**Fabrication of Silicon VLSI Circuits Using the MOS Technology**
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**Lecture 10**
**Solid State Diffusion (Continued)**

Okay, so here we go. Today maybe the last lecture in which we talk about diffusions and we will next time start with thermal oxidation. Let me quickly revisit something which we did earlier but little more carefully we look into some more problems. In actual diffusion profiles we look to theory again.

What we see now that the flux density was given as minus D d N by d x from the Fick's First Law but one can see from here at a given temperature of diffusion which may be around 900 degree plus, the intrinsic carrier concentration of silicon itself will be large enough. Large electrons are pairs are we knew available so n i is higher. However at diffusion temperature if the n i impurities are created larger than this n i e they create a gradient actually and that essentially leads to space charge and because of that we say there is an electric field. Now this additional electric field actually provides mobility to ions, okay.

So the diffusion specie which are ionic actually find that there is not only of force due to the diffusion gradient but also there is a field added flux available which is mu times n into eta e which is the electric field. I hope you have done some devices somewhere which has Einstein relation plus D k T by q plus we can always have build in electric field essentially minus k T by q 1 upon n d n by d x. Look for theory of devices or any other book, this is the standard expression.

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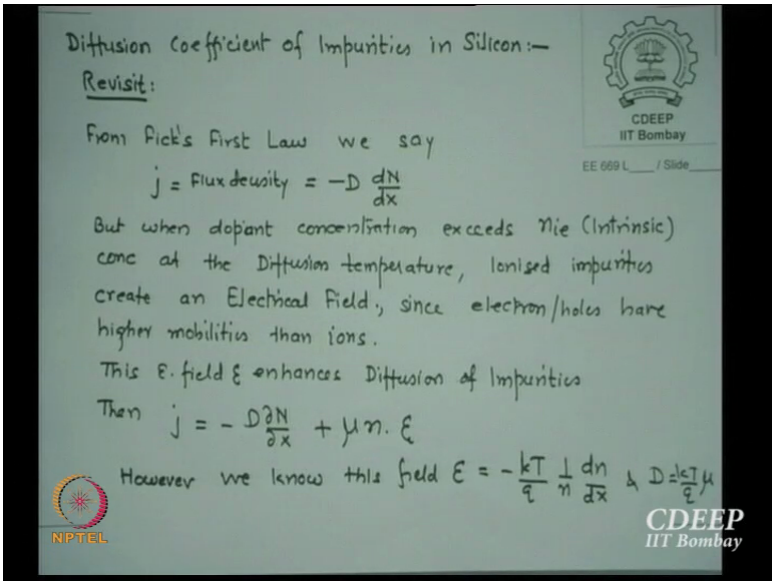


In our case n of course is the carrier available which you can say capital N is the number of impurities and n are electrons. Please remember n are electrons. So in real life if you have noted down the flux has now two terms, one due to gradient the other due to electric field. And one can see from there if the electric field is in the direction more diffusion will actually occur so impurities can go deeper during this higher gradient and because of that higher electric field. These relations are standard.

If you wish I can even derive them. This is very simple derivations but those who want to see some other book and devices you see that, okay. So why are we doing this is some one example at least or maybe two examples I will give you why are we so keen about doing this because we figured out in some species at some temperature did go more than what we thought by normal diffusion equations. So why did they go? So we came back and say there must be some additional force on that which carried them ahead, okay.

Or in some cases the profiles suddenly drops down. So what has happen suddenly? So some reasons which we saw in real profiles we wanted to explain and base for them we created some more physics and this is what it is. Have you noted down now? Major interest to us is these two equations which I wrote. J is flux density, D d N by d x minus of course even now I am assuming these constants. In fact D is also function of N itself. So there is additional term may appear but that we will see little later.

So if I expand this in real term it comes as minus D 1 plus d n by d N into d N by d x and this term in the bracket 1 plus d n by d N, n is the electron concentration, capital N is the impurity

concentration. Then that factor 1 plus d N by d x is given a name h which is enhancement factor. So D into h is essentially now effective D. D into h is now effective D and therefore we can even find what is h which I did. I hope that you know these two equations again as I said. If you do not know equations read again.

The charge neutrality means P plus n d is equal to n h plus n h minus so charge neutrality holds. So this is the first equation we use. And law of mass action is what? P n is equal to n i square. So using these two equations you can write this expression n by n i is equal to capital N by 2 n i plus bracketed N by 2 n i square plus 1 to the power half. In this case either n d or n h will be used because you will have only one kind of species. N will be either n d or n h because you are only diffusing h specie.

So if I solve this and use binomial expansion assuming that N is larger than n i that is the condition I said. Then this can be expanded and roughly this can be written as 1 plus N upon N square plus 4 n i square. This is roughly good enough.

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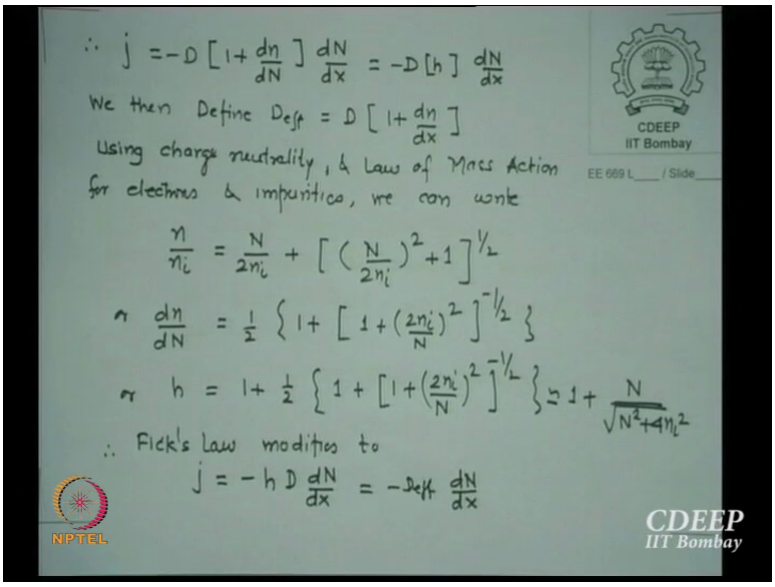


This maybe around if you calculate this value, point 1 to point 2 or sometimes even point 8. If n i is comparable to N it can be as high as point 8, okay. So depending on the value of N and n i at that temperature one gets the coefficient h which can be as I said can go up to maximum up to 2 but minimum at least is not 2 means 1, 1 plus 1 is 2, but typically 1 point 2 to 1 point 4 is the value which you get total. H is the factor which is 1 point.

So what does this mean? That the diffusivity will increase in the presence of large dopants if the temperature is high, n i is higher but dopants are even higher. So for higher doping cases

additional diffusion appears simply because this field enhancement factor h. Another effect people see which is very important and we will see that but if you have noted down as I said this is my expansion.

I solved it so you do not have to solve every step. This is the expression. You may write this expression. I write everything because I do not copy so I have to solve myself. So when I solve, steps have to be written. But you do not have to, okay. I already solved it, okay.

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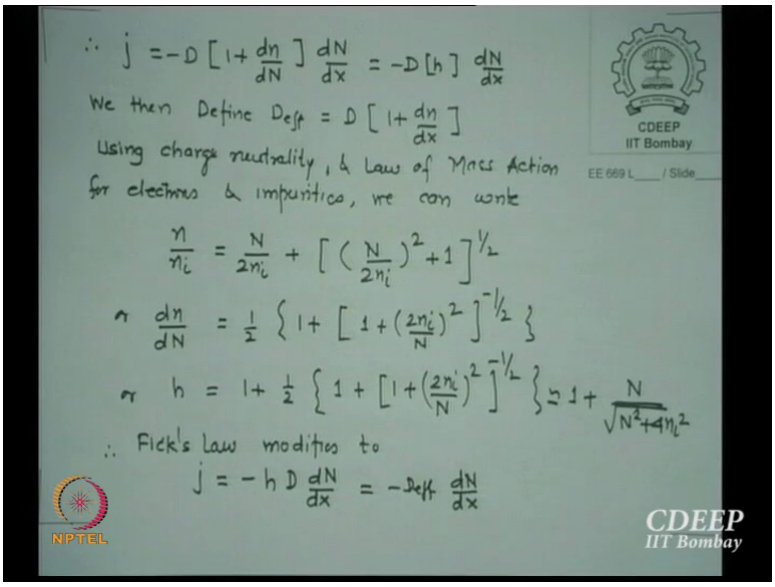


I just want to tell that how it is done because most people believe that books are final answer they give. No, it is derivable from basics. That is why I wrote two equations and everything is solvable, okay. Okay, so j is minus h D N by d x so D effective d N by d x. If you have noted down here is another effect what it can give. Let us say initial profile was this one and there are impurities here and electrons here which are higher mobility. Remember electrons have higher mobility than ions.

Since electrons have higher mobility than ions, electrons move faster and that is why there is a depletion layer created which increases the electric fields. If there is enhanced electric field, impurities try to follow the electric field and since they follow the new profile is something which is different. This was initial profile and now this is additional diffusivity has been seen.

So it actually goes in, okay. But net concentration remaining same, surface concentration slightly reduces to adjust the number of impurities which you are pushing. So, another effect which not so obvious from here, this is called isotropic diffusion which is also worrying part to many solid state diffusion people.

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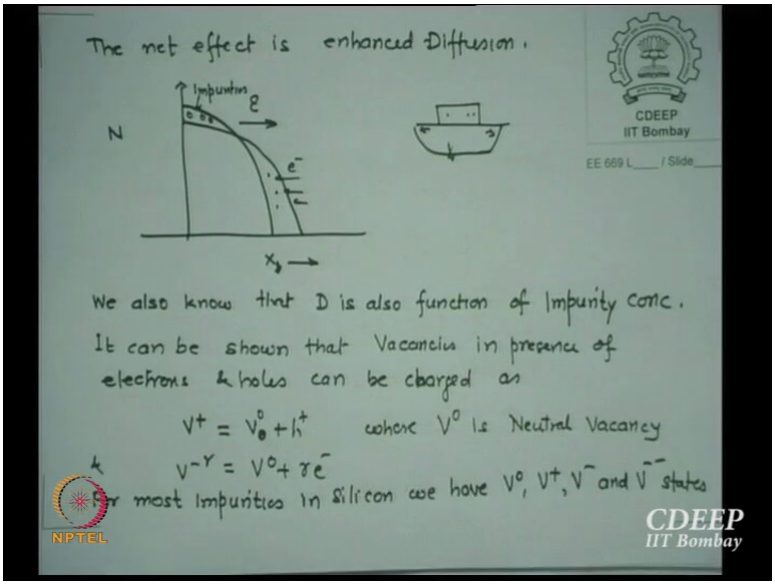


If I am actually introducing impurities inside of a silicon substrate, this is one effect, this is another effect. So the impurities do not travel essentially. The electric field to great extent pushes them down but there is diffusion also sideways, okay. This is called lateral diffusion. This is because the impurities are isotropic in their getting inside material. There is except little direct I get it because electric field is with me but even then there is side diffusion goes on.

So the actual source of drain if I create and I am allowing some window and through which I am putting impurities, the source drain will not be of the same size through which the window I pushed in but they will be also lateral on the sides, okay. And that sometimes worrying because essentially it helps in some cases because channel length may reduce if I did but in some cases it will actually improve. It will allow more depletion there and more bulk charge will appear. So there are issues diffusion will increase.

So there are issues in which one has to worry how much lateral diffusion. So if your electric field is stronger, these lateral diffusions are smaller. So larger the doping you are doing, this is possible. For the normal mode of diffusion this is not possible, okay. Because n i is equal or less than larger than this at that temperature then it will not have enhanced effect. It will only go through lateral as well as anywhere, okay. This is not just three dimensional, it can go all directions. Isotropic is the word.

If anything goes in one direction, what is the word used? Anisotropic. So we are actually looking for anisotropic situation but we never get it in normal diffusivities. What is that? No,

in a way inside furnace there is no voltage. This is called built in fields, okay. These are called because as I say electrons are higher and they move faster compared to because of their mobility is higher. So as they move out the depletion layer is created and that depletion layer essentially creates electric field, okay.

Space charge Poison Law, okay. So more impurities are then sucked in because the electrons going in means field is higher on the other side. Yes, only at higher doping this is seen. At lower doping this is not so strong in effect. That is why I say h is close to 1 point 1 to 2 depending on doping actually you are going through, okay. This is two effects which I seen. The third also there is another problem which we see in many cases. We also know that D is also function of impurity concentration.

That is what I said and it can be shown that the vacancy in presence of electrons and holes can be charged species. The figure maybe I can draw for you. This is your lettuce and let us say this is your vacancy and this is your impurity. So this impurity finds a vacancy here but it does not really immediately go there because it will create a vacancy here.

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But normally what happens it exchanges something like this. This is called vacancy ions pair. It is called vacancy ion pair, okay. And actually this whole vacancy ion pair actually jumps, okay. So when this goes ahead or this goes ahead it will create another vacancy and ion will move ahead of it, okay. So essentially what happens this whenever vacancy is larger and earlier there is a gradient so more and more impurities in a pair starts getting in. So this is similarly it can also occur with intrinsic shells but that diffusion is not very dominant for us.

Why? Because they are not contraband electrically but in real life even that diffusion is interstitial vacancy pair is also formed, okay. So we are not looking that so carefully because they do not contribute to resistivity or currents. However in real life many things happen in materials which we do not look into it because they are not electrically active situations. Whereas in other case if the electron holes are available, this normal vacancy is called neutral. there is no charge with it.

But if it forms a pair, it picks up a whole, okay, then it is called V plus. And if it can pick up more than one electron that is two vacancies or two ions close to one vacancy, die vacancy as it is called or maybe (())(13:39) vacancy as it is called, so the neutral vacancy plus r number of electrons. R can be 1, 2, 3 but not more than 3 in different materials. R e minus is V, this is the definition I given.

It picks up a hole then it becomes positively charged vacancy. If it picks up an electron it becomes negatively charged and it can pick up one electron, two electrons and even three electrons. So that is called charged vacancies.

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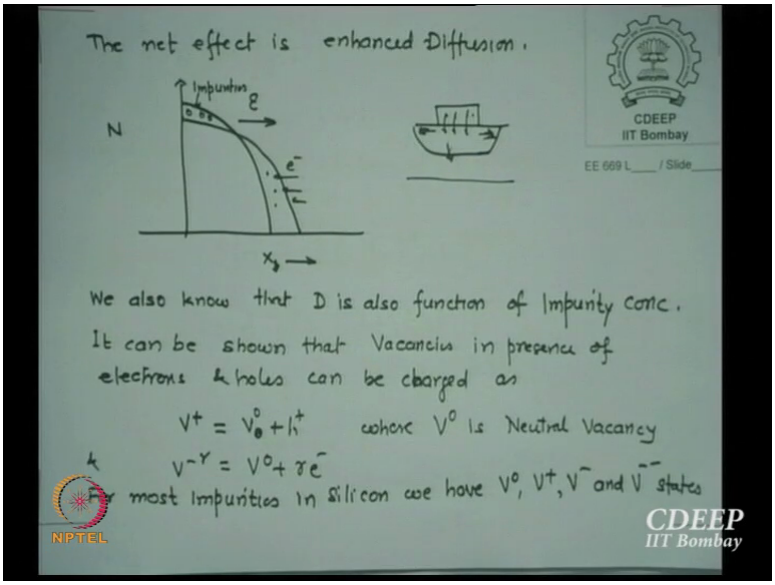


Now if there is a charged vacancy in a (())(14:13) of silicon what does that mean and if these vacancies have their energy state in the band gap then we have worries. If they are outside we may not be worried. May be the conduction band above who carries. However when we did lot of extra other experiments, (())(14:31) many others, it has been found by many experiments that these energy particularly for impurities in silicon there are two electrons

states, vacancy state minus 1 minus V minus and V minus 2 which is energy minus 1, energy minus minus.

The upper one is only point 11 e V from conduction band. The other one is point 44 electron volt in the conduction band. Whereas in the case of holes there is only one possible mechanism in silicon V plus. So that also varies in different materials. For example if you have an Indian specie and with a vacancy it may have around point 16 electron volts as the energy here but in the case of Boron or any other specie it can be as low as point 08, point 1, point 01 or point 1 in many cases.

So depends on specie and it depends on material you are using this V plus. So please remember even V plus plus in some other material with some other impurity is possible. In silicon only V plus is observed within the band gap whereas two electrons states V minus and V minus minus or 2 minus as we call are also available.

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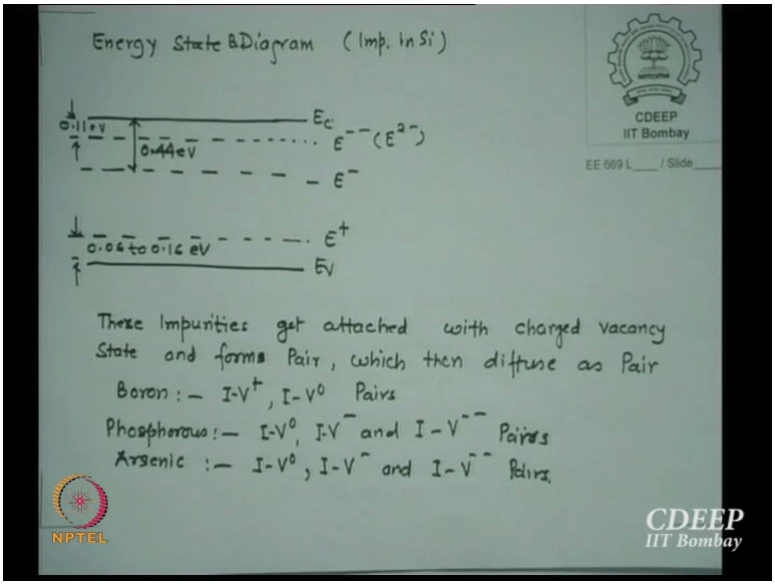


Now because of availability of these states. Yes this act like a trap. That is what the vacancy is. Therefore the impurities are actually trapped on these charge vacancy sides, okay. So they may form now pair like for Boron it may form an I V plus or I V 0. In case of phosphorus it may form I V 0. I is impurity, I V minus and I V minus minus. These are pairs. In arsenic same as phosphorus, I V 0, I V minus, I V minus minus.

So what is the implication? Boron otherwise impurities are going and picking up vacancy side but there is additional mechanism diffusion which is adding to the movement of ions and that means there will be additional diffusivity in the presence of vacancy ion pairs. One of

course is actual jumps which we have already done. That is how we calculated D. There is a jump frequency one point to the other. This is the energy barricade crosses, reaches the next side. But there is an additional mechanism we see at least for higher doping cases in most cases.

Then they form a pair and these pairs may contribute to additional diffusivity. If you have noted down please remember this has been verified by number of experiments including infrared, spectroscopy, many other analytical tools that there are charged vacancies. Is that okay? Everyone, why I am doing all this? I am show you one example and why I thought of show you because of course these days very few people are working on phosphorus diffusion in (())(17:53) but mostly we are going for arsenic. Why we like to go arsenic?

Student: Light.

No it is not light. Not mass part.

Student: Shallow junction.

Shallow junction, one is this but that is not the only reason. Arsenic can give me highest solid solubility. Its (())(18:20) factor is zero. Same radius that of silicon, 1 point 18 armstrong. So the largest number of impurities which I can push in if arsenic is only possible in silicon. So 4 into 10 to the power 21 per cc I can get to you. No other species can go to this concentration. Is that clear? Phosphorus has this around 1 point 1 or something so it will give point 25 or something as (())(18:47) factor which means it cannot go to all the way.

It may go to 21 but will not go 4 into 21 or 5 into 21 which is possible in arsenic. So for larger surface concentrations arsenic is ideal. And the second of course is the diffusivity of arsenic as that figure other day showed has the least of diffusivity among all other species. What is the advantage? Shallow junctions, very good. So of course you can solve this but I just wrote the final answer to show you.

The diffusivity then effectively is h time additional diffusivity because of pairs. This P is the hole concentration with reference to n i. N is to the n i and remember that there are two possible vacancy mechanisms, one with positive D, negative two Ds and however this is general expression. Both have P or n.

So if you look for n alone this plus will be not there because there will not be any I V plus formation because phosphorus is already having additional electron with us, okay, or arsenic

having additional electron with it. So they form only D minus and D minus minus pairs so D effective for n is D 0 plus D minus n by n i plus this.

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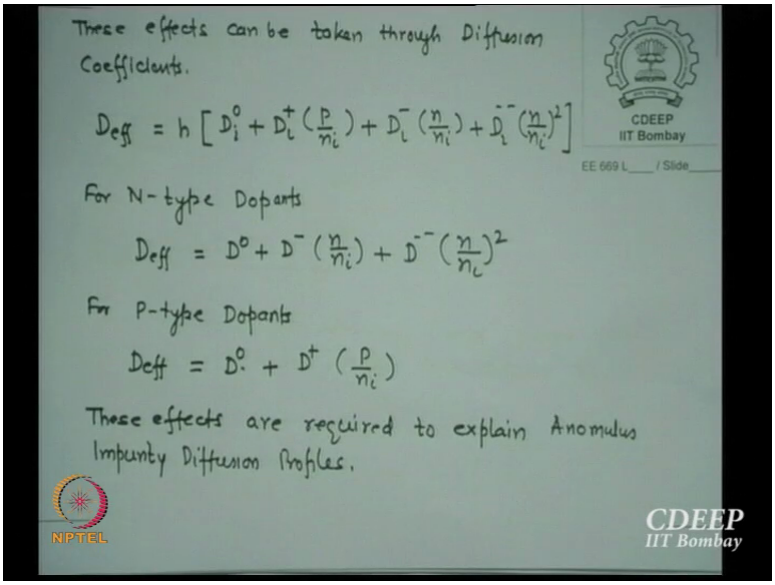


Actually n by n i is the ratio vacancies to the intrinsic vacancy at a given time. Some other (())(20:20). Extrinsic case the number of vacancies available to the intrinsic case number, the ratio of that is essentially n by n i. You just listen me what I said. This is good enough. D effective for P dopant would be D 0 plus D plus only because boron are P minus ions, okay. So this will only give one term. So now we see that for a given doping situation with that temperature we find D.

I know P and n so n i and then I find how much is D effective for that specie. Now all that we did for two reasons. Here is something an example, you note down and then I show you where these examples were used. There are two popular effects particularly in bipolar processes. One of them is very important. Please remember I keep saying mass circuits are taken over bipolars by huge numbers but there is still 8 to 10 percent bipolar market. So do not think that bipolars are zero, okay.

So and firstly I like bipolar because it gives lot of physics of semiconductor junctions. You use anything in mass later about basic thinking is far better in bipolar then only you can think why mass did not do as bad as bipolar, how I did it better than bipolar? So in some sense do not think that bipolars are out. The only thing silicon bipolars are out, okay. That much I can say. All high frequency HEMT or whatever devices now are (())(21:57) or 3-5 material based bipolars but they are very much there.

They are in optical devices everywhere and therefore do not think that BJTs are over, okay. Their application area has certainly changed, okay. So I want to show two cases quickly. If let us say I am making an NPN transistor vertical. This is my base diffusion, this is in substrate n and I make n plus diffusion for making emitter. Actually it is also here, collector. This is a BJT.

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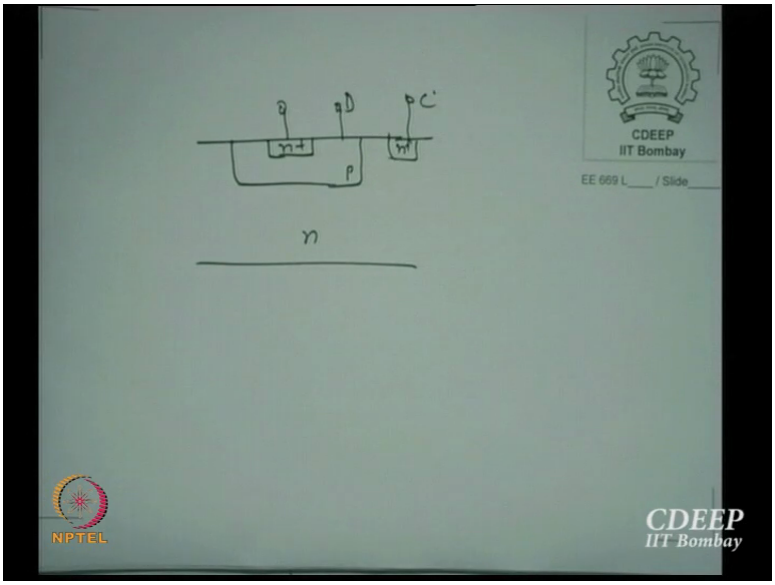


Now what I thought that if I diffuse emitter here, the base width actually is this much, okay. So it is good if I diffuse emitter then I will get smaller base width and better gains. Of course this is not very true because it will also go in all directions. But the minimum base width is available to you. But it does not occur like this. In fact in real life exactly below emitter there is a dip in the base region. It is called emitter dip effect. So what happens, the base width did not change, okay.

It remains same and therefore your gain did not get improved as we all thought that it should but it did not, okay. So this was an anomalous situation we thought it should do something but it did not. So we thought wherever n plus was coming why there was an additional diffusivity of boron down, okay. Please remember boron is going down, okay. So we figure out that emitter is heavily doped material n plus maybe phosphorus or something.

What kind of vacancies pair it can form phosphorus or even if arsenic? It can form V minus and V minus minus. So there is a diffusivity which is essentially available with this. But as soon as it tries to go below the concentration itself reduces. Surface is highest but as emitter

diffusion happens the concentration at this junction point is smaller. It becomes smaller and smaller.

So now what time this pair formation was declared by us? When n is larger than n i. But as n decreases this pairs do not remain paired and vacancies are released, okay. I V minus let us say becomes I plus V minus so vacancies are released.

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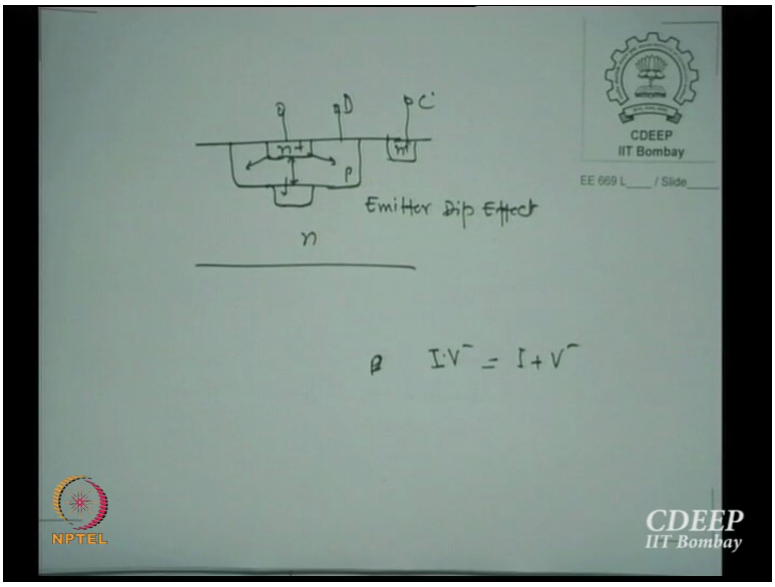


As the vacancies are released vacancy does not mind and they are mostly initially minus but it may also happen that it may become I minus plus V 0. If there are neutral vacancies created there, the boron now finds there is an additional place where they can go, okay. And therefore whenever this vacancy drifts down which was the h factor going down so it finds that more and more vacancies are available just below that so more and more boron goes down through this.

So first thing it happens that at high concentration the pairs occur but at lower it did not, okay. So this was one reason we said that look this is one possibility that pair might have broken down. In the case of phosphorus there are many effect but major effect I can show you. Let us say this is ideal profile I want for phosphorus N 0 at here I want to create somewhere here in B.

But what I figured out in real life this is the profile some whether (())(26:21) or something like this. But in real life the profile is not like this. There is a kink at some point and suddenly more impurities get out.

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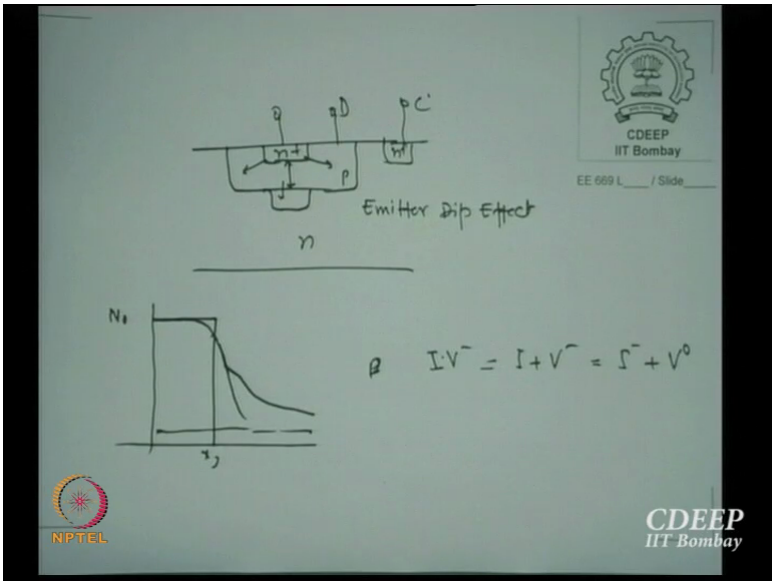


The same reason one can ascribe that as the concentration of this impurity goes down below n i e the vacancy pair both V minus minus as well as V minus actually are broken down, they come out. And as more and more vacancies are available for you, phosphorus starts following these vacancies and start getting more and more inside. So now the junction depth many times is orders of higher than what you thought in your process. You thought it is point 1 micron junction it may become a micron junction, okay.

Now this effect has to be known (())(27:12) because otherwise the junction depth which is deciding the base width or any other parameter may actually go so (())(27:20) that your performance of the circuit will never be as what you wanted. Therefore this anomalous effect when first time we observed many years ago people realised that there must be something more to it and therefore they let look into physics once again and they say, okay there is a additional diffusivity and breaking down of pair the which causes vacancy creation which allows access diffusivity, okay.

This issues which I am talking about are real life issues. Of course I think Plummer has given this diffusivity term but I think he did not explain much about the actual profiles which he could observe, okay. May be dip effect everyone talks. They so first worry because they were only making in 70s BJTs and every time we used to figure it out that the gain has not improved, okay, which we thought by so much diffusion will happen.

So we have to re plan ourself how much we should do ? So all these issues came and BJT gains were not attainable and then we started looking (())(28:25). Is it okay? So these issues

are essentially what I must say are physics based and one can explain. There are many anomalous effects. There are 12 or so. I am not going to each of them. I am just trying to say this is the physics one can think of and can explain the real results. Why I am interested in these models?

Because, if I am going this whole processing of the chip on computer then computer cannot think hopefully so good. Of course there is an artificial intelligence word is used but AI is how much you teach so that is not real artificial, okay. AI is only as much as you teach. It is you teach neuron that much it remembers like putting in memory there. However in real life that cannot do the job of a humans.

So what we figured out that some results which we are getting are not so ready but the actual process has shown something else so the computer should also know what could have gone through. So the models have to be substituted there, okay. That is why these models were created because the CAT tool one needs to have exact models. Not exactly of course what do we do? In spite of all this let us say I am not able to get the profile then I will add some 1 plus k time some factor, okay, and try to fit there first.

And then I start explaining k after I find it is fitting, okay. Due regards to all modelling people but that is what they will do. They will add 1 plus k and if k does not fit linearly they will put some number and then also get a physics, okay. Oh, this must be thermodynamic issue, comeback. Okay but anyway at the end of the day computer has to give the values which we observe closest to what it should be.

Having done modelling, having done the physics, having done the possible profiles you can get, okay, how do I calculate time temperatures for given depths and surface concentration? Now we actually want to see how it is done in a lab, okay, because unless we do in a lab there is no issue. So essentially if you are looking for diffusion processes in a lab first start looking into what are the requirements, okay. What are the requirements for a good diffusion system? These are some of my thoughts over the years.

If you have seen it that diffusing impurity should be always brought in contact with the pre-cleaned silicon surface only then impurities can go. So they must touch somewhere. Gaseous form, solid form, whatever form they must touch the surface of silicon. So first system whichever you are going to create must have possibility of see that the source is touching silicon, okay. So that kind of system you must built something, okay.

It should also remain in contact as long as your diffusion process is going to be done or given temperature time cycle the impurities must keep touching those silicon surfaces. If you are depositing something you must remain uniform there. So there must be constancy available which should not vary then. You know suddenly some impurities gone away, suddenly they come. No, uniform there should remain there. So that is another issue.

The third requirement for a diffusion system should be such that it should be possible to vary surface concentrations N S up to its solid solubility limits. It should allow me to reach the solid solubility limits at highest of temperatures, 4 into 10 to the power 21 or kind of that value. If I cannot reach that that means I am limited by the diffusing system which I do not want, okay. Of course these are all obvious but whatever is obvious is stated, okay.

The diffusion process be such that it does not damage the surface of the wafer because if surface damage occurs then there are more issues of what we call trans created and random diffusivity will start.

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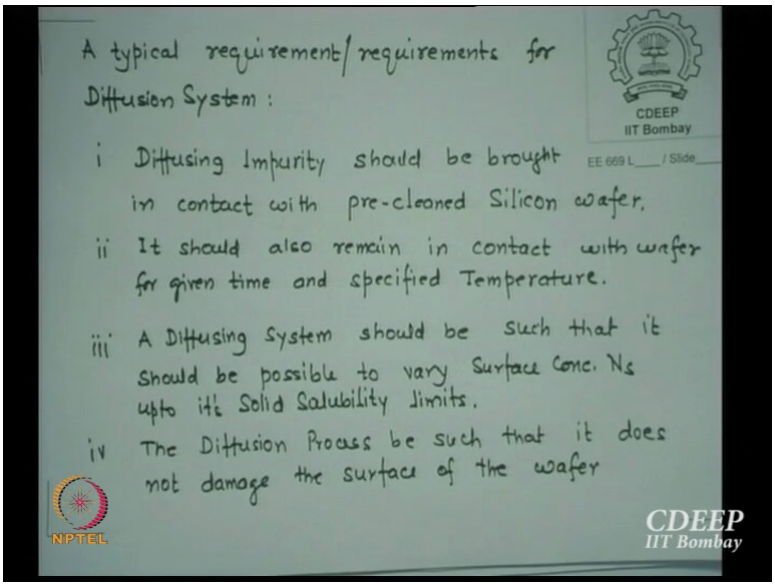


So it should not actually damage the surface of silicon, okay. It is very important. The reason why I say that many materials we did not use because it started surface damages. please remember the wafer which we created first time was polished surface and polish is of the order of point 01 micron. That is the level at which our polish was and that is what I said, it is better than normal mirror finish, okay. It is such a flat surface. So anything pits goes on it which you do not see by eye but maybe hundreds of nanometre pits it will create different diffusivities, okay.

And therefore we do not want anything which goes there. Of course you can say I remove that. Yes, that exist that possibility that okay I will do some way that I will further polish it out after my process. That is done. This process is called CMP, okay, chemical mechanical polishing which is allowed now. Earlier it was not, now it is allowed. So it is not that this criterion is not so valid now. We can say okay I have a CMP I will do that, okay. Okay, so these are four, there are few more which we will look into. Is that okay?

First is contact, second is till diffusion all impurities should remain in contact. It should be allowed to get me the best of surface concentration I need. And the process should be such that it does not damage the wafer. These are four requirements. After the diffusion process, the impurities and other materials on the wafer surface should be easily removable. That is most important. For example other day I said the silicate glasses, borosilicate or silicate glass I should be able to remove that and not by great polish.

I should just do something and it should get a mirror polish again. So this is an essential part of the system. Whichever gases sources you are using you must see that they finally give me etch ability of any surface which I want. One of the major interest in companies are the last two. The diffusion system should be able to give reproducible results. If I do today maybe another half an hour later some other diffusion it should be reproducible.

If the one result is not matching the other then I have a problem of reliability. These are two slightly same but different. Reproducible essentially means for given process the number of wafers in a run should have same result. And if I do number of such runs they also should produce same results, okay. If there is a huge variation then my process is not standard, my system is not standard because the yield is money.

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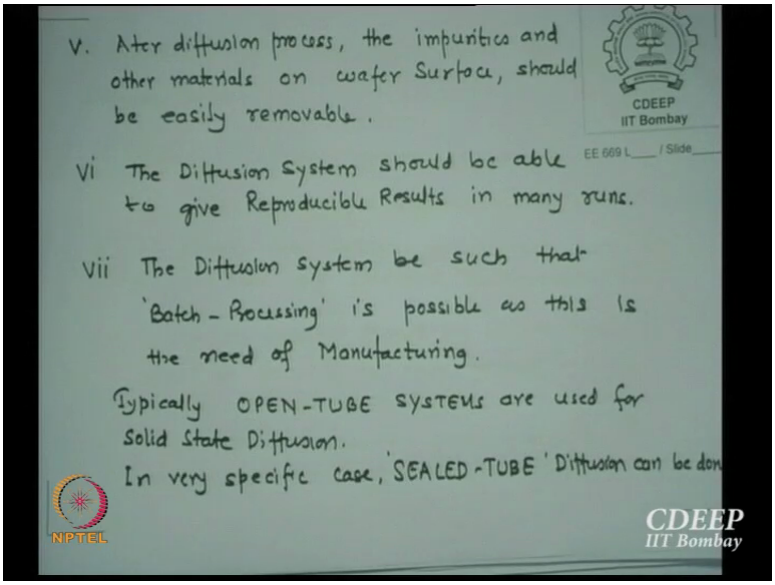


I want almost 100 percent yield so as close as I reach that much money I have, okay. So these are manufacturing requirements that the process has to be 100 percent uniform throughout that, any number of times I do and that is very important, okay. There are two kinds of systems for diffusion we use, one is called open tube system the other is sealed tube which is rarely used but possible. We will see at least this one. I have photograph of a furnace which will probably give some idea. I do not know whether, yes I have, okay.

First have you written down? Typical furnace is shown here. Another photograph is better but this is just to show you.

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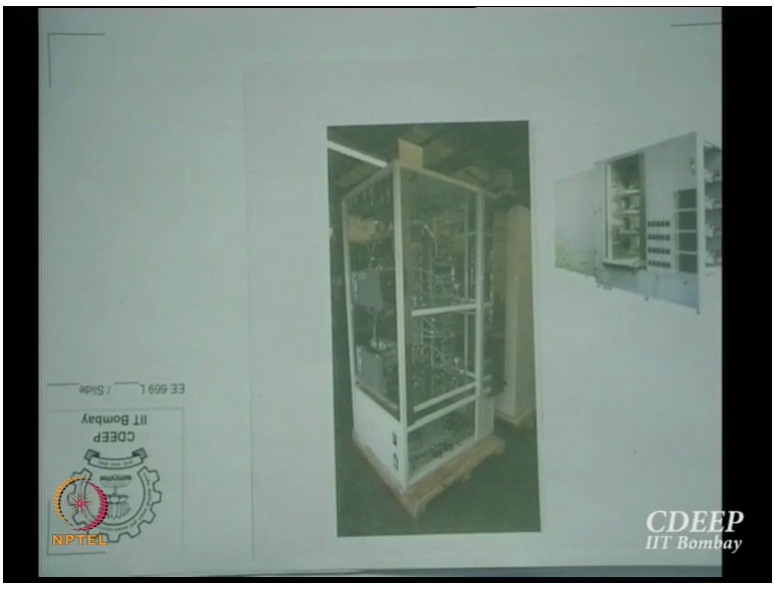

This is typically what a furnace looks like, okay. It depends on how many tubes you want. This is a four stag furnace. One tube, two tubes, three tubes, four tubes, four stag furnace. This part of the backside of this essentially has all gas entry systems. Different kind of gases are required at different flow rates and they have to be given to different tubes. So this is a gas flow system which is just rear side of the entrance of every tube for that. So this is very huge system.

Typically a furnace may be height around 9 feet to 12 feet depends on how many tubes you have and what size of tubes you are actually going to use. The better figure is somewhere here. This is a typical four stag furnace shown here and one can see these are the exits. You can see here a small ladder is kept so that you can go and put something above.

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So height you can guess what it is, okay. The kind of clean room requirement dresses is shown here bungee suits. Absolutely not known who is inside, okay. That is the catch in that. It should be so much covered that accept for your eyes nothing should be visible and you have two specs on that, one internal specs, one upper specs. So you will not be able to see who is in, okay. This is how wafers are loaded. I will show, this is not very good. Wafers are put in a rack and loaded, okay.

This is a quartz tube which is used in all diffusion furnaces. Quartz is the highest purity glass and it is crystalline. Its melting temperature is as high is 1812 degree centigrade so it is all used up to 1400 degree centigrade quartz tubes can be used, okay. Now this is the cap which

sits on that, okay. This whole is inside. So the way it is done is this furnace is in a semi clean area which may be class 1000 or class 100 area.

But this tube outlet is projected in clean area so wafers are introduced from clean area, clean benches and a clean environment. So no dust sits on wafers. So that is the kind of furnaces we used and as I say each furnace per stag as I say, per tube these days. Please remember this size is roughly 3 inch wafer size. It is a 4 inch tube, can handle 3 inch wafer or preferably 2 inch wafers. If you have a 12 inch wafers you need to have 16 inch tube, okay.

So what is the importance in that? Larger the tube means larger heating element has to be provided so much that larger amount of gases has to be flown. Volume is so high, okay. However larger the size of the wafer more chips will come out of a single wafer in one run. So that is why we still want to go higher and higher for the sake of profitability, okay. I have started work in 60s with 1 inch wafer, 2 inch wafer, I went 3 inch wafers and then of course then I came here and even say why not make a 6 inch wafer furnace.

I say the cost of 6 inch wafer furnace is 12 times that of 3 inch wafer furnace. So I just wanted to show you that the furnace is as such you see are very crucial and the kind of furnace system at the end maybe we will talk more about it. Types of sources which we use in diffusion are three kinds, solid source, liquid source and gaseous source. The solid sources which sits actually on the wafer is called primary source.

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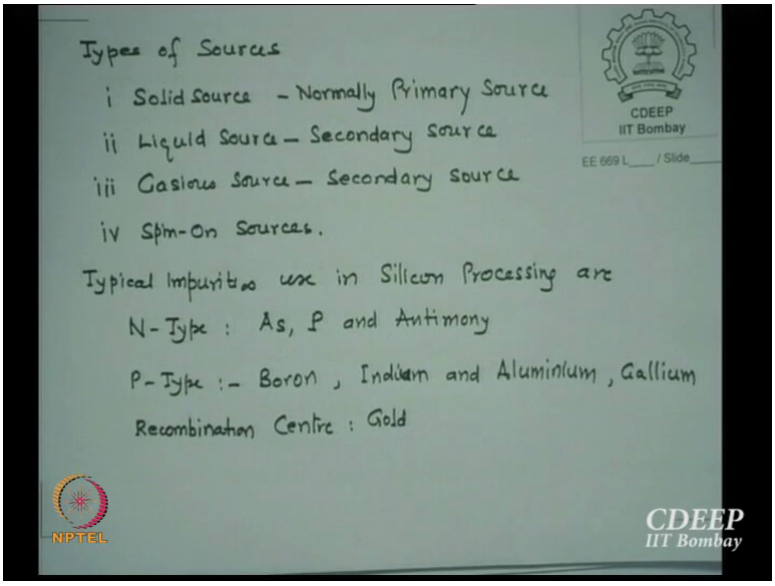


The impurities source which actually gets impure is in silicon is called its primary source. You may have any other source but first must convert it into primary source, okay. So that

diffusion will only occur through primary source, okay. There is also fourth possibility which is called spin-on sources, good for solar cells, cheaper, okay. Typical impurities used in silicon processing are N type arsenic, phosphorus, antimony. P type, boron, Indian and I intentionally put here because aluminium, gallium are rarely used but they are available.

They can be (imp) implemented. Everyone thought Indian has a very large energy from the balance point 16 so it will never be used because how many holes it will create. Since the energy is higher e to the power minus e S by k T. So larger the energy smaller number of holes it will create. Boron has point 08 or point 06 so it will create almost at room temperature all can be n i so all holes can be achieved. Whereas in Indian unlikely to get larger concentrations. So Indian is not used.

Aluminium has another problem. What aluminium is also has a diffusivity in silicon but also is alloy with silicon. Now if it does both then one does not know whether aluminium is going or not going and how much it is going. It also gets too fast oxidized. What is aluminium oxide is called? What is the commercial anodized? Whatever aluminium you see they are all oxidized and polished and called anodized alumina only, okay.

So aluminium is not a very good impurity to diffuse because it may form an alloy quicker than it diffuses down. But it does, it is not that it cannot be. So type three impurities it will create holes, okay. But it has a slightly higher energy of this. So one does not use aluminium as anytime impurities source. The aluminium has a strong advantage in source drain contacts because let us say I have a P type source and P type drain and I put aluminium contact.

So even if P is not heavily doped this aluminium top doping during the higher temperature processing will make a good alloy and good omissity. So it is good for P channel devices particularly putting aluminium contact. But aluminium is now almost out of all IC processors barring exceptions. We are looking for higher conductivity materials. Aluminium is very good conductor everyone thought but copper is even better so why we did not use copper? Copper is very strong oxidizing itself.

It forms copper oxide which is insulating. So now we put it oxidation but we run copper line, okay. Earlier when we made first lab in 80s there was not a single copper tubing or copper material in whole lab because copper is a poison. It gives almost a level in the silicon which is near mid gap. So you wanted to avoid copper everywhere. Nowadays the copper is the

major interconnect, okay. 20 years earlier they started in 98 from IBM (())(44:34). They actually first time introduced copper interconnects.

What is the advantage? The resistivity ratio of aluminium to copper is 3 times. So obviously for the resistance of the line will be 3 times smaller compared to aluminium for same size which means the R C time constant will go down which means pits can be improved. The issue came, circuit devices could give faster outputs but running from one point to other is slowing down. So, interconnected related problems so attempt was made to improve interconnect itself, okay, so that is why aluminium.

So this is additional features you should know. Gallium has even deeper impurities so it hardly used, okay. There are some sensors now being used with gallium, okay. But you read some maybe (())(45:22). Antimony is N type dopant, can be used but again it has a larger energy gap therefore rarely used and it is much bigger. Of course its misfit factor is small so do not think it has a better compared to both phosphorus and that. Arsenic of course is the best.

But as I say size is bigger and energy is too high to create large number of electrons, okay. There are also other impurities we introduced is gold. Very important for us because faster devices. Particularly the bipolar devices speed can be improved by gold dopings, okay. These are called recombination centres, okay.

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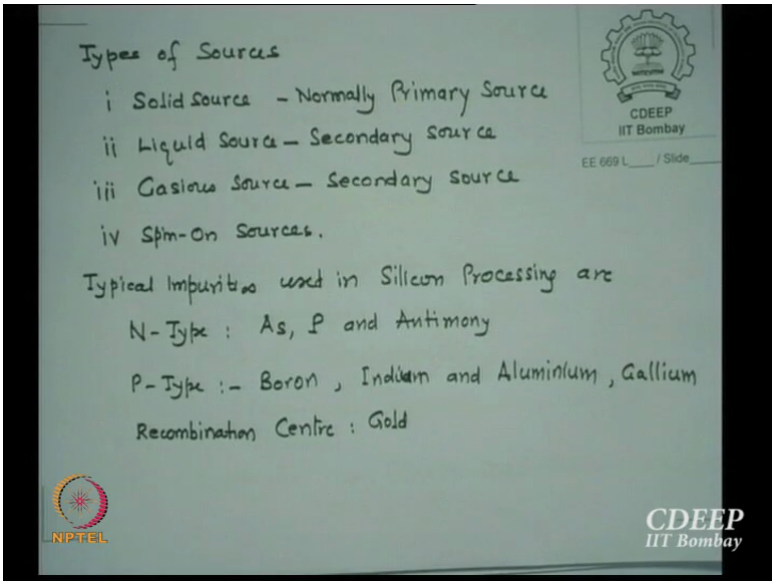


I will leave a word for you. Gold is amphoteric. What does that mean? Yes, so it is an amphoteric impurity. It gives both levels. Acceptor level is higher than the donor level. If you

look at phosphorus the impurities sources are solid sources. The phosphorus available in the market even if it is purified is called red phosphorus. It is a powder form and it is available as red phosphorus. The red essentially word came because it gets little bit oxidized and it gives reddish colour so people used to call that phosphorus as a red phosphorus.

But it is essentially only a phosphorus with little oxidation on that. So you will have to (re) reduce it to make full phosphorus. Another source is what is called dibasic or even (chloro) tri basic ammonium phosphate, monobasic ammonium phosphate but mostly used is dibasic N H 4 2, H P O 4. What will be mono? 1 here 3 here, okay.

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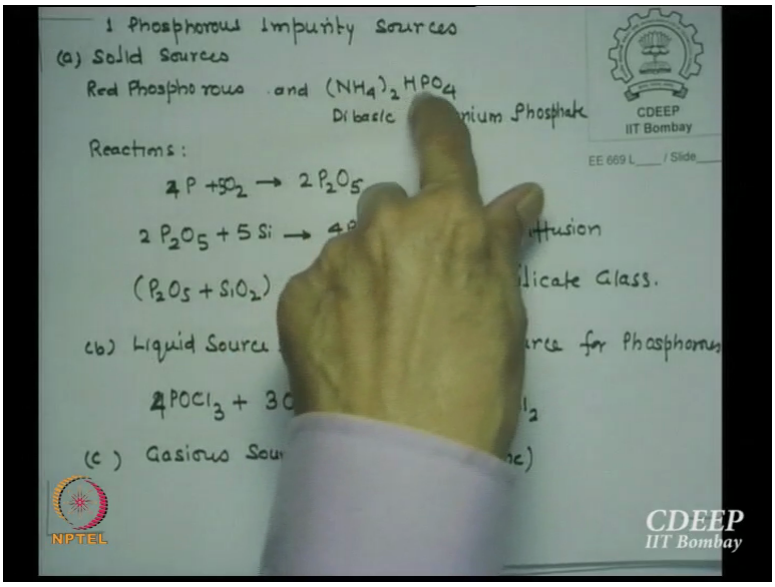


So if you keep changing the phosphate with reference to N H 4 it can be all three possibilities. But most used source is (di) dibasic ammonium phosphate. 4 phosphorous plus 5 O 2 forms 2 P 2 O 5. Please remember P 2 O 5 is the basic source for phosphorus. It is the primary source for phosphorus. P 2 O 5 is the primary source for phosphorus diffusion. So if I oxidize it I shall create P 2 O 5.

The reaction further during diffusion will be, once I have P 2 O 5 on the surface of silicon, P 2 O 5 will react with silicon and will form phosphorus and S i O 2, okay. So phosphorus will get in and outside will be on the top, okay. This is process of diffusion, phosphorus in, oxide top, okay.

Student: (())(48:18)

It does but still thin enough and since you have a gas flow down it has a more concentration in the outside so the diffusivity is much stronger in than what is coming out. Internally there is no gradient. It is opposing the gradient. So floor impurities will come out but larger will go in. There is a flux both sides. In any thermodynamic system y will come to x, okay. It depends on the given temperature forward reaction is favoured or the reverse reaction is favoured.

Actually you must have seen I have not to put equal anywhere. Arrow essentially says that at different temperatures reaction can be either way, okay. Can be from right to left or left to right, okay. This mixture which is mixture of S i O 2 and P 2 O 5 is called phosphosilicate glass, okay. What is it called? Phosphosilicate glass and actually that is the source of impurity in fact, okay.

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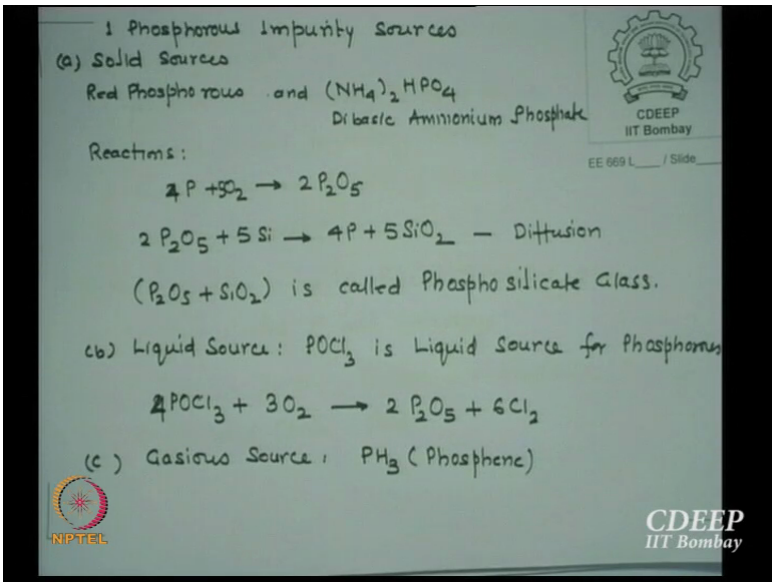


The liquid source which I may use is only known source of phosphorus is phosphorus oxychloride which is P O C L 3 and it is a liquid at room temperature and the reaction is 4 P O C L 3 plus 3 O 2 is 2 P 2 O 5 plus 6 C L 2. Now we will see that this is not very favoured because chlorine is a halogen which pits silicon, okay. Silicon has a reaction with chlorine. Silicon plus chlorine is silicon chloride. Three forms, four forms so any of that may actually remove some part of silicon.

Then there is a source which is gaseous which is called phosphene, okay. There was a gas called phosgene. What is that gas? Oh so you are all born after that so I thought you may not be knowing. Bhopal tragedy is very bad because of the phosgene gas which is methyl

isocyanide now M i C. So the problem with all these gaseous sources which I am using in specific are extremely toxicity.

For example let us say if it is one part per million in 10 to the power 6 one molecule is the level at which phosgene was toxic to human body. Of course it was much higher than that. It was actually released so there was nothing stopping it. But P H 3 is 10 ppb, okay. So if you can see even 10 ppb can be released and you have a problem. The only advantage of P H 3 which I may say since I have used it and maybe I do not know whether I have inhaled but I ran for my life, it has a fishy smell.

So when it leaks you can run. You have all oxygen, just run outside as fast as you can, okay. Break every door if possible, okay. But do not think it, there were hardly any accidents in the labs. Many years ago there were few but now we take so much precaution that it is unlikely things will fail. So it is called fail safe operations, okay. If things happen some valves will be closed immediately automatically. We do not do it.

Such much volume increases it will switch off everything, okay. The phosphene gas at 440 degree centigrade breaks into 3 hydrogen plus 2 P, okay. Of course these equations are not every time balanced. In case they are not balance you balance this. That arrow is only showing left to right that is it. But I tried to balance but I am still telling you they are not balance just balance them out.

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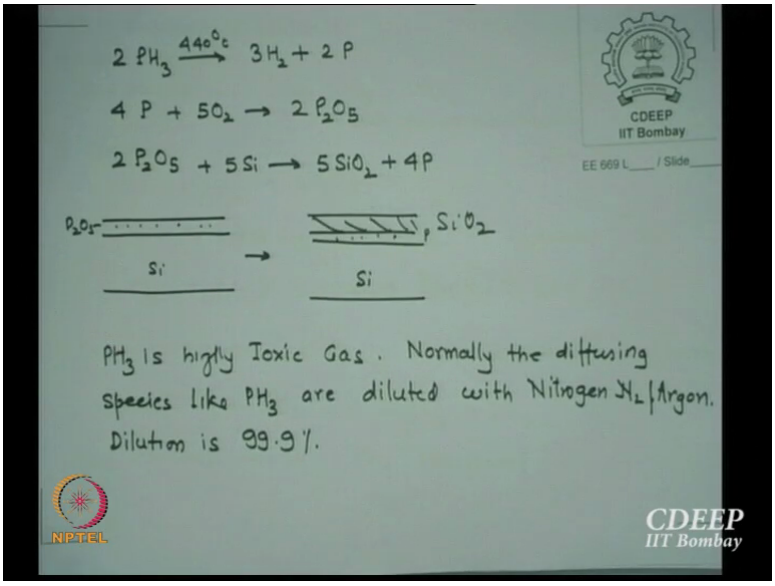


So this 2 P that is phosphorus which is coming out of phosphene at 440 degree so this reacts with oxygen and form P 2 O 5. So your basic source you wanted it. So this phosphorus then

will react with oxygen and form this. And if you have silicon around it will also form silicon dioxide so phosphosilicate glass which is the source of impurities, 5 S i O 2 plus phosphorous, okay. Example shown here this is your P 2 O 5 sitting on silicon.

When I drive in or when I push or continue this, these impurities get inside and S i O 2 is created, okay. This may also contain phosphorus but that I will etch so I will have fresh surface of N type N p, okay. As I said I have really written there P H 3 is highly toxic gas. So what we used for safety is we diluted with nitrogen. Typical dilution ratio is 99 point 9 nitrogen to point 1 phosphene. So 100 litres of nitrogen I will add 1 cc of phosphene to that.

Whenever I work in a lab I take lot of precautions that it does not leak through anywhere but luck is bad. If your luck is bad we had a student who was working earlier. I am talking about 80s. Everyone probably I do not know how much hydrogen is extremely flammable gas but we actually burn hydrogen. That is the way the hydrogen is removed in fact. But it should come out of a capillary it you should actually fire it, okay. This is the typical diffusion system shown here.

The furnace internal part is shown here. This is my quartz tube, this is the cap which I showed you earlier. Just a minute, this is the tube and this is the cap with exit tube, okay. There is a heater here all around. This is only shown cross section. This heating element is resistive heaters. Actually the tube is surrounded by some kind of a former which is made out of a material called mullite.

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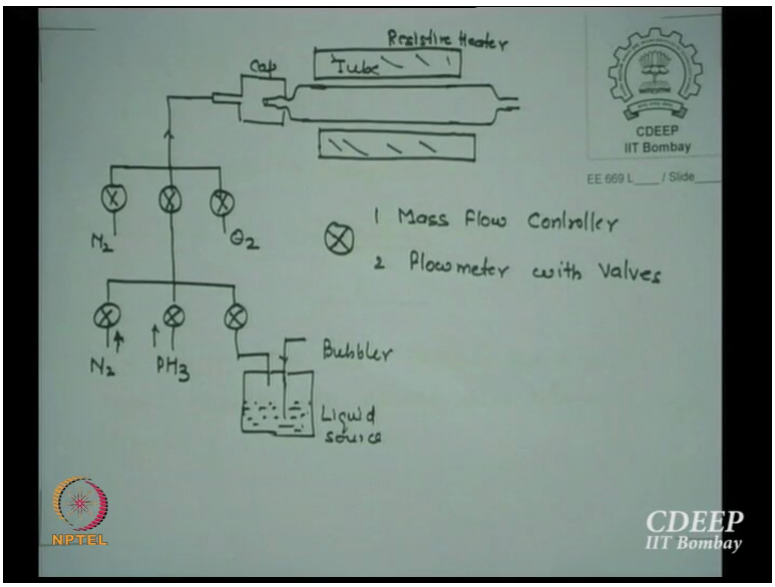

What is it? Okay. Mullite is a plastic created rexine which is like a bricks of white you know ceramics you must have seen white bricks. So they are mostly mullites. So actually there is a mullite rods are made, hollow rods and tube gets inside. And there is a slot in the mullite when making like a brick making. And then there is a heating wire which is bound around this mullite which covers this tube and you give a normal enough current 200 amps current to heat this filament.

Now the important is what material I should use for good resistivity in this. It should be very high in resistive and stand to higher temperatures. So what could be? No, the wire should be what, heating wires? I want. Tungsten is a good material. Firstly tungsten is a little fragile so when you form it, it breaks many times so one does not use tungsten.

Student: Nickel chrome.

Nickel chrome, nichrome as the world. So nichrome wires they have more malleable and therefore they are bound around this. Now there are three coils. One in the centre area, one in this two ends of the furnace. There are also thermal sensors, two here, three here and two here. Now what is the purpose of this sensor, because the problem is depending on your run number of wafers.

The wafers are of course, it is not shown here. There is a quartz rack and there are slots inside and vapours wafers are sitting inside like this, same height of course. Now since each wafer should see same temperature and same flows, this is called center zone.

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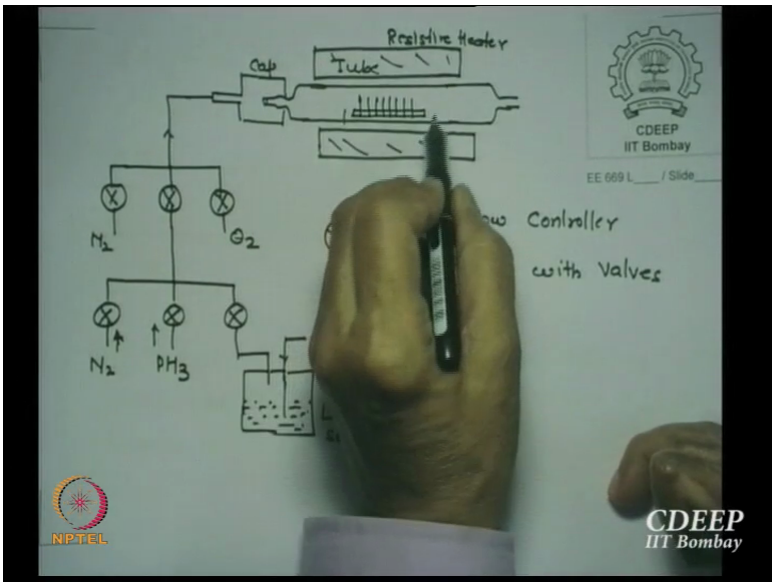

So the center zone temperature should remain unaffected by the flow as well as by the change in your current, okay. So what they do is you have a end temperature monitoring, early temperature monitoring as well as center zone three monitors, okay. These are (())(57:22) controller and we keep on monitoring when to switch on or when to switch off the power to the individual coils.

And therefore since PID controls are very fast we are able to control the temperature in the central zone plus minus point 25 degrees centigrade. So if you have a furnace I may have 1100 plus minus quarter degree centigrade accuracy which is very good in any sense, okay. So these are called resistive heaters. There are other heaters which are not resistive. What are those called? Inductive heaters. So we will see in other processes we may use that is called cold furnaces.

Inductive heaters are normally called cold furnaces. These are actually hard furnaces, huge heat. Now to monitor this there are variety of thermal inside. RTD is one, the thermistors are others but thermistor at that temperature we cannot. So we normally use thermocouples which is typically of the constant in copper if it is outside. If it is inside it should be radium platinum inside a quartz tube. There are new sensors are also appearing using (())(58:32), okay.

They are also very accurate so we can monitor better temperature sensitivities. And these are all newer techniques with new things. But PID controller is still as it was, okay. It has a microprocessor which is sitting along with PID and you set the temperature before hand past gas flows till you do not load the wafers and when the temperature settles down then only you push it. There are all digital displays to know where is what temperatures, okay. The gas flow control is something like this.

For example I want O 2 gas so there is a flow metre here with a valve. I can pass oxygen, I can pass nitrogen, I can open both valve and pass nitrogen and oxygen together. I can have a gas flow of phosphene. I can have phosphene with nitrogen. Both of them I can go through this. If I have a liquid source so I have a bubbler, I pass nitrogen inside or argon sometimes and vapour of this liquid is picked up and passed inside, okay.

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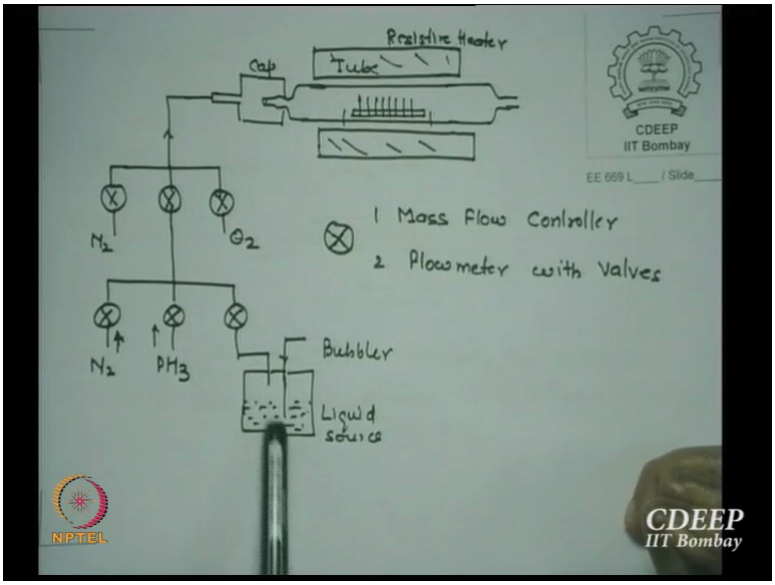


If you have a solid source then actually solid source is kept right here, small tube which is rarely used. No one put phosphorous oxide or red phosphorous near the wafers, okay. The importance of all this is that when the gas is going whichever form they go in there must form a laminar flow, okay. And that is very important. Two parameters which we control in this is called which numbers? Reynolds numbers and Rayleigh numbers.

So we actually monitor the Rayleigh number and Reynolds number to get laminar inside so that every wafer when the gas goes it sees uniform flow like this. This is very important in processes. Please remember there are two kinds of flow metre which we use. What are these two? Anyone heard of them? One is called rotameters, okay. The rotameters are used in almost every industry whether it is a food, chemical, liquid flow or gaseous flow. It is essentially a capillary which is graduated for particular gas densities.

You pass the gas and there is a some float inside it may be stainless steel or plastic depends on the gas density. And this small capillary is around 8 inch height or 10 inch height. The gas flows and since the gas flow pressure is from below, it pushes the float up, okay. And it is balanced by the actual atmospheric pressure from the down. So depending on the gas flow you can calibrate where this float will, so you can see the graduated scale is say okay 100 cc or 200 cc, litre whatever scales you want you can get.

These are called standard flow metres which are not very accurate because every flow metre is for different gases and their graduation is not very accurate. But let us say I am passing 20 litres or say maybe 50 litres in a large tube. It does not matter if it is 51, okay. It does not

matter if it is 49. But if I am passing 100 cc, I want 100 cc there, okay. So the accuracy of flow is a required in certain cases otherwise it is not. To make a very accurate flow inside it should be independent of pressures.

So what are those called? These are called mass flow metres. They are very costly MFCs, mass flow metres. MFCs have the advantage that you know it is like a tube here, the gas go there. There is a small additional capillary tube goes up. Maybe I can show you how it is. This is your main tube. This is something like this another tube, okay. Then depending on the gas you enter there are three elements here. This is a heater element. This is heated. So what happens if the gas flow is larger and if it is already heated sensor? It cools, okay.

So there is a temperature initially because of the gas is T 1. But since there is a heater here it actually increases the temperature here. The difference between the temperatures of two sensors is essentially monitor of the flow going in, okay.

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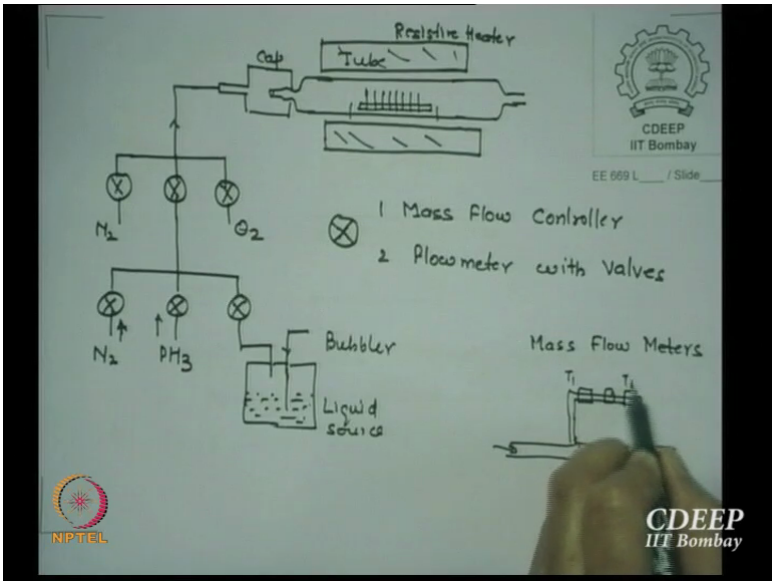


So you can set this temperature initially which is called set points and if the gas is larger then it shuts off. This valve here will be shutting off. If it is smaller it will allow more gas to come in and very accurate amount of flow can be adjusted through this. This whole electronic system this is huge circuit here. The mass flow metre is typically around 8 inch by 8 inch kind of system and it costs, there is a magnetic plunger. There are too many things inside to close or open and these are very costly. Typical flow metres are 25000 and above, okay.

Whereas the rotameters are available for 150 rupees, okay. So accuracy to money. Many a times this do not work so over experience is we open it and clean it and do it again. But 90

percent of the scientists do not do it, buy another one, okay. Okay, so this is a typical diffusion system and I just gave you all this which otherwise no one will tell you or no one will write about it. This is only we did many furnaces ourselves so we know what we did, okay.

So the better part of our technology was that we were making our own systems. There was nothing available so we made our system. Then we have seen phosphorus. Let us look for boron. This figure is nothing to do with phosphorus. This is for all kinds of diffusing systems. There are as I say aluminium and gallium has a better misfit factor than boron. Indium has point 22, boron has point 254, okay. Even then we only use boron.

As I already said aluminium is bad, it forms an alloy so we do not want to use. Then gallium is essentially a very high energy. It has a very large activity energy so we do not want to create very few holes, okay. Then indium also is point 16 electron volt so we do not want to use it. Boron has point 086 as the activation energy so it is used very extensively.

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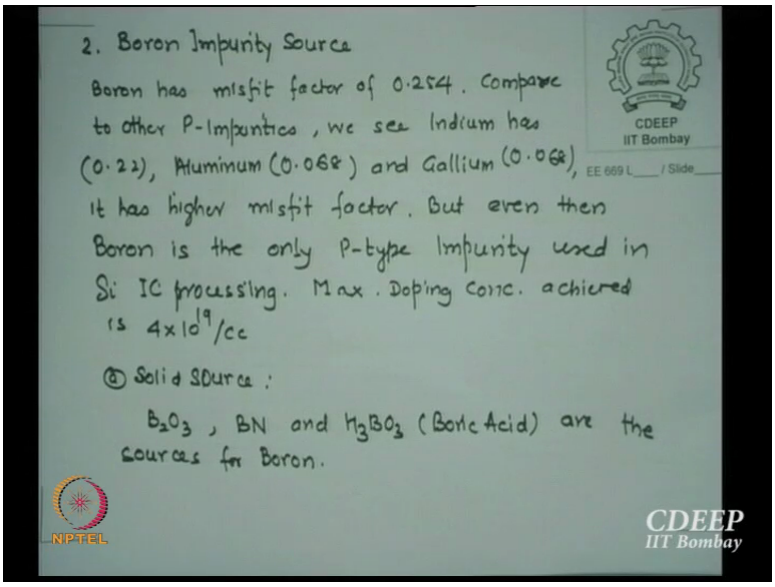


Since its misfit factor is larger so what is the effect? Its solid already will be relatively smaller so it is 4 into 10 to the power 19. In some cases may be 5 into 10 to the power 19 per cc all that boron. So P plus doping is always less than N plus doping simply because the misfit factor of boron is larger than phosphorus or arsenic of course is the best. But arsenic as this gentleman also said that it is a slow diffuser so in shallow junction they are good but if you are looking for deep junctions phosphate is the only solution. For why others are not?

So I just gave you why others are not used. Solid sources is B 2 O 3 powder is available, boron nitride wafers are available and very marketable material boric acid which is used in preservation of grains, okay, so H 3 B O 3. These are the three solid sources. Of course the one which we use in the market is not electronic grade. They are only industrial grade and they have lot many impurities so never used in labs anyway, okay.

We already said the kind of grades we are looking for is minimum 69 and above impurities. 69 is the minimum impurity which we use preferably 99, okay, 79 point 99, okay. Okay, so these are the solid sources. I mean I already said twice why not aluminium, why not gallium, why not any other? Only boron, okay. There are reactions. The B 2 O 3 plus 3 silicon is 4 boron plus 3 S i O 2 and mixture of B 2 O 3 plus S i O 2 is called borosilicate glass. Popularly there are three kinds of glasses available in market.

Borosil is exactly this borosilicate glass. It is called Pyrex. Very famous named Pyrex which is coming from Borosil company, okay. So it is a Pyrex glass but is not very pure and it is not very good. Which is worse glass than this? Soda glass, the whole drinks all the time, I do not know these days I do not see many people taking cold drinks but in our time I think it was much popular. So all cold drink bottles are essentially of soda or it contains sodium.

And no glass which has sodium is allowed inside our lab because if that happens everything will be (())(01:08:38) for us. So sodium is avoided. So soda glass is never allowed. Pyrex at higher temperature may release impurities, okay. So we do not want high Pyrex around glasses except when they are not used in heating areas we may use Pyrex systems. But anytime when we are going we should use only quartz plus this. So that is the catch in word everywhere, okay.

There is another as I say boric acid also can reduce to 185 degree B 2 O 3 plus water steam and you have a B 2 O 3 source. For this case two zone furnace first you put H 3 B O 3, oxidize it little bit and when it pass it forms a B 2 O 3 near the surface and that is picked up on silicon. There is also possibility of making a solar cell with cheaper sources which is called boron nitride sources. There are wafers of boron nitride. So you put silicon wafer in touch with boron nitride, both side silicon.

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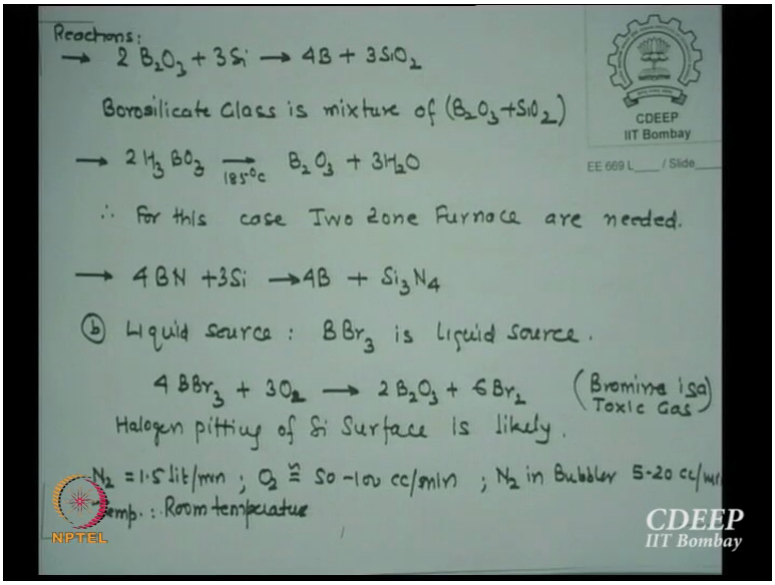


So both sides are polished surfaces of silicon, touches the boron nitride wafer in a slot and slot is sold. All three wafers are tied each other, okay. Two silicon one boron nitride, two silicon one boron nitride and that is heated to create. Boron nitride breaks with silicon into 4 boron and nitride. Instead of S i O 2 now silicon nitride is the upper layer which is also a mask for impurities.

Of course not good a mask as S i O 2 but it still a mask. The last source is liquid which is boron tribromide B B r 3. B B r 3 reacts with oxygen to form B 2 O 3. So what was our primary source of boron? B 2 O 3 is our primary source. So whichever source you may have you must convert this into B 2 O 3 at the surface of silicon. Then only the next reaction is possible. Now there is a problem. Boron is highly toxic as well as it is very highly reactive to silicon so it gives what is called as halogen pitting.

So when we are making 5 micron devices or depth of 3 micron junction there, that pitting was relevant. But with 100 nanometre junctions the pitting maybe of hundred nanometres, okay. So there are issues now which 25-30 years we never bothered, okay. But now no one uses B B r 3. Earlier time almost everyone used B B r 3, okay. So this is a progression. Now mostly people will not even use either of them, okay. If you want still a liquid source then there is a source called tri methyle borate which is used now.

TMB is very popularly known. TMB when it oxidizes it creates B 2 O 3, carbon dioxide and water, okay. TMB has a problem that it has a very high vapour pressure so it has to be refrigerated, okay, to keep vapour pressure down. Otherwise it will blast out.

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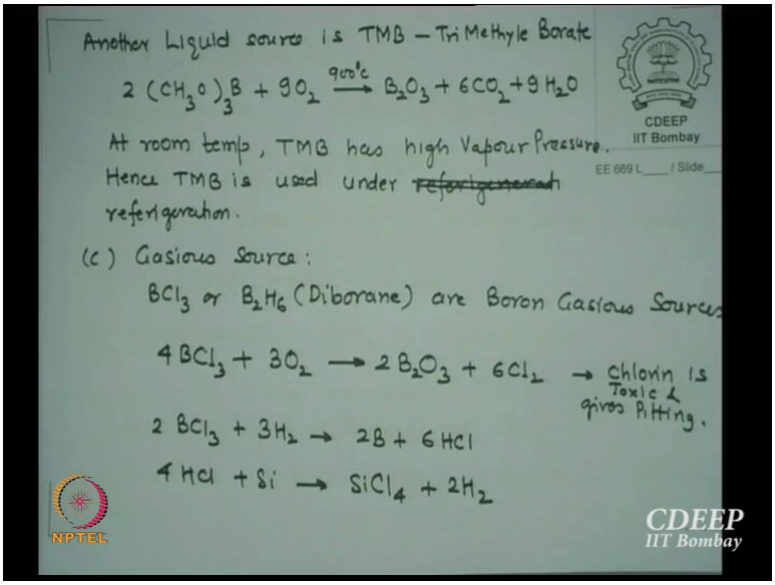


So it is always kept refrigerated and even when you put it, put in a water bath and then only use, okay. So the pressure says this is tri methyle borate, tri. This is methyle group so 2 C H 3 O B plus 9 O 2 at 900 degree become B 2 O 3, 6 C O 2 plus 9 H 2 O, okay. Very popular source, okay. It also is very controllable source and therefore even now in many ICs some lab of course Intel is not using but of course TI is now selling off all his process but TI had TMB process, okay.

Many a time people do not change to something else. Similar if it is working, just for the heck of it why should I change, okay. If it is not working for my requirement I will change. So many companies have been doing something which they think is working so why change so why money, okay. But we know better sources will be gaseous but it is a matter of your decision how much money you have, okay. The other possible gaseous sources are boron chloride or boron (hy) (boro) diborane as it is called B 2 H 6.

They are all gas sources. B C L 3 reacts with 3 O 2 to form B 2 O 3 and 6 C L 2 and again the same issue it may pit, okay. Normally chlorine does not pit as much unless there is a hydrogen around. If H C L is around it will definitely pit. But if your system has hydrogen free it will not give that much pitting. It does react but it has a very marginal silicon reaction. With H around H C L it will pit it, okay.

Why I am saying you because some of the gate oxide (())(01:13:53) were earlier using chlorine as a improving specie for inter states and we used to use chlorinated oxide and then we realise that it is actually creating more problem than this. So we changed to other TCAs

and other chlorine sources. B C L 3 plus 3 H 2 boron plus 6 H C L and here is that issue. If there is a H C L, there is a pitting. 4 H C L plus S i, this is what it means silicon chloride will form. So some spurts this may go, okay.

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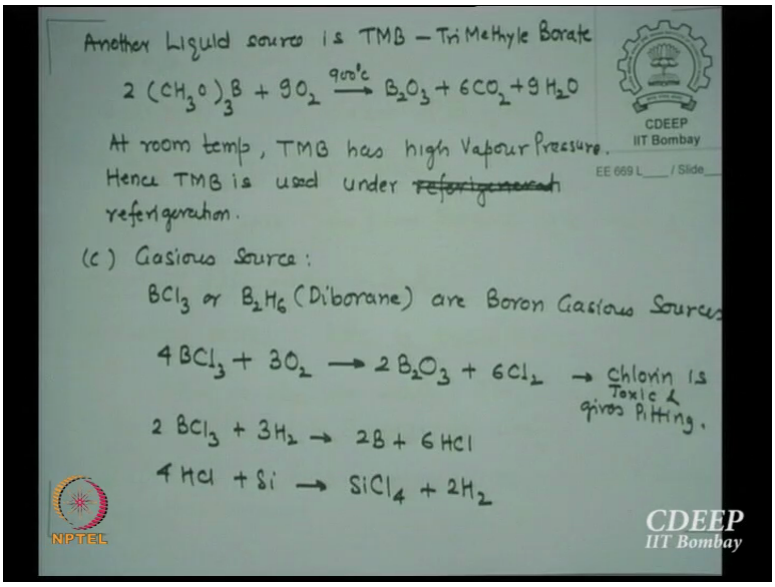


If it is hydrogen free absolutely no issue. Quickly diborane is a highly toxic gas, very carefully has to be handled and it oxidizes at 300 degree to form B 2 O 3. The gas flow is one parameter for amount of oxygen plus this mixture of these two gases. Mixture decides how much concentration you are going to get, okay. As I said it should be laminar decided by Reynolds number and Rayleigh numbers, okay. How do I test that the boron diffusion is okay?

This is not advised by from many but people like us have done that. You see at the other end of the tube and if you see a two good (hea) lobes of heart you say you are perfectly laminar flow going in, okay.

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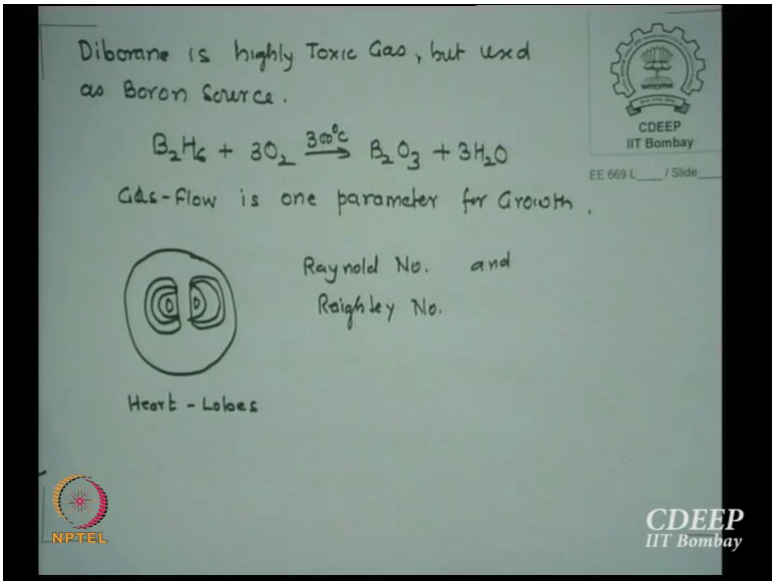


This is called boron lobes where you actually see otherwise it will be meshed up. You will see a mixture of everything. If you see a good lobes you say you are perfectly handled this, okay. So I just told you how do we found out that it is okay? This is how we figured out. Last source, is that okay? B 2 O 6 plus 3 O 2 at 300 degree becomes what is primary source I declared? B 2 O 3, so all reactions I show to convert that whatever source you use into B 2 O 3 at the silicon surface, okay.

Primary source, so we are always converting all secondary sources to the primary sources. That is the way. Last slide for the day, not last for the course. I have many more to come. Just a minute, we will finish and come back. The last is arsenic impurity which may use very often these days. For example the solid is arsenic oxide when arsenic oxide plus S i O 2 is called arsenosilicate glass. Rarely used because S 2 O 3 is also little poisonous so it is hardly used or hardly sold. Of course sold I do not know.

These days anything is available. Yesterday there was something that cobra venom people like so I am surprised, okay. I just fear so much cobra and they take venoms, okay. Fine, so A S H 3 reduces around 325 degree to arsenic and hydrogen. Arsenic reacts with oxygen to form A S 2 O 3 and A S 2 O 3 plus S i is S i O 2 plus arsenic.

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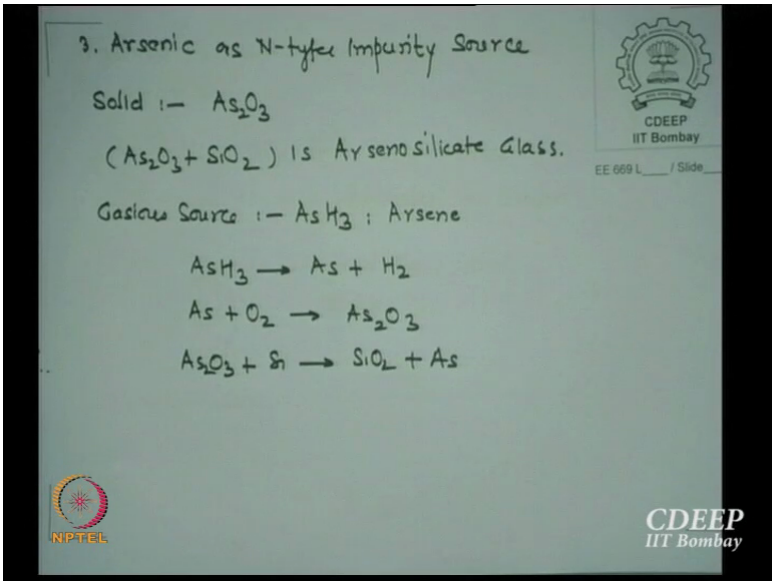


So that is how arsenic gets in and S i O 2 is created on the top. Is that okay? So next, yes?

Student: (())(01:17:20)

They are exhausted at least 30 feet up and then if there are toxic gases there is something called scrubbers, okay. So we pass through solution where they are converted into solids or solubles which are non toxic.