VLSI Technology
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Lecture - 8
Epitaxy II –Vapour Phase Epitaxy

So, we have been discussing the general principles of vapour phase epitaxy and you have seen the three basic reactor design.

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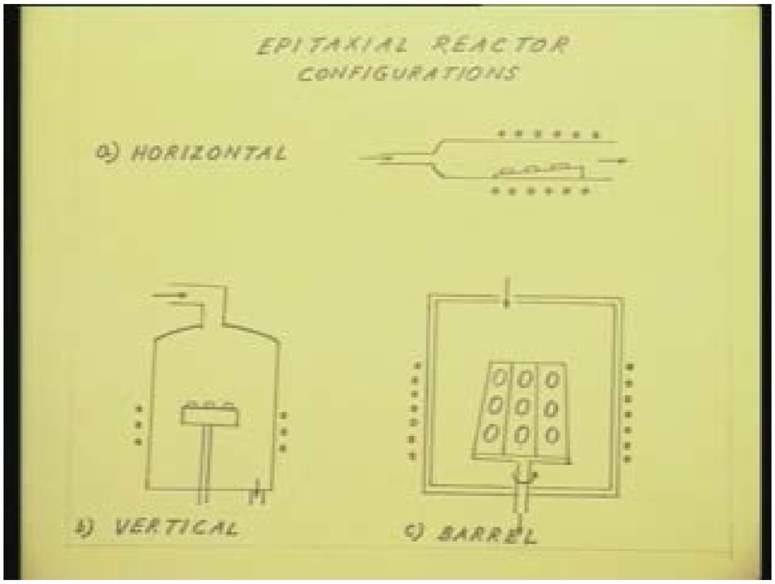

It can be horizontal or vertical or a barrel shaped reactor, for better mass through put. For a commercial system usually a barrel shaped reactor is used. Now, one thing, very important thing to be noted is the type of the reactor is specified by the direction of the flow of gas with respect to the semiconductor surface. So, that is why a horizontal reactor is actually called a horizontal reactor, because the flow of the gas is parallel to the direction of the semiconductor surface. In a vertical reactor, the flow of the gas is normal to the sample surface. See, the sample surface is here like this and the flow of the gas is perpendicular to that, normal to the semiconductor surface.

In a barrel shaped reactor, this is where you can easily get confused, if you just compare these two figures, they look very alike - the vertical reactor and the barrel shaped reactor. The flow of the gas is like this, but please do not get confused. The barrel shaped reactor is actually a horizontal type of reactor, because the flow of the gas is actually parallel to the semiconductor surface.

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You can assume that this is the barrel, that this is the sample holder, this is the sample holder and along its surface, samples are placed like this. Actually, small grooves are carved out in this surface of the barrel and samples are placed like this, so that the flow of the gas is actually like this. It is parallel to the surface of the sample. That is why I am saying that a barrel shaped reactor is actually a horizontal type of a reactor, even though looking at the figure it is very easy to think that it looks like, somewhat like the vertical reactor. But, it is not so. The flow of the gas is parallel to the semiconductor surface.

Now, in discussing the VLSI technology processes, very often we will have to use the term optimization. We have to optimize these. That is because, we have conflicting requirements. Any process, epitaxy for example, is a process where the adjustment of the different parameters, we have to optimize the parameters. There is no absolute good or bad. Do you understand what I mean by adjusting the parameters? What I mean basically is the system is operating at a particular temperature, at a particular pressure. What is the best temperature, what is the best pressure, there is nothing like that. It all depends on your particular requirements and it is always a question of a balancing act. We have to optimize the different parameters. We have various conflicting requirements. For certain requirements, I may need high temperature; for certain other requirements, I need as low a temperature as possible. Therefore, for your particular application you have to decide which temperature or which pressure you are going to use.

So, I will just give you an example say, how to decide the temperature during epitaxy. What should be the process temperature? Now here, ideally speaking, higher growth temperature is good in certain ways. Why is it good? The higher the temperature, the higher will be the surface mobility of the atoms. See, the atoms will have to come and deposit on the substrate surface. So, if they have higher surface mobility, that means they have a greater time, they have more time to get themselves oriented in a particular direction, maintaining the crystal orientation of the substrate. So, the higher the mobility, the better should be the crystal quality. But, higher temperature will also mean that you are stressing the wafer, thermal stress and at the same time, the higher the temperature is the more is the chance of intermixing of the dopants. That is to say, suppose your substrate is p-type, you want to grow an n-type epitaxial layer, which is our requirement for a bipolar junction transistor fabrication, remember.

So, in that case the higher the temperature is, the more chance there is for the p-type dopant from the substrate to come into the epitaxial layer and the n-type dopant from the epitaxial layer to come into the p-type substrate, intermixing of dopants. So you see, you always have to do this balancing act.

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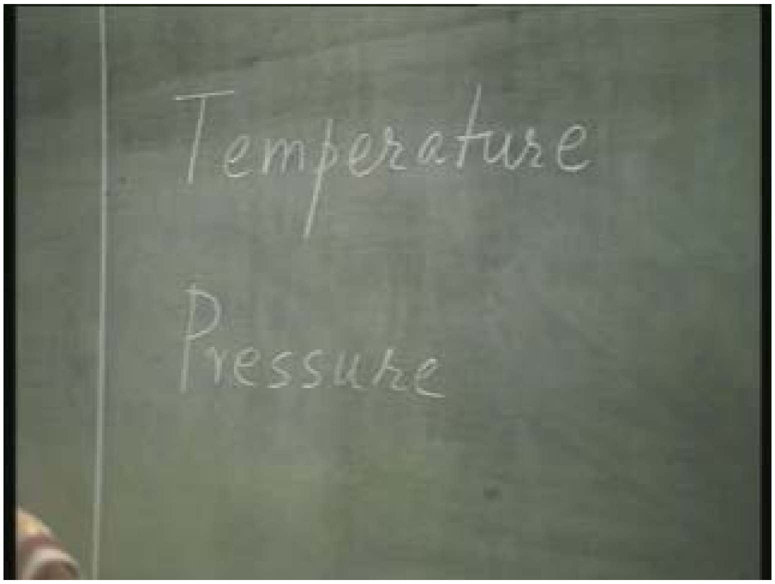

Temperature

Pressure

So, this is one process parameter, you have to carefully optimize, temperature. Higher temperature, better crystal quality, but higher temperature also means increased thermal stress and intermixing of dopants. So, accordingly you have to adjust the temperature. The other parameter that I would like to talk about is pressure. Now, remember this equation that we wrote yesterday, particularly the second one.

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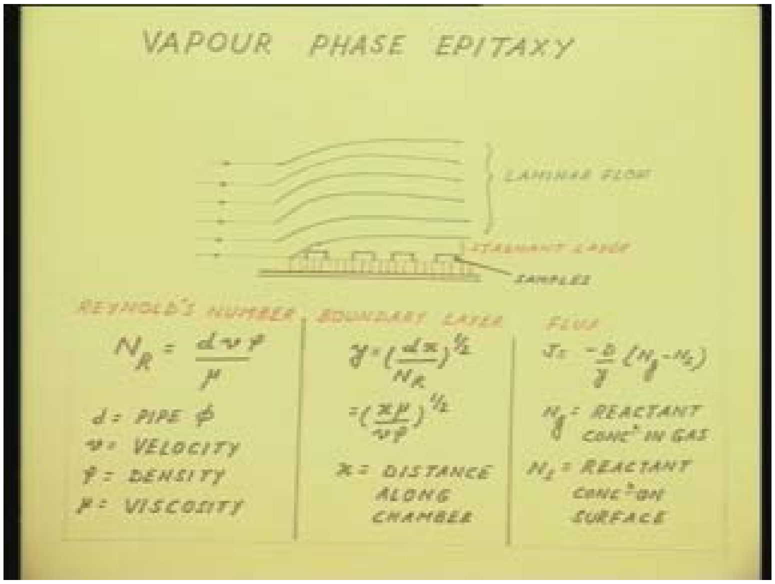

VAPOUR PHASE EPITAXY

REYNOLD'S NUMBER

$$N_R = \frac{d v \rho}{\mu}$$

d = PIPE ϕ
v = VELOCITY
ρ = DENSITY
μ = VISCOSITY

BOUNDARY LAYER

$$y = \left(\frac{d x}{N_R}\right)^{1/2} = \left(\frac{x \mu}{v \rho}\right)^{1/2}$$

x = DISTANCE ALONG CHAMBER

FLUX

$$J = \frac{-D}{y}(N_g - N_s)$$

N_g = REACTANT CONC^n IN GAS
N_s = REACTANT CONC^n ON SURFACE

The thickness of the boundary layer was shown to be proportional to x times mu divided by v times rho to the power half and therefore, we said that if the velocity of the gas flow is increased, the boundary layer thickness will decrease. I will have lesser of a boundary layer problem. But, in a practical system you are always concerned about the cost. So, if you have a higher flow velocity that means more consumption of gas, more consumption of reactant materials and that costs money. So, one way out will be to reduce the pressure of the system. If you reduce the pressure of the system, then if you are operating on the low pressure, then you can afford to increase the velocity of the gas; for the same consumption of reactant material, you can afford to increase the velocity of the gas flow and therefore you can reduce the boundary layer problem.

There are also some additional benefits like if you reduce the pressure, then the convection effects can also be minimized, you can maintain a better temperature stability. So, variation of epitaxy is called LPCVD or low pressure chemical vapour deposition.

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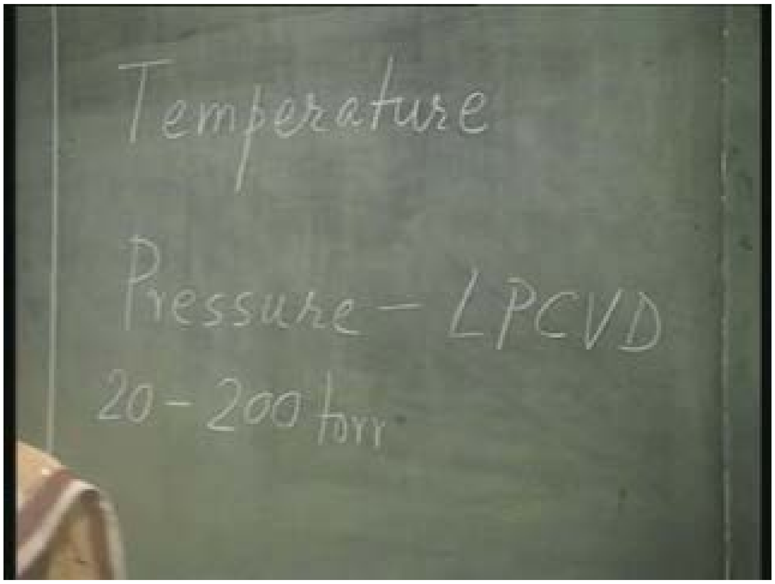

Temperature

Pressure – LPCVD

20 – 200 torr

In this case, the pressure is in the range of 20 to 200 torr. You will find, the term chemical vapour deposition and vapour phase epitaxy are used almost indiscriminately. That is not much difference between these two terms. Essentially speaking, vapour phase epitaxy is nothing but a chemical vapour deposition process. Only thing is, when we say chemical vapour deposition, we do not specify whether the layer is going to be crystalline or not. You see, you can also have chemical vapour deposition of silicon dioxide or silicon nitride which will form amorphous layers, not crystalline layers. In contrast, when we say vapour phase epitaxy, we always mean that it is a crystalline layer. But essentially you could then say that VPE is a subset of CVD. All VPEs, all vapour phase epitaxies, necessarily they have to be chemical vapour deposition processes, but all chemical vapour deposition may not result in an epitaxial layer. Understood? So, that is why this low pressure epitaxial reactors are called LPCVD, low pressure chemical vapour deposition system. That is a more generic term.

Now, coming to the particular problem of silicon epitaxy, essentially it is very simple. Essentially what is done is you have certain compound of silicon, usually silicon tetra chloride or chlorosilane as they are called and you reduce it by using hydrogen. So, this reaction actually takes place in two parts.

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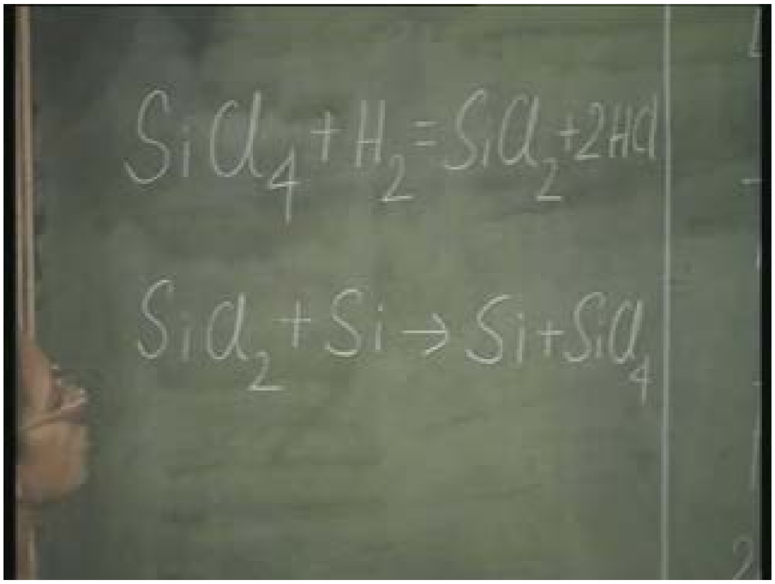

In the first part, the silicon tetra chloride for example, silicon tetra chloride, it reacts with hydrogen and it forms SiCl 2 and HCl. This SiCl 2 then gets adsorbed on the sample surface and it forms silicon and SiCl 4. That is in presence of the sample surface, it forms silicon and silicon tetra chloride. There are many sub reactions going on here. For example, the starting material can be silicon tetra chloride or it can be chlorosilane. That is silane is, you know, SiH 4. Chlorosilane is when one or more hydrogen atoms are replaced by chlorine.

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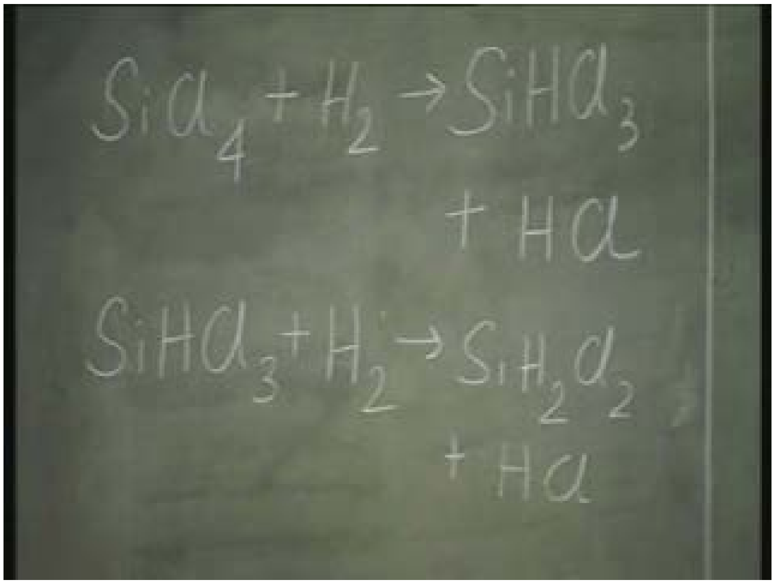

$$SiCl_4 + H_2 \rightarrow SiHCl_3 + HCl$$

$$SiHCl_3 + H_2 \rightarrow SiH_2Cl_2 + HCl$$

So, like I said the basic reaction can be something like, so you have formed a trichlorosilane, SiHCl 3. This is one possible sub reaction. Now that you have this SiHCl 3, this can further react with hydrogen and form SiH 2 Cl 2 plus HCl.

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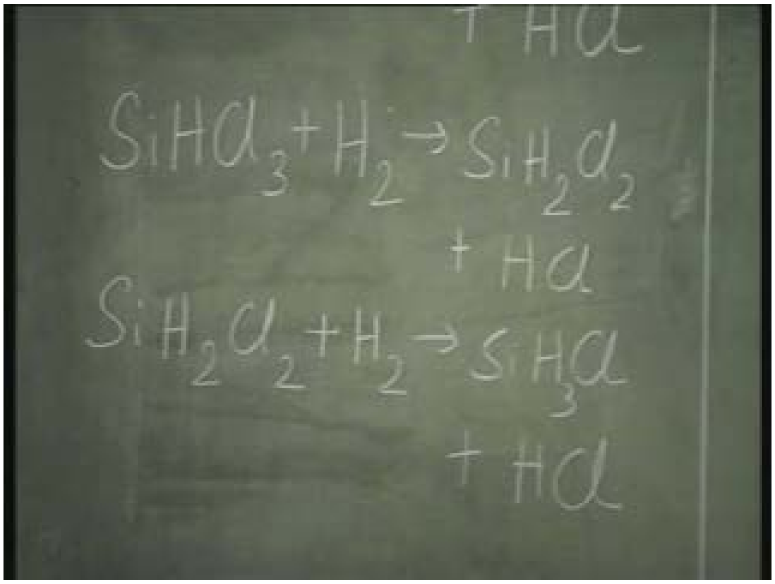

This SiH 2 Cl 2 can further react with hydrogen to form SiH SiH 3 Cl plus HCl and like that and finally what we have is, from all these intermediate components finally what we have is, SiCl 2.

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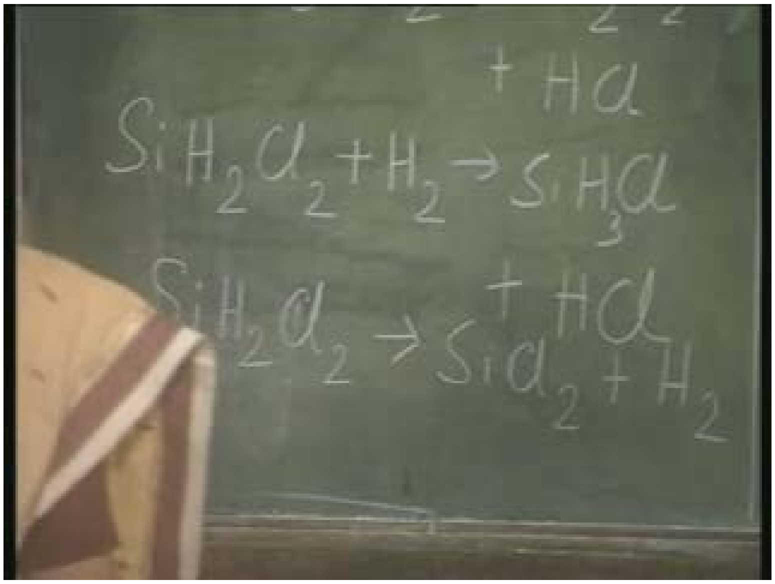

Finally what we have is, from all these steps ..... So, various side reactions are going on. If you have silicon tetra chloride or tri chloride. That is why your starting reactant can be silicon tetra chloride or it can be SiHCl 3 or it can be SiH 2 Cl 2, because all of them will eventually give rise to SiCl 2. This SiCl 2 is your active reactant species. This SiCl 2 in contact with the sample will give rise to silicon and HCl. In presence of hydrogen gas, it will get adsorbed on the sample surface and it will give rise to silicon and HCl. So, there are a few critical points to remember about this equation, this chemical reaction.

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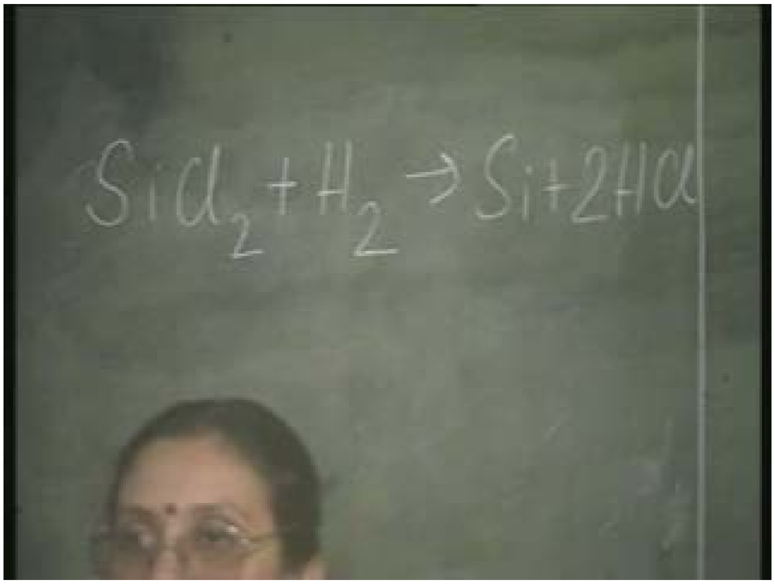

$SiCl_2 + H_2 \rightarrow Si + 2HCl$

First of all, this reaction is called surface catalyzed that is this, this reaction will take place only in the presence of sample surface. Only when SiCl 2 is adsorbed on the sample surface, this reaction is going to take place.

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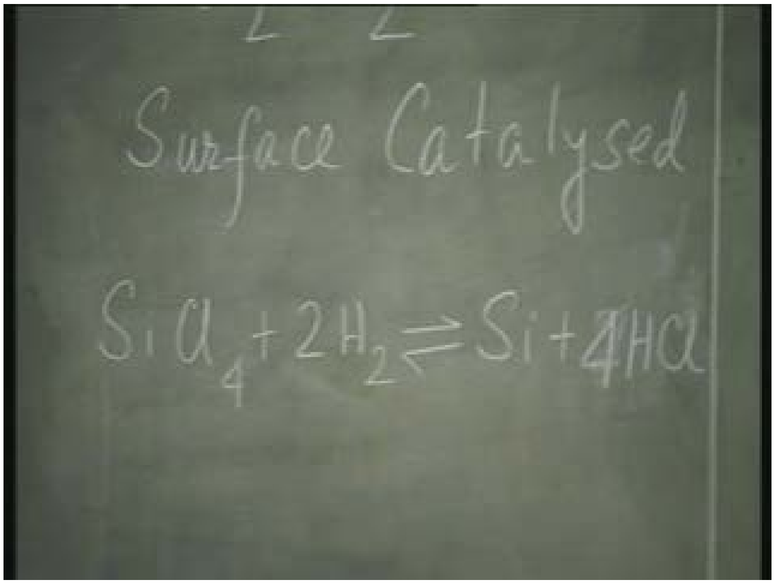

Surface Catalysed

$$SiCl_4 + 2H_2 \rightleftharpoons Si + 4HCl$$

So, this is called a surface catalysed reaction, surface catalysed reaction. Secondly, as the concentration of SiCl 4 increases, you see, as the concentration of SiCl 4 increases, see the overall reaction can also be written like this. This is the overall reaction, overall reversible reaction. Of course this is all, the sub reactions, SiCl 4 first it is making SiHCl 3, then it is making SiH 2 Cl 2, then from each one of these finally SiCl 2 is formed and then that is adsorbed on the surface to give silicon. But, the overall reaction can be written as this - SiCl 4 reacting with hydrogen to give silicon and HCl.

Now here, if the concentration of this SiCl 4 is increased, what do you expect to happen? First as this is increased, of course, we are going to have more reaction in the forward direction. that is the growth rate of silicon is going to increase. Isn’t it? By law of mass action, if the concentration of SiCl 4 is increased, then this also has to increase and therefore the growth rate is going to increase, but only up to a certain point. If the concentration of silicon tetra chloride is increased beyond a certain point, then instead of growth, what we are going to have is etching.

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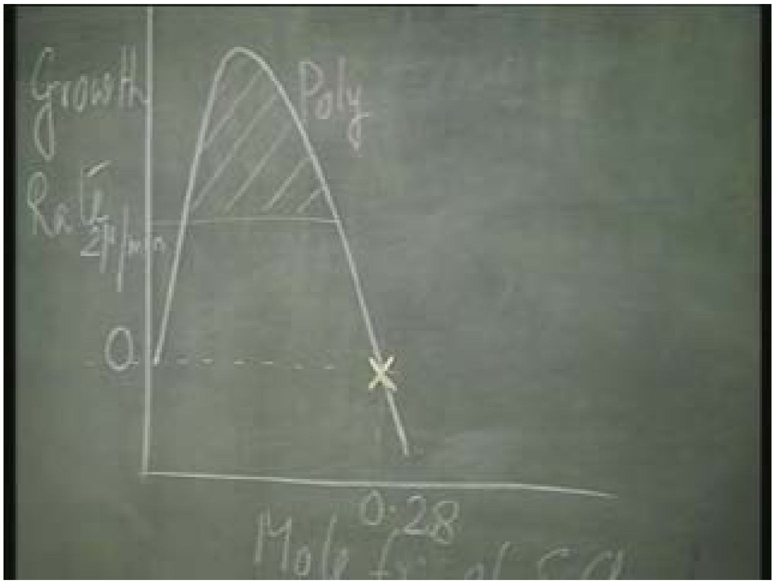

The reaction will take place in the reverse direction and we will have etching and that is why the growth curve can be plotted like this, growth rate versus the concentration of SiCl 4, mole fraction of SiCl 4. It starts and then it decreases and finally it crosses; this is the zero point. That is as the mole fraction of silicon tetra chloride is increased, initially you see that the growth rate increases. But, beyond a certain point that is beyond a certain point you find that the growth rate falls again and eventually it crosses the zero growth rate point that is we have a negative growth rate or in other words, we have etching.

The other interesting thing to notice is that as you increase the growth rate, the epitaxial layer is no longer going to be single crystal. We will have poly crystalline growth when the growth rate has become too high say, greater than 2 micro meter per minute. So, for a very high growth rate, single crystal layer is not possible to be achieved. So, then you will have poly crystalline layer and as you keep on increasing the silicon tetra chloride mole fraction, there will be a point when instead of growth it will start etching and that point is approximately at about 0.28. When the mole fraction of silicon tetra chloride exceeds 0.28, etching is seem to occur.

Now, the next point is I have already told you that we can use either silicon tetra chloride or some chlorosilane, SiHCl 3 or SiH 2 Cl 2. Which one do we use? Which one is most convenient? Silicon tetra chloride is the most stable material. Among all these silicon tetra chloride is the most stable material and it is also relatively insensitive to trace amount of oxygen present in the reactor chamber. That is why silicon tetra chloride was widely used. This is in fact the most extensively studied material for silicon epitaxy, but the point is you see, eventually whether you use silicon tetra chloride or SiHCl 3 or SiH 2 Cl 2, your active reactant is going to be SiCl 2. So, it all boils down to how effective are these materials in generating SiCl 2.

It is found that when silicon tetra chloride is used, then this SiCl 2 formation takes place only above 1000 K, 1000 degree Kelvin, while if you use SiHCl 3 or SiH 2 Cl 2, then SiCl 2 generation takes place at a comparatively lower temperature about 100 or 200 degree centigrade less. So, temperature wise, SiHCl 3 or SiH 2 Cl 2 offer a certain advantage. That is the temperature can be reduced by a small margin, not a very large margin but by a small margin. The other point is which is called the efficiency of deposition. The efficiency is defined as the ratio between the amount of silicon that is deposited to the amount of silicon that is present in the reactant gas, so efficiency or eta.

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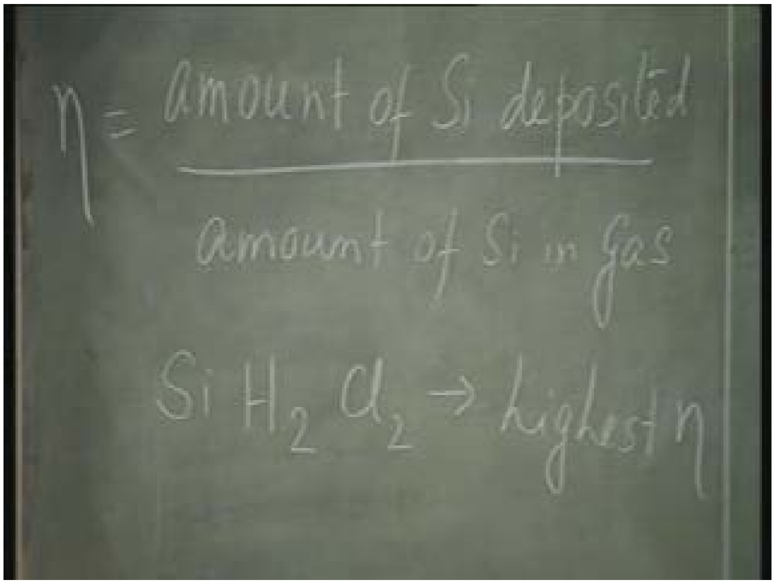

$$\eta = \frac{\text{amount of Si deposited}}{\text{amount of Si in gas}}$$

$$SiH_2Cl_2 \rightarrow \text{highest } \eta$$

That is the reactant gas contains so much silicon and only a certain percentage of that silicon is finally being utilized, it is getting deposited. So, the ratio will determine the efficiency of the epitaxy process and in this context also it is found that silicon tetra chloride is least efficient. The most efficient is SiH_2Cl_2. So, you see SiH_2Cl_2 offers two advantages - highest efficiency, also the formation of $SiCl_2$ takes place at a comparatively lower temperature. But again, in favor of silicon tetra chloride we have these two factors, that is it is the very stable compound and it is relatively insensitive to presence of oxygen in the reactant chamber. So, this is one route of silicon epitaxy, the most commonly used route, the route of chlorosilane . Silicon tetra chloride or $SiHCl_3$ or SiH_2Cl_2, they are all called part of the chloro silane route of silicon, chloro silane route to silicon epitaxy.

Remember, all of them will have as a byproduct, HCl, which is a very dangerous gas. Therefore, all the epitaxial reactors, all silicon epitaxial reactors must have excellent venting system. Otherwise you are not allowed to use that epitaxial reactor. It is hazardous. So, all of the them must have excellent venting system in order to take care of HCl. Remember, does not matter which one you use, $SiCl_4$ or $SiCl_3$ or SiH_2Cl_2, you are always having a lot of HCl as byproduct. Is there another route by which we can still have silicon deposition, but without the presence of HCl? The other route is the pyrolytic decomposition of silane. That reaction is very, very straight forward.

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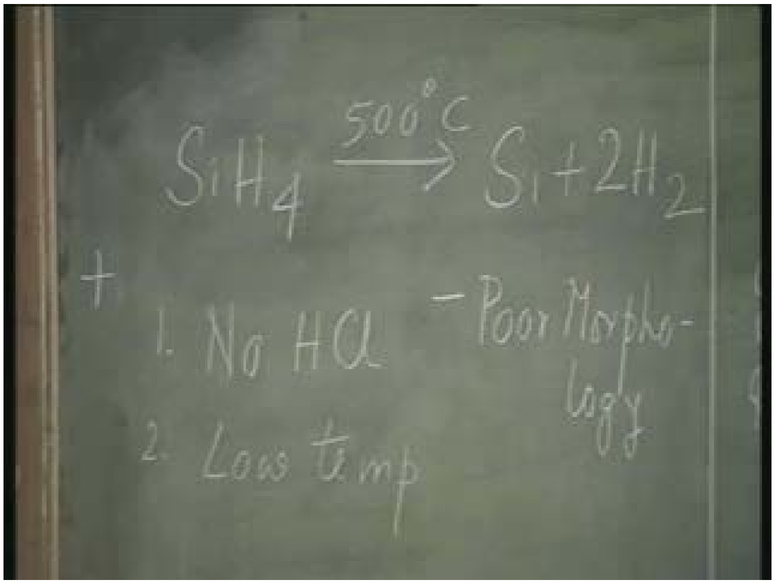

$SiH_4 \xrightarrow{500^{\circ}C} Si + 2H_2$

\+

1. No HCl
2. Low temp

− Poor Morphology

So, silane that is SiH 4 is pyrolytically decomposed into Si and hydrogen. So, the advantages of using a silane process over a chlorosilane process is, number 1, no HCl. Number 2, this reaction takes place relatively at a lower temperature. By 500 degree centigrade silane will start decomposing and finally this reaction is non-reversible. See, I have just put one arrow there. It can only move in the forward direction. In contrast all the chlorosilane reactions are reversible reactions. This is a non-reversible reaction. So, you can get very abrupt layer. It is possible to have very abrupt layer. So, these are the advantages of the silane route, but again as I said, there is nothing like absolutely good or absolutely bad, particularly when processing technology is concerned.

Therefore silane route also has a lot of flip side. The flip side is this. In the chlorosilane reaction, you remember, I said that this reaction is surface catalyzed. That is silicon is going to be deposited only on the surface. SiCl 2, only in presence of the sample will form silicon. In this case however, there is no such provision. This reaction can take place anywhere, all through, all inside the chamber this reaction can take place. So, the nucleation can take place in the gas phase itself. It does not have to be on the surface. So, in general, in a silane route the morphology will be poorer, right. Morphology that is the surface structure will be poorer, you will have poorer crystal quality. These are the advantages. On the negative side, we have poor morphology and I told you that one major advantage of silicon tetra chloride was that it is relatively insensitive to trace amount of oxygen.

All those who have ever worked in a high vacuum system will know that it is extremely difficult to really get rid of oxygen. Trace amount of oxygen will always be present, it is extremely difficult to remove it. So, if your reaction is very sensitive to the presence of oxygen, it becomes that much more difficult to attain the quality, for quality control. So, silicon tetra chloride has a major advantage that it is relatively insensitive. By that I do not mean that you can have the system full of oxygen. But, if there are trace amount of oxygen, the reaction is more tolerant to that. In contrast, the silane reaction is extremely sensitive to the presence of oxygen. So, that is a major practical concern, because in practice it is going to be very, very difficult to really, really get rid of oxygen.

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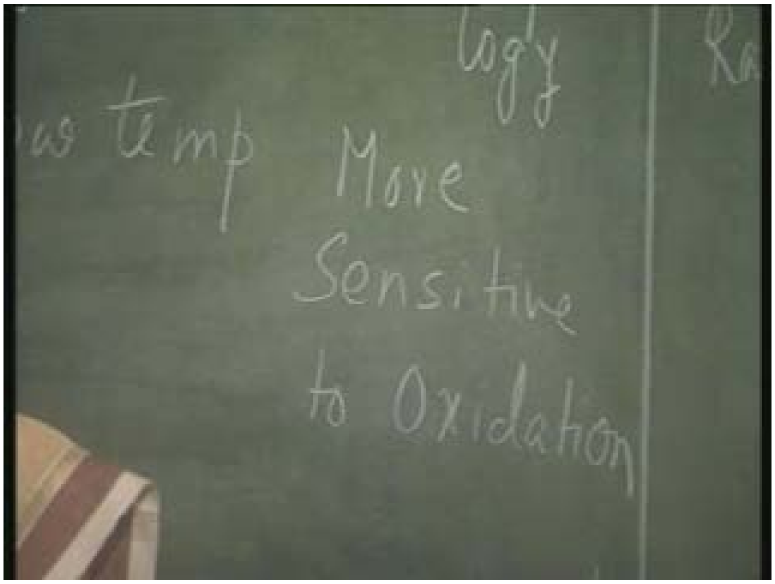

So, it is also more sensitive to oxidation. Essentially, these are the two routes of silicon epitaxy. You can either use chlorosilane or you can use simple silane. They all have their plus points and minus points. So, depending on the particular application, you choose the route. The other point is of course, during epitaxy there should be a provision for doping the epitaxial layer. As you have seen, for example, taking again the example of the bipolar junction transistor, we had to grow an n-type epitaxial layer. That is going to be the collector, so n-type epitaxial layer with a particular doping concentration. Similarly for other applications you may have to grow a p-type or sometimes even very highly doped layers, you may have to grow this.

So, how does one incorporate the dopants into the epitaxial layer? Doping during epitaxy is also done and that also essentially follows the same principle.

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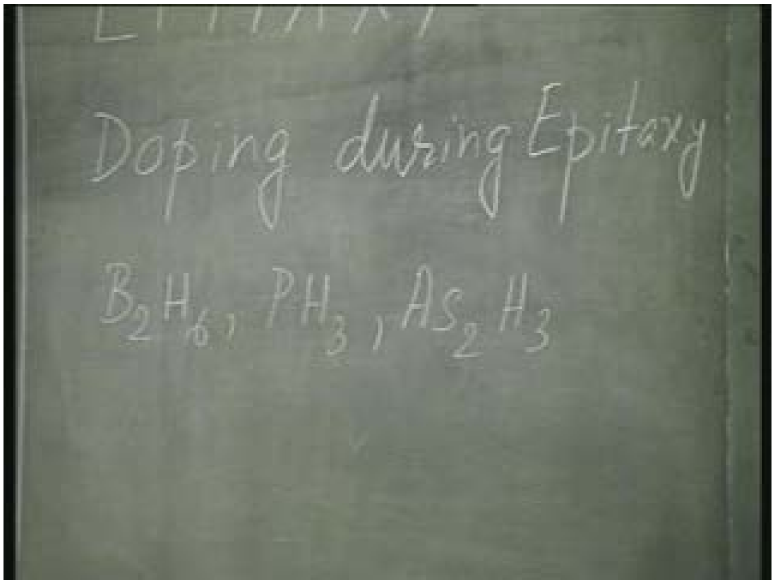

Doping during Epitaxy

B_2H_6, PH_3, As_2H_3

What you do is you use hydrides of the dopants. You know the common dopants are boron, phosphorus and arsenic. So, you can use and they will decompose and introduce the dopants into the silicon. So, as the epitaxial layer is growing, you can have it doped in a proper way. So, doping during epitaxy that is deliberate doping during epitaxy can be done very simply. Now, let me remind you that one important consideration during epitaxy is that the surface must be absolutely clean, surface must be absolutely clean. We must have a totally oxide free and damage free surface. If there is a damage present on the surface, that damage will travel in the epitaxial layer also. If there is a stacking fault on the surface, that will travel inside the epitaxial layer.

If however you have patches of oxides, you know that the silicon, silicon tetrahedral radius it has a certain value. From the, from our discussion on crystal orientation, we have shown that the tetrahedral radius is how it is related to the lattice constant. But, if you have oxide, then you will have Si O Si bonds, that has a different tetrahedral radius. So, if you have patches of oxide on the surface and then you are growing an epitaxial layer, there will be stresses generated in the epitaxial layer, because of this difference in the tetrahedral radius. So, if you have stresses, it might result in dislocations. That is why it is absolutely essential to have a perfectly damage free and oxide free surface. So, there must be a provision for in-situ cleaning and etching of the wafer.

As I have already mentioned, by in-situ cleaning and etching, I mean after the wafer, after the sample has been loaded into the reactor chamber, without having to take it out, inside the chamber there must be a provision for cleaning and etching the sample. This cleaning and etching is done normally in two steps.

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First of all, after the wafers are introduced in the reactor, they are flushed in dry hydrogen at about 1200 degree centigrade, quite high temperature. 1200 centigrade, it is, dry hydrogen is passed through the chamber and the samples are flushed in dry hydrogen.

The idea is to reduce any oxide that might have been present on the sample and this is a very, very, very important step. The sample surface must be absolutely free of oxygen and this can only be achieved by flushing it in dry hydrogen at a pretty high temperature.

Now that you have done this and you have made sure that no traces of native oxide is present, next anhydrous hydrogen chloride is passed. Anhydrous hydrogen chloride diluted with hydrogen is passed and the etching proceeds exactly the previous reaction, only in the opposite direction. Remember, the opposite direction was this.

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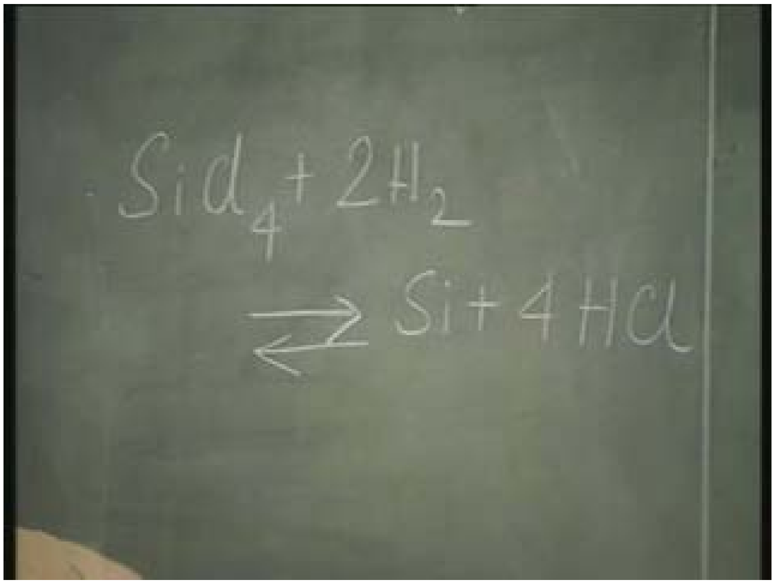

$$SiCl_4 + 2H_2 \rightleftharpoons Si + 4HCl$$

This is the epitaxy reaction, epitaxial reaction. Silicon tetra chloride plus two hydrogen gives rise to silicon and four HCl. But, I told you that these reactions are reversible. So, now you have silicon that is the sample surface and you are passing anhydrous hydrogen chloride diluted with hydrogen. Therefore the reaction proceeds in this direction and you have etching of the sample. Usually 1 to 5 mole fraction of hydrogen chloride is used.

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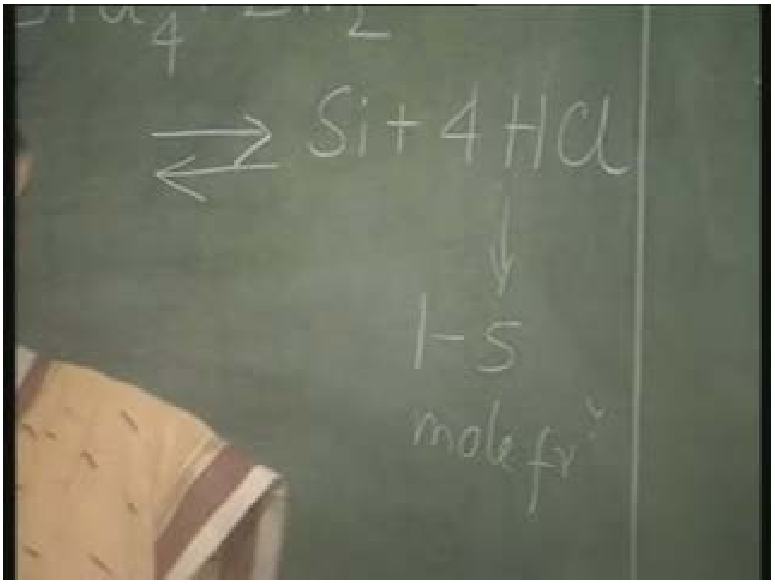

This is usually 1 to 5 mole fraction, not more than that. Etching rate is from a fraction of a micron that is say, from 0.5 micron to 2 microns per minute. The limit on this anhydrous HCl is because if you have excessive hydrogen chloride, there will be more damage on the surface. It will cause pitting. That is called halogen pitting. In various other processing also, you will find that chlorine in small quantity, chlorine or hydrogen chloride, chlorine bearing compound, in very small quantities they are usually good for semiconductor processing. But, excessive chlorine or excessive hydrogen chloride will cause pitting of the surface. So, that is called halogen pitting. That is why always, not just for epitaxy, but for various other processes as we encounter then, you will find that there is always an upper limit on the amount of chlorine that you can use. In this particular case, it is 1 to 5 mole fraction.

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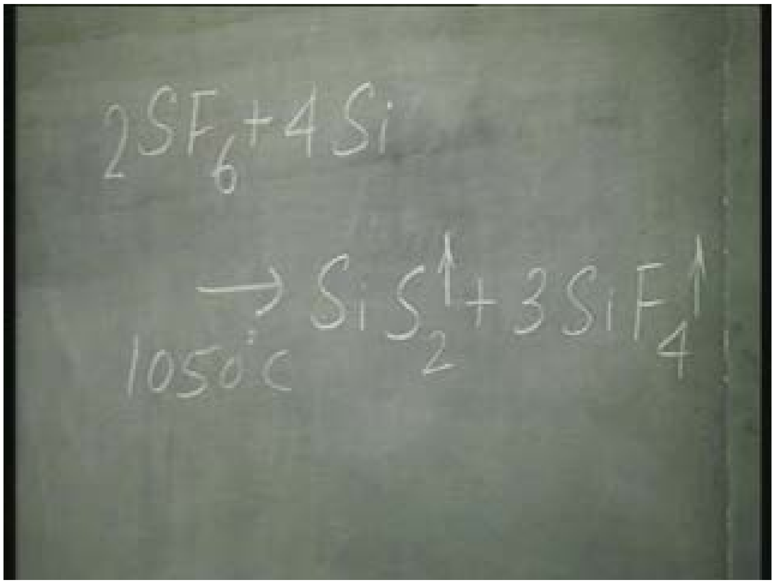

$$2SF_6 + 4Si \xrightarrow[1050^\circ C]{} SiS_2\uparrow + 3SiF_4\uparrow$$

If you do not want to use hydrogen chloride, there is another material SF 6. That is an alternative agent. Instead of introducing hydrogen chloride, you can put SF 6 and silicon sulphide plus 3 SiF 4. They are both volatile compounds. So, SF 6 is an alternative agent, it is a newer agent. Because there were potential problems with using hydrogen chloride, as the technology advanced people found that there is another agent. The advantage, advantages are two fold. First of all there is no question of any hydrogen chloride. You do not have to handle HCl, which is an hazardous gas and secondly you can lower the temperature to achieve comparable etch rate. If you compare the etch rates, say here at 1200 degree centigrade that compares with 1050 degree centigrade. So, you can lower the temperature by about 150 degree centigrade and still have comparable etch rates.

Lowering the temperature by even 150 degree matters, because in actual production we are very concerned about the thermal budget. To increase the temperature of the furnace and run them continuously costs a lot of money. So, in VLSI technology you will find that the trend is more and more towards low temperature processing, towards lower temperature processing. So, SF 6 offers these following advantages. It is non toxic, non hazardous and therefore, easier to handle and also the temperature can be lowered. But, from all these it may seem that silicon epitaxy is quite a simple or let us say, well established process. It is so, but it has certain problems.

See, I told you about how doping can be done during epitaxy. We can use the hydrides of the dopant material, but in addition to all these things there are inadvertent or non deliberate doping of the epitaxial layer, which is called, usually the term given to it is auto doping. Automatically it gets doped, even though you did not intend it to be doped in this particular way, it gets automatically doped. So, this is actually quite a major problem for epitaxy. I will just briefly outline why this happens and then, may be in the next class we can continue on that and show what are the adverse fall outs of this.

You have started out, during epitaxy you have started out, with a sample. Sample had some particular doping concentration. Now, even before the deposition has started, the sample was subjected to a lot of high temperature steps like the hydrogen flushing, like the HCl etching. So, during all these things it is possible for the dopants to diffuse out of the sample. So, the dopants will diffuse out of the original substrate and get mixed in the gas stream. So, that will alter the composition of the gas stream, agreed. Now, there is a possibility that when the epitaxial layer is getting deposited, from the gas stream these dopants which were not intended to be introduced in the epitaxial layer, it just came because of the out diffusion from the original sample surface, they get introduced into the epitaxial layer. This is one possibility. This is called gas phase auto doping.

The other possibility is you have the substrate with a certain doping concentration, you have the epitaxial layer also with a different doping concentration. At the interface, it is possible for both of them to get diffused across the interface. That is let us say, if my sample is p-type and the epitaxial layer is n-type. So at the boundary between the sample, bulk sample and the epitaxial layer I have a pn junction.

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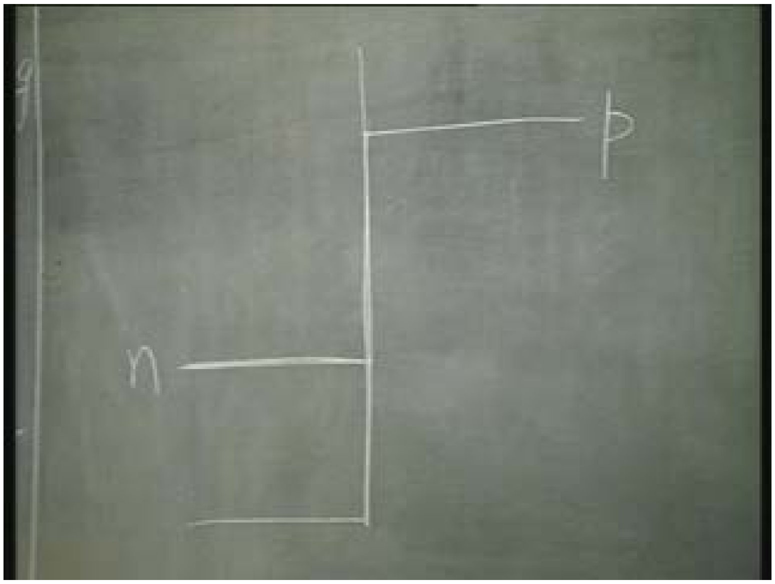

Now therefore on the epitaxial layer side, say this is my n epitaxial layer and this is my p bulk sample, this is the boundary. Across this boundary, you see on this side, the concentration of n-type dopant is small. Therefore, it may try to diffuse in here and across the boundary on this side, the concentration of p-type dopant is small. Therefore, the p-type dopant will try to diffuse in here. Therefore, even though ideally I have shown the boundary like an abrupt straight line, it will not actually be something like this, because of both these effects. One is the solid state diffusion across the boundary, the other is because of the gas phase auto doping. These are the two major reasons of unintentional doping during epitaxy and this can really pose a lot of problems for epitaxy.

For example, it can, it can determine what is the, what is the minimum thickness of the layer that you must grow, because you see there will be a transition layer between the substrate and the epitaxial layer, there will be a transition layer. So, this will dictate what is the minimum thickness of the layer that must be grown in order to get the specified doping concentration requirements. We will discuss more about this in the next class, the problems of auto doping and how they can be circumvented.