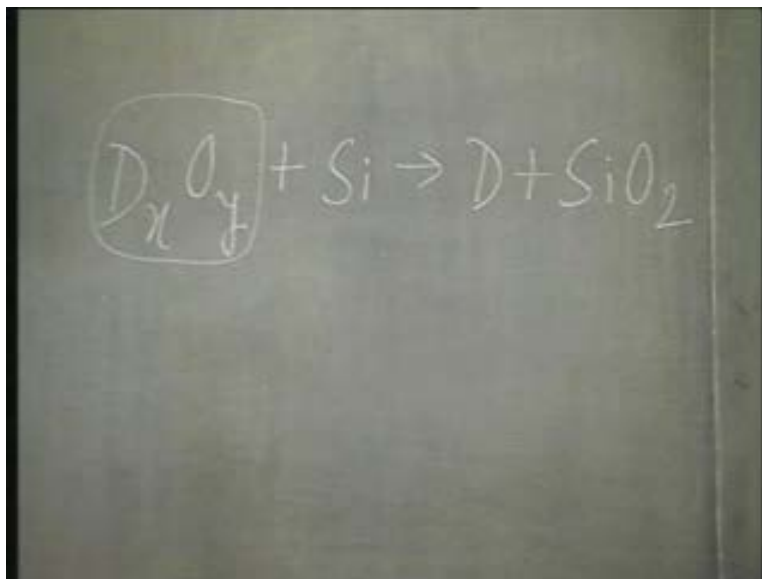


VLSI Technology
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Lecture - 18
Diffusion IV - Diffusion systems
+
Comparison with ion implantation

So far we have talked about the diffusion in silicon, first of all diffusion in general and then the case of some major dopants in silicon; what their diffusion profile is going to look like, what the diffusion co-efficient is going to be and so on. So, today we are going to discuss the actual, practical diffusion systems. That is to say how exactly in practice the diffusion in silicon is carried out. Well you know, diffusion is a high temperature process. The temperature ranges from say, 800 degree centigrade to 1200 degree centigrade and it is carried out in a fused quartz tube, inside a fused quartz tube; use a furnace and the fused quartz tube is there and inside silicon is kept. Silicon sample is placed inside in a quartz boat and then it is exposed to the ambient in which the dopants are present. So, essentially most of the silicon diffusion process we have the oxide of the dopant.

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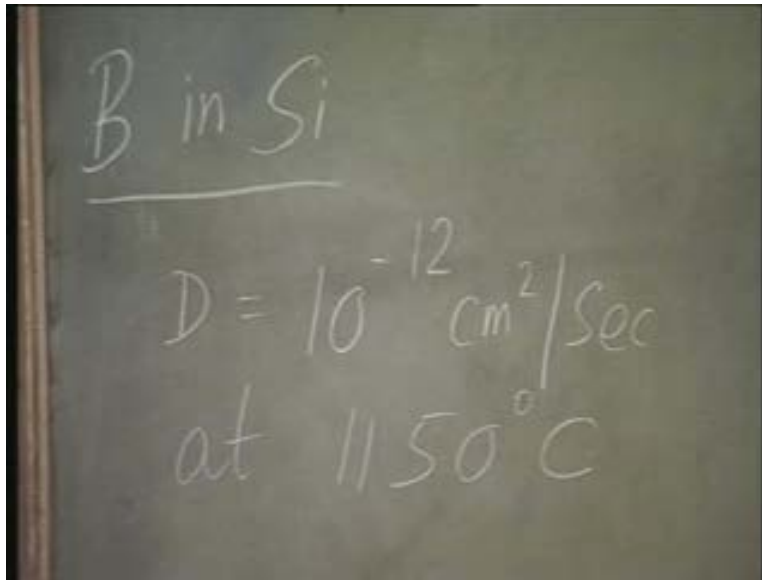


If I can put it like generally as $D_x O_y$, D stands for the dopant, some oxide compound of the dopant, it reacts with silicon to release Because silicon has a great affinity for oxygen, this is what is going to happen in most of the cases. So, this dopant will be introduced into the silicon and at the same time the silicon dioxide that will be formed on top of the surface, it will act as a barrier against out diffusion of the dopant. So, this is essentially what is going to happen at the time of the diffusion. Now, this $D_x O_y$ can be used just as it is like for example, you can use $B_2 O_3$ or $P_2 O_5$ or more generally what is done is you take some other compound of the dopant, make it react with oxygen insitu, so that this is formed and then from this the dopant is incorporated into the silicon.

This source material, the compound of the dopant which is going to be used, it is called the source material. This source can be either solid or liquid or gas and depending on whether it is solid or liquid or gas, there will be slight changes in the diffusion system, like for example, if it is a solid source, then you will place it close to the silicon sample itself. If it is a liquid source, then that will be taken in a container, gas will be bubbled through that liquid, so that the out coming gas is full of, saturated with that liquid vapour. If it gaseous, then of course we will pass it in the gas stream inside the furnace. Depending on whether it is solid or liquid or gaseous, there will be some modifications in the diffusion system.

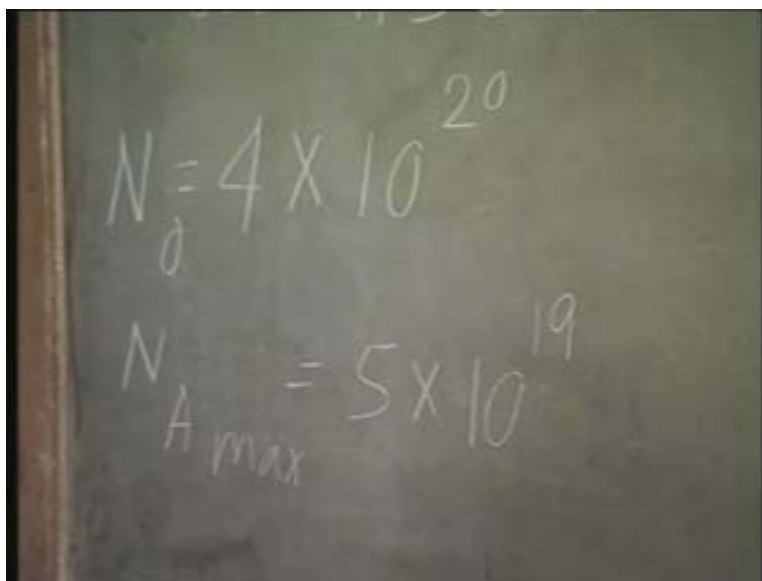
Now, let us talk about one of the most important dopant material in silicon, the only one available p-type material that is boron. In order to diffuse boron in silicon what are the things that I should know? First of all, what is the diffusivity of boron, diffusion coefficient or the diffusivity of boron? The diffusion coefficient of boron, of any material for that matter, is going to be dependent on temperature.

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So, at 1150 degree centigrade the diffusion coefficient of boron is about 10 power minus 12 centimeter square per second and of course you know in case of infinite source diffusion, the surface concentration is going to be limited by the solid solubility and the solid solubility of boron is, at this temperature, it is 4 into 10 power 20 per centimeter cube.

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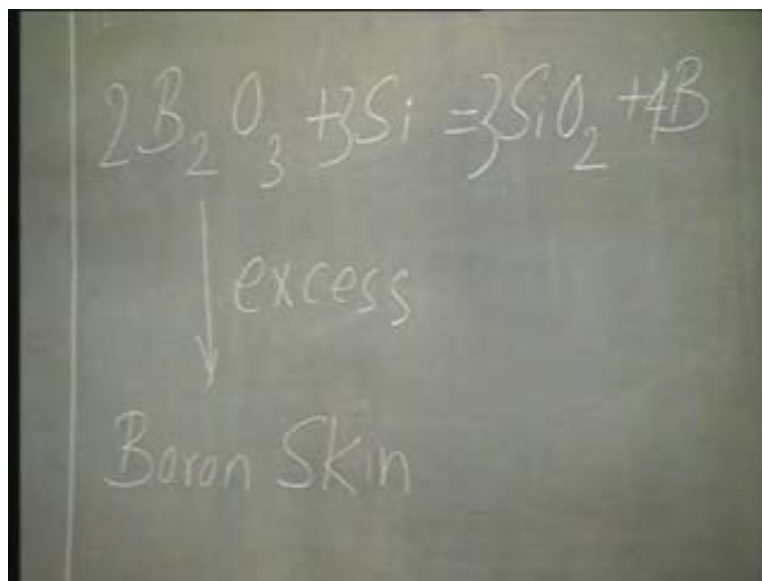
A chalkboard with handwritten equations. The first equation is $N_0 = 4 \times 10^{20}$. The second equation is $N_{A \text{ max}} = 5 \times 10^{19}$.

But that does not mean that all of this boron which you can introduce is going to be electronically active. The electronic activity will be determined in part by the misfit factor and remember boron has quite a large misfit factor of 0.254. Therefore, even though you can put in so much boron inside silicon, the surface concentration of boron can be as high as 4×10^{20} , you get the active concentration only around 5×10^{19} per centimeter cube, because of the misfit factor, N_A max is going to be 5×10^{19} .

So, let me in passing mention something. I told you that in VLSI, npn transistors are preferred over pnp transistors and I gave you a lot of reasons. This is one more reason, you know. If you are using a pnp transistor, then your emitter has to be p-type. The only dopant is boron. But, using boron you can only go as high as 5×10^{19} . So, you cannot really get a very highly doped emitter. Whereas for npn transistor whether you use phosphorus or arsenic, arsenic has zero misfit factor, phosphorus has also a very small misfit factor, 0.06. Therefore, the active carrier concentration will be much higher. So, so much about the diffusion coefficient and solid solubility limit of boron.

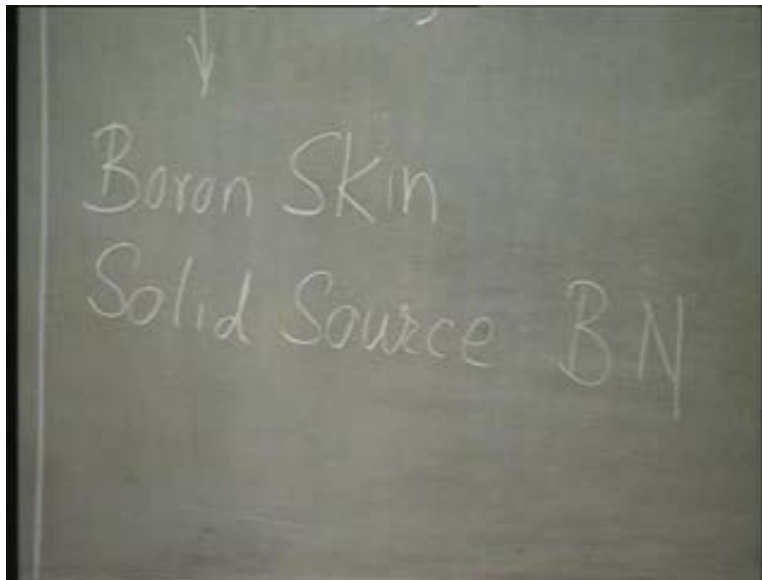
How do we really incorporate this boron into silicon?

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So, going by what I have said so far, the reaction should be something like this: B_2O_3 reacting with silicon to form silicon dioxide and release boron and this boron is going to be incorporated into the silicon. But in practice, B_2O_3 is not really used directly. You know why? Because, if you have only B_2O_3 , excess B_2O_3 will form a dark brown surface layer which is called the boron skin. It will form a dark brown layer on the silicon surface which is very difficult to remove. So, your surface will get completely spoiled. Now, only way to remove this boron skin is to oxidize it, so that it will form borosilicate glass and then etch that oxide; very slow and very difficult process, so one does not use B_2O_3 as it is, because there is always the problem of formation of boron skin. So you see, even though this is my basic reaction, I must somehow control the formation of B_2O_3 . So, what is preferred for boron is the use of a solid source called boron nitride.

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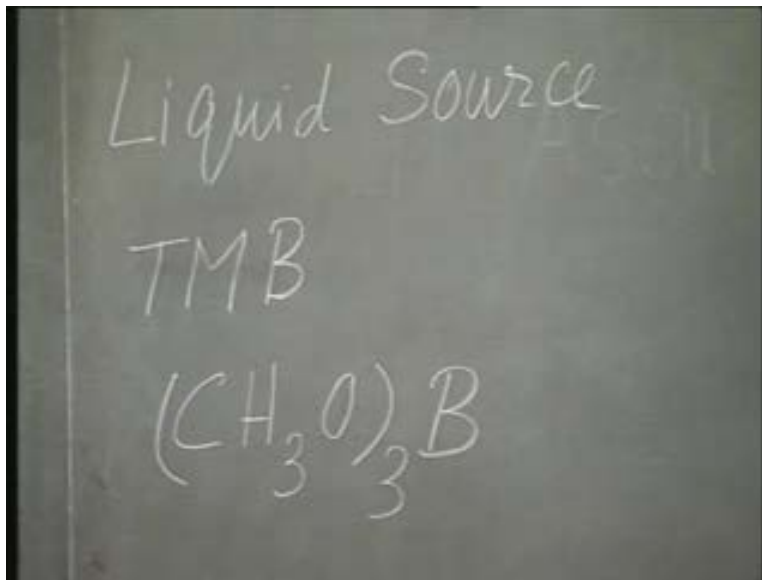


So, actually what is done is one uses boron nitride. This boron nitride is activated; before the actual diffusion process it is activated in an oxidizing ambient. So, what happens? This boron nitride reacts with oxygen and it forms a thin surface layer of B_2O_3 . Usually this boron nitride comes also in form of a thin disc. Like a silicon wafer itself, you have a boron nitride wafer, a thin disc of boron nitride. This boron nitride first has to be activated. The temperature range is also specified for the particular type of boron

nitride wafer. It can be anything between 750 to 1100 degree centigrade. It will be mentioned, you know it will be called say, BN 975. Then you know that the activation temperature of this particular boron nitride wafer is 975 degrees.

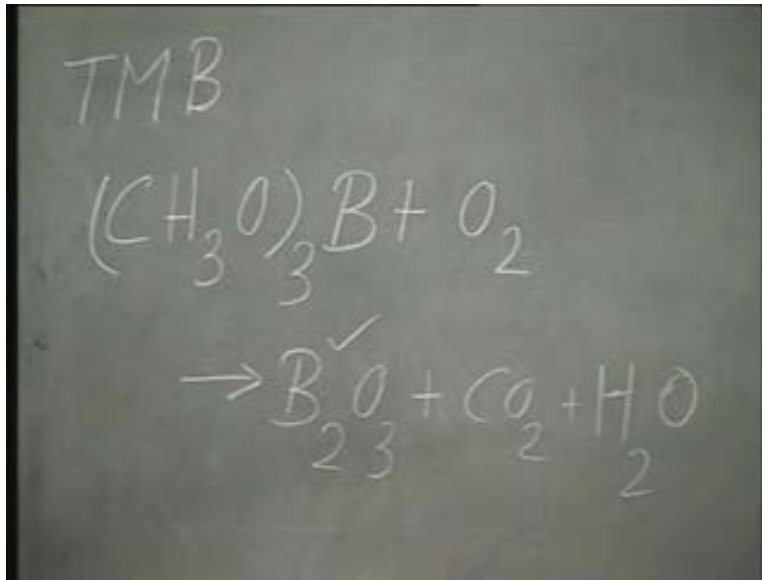
You activate it in oxygen ambient, so that a thin layer of B_2O_3 is formed on the boron nitride surface and then this oxidized boron nitride wafer is placed close to the silicon wafer and you use a weakly oxidizing ambient, so that from this B_2O_3 , the thin surface layer of B_2O_3 , boron gets incorporated into the silicon. You are controlling the formation of B_2O_3 . You are just activating the boron nitride wafer prior to the diffusion, when only a thin region is converted into B_2O_3 and that is going to act as the solid source. This is one choice of source for boron, the solid source of boron nitride, a very popular choice, but there are other possibilities also. Like for example, another quite common source for boron is a liquid source and that is trimethyl borate.

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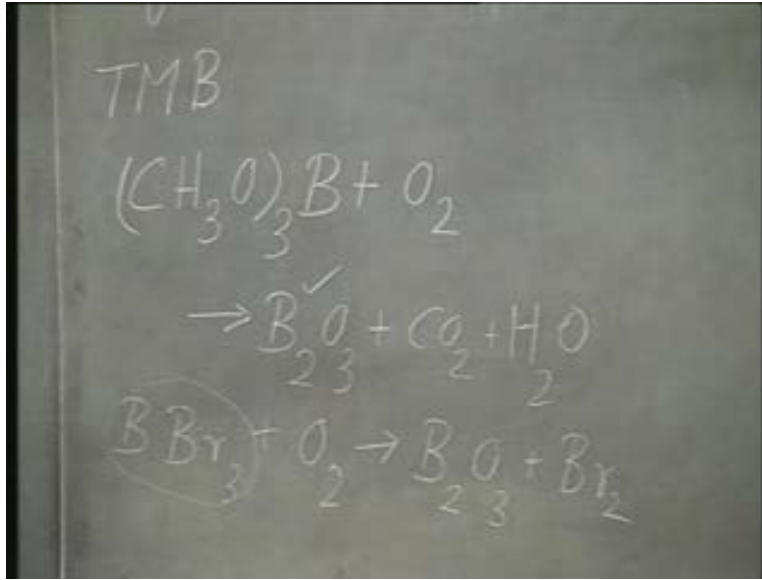
Trimethyl borate or TMB, commonly called TMB, trimethyl borate. It has three methyl groups. This is the trimethyl borate CH_2OH or CH_3O . This methyl group is there, three of them, so trimethyl borate.

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So, this trimethyl borate can also be made to react with oxygen to form B₂O₃ plus carbon dioxide plus water. But, what we are interested in is the formation of B₂O₃. So, this trimethyl borate is a liquid source. What you can do is you can take this liquid in a container, pass oxygen through that, so that at the output of the container you have oxygen saturated with trimethyl borate. Then, at the mouth of the furnace this oxygen will react with the trimethyl borate to release B₂O₃ and then this B₂O₃ can go and react with the silicon sample to form silicon dioxide and boron which will be incorporated into the silicon sample. So, this is another popular source for boron diffusion.

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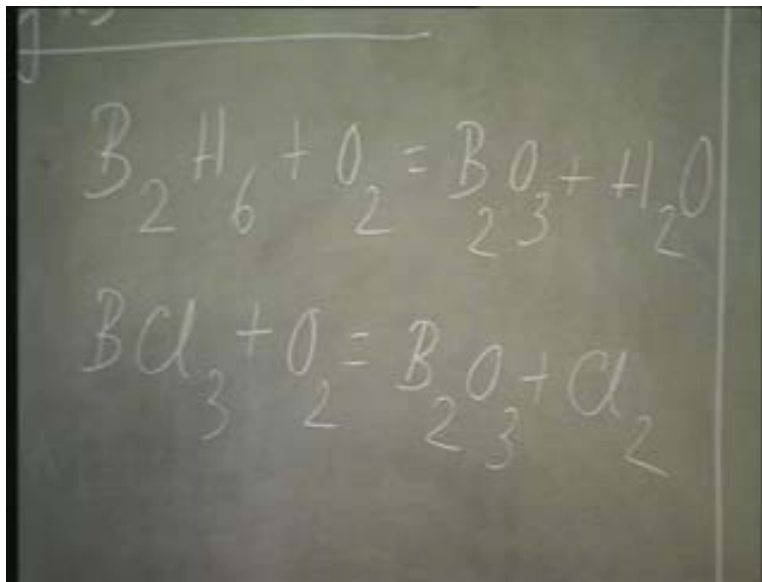


There is another choice of liquid source and that is boron tribromide. This is boron tribromide, BBr_3 . This can also be made to react with oxygen to form B_2O_3 and release bromine and again you know, after that B_2O_3 is going to react. So, see everywhere the eventual reaction is going to be between silicon and B_2O_3 . It is only how we generate this B_2O_3 that is the problem. We cannot directly use B_2O_3 , because then this boron skin formation will be there. Therefore we would like to use some other source from which a controlled amount of B_2O_3 will be generated and then that B_2O_3 will be made to react with silicon.

So, therefore you can use either solid source of boron nitride or liquid source of trimethyl borate or of boron tribromide. Now, boron tribromide of course, it offers you an advantage, an additional advantage and a disadvantage also. That is because bromine is released due to this reaction. Now you see, whenever you are releasing any halogen, you must have adequate venting. Bromine, chlorine, all these things must be vented properly; you cannot just let it loose in the atmosphere. Adequate venting, exhaust should be provided. That is one disadvantage.

The second disadvantage is you know, if these halogens - chlorine, bromine, etc, are present in excess it will cause halogen pitting of the semiconductor surface. So excess bromine, pitting might occur. So, you have to control the amount of this boron tribromide. But, there is an advantage also. You know, in small quantities, halogens will act as gettering agents. You have seen this for chlorine; similarly bromine can also be used for gettering. So, this is about the solid and liquid sources and then, what about the gaseous sources?

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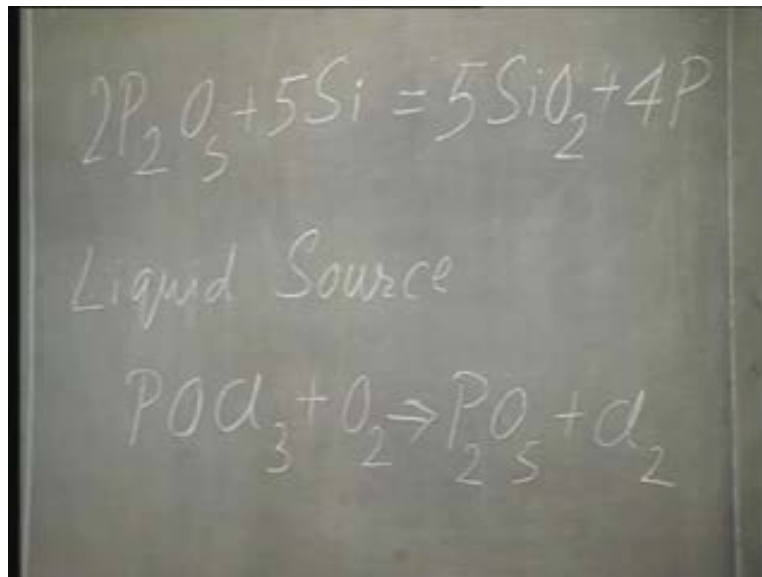


Actually a gaseous source is the easiest to handle, because you do not have to do anything. You just have to mix it with a diluent gas and then let it be inside the furnace. That is all you have to do, right. So, it is the easiest that way. But for boron, we have a bit of a problem, because the gaseous compound for example, diborane, B_2H_6 , B_2H_6 is a very dangerous gas. It is a very highly poisonous gas, as well as an explosive. So, even though it is possible theoretically to use B_2H_6 and make it to react with oxygen, again to give me B_2O_3 and, but one must be very careful about using this diborane, because it is a highly poisonous gas and also an explosive gas.

The other possibility is of course to use boron trichloride. Just as you have used boron dibromide, the liquid source, you can use the gaseous source of BCl_3 , but again in this case, remember you have to have adequate venting, because you are releasing chlorine and you must carefully control the amount of chlorine, otherwise halogen pitting will occur. But then, again in small quantities chlorine is not bad, it will help in gettering. In fact sometimes boron trichloride is used for this purpose, although the more popular sources are boron nitride and trimethyl borate. So, these are the choices of solid, liquid and gas sources for boron.

Now, let us go to the other major dopant in silicon that is phosphorus. For phosphorus, the diffusion coefficient is approximately of the same order as that of boron. That is about 10^{-12} cm²/s at 1150 degree Centigrade. Phosphorus can however give you a much higher active carrier concentration because its misfit factor is so low. Therefore it is possible, practically achievable impurity concentration can be as high as 10^{21} per centimeter cube. So you see, for npn transistor phosphorus is a good choice for making the emitter, because you can get very high concentration of phosphorus; very high carrier concentration. It is limited only by the solid solubility.

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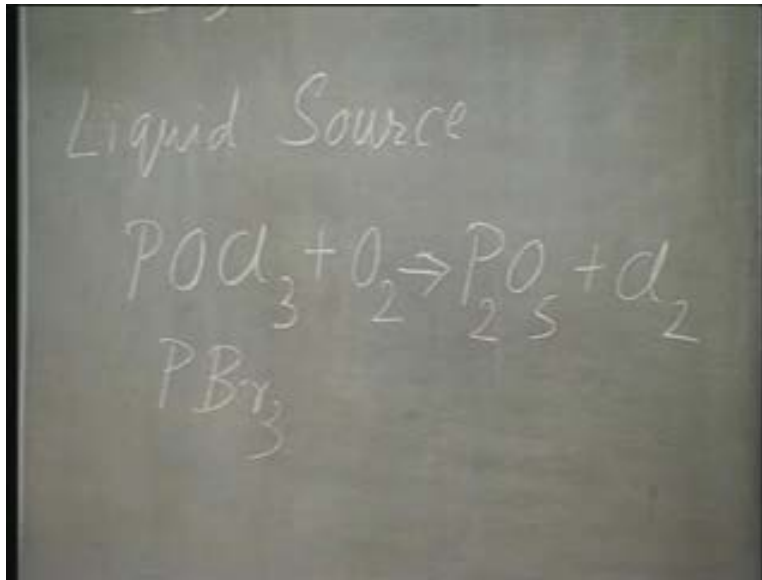


Again in case of phosphorus you know, the basic reaction is going to be, the basic reaction is going to be between P_2O_5 and silicon to give phosphorus, which will be incorporated in silicon and form a layer of silicon dioxide. That is essentially the basic reaction, but again here P_2O_5 directly is hardly ever used. P_2O_5 as it is, it is almost never used because it is hygroscopic. So, it will get contaminated very easily. It will absorb moisture from the atmosphere; it will get contaminated very easily. So, one does not use P_2O_5 . What one uses is a liquid source. For phosphorus, this liquid source is almost universally used. This is called phosphorus oxy chloride, phosphorus oxy chloride $POCl_3$. This is almost universally used. This $POCl_3$ will react with oxygen to form P_2O_5 and release chlorine and then of course, this P_2O_5 will react with silicon to form, to give phosphorus in silicon and you see, again here you are releasing chlorine. So, venting is a major concern, but again because of this chlorine one can get the gettering effect.

So, what happens is $POCl_3$ is also a colorless liquid. It is kept at zero degree centigrade, kept in icepack and oxygen is bubbled through this $POCl_3$ source. Then, at the mouth of the furnace, where the temperature is about 600 degree centigrade or so, there this reaction is going to take place. So, P_2O_5 is going to be formed. This P_2O_5 is carried in the gas stream to the silicon which is kept at a higher temperature. So, there this reaction is going to take place. P_2O_5 is going to react with silicon to form phosphorus, release phosphorus and this phosphorus will be incorporated in silicon.

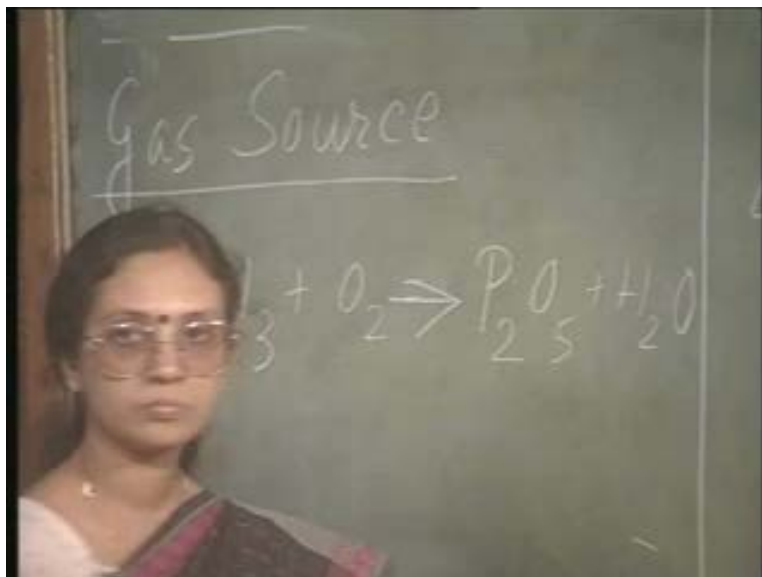
$POCl_3$ is almost the universal choice for phosphorus diffusion. Of course, instead of $POCl_3$, PBr_3 can also be used.

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This apparently gives a better gettering action. It releases bromine. Analogues to this, it will react with oxygen, form P_2O_5 and release bromine that apparently gives a better gettering action. But, $POCl_3$ is very well understood, very well studied and $POCl_3$ is used. As far as the gas sources of phosphorus is concerned, you see, one could use phosphine that is PH_3 . Just as you have used diborane in case of boron, one can use phosphine.

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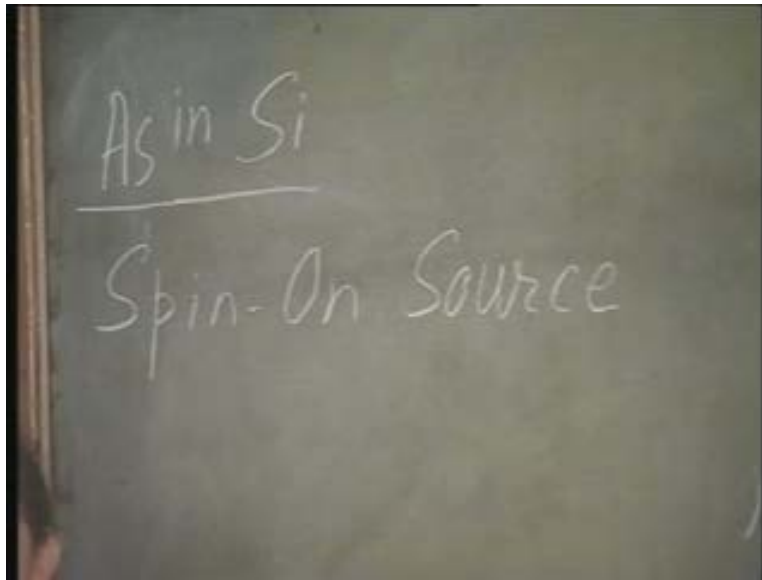
But again, phosphine is a highly toxic gas. So, one must be very careful while using phosphine. That is why for phosphorus almost the single choice of source is POCl_3 . You will always use POCl_3 for phosphorus diffusion.

Apart from phosphorus, the other important n-type dopant in silicon is arsenic. Arsenic is in a sense very good, because it has a misfit factor of zero. Its tetrahedral radius matches exactly with silicon, so it has a zero misfit factor. It has a lower diffusion coefficient than phosphorus or boron. The diffusion coefficient for arsenic is about one tenth of that of boron or phosphorus. That is if it was 10^{-12} in case of boron or phosphorus, it will be 10^{-13} , at the same temperature and again essentially it is the same reaction - arsenic trioxide, As_2O_3 reacting with silicon to release arsenic and form silicon dioxide. But, when you are using arsenic as the n-type dopant, there are some factors you must be very careful about.

First of all if arsenic is going to be diffused, the ambient must be free of oxygen. That is because arsenic is readily masked by oxygen. Even a thin silicon dioxide layer if it is formed, will be enough to prevent arsenic from going inside. So, arsenic diffusion is not done in an oxygen ambient, it is done usually in the neutral, nitrogen ambient, inert ambient. Secondly, the most important problem with arsenic is that it is a highly volatile material. As_2O_3 is even more volatile and arsenic itself is very highly volatile. So, what will happen? Since you cannot use an oxygen ambient, it is going to be diffusing out, so that your surface concentration that is carrier concentration, all these will be decided not by the case of zero misfit factor, but by the out diffusion problem. So, that is why even for arsenic it is difficult to achieve a concentration of more than 10^{19} per centimeter cube.

However another technique is usually used for arsenic diffusion. That is you use a spin-on source.

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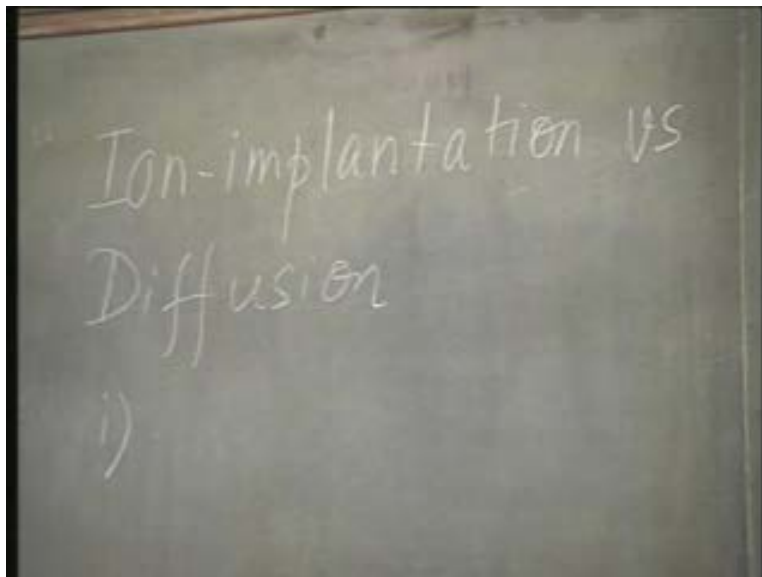
The spin-on technique is somewhat different from what we have talked so far. In spin-on technique, what is done is you take an organic compound of arsenic, usually arsenosiloxane or something like that. This comes as a liquid. You put a few drops of this liquid on the silicon surface at room temperature. You have your silicon wafer in which you want to diffuse arsenic. You put one or two drops of this arsenosiloxane in this and then you spin it at very high speed say, 4000 rpm or 5000 rpm you spin, so that there is a thin, even coating of this liquid on the silicon.

Now you bake it, prebake. You bake it at comparatively lower temperature say, 250 to 450 degree centigrade. When you bake this, then it forms a layer of arsenosilicate glass on top of the silicon. See, it is an organic compound. You are baking it, so all the hydrocarbons, they are going to go away. What you have is just a thin layer of arsenosilicate glass on top of silicon and then you push it inside the furnace at high temperature. So, what is going to happen? This arsenosilicate glass, what is arsenosilicate glass? It is a combination of As_2O_3 and SiO_2 , just like borosilicate glass, arsenosilicate glass, right. So, you push this sample now inside the furnace. This arsenosilicate glass which is formed on top of the silicon surface is now going to act as the source for arsenic, as well as it is going to prevent the out diffusion of arsenic, right.

So, you are going to prevent the out diffusion of arsenic to certain extent and by doing this, you can get higher concentration than that would have been normally possible. So, this is called the spin-on technique using arsenosiloxane. It is an organic liquid. Put a few drops, spin it at high speed, bake it, so that a layer of arsenosilicate glass is formed and that is going to act as your secondary source, as well as that is going to prevent the out diffusion of arsenic. So, so far, we have discussed the practical diffusion systems for silicon. That is we have seen what is needed to be done in order to diffuse boron or phosphorus or arsenic in silicon.

Now, you will remember that at the beginning of discussing the various processing steps, we said that doping can be done either by diffusion or by ion implantation. Now that you know what diffusion is all about, what kind of doping profile we get, what kind of system we need, let us now discuss the relative merits and demerits of ion implantation process diffusion. After that, we will go to discuss about ion implantation. What we are going to do is, we are going to take each point about diffusion and compare it. I am going to tell you, in ion implantation how it is done or what is done in case of ion implantation, right. So, we are now going to discuss ion implantation versus diffusion.

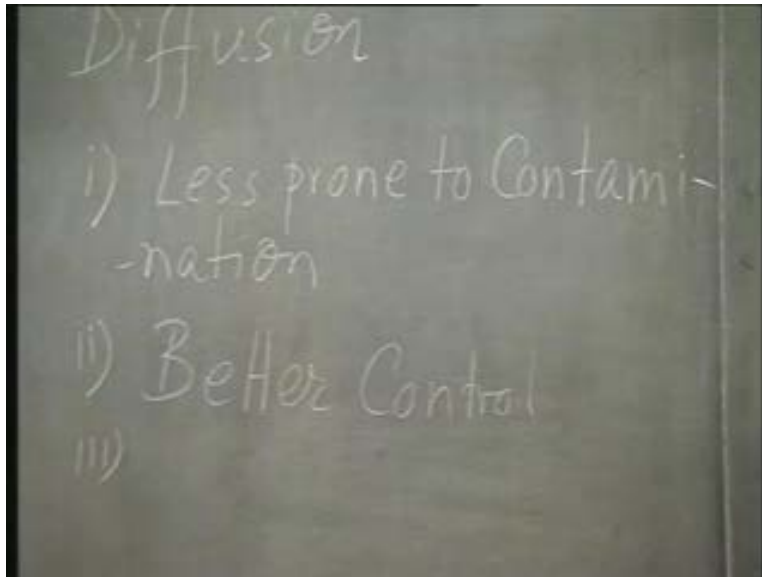
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In diffusion one of the major considerations is contamination. That is to say you cannot use the same furnace for diffusing say, boron and phosphorus, right, because inside the furnace there will always be a lot of contamination; like phosphorus diffusion furnace inside you will have a lot of P_2O_5 deposition. You cannot use that same furnace for boron diffusion. For those who have already been exposed to the fabrication lab, you know it is almost a sacrilege. You cannot even use, why the furnace, you cannot use the same boat or the same push dot for the diffusion furnace. Push dot is the dot by which you push the sample inside. You cannot even use those things of one furnace for another, because it will contaminate the entire system irrevocably. So, diffusion is highly prone to contamination. One must have separate furnaces, separate quartz tubes, separate boats, separate set of everything for different diffusion system.

On the other hand, ion implantation is much less prone to contamination. That is the same system can be used to implant various dopants. Ion implantation is an inherently cleaner process, because it is done under high vacuum. Any high vacuum system is obviously going to be much cleaner, right; you are going to pump out all the contamination.

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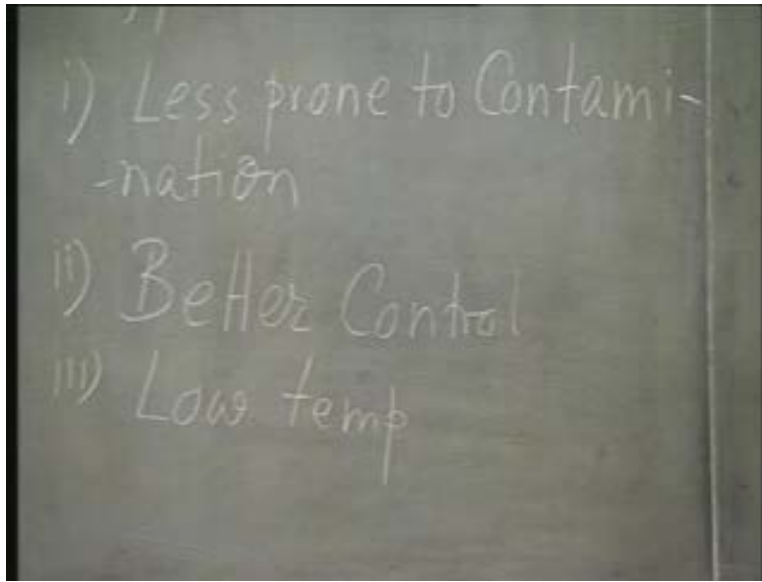


So, ion implantation is less prone to contamination. In diffusion, the control of the doping profile is usually within 5 to 10% of the predicted value. Well, that is because of various factors; you cannot really control the ambient conditions so accurately. That is why the profile or the amount of dopant that you want to put in is usually within 5 to 10%. On the other hand, in ion implantation it can be controlled within plus minus 1%. That is because, in ion implantation what you are doing? You are directing an ion beam on to the surface and you can adjust the dose of the ion beam by simply adjusting the ion beam current. It is much easier to control, you do not have to control the host of ambient system, you see. You are just controlling the ion beam current and you can very accurately control the ion dose. Therefore, in ion implantation you obtain a much better control of total impurity.

The third point is of course quite evident. Diffusion is a high temperature process; as I said, 800 to 1200 degree centigrade. In contrast, ion implantation is a room temperature process. So, not only that your thermal budget is reduced, but also remember whether I do diffusion or ion implantation, most often we will be doing selective doping, right. That is some portions of the silicon will have the impurities, some portions will have to be masked against. So, for diffusion, since it is a high temperature process, your only choice of mask material is silicon dioxide.

In case of ion implantation however, since it is a room temperature process, you can even use photoresist as a mask. So, that gives you a much better flexibility. You do not have to, before every diffusion step you have to grow an oxide. Here, you do not have to do it.

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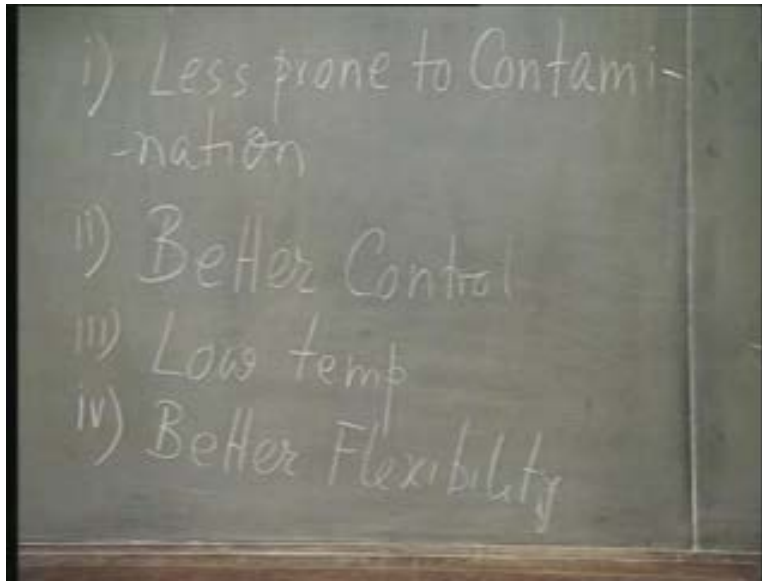
So, these are all the advantages coming with low temperature. Then again, there is a question of flexibility. In case of diffusion, you know that well, at most I can get the solid solubility limit on the surface for the infinite source diffusion and then as I do the drive-in, it is going to go down. The surface concentration is going to go down and the junction is going to move in. So for example, let us say suppose you want to have a junction with a low surface concentration and at the same time it should be shallow. You want a shallow junction that is the junction depth is low and the surface concentration is also low. If I ask you to realize this, you will be in trouble. Is it not? Because, remember what the diffusion profile looks like?

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This is the complementary error function profile. I have a high surface concentration and a shallow junction and if I want to reduce this surface concentration, I have a low surface concentration, but a deep junction. But, how do I get a low surface concentration and a shallow junction? This is going to be quite difficult for a diffused system. Is it not? You can however do it very easily with the ion implantation, because in ion implantation you have two different factors. One is the ion dose, which will control the total impurity and the other is the ion energy, which will determine how deep the ions are going to go in. So, you have independent control of the two unlike in diffusion, right. Because you have independent control, you can choose that I will put a small dose and I will also use a lesser energy, so that all these ions come to rest very close to the surface, so that I have shallow junction and at the same time because I have a low dose, the surface concentration is going to be low, right. So, ion implantation does offer you better flexibility.

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Other, another advantage associated with ion implantation is this. See, in a diffusion you are, you have been governed by a set of rules which are, let us say, in equilibrium that is to say your surface concentration is governed by maximum, the solid solubility limit. Is it not? The entire diffusion process is governed by the concentration gradient. On the other hand, in ion implantation it is a basically a known equilibrium process, because what you are doing is you are directing an ion beam of high energy inside the silicon. It is not governed either by concentration gradient or by the solid solubility limit. I can, by force I am pushing these dopants inside the semiconductor, right. So, therefore it is possible for you to obtain a peak carrier concentration, even in excess of the solid solubility limit.

See, what I am trying to say is this. Even when you have an abundance of dopant material, in case of diffusion your peak concentration, in case of diffusion that is at the surface; you cannot move the peak anywhere else. The peak always has to be at the surface, right. At the same time, the peak concentration is at most, it can be equal to the solid solubility limit. But suppose for some reason, for various reasons, we will see I want to have a sort of kind of a junction. That is I want the peak to be inside the surface. I cannot obtain that with diffusion, but I can obtain it with ion implantation. I can adjust the energy, so that the peak is somewhere inside the semiconductor surface, inside

the, underneath the surface, not at the surface, right. At the same time, I can adjust the peak concentration. I am no longer governed by the solid solubility criteria. The peak concentration can be even in excess of the solid solubility limit. So, all these things in fact, you know, you can put them in better flexibility.

There are various things one can do with ion implantation which is not possible with diffusion. But then, always this is a maxim in life that is always if you have to get something you have to give something, you have to pay something, right. In case of ion implantation also this is very true. If everything is so positive about ion implantation, how come then we are still using diffusion? Well, most commercial systems have really gone totally ion implantation. But, the flip side is this: ion implantation is a very expensive process. So, unless you are a commercial system, we do not have money to buy an ion implantation system. It is very expensive; very expensive and very sophisticated, therefore its maintenance is also quite expensive. That is one thing.

Even when you have the money, again think about the ion implantation process. What are you doing? You are directing an ion beam of high energy particles onto the semiconductor surface. In the process, obviously you are going to create damage. Are you not? You are heating the silicon surface with this high energy beam. In the process you are going to create damage. Fortunately these damages can be thermally annealed; not at very high temperature, by 800, 850, maximum 900, 950 degree centigrade, most of the ion implantation damages can be annealed out. But, whenever ion implantation is followed by annealing, it has to be followed by annealing, because immediately after ion implantation you will have no carrier activation. The layer will be completely damaged, there will be no electronic activity.

In order to get back the electronic activity it must be annealed, but when you are annealing there is always an associated diffusion process. So, your doping profile is going to get modified. It will be determined not merely by the ion implantation parameters, but also by the diffusion parameters. Fortunately for silicon these annealing, since they are done at comparatively lesser temperature, you know by 950 centigrade as I said, so at that

temperature the square root of $D t$ is not very high, it is quite small. Remember, the square root of $D t$ is a very important parameter, right. This actually determines the diffusion depth. So, this square root of $D t$ at this temperature range is fairly low, so that the ion implantation profile is not really modified that much. But, if you go to compound semiconductor processing, there you will have problem. Anyway that is beyond the scope of our present discussion. Let us for the time being focus only on silicon as the semiconductor material of our choice. So, in silicon, ion implantation does offer a lot of advantages and the disadvantages, except for the cost, can be easily combated. The major disadvantage is that of damage. Damage can be thermally annealed and this thermal annealing is done not at a very high temperature, so as to alter the implantation profile drastically and this ion implantation has been a boon to the silicon devices, particularly for mosfets.

Before I end this class, let me just tell you, remember in case of n-mosfets we had a tough time. Because of the presence of the fixed oxide charges, the threshold voltage kept going to the negative direction. Instead of an enhancement mode device, you were getting a depletion mode device. Now, ion implementation offers you, even when, even if you have a small amount of fixed oxide charge, ion implantation offers you a way to tailor the threshold voltage by simply putting a thin layer of dopant materials very close to the surface; n-mos, p-type substrate. You do not want to increase the p-type substrate doping because it will affect the body effect. So, you do not want to increase the substrate doping. Instead of that you put a thin layer of boron very close the surface, so that as well as the depletion region is concerned, the doping concentration is unaltered at the edge of the depletion region. But, very close to the surface you have a thin sheet of boron, which will alter only the threshold voltage. It will be like having another additional component.

All these borons they will be ionized; acceptor like, they will be ionized, so you are putting a thin sheet of negative charge very close to surface. So, that will act in a direction opposite to that of the fixed oxide charge and then combat the effects of the fixed oxide charge; you can tailor the threshold voltage. This is one major advantage of ion implantation and there are various other advantages which we will see as and when

we discuss the particular technologies. So, I think I have sold it to you that ion implantation offers you a better choice in terms of flexibility and control. So, the more stringent your requirements of doping profile becomes there is no other go, but to shift to ion implementation. We will start on ion implantation as it is in the next class.