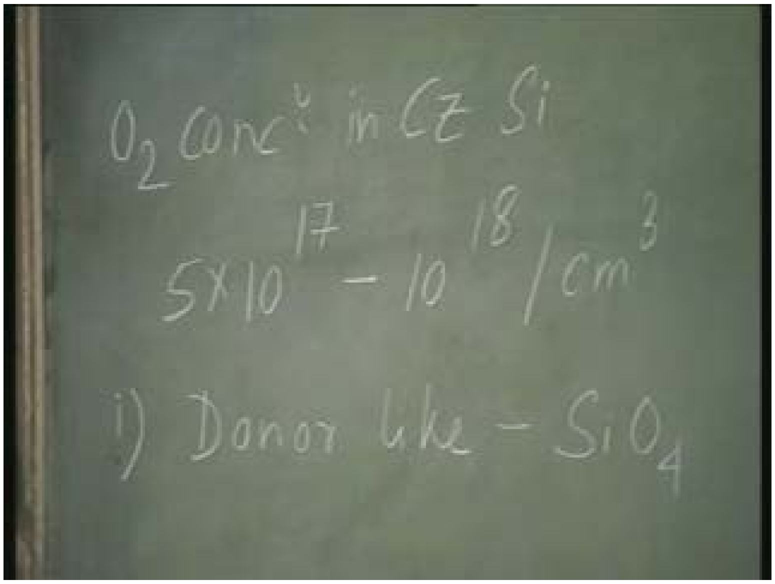
(Refer Slide Time: 34:05)



So, this is given by the segregation coefficient, this difference is given by the segregation coefficient, usually referred to as K naught and K naught is given as the ratio between C S and C L, where C S is the solid solubility in solid silicon, solid solubility of the dopant in silicon and C L is the equilibrium solubility in the melt. Now, usually for most common impurities this K 0 is less than 1; for most common impurities K 0 is less than 1. What is the implication? The implication is that the solid solubility is less than the equilibrium solubility, equilibrium solubility in melt. That means as you grow the crystal, these impurities are preferentially left inside the melt, they do not come into the solid. They are rejected by the solid, they prefer to be in the melt. That is because C S by C L is less than 1. That means as you are drawing the crystal, the melt is becoming progressively richer in the impurity. So, when you grow a crystal, we will find that the doping concentration will vary from one end to the other.

The top end will have relatively less dopant concentration and the bottom end will be relatively more doped. That is true for most common impurities with the notable exception of oxygen. That is oxygen will have a segregation coefficient greater than 1. That is oxygen will come preferentially into the crystal, it will try to come preferentially into the crystal. That is a cause for concern, because you know in the furnace itself we have a source of oxygen. We are using quartz crucible, we are using quartz envelopes. Although the envelope is water cooled, but the crucible is heated. So, there is a possibility of oxygen incorporation during the crystal growth, oxygen incorporation into the silicon during the crystal growth. Is it detrimental? What are effects of oxygen in the single crystal silicon?

(Refer Slide Time: 37:37)



O_2 conc^{n} in Cz Si

$5\times10^{17} - 10^{18}/cm^3$

i) Donor like – SiO_4

Usually in a Czochralski grown crystal, the amount of oxygen will vary from 5 into 10 to the power 17 to about 10 power 18 per centimeter cube; 5 into 10 to the power 17 to about 10 to the power 18 per centimeter cube. Now, this oxygen in the silicon will have three possible defects. First of all within a limit this oxygen, 95% of it, will be in the interstitial sites, 95% will stay in the interstitial sites. That is it will find the space in between the regular array of silicon atoms and go and sit there. The rest 5%, however it can form a complex like SiO 4 and that complex will be donor like. This complex will be electronically active, it will be donor like, therefore it will affect the resistivity of the grown crystal and the formation temperature of these complexes are around 450 to 500 centigrade.

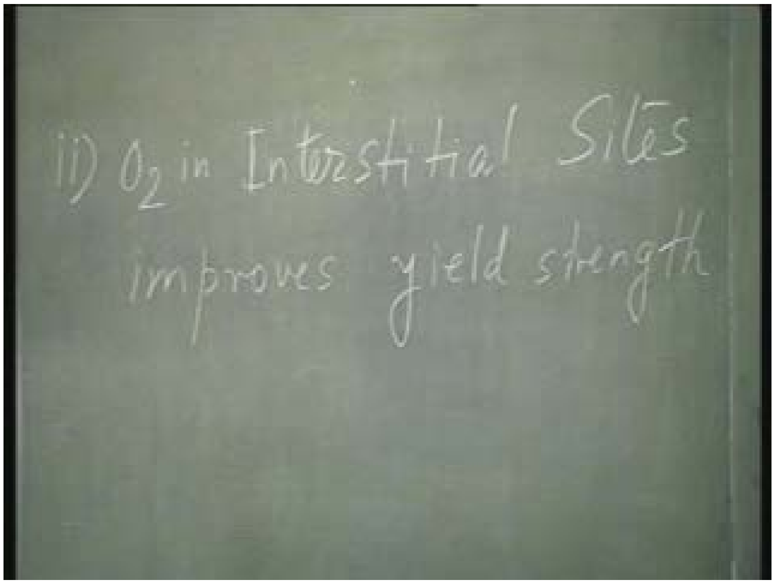
(Refer Slide Time: 39:28)

So, when the crystal is being cooled, this SiO 4 complexes will be formed. They will make the silicon n-type, donor like complexes.

One possible remedy to reduce this is, you form the crystal, you cut them into wafers that is thin slices and then you heat these slices to temperature above 600 degree centigrade and then, when you heat it above 600 degree centigrade, these complexes are dissolved, because the formation temperature is only around 450 to 500 degree centigrade. You heat it above that and the complexes separate, it dissolves and then, when you cool it down, see, a wafer is going to cool much faster than the entire single crystal. It has got a much smaller thermal mass, it is going to cool much faster. So, when you are cooling down the wafer, the complexes have less time to form. Therefore, their concentration is going to be reduced. It is much easier to cool down a wafer than cooling down the entire large single crystal. So, this is a common practice in order to reduce the donor complexes due to oxygen is after the crystal is grown, the wafer slices are cut, do a thermal treatment on these wafers; heat them up and then cool them down, so that the complexes are dissolved at the high temperature and they do not have sufficient time to form back when the wafer cools quickly.

This is one effect of oxygen. Remember, this is only the 5% of oxygen that is not there in the interstitial site. 95% of the oxygen that is incorporated, that is incorporated in the interstitial sites. So, these oxygen in the interstitial site actually is, you could say, beneficial to silicon. It improves the mechanical properties of silicon, it improves its yield strength.

(Refer Slide Time: 42:13)

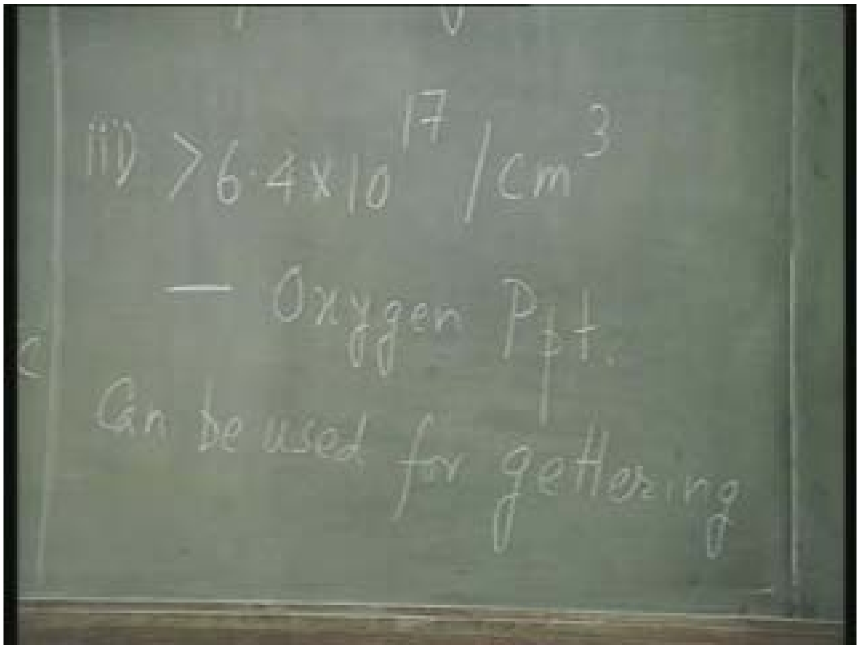


ii) O_2 in Interstitial Sites

improves yield strength

But, all this is true when I have relatively less amount of oxygen incorporated during crystal growth. That is when I am at the, towards the lower limit of the oxygen concentration, up to 6.4 into 10 power 17.

(Refer Slide Time: 43:18)



(iii) $> 6.4 \times 10^{17} / cm^3$

— Oxygen Ppt.

Can be used for gettering

If the oxygen concentration in silicon is greater than 6.4 into 10 power 17, then we come to the third problem and that is the problem of oxygen precipitate. Remember what we said about precipitate formation. The solubility is going to reduce with decrease in temperature. Therefore, when the crystal is being pulled down, if the oxygen concentration is greater than 6.4 into 10 power 17 per centimeter cube, this is going to be precipitated in silicon and once it precipitates, you have all kinds of problem, because this precipitates will give rise to compressive strength. That will stress the crystal and will start shooting off dislocations from that site.

So, the precipitate formation, you know, generally it is highly undesirable, because it will give rise to dislocations in the crystal. However, they can sometimes be used to our advantage. That is you know the precipitates will attract the metallic impurities. It can be made to act as a sink for metallic impurities. They are also called as the gettering centers, gettering. Only thing you have to make sure is that these gettering centers are not coming in the active region. That is this is not where your devices are found. If they are found lowered down in the bulk of the material, you do not mind, because there it is going to act as a sink for metallic impurities, leaving your active region free from metallic contamination. So, they can be used to your advantage, can be used as gettering center. So, oxygen concentration in the Czochralski grown crystal is quite a problem. It has three effects. Some of them are beneficial, some of them are not so.

So, particularly if you are very keen on the performance of the device like for example, if you are making power devices where the break down voltage needs to be very high, the leakage voltage has to be very low, then this oxygen concentration in silicon may not be acceptable, because you know, dislocations are generally going to deteriorate the device performance. Particularly it is going to lower the breakdown voltage and it is going to increase the leakage. So, in that case we may have to resort to further processing, further refining in order to remove the oxygen from the Czochralski grown crystal.

So, essentially if we try to sum up what we have done so far, as far as the crystal growth technique is concerned, the Bridgman technique is a simpler process. But, since during Bridgman, during Bridgman growth, the crystal is in contact with the boat and therefore is subjected to a lot of stress, there will be a lot of dislocations present in Bridgman grown crystal. In contrast, in Czochralski the crystal is not hampered by any confining surface. It is pulled out of the melt by the seed crystal. The crystal when it is growing is not constricted by any confining surface. Therefore, the amount of defects present in this crystal will be much less.

However, because of the quartz crucible there will be some oxygen present in the silicon and the problem is more aggravated, because oxygen has a segregation coefficient greater than 1, so that it will preferentially come inside the silicon. This oxygen may cause some detrimental effects, may have some detrimental effects, in the final device performance, particularly in lowering down the break down voltage and increasing the leakage current. Therefore, further refining may be necessary if one is very, very particular about the device performance requirements. I will stop here today.