VLSI Technology
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Lecture – 28
Etching of Si, SiO_2, SiN and other materials.

In the last class, I told you that dry etching of silicon can be done by using either a chlorine route or a fluorine route. Let us now investigate what happens if we use the fluorine route and what happens if we use the chlorine route and then finally what happens if we use of mixture of fluorine and chlorine as the feed gas. Now, for silicon etching, the fluorine route has been used for a long time; very well understood, everybody knows what actually happens.

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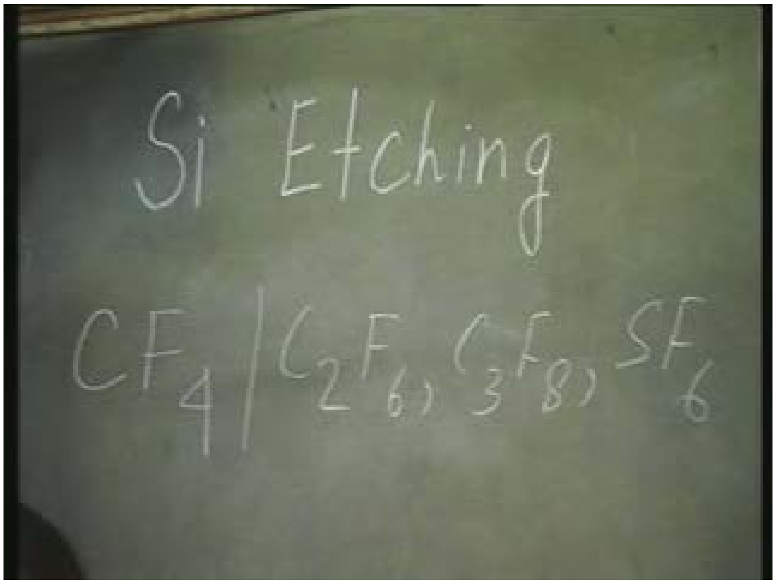

So, in this fluorine based etching CF 4 is most commonly used; that is most commonly used. Of course, you can use any other fluorocarbon that is you can use C 2 F 6 or you can use C 3 F 8 or a newer gas like sulphur hexafluoride; SF 6, can also be used. So, you can use CF 4 or C 2 F 6, C 3 F 8 or SF 6. They all behave pretty much in the same way. So, we will focus our discussion with respect to CF 4. Inside the plasma, we have this reaction.

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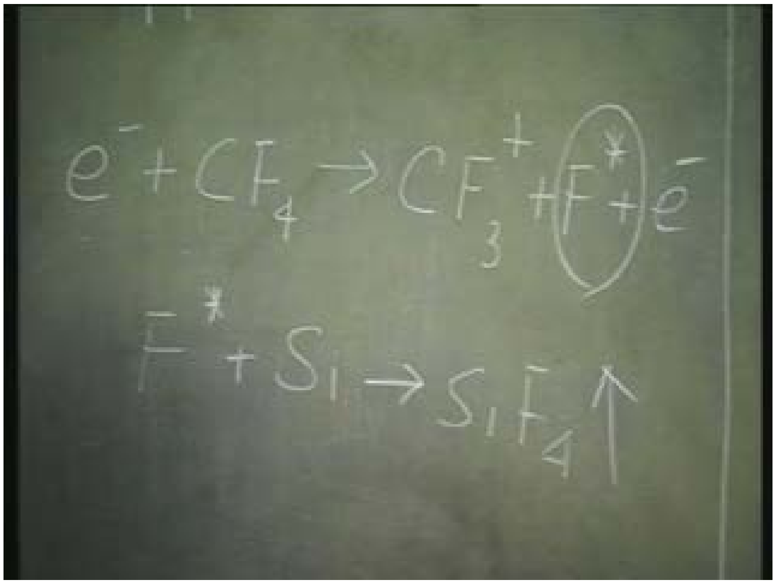

$$e^- + CF_4 \rightarrow CF_3^+ + \boxed{F^* +} e^-$$

$$F^* + Si \rightarrow SiF_4 \uparrow$$

The high energy electrons, they cause the CF 4 to break. Remember, inside the plasma we have very high energy electrons. The electron temperature can actually go as high as 10,000 Kelvin. So, therefore it is possible to have a lot of reactions which are not otherwise possible at low temperature. So, this is one such reaction. I have energetic electrons reacting with CF 4. In the process CF 3 plus radicals are being created and most importantly, the fluorine, F star is being created. F star is actually a neutral reactive fluorine species and to maintain the charge neutrality, I have the electrons again, so that this reaction can keep on happening.

Now, for silicon etching this is the most important item. Silicon is etched by this free F star. This is the primary active species which is going to etch silicon and how does it etch silicon? It reacts with the surface atoms of silicon and it forms a volatile product, SiF 4. This is another very important criterion. The reaction product must be volatile. If it is not volatile, the process will automatically stop. Remember, the reaction product has to be carried away from the site. So, unless it is volatile, it will not be carried away from the site; therefore, the reaction will automatically stop. So, for any dry etching to progress, the reaction product must be volatile.

Now, how can I improve the etch rate of silicon? One possibility is by adding a small amount of oxygen in the feed gas. The feed gas is CF 4 or C 2 F 6 or C 3 F 8 or SF 6. If you add a small amount of oxygen with the feed gas, then this extra, additional reaction is going to take place.

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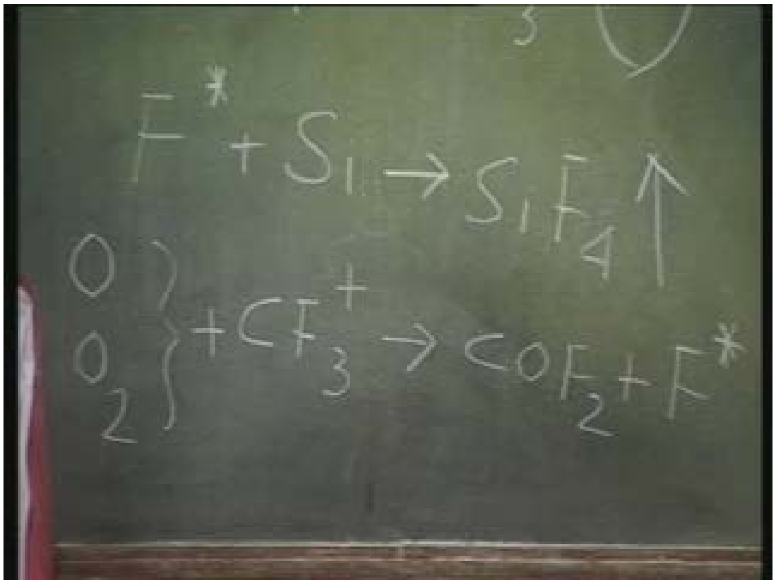

$$\bar{F}^* + Si \rightarrow SiF_4 \uparrow$$

$$\left.\begin{matrix} O \\ O_2 \end{matrix}\right\} + CF_3^+ \rightarrow COF_2 + F^*$$

I have oxygen atom or molecule. They are going to react with CF 3 plus and they are going to release extra fluorine. So, if you have a small amount of oxygen that is going to react with CF 3 and it is going to release extra fluorine and the more fluorine, active fluorine, you have more will be the silicon etching.

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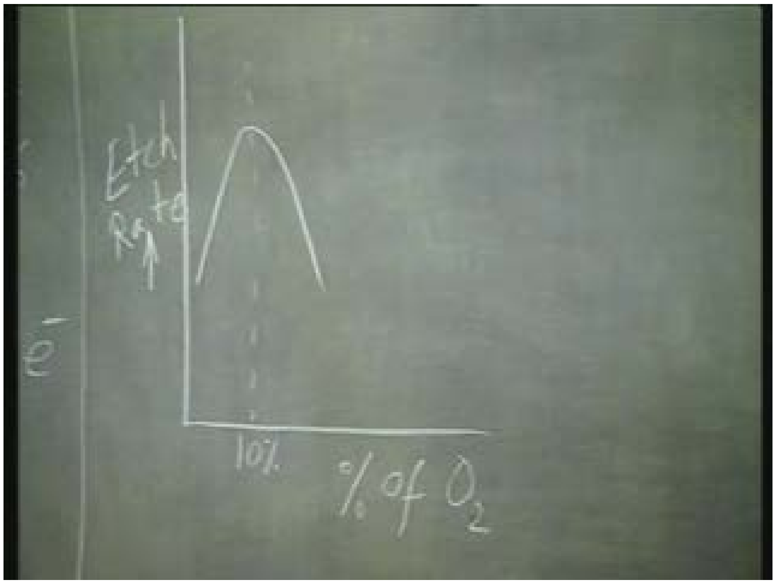

So, if I want to plot the etch rate versus percentage of oxygen, then it is going to increase like this. But then, it reaches a peak at around 10% of oxygen in the feed gas and then again it begins to fall. This peak is around 10%. So, the increase is easy to understand. It is because of extra generation of active fluorine species. Why then the fall? The fall happens when you have too much oxygen in the feed gas, so that the surface of silicon looks not like silicon, but like silicon dioxide and the etch rate of silicon dioxide in this feed gas is much smaller than that of silicon. So, so long as you have a small quantity of oxygen, everything is fine; you have more generation of fluorine species, it is going to facilitate etching of silicon, but not beyond a certain point when the silicon surface starts to resemble not silicon but silicon dioxide, at which time the etch rate is going to decrease.

So, from this you see, we have actually pointed out quite an important fact. That is the selectivity of fluorine based etching; selectivity. The most common two things you need to distinguish between is silicon and silicon dioxide, right and I have already told you that the etch rate of silicon dioxide is going to be much smaller than that of silicon, when you use fluorine. That is why here you see the etch rate is decreasing. If you have actual silicon dioxide the etch rate is going to be much, much smaller, right. So, you have good selectivity if you use fluorine, because you see the etching is taking place by the chemical reaction the reaction of active fluorine species with silicon and its selectivity over silicon dioxide is quite good.

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In fact, you can realize a selectivity of 40 is to 1. If you use CF 4, fluorine based etching, then it is possible realize a relative etch rate of silicon to silicon dioxide 40 is to 1. That is the etchant will etch silicon at a rate 40 times faster than the rate at which it will attack silicon dioxide. So, you have very good selectivity of silicon over silicon dioxide. But whenever I have good selectivity, the next question automatically comes, what about the anisotropy. Here, the fluorine based etching is found to be severely limited, because the reaction is spontaneous and vigorous that is why the etch profile is going to be absolutely isotropic.

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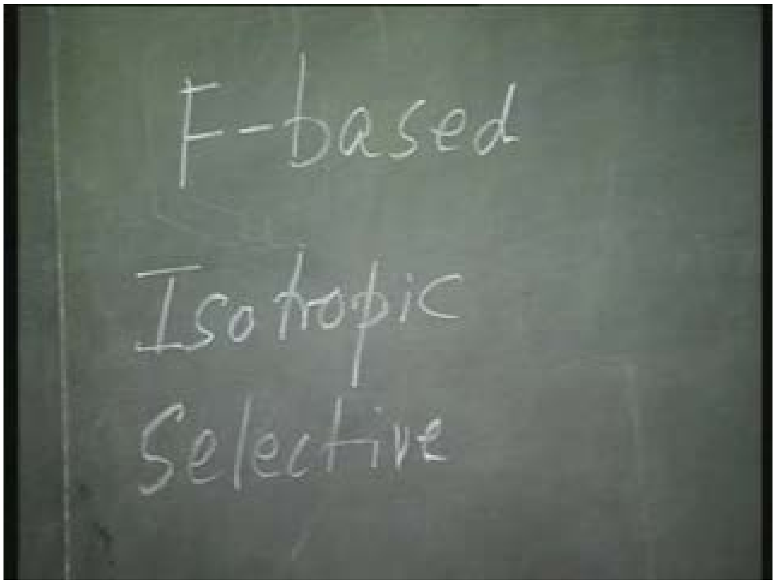

So, by fluorine based etching, you have isotropic etching, but it is selective. You have good selectivity, but you have poor anisotropy. The same feed gas can be used also to etch silicon dioxide and silicon nitride. Of course, the etch rate of silicon dioxide will be much smaller than in case of silicon, but it will still etch silicon dioxide. How can we improve the etch rate of silicon dioxide? One possibility is again by putting oxygen, putting a small amount of oxygen, just as in the previous case; you will have extra generation of active fluorine species and that will etch silicon dioxide.

The problem is in this process I cannot get any selectivity over silicon. In fact you see, most commonly what do we have to do? We have a silicon dioxide grown on top of silicon and we would like to open a window in that silicon dioxide. That is we would like to preferentially etch that silicon dioxide, but we want the etching to be stopped when it encounter silicon, isn’t it. So there, therefore using this feed gas with small amount of oxygen is not going to help us, because the etch rate of silicon will be much, much faster. So, I cannot get any selectivity. Instead of that, therefore what is done is this.

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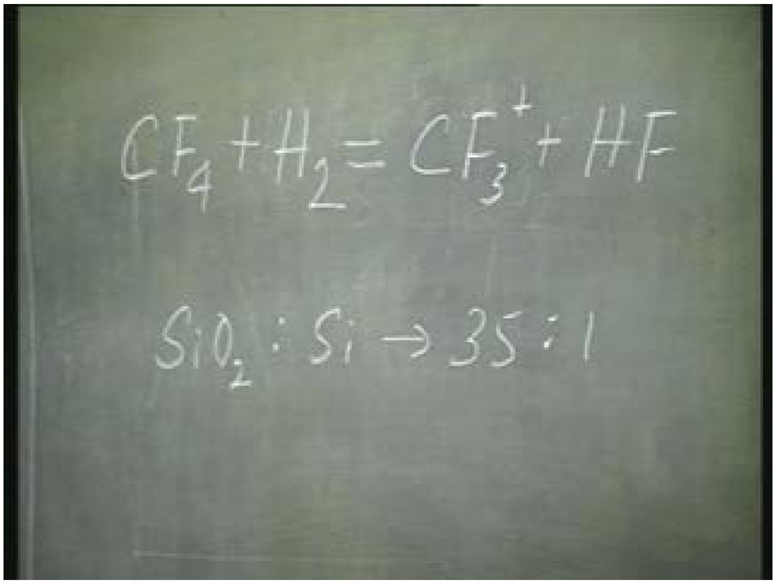

$$CF_4 + H_2 = CF_3^+ + HF$$

$$SiO_2 : Si \rightarrow 35 : 1$$

You use a small quantity of hydrogen along with CF 4. So, what will hydrogen do? Remember, CF 4, inside the plasma, it gives rise to CF 3 plus plus active fluorine species. Hydrogen is going to suppress the formation of this active fluorine species, so that you have …… So, you have suppressed the formation of the active fluorine species, therefore etching of silicon will be suppressed. Fortunately, silicon dioxide is also etched by this, right. So, the etching of the silicon dioxide will progress, whereas the etching of silicon will get suppressed and by doing so, it is possible to obtain a selectivity of silicon dioxide over silicon as 35 is to 1. In the previous case, when we added oxygen to the feed gas, it was possible to selectively etch silicon. Silicon was getting etched at a rate 40 times faster. Now, by adding hydrogen, it is possible to etch silicon dioxide at a much faster rate, 35 times faster than that of silicon. So, you see, dry etching I have so much flexibility; I use the same feed gas, I only modify the composition of the feed gas slightly, so that I can etch either silicon or silicon dioxide with very good selectivity.

The other thing is of course, etching silicon nitride. Next to silicon dioxide, the dielectric mostly used in VLSI technology is silicon nitride and we would like to etch silicon nitride. So, silicon nitride is also etched by this active fluorine species. You know, fluorine reacts silicon nitride again to give rise to silicon tetrafluoride, Si F 4 and nitrogen is released in the process. So now, the question is whether you want to have selectivity over silicon or selectivity over silicon dioxide. It may not be possible to etch silicon nitride with good selectivity over both silicon and silicon dioxide at the same time.

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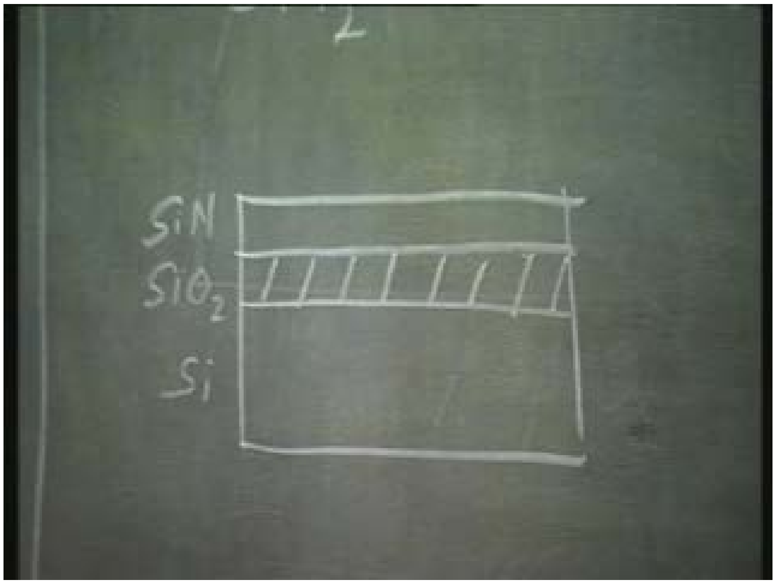

So, depending on whether your substrate is like this that is if you have a structure like this the top layer is silicon nitride, then I have silicon dioxide and underlying is the bulk silicon substrate; in that case you want, when you are etching silicon nitride you want, good selectivity over silicon dioxide.

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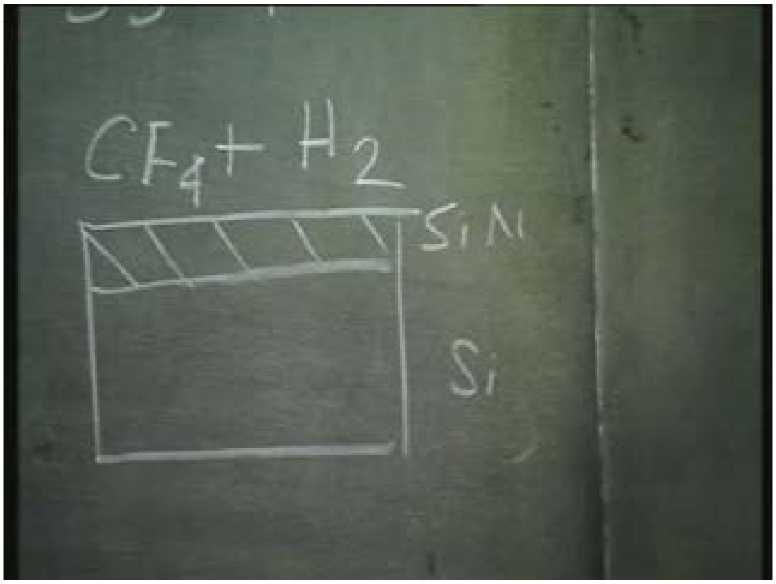

On the other hand, if you simply had silicon nitride and silicon, then you would want to have good selectivity over silicon. So, depending on what you substrate is like, you should choose the feed gas composition. So, you have two options. You can either use the feed gas with a little bit of hydrogen just as in this previous case, so that the formation of this active fluorine species is suppressed and therefore silicon will not get etched, so you will have good selectivity over silicon; good selectivity of etching silicon nitride over silicon. That is one possibility. So, if you have this kind of a composition, use CF 4 plus hydrogen; that will give you good selectivity over silicon. If however you want to have good selectivity over silicon dioxide, in that case you have to use, probably you should use a feed gas with a little bit of chlorine in it; chlorine or ClF 3 in it.

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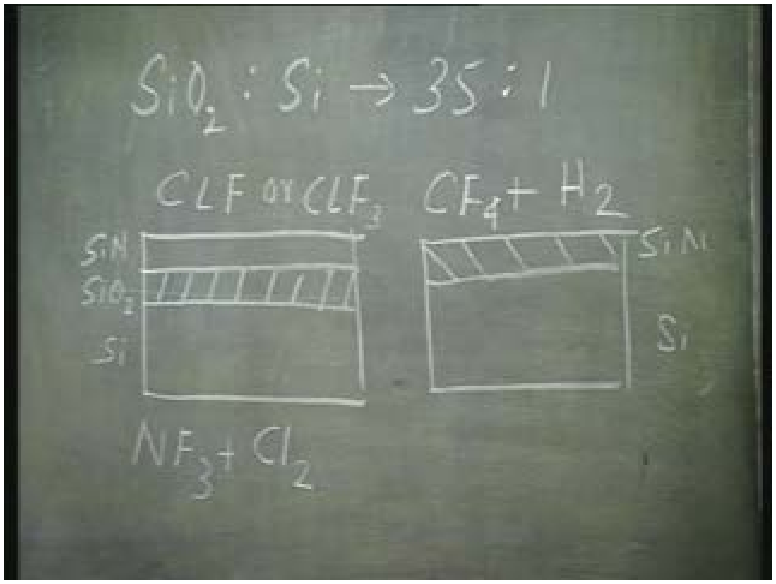

So, when ClF or ClF 3 is the active species, then silicon dioxide is not attacked, so you have good selectivity over silicon dioxide. In fact, the feed gas composition used in such cases will usually be NF 3 plus chlorine which will give rise to the active species of ClF or ClF 3 that will not attack silicon dioxide. But, it will attack silicon. That is what I meant that you cannot have good selectivity over both silicon and silicon dioxide at the same time. You can choose a feed gas composition which will give you, which will preferentially etch silicon nitride with respect to silicon or you can use another feed gas composition which will preferentially etch silicon nitride and will not attack silicon dioxide. So, depending on what you want, which of these two structures you have, whether you want to have good selectivity over silicon or silicon dioxide, you should choose the feed gas accordingly. So, this is actually the fluorine based etching of silicon and silicon based compounds. We have talked about etching of silicon, silicon nitride as well as silicon dioxide.

The common feature is this. Silicon is etched very easily using CF 4 feed gas. You can improve the etch rate by adding a little bit of oxygen, so that you have more generation of active fluorine species which is going to react with silicon and gives SiF 4, which is a volatile product. The same feed gas will also etch silicon nitride and silicon dioxide, but with lesser degree. So, if you want to have selectivity of etching of silicon dioxide or silicon nitride over silicon, you should use this feed gas with a little bit of hydrogen. Hydrogen will suppress the active fluorine species. It will form HF and therefore, it will suppress the formation of active fluorine species and therefore, the etching of silicon will be hindered. But, the etching of silicon dioxide and silicon nitride will go on and in the process it is possible to have a high selectivity; like I told you, in case of silicon dioxide over silicon, it is possible to have 35 is to 1.

Same thing also holds good for silicon nitride. But, the problem is when I want to obtain selectivity of etching silicon nitride over silicon dioxide. In that case, I may have to use a different feed gas, something like NF 3 plus chlorine, where the active species of etching will be ClF or ClF 3 which will not attack silicon dioxide, but it will etch silicon nitride. But remember, if you use these feed gases, then you do not have selectivity over silicon etching. This is the fluorine based etching of silicon.

Let as now talk about the chlorine based etching of silicon. In chlorine based etching of silicon, there are a few ground rules. First ground rule is that chlorine will not spontaneously etch undoped silicon or we can say that the etch rate will be extremely small. So, undoped silicon cannot be etched in chlorine, just in chlorine; I do not mean plasma. What I am trying to say is it cannot be etched spontaneously in chlorine. There is no spontaneous chemical reaction between chlorine and undoped silicon.

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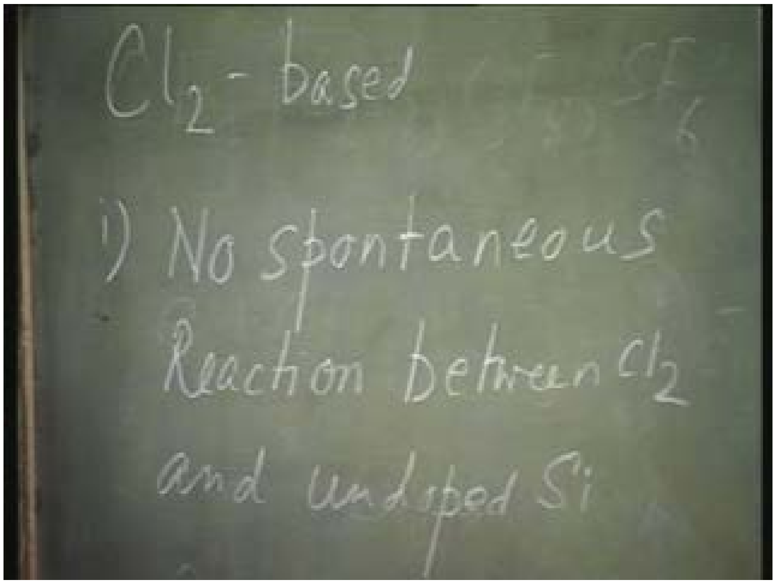

Cl_2- based SF_6

i) No spontaneous Reaction between Cl_2 and undoped Si

So, that is the first ground rule - no spontaneous reaction between chlorine and undoped silicon. Rule number 2 - however in presence of energetic ions, when I have energetic ion bombardment, then the reactivity of the surface can be made sufficiently high, so that it reacts with chlorine. I have already mentioned this in the last class that is the energetic ion-enhanced etching. If we have energetic ions bombarding a particular surface, the reactivity of that surface can be modified, so that, may be in the absence of plasma the surface would not have reacted with the feed gas, but now the reactive surface is going to react.

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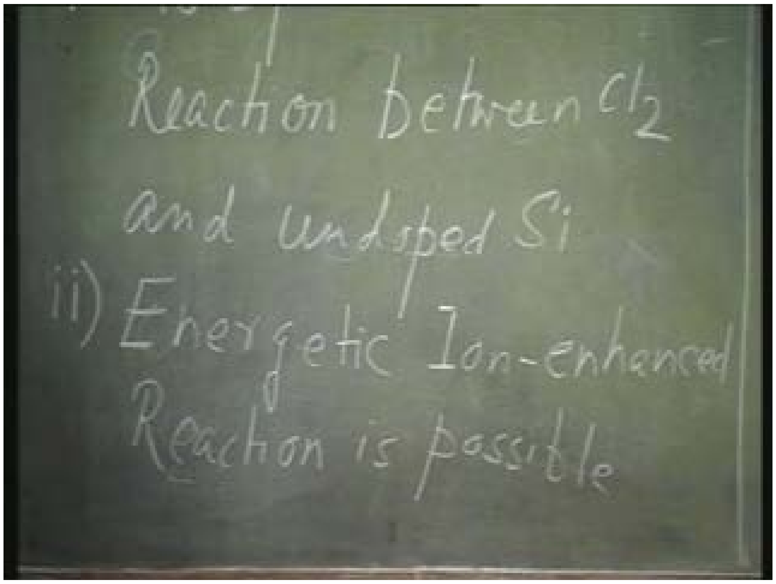

Reaction between Cl_2 and undoped Si

ii) Energetic Ion-enhanced Reaction is possible

So, it is possible to have energetic ion-enhanced reaction; energetic ion-enhanced reaction is possible and point number 3 is however all these are applicable to undoped silicon. If I have heavily doped silicon, then chlorine is going to react spontaneously with the surface.

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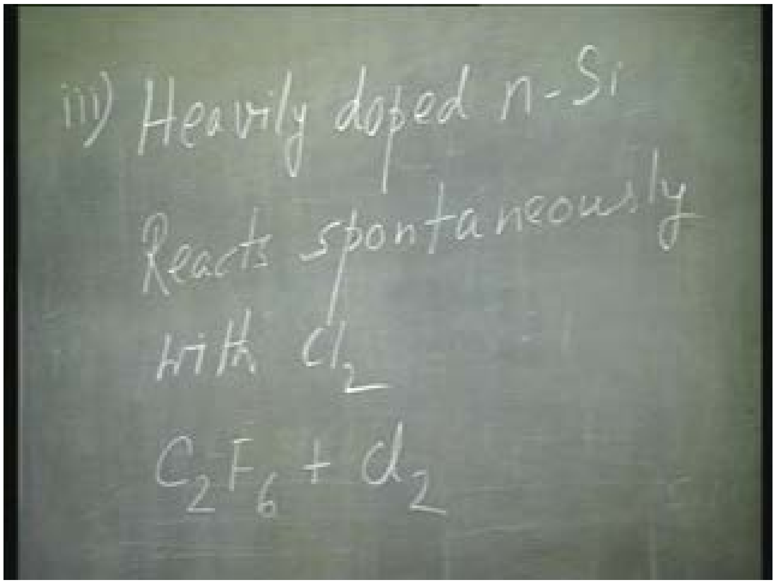

iii) Heavily doped n-Si Reacts spontaneously with Cl_2

$C_2F_6 + Cl_2$

Heavily doped n-type silicon will react spontaneously with chlorine. So, you see, chlorine actually offers you a lot of possibilities. First of all, if you have intrinsic or undoped silicon, you can have energetic ion-enhanced reaction, in which case you will have very good anisotropy and also good selectivity. On the other hand, if silicon is very heavily doped, then chlorine is going to react spontaneously, right. In that case you would expect that the etching profile will be isotropic; anisotropy will suffer, because it is going to take place by spontaneous chemical reaction.

You can even, here you can get anisotropic etch profile by using an inhibitor along with the feed gas and the very common inhibitor is C 2 F 6. Use C 2 F 6 with chlorine; C 2 F 6 is going to form an inhibitor film on the side walls. On the side walls, this inhibitor film is going to remain; on the surface which is bombarded by the energetic ions, the film will get removed. So, again it is possible for you to have anisotropic etch profile. However here, the feed gas composition has to be carefully monitored. That is there should be sufficient C 2 F 6 to form the inhibitor. Otherwise we will get isotropic profile. So, you see, even here you have a lot of flexibility. By using the same feed gas with varying amount of relative percentage of chlorine and C 2 F 6, you can get isotropic or anisotropic profile. So, altogether chlorine offers you much more possibility than fluorine.

In fluorine based reaction, as I said, we are always stuck with very poor anisotropy, because the reaction is so vigorous, it is not even possible to have any inhibitor forming mechanism; so vigorous reaction, that nothing works. You always get isotropic profile. In contrast, chlorine offers you a lot of possibilities and particularly this is a very interesting reaction. See, I am using C 2 F 6 and chlorine. Now, silicon dioxide does not get etched by chlorine; silicon dioxide does not react with chlorine, does not get etched by chlorine. But you know, your native silicon, the basic silicon wafer will always have some native oxide present on that. So, if you try to etch it simply using chlorine plasma, etching may not be very fruitful, because you have some traces of oxide present on the surface; that oxide is not getting etched, therefore etching cannot progress. So even there, this feed gas is going to help, C 2 F 6 plus chlorine. How? C 2 F 6 can etch silicon dioxide.

Remember, I told you that you can use CF 4 or C 2 F 6 or C 3 F 8, so that will etch silicon dioxide. So remember, C 2 F 6 therefore serves a double purpose; it does two jobs.

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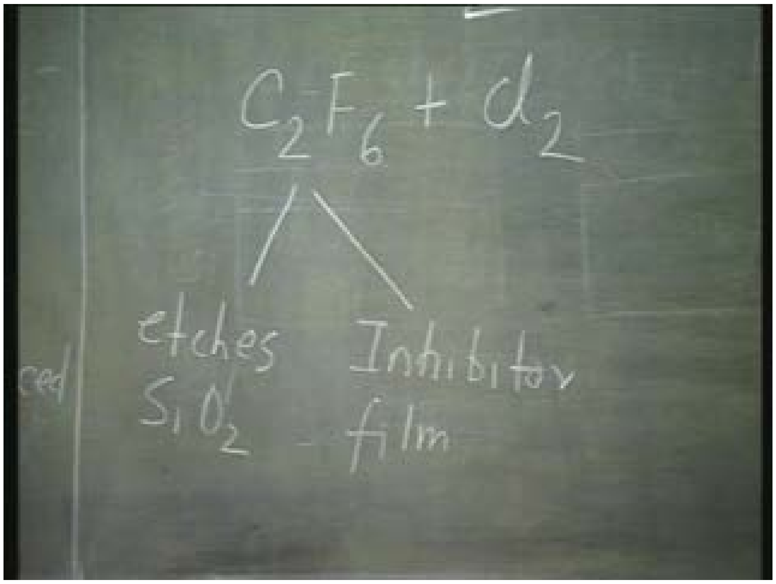

One job is it etches silicon dioxide, the native oxide that is always present on any silicon surface and secondly, it forms inhibitor film, so that you get very good anisotropy even when you are etching heavily n-type silicon.

You can of course play with a combination of chlorine and fluorine. In that case, usually ClF 3 and chlorine, ClF 3 and Cl 2, these are used as the feed gas. That is the feed gas has two constituents; one is chlorine, the other is ClF 3.

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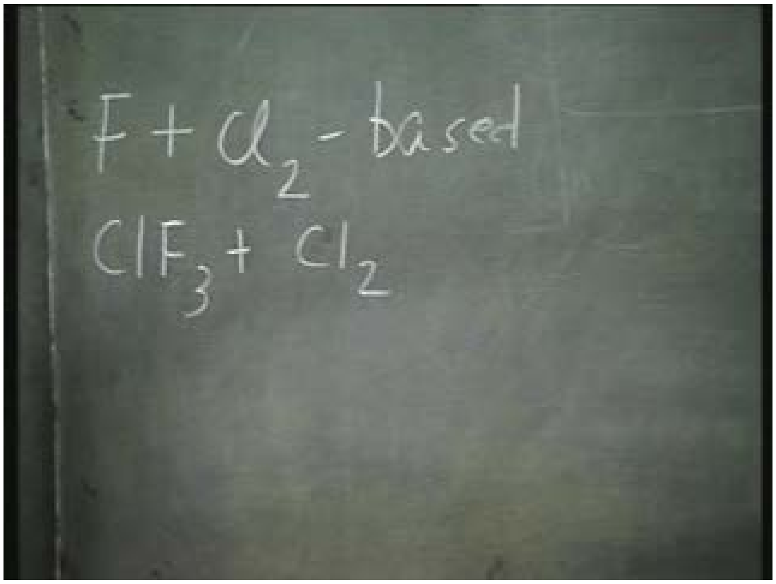

$F + Cl_2$ - based

$ClF_3 + Cl_2$

So, I can have fluorine plus chlorine based etching. Feed gas is going to be ClF 3 plus Cl 2. What you have is you start with POClF 3. So, ClF 3, POClF 3 is going to give you most fluorine; mostly the active species obtained in ClF 3 plasma is going to be fluorine. So, the etch profile will be isotropic. Fluorine based etching; I am going to have isotropic profile. You start increasing the percentage of chlorine slowly. What will happen? Slowly the anisotropy in the profile will start increasing, right.

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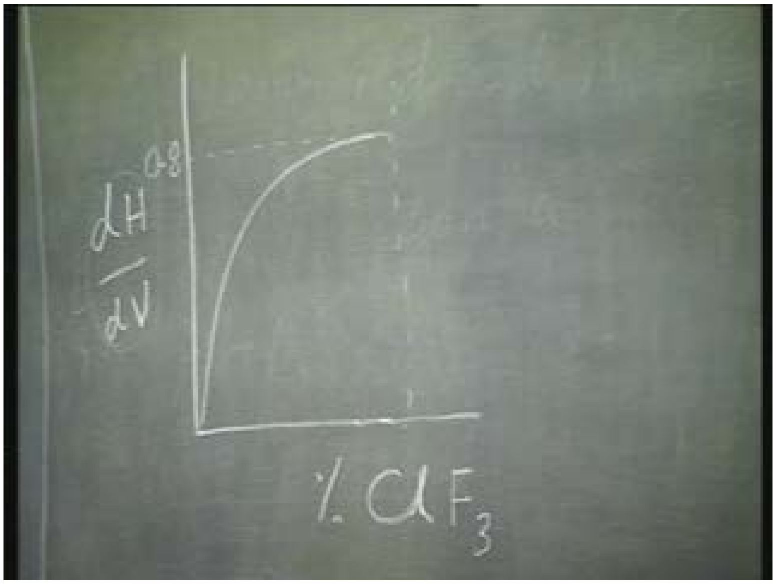

So, actually if I plot dH dV, dH dV is the rate of etching of the horizontal surface relative to the rate of etching of the vertical surface; dH dV. You want dH dV to be, you want the horizontal surface to be etched, not the vertical surface, right. Therefore, you want dH dV to be as high as possible, right. So, if I plot it as a function of the percentage of ClF 3 in the feed gas, then it is going to increase like this. So, as I keep on increasing the percentage of chlorine, the rate of, ratio of dH dV approaches 1, about 0.8. That is here I have more or less isotropic doping profile. When I have the feed gas composition mostly ClF 3, nearly 100% ClF 3, I have an almost isotropic etch profile. As the percentage of CLF 3 is slowly decreased, it falls, right. The etch profile can also be shown like this.

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Let us say, I have silicon surface and I have a very small percentage of ClF 3. Then, I have an almost vertical profile like this, almost vertical; not exactly, but almost that is when I have 6% of ClF 3. Let me increase this percentage of ClF 3 from 6% to let us say 30%.

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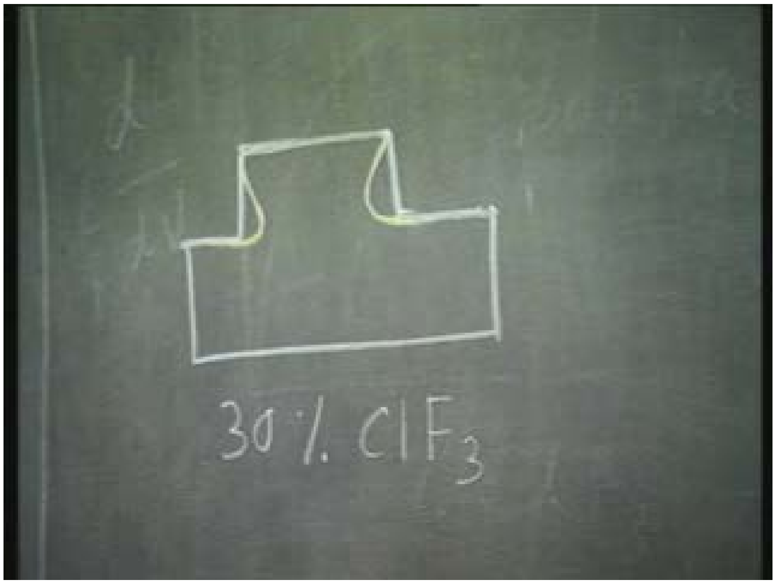

What I am going to have is you will find under cuts, right.

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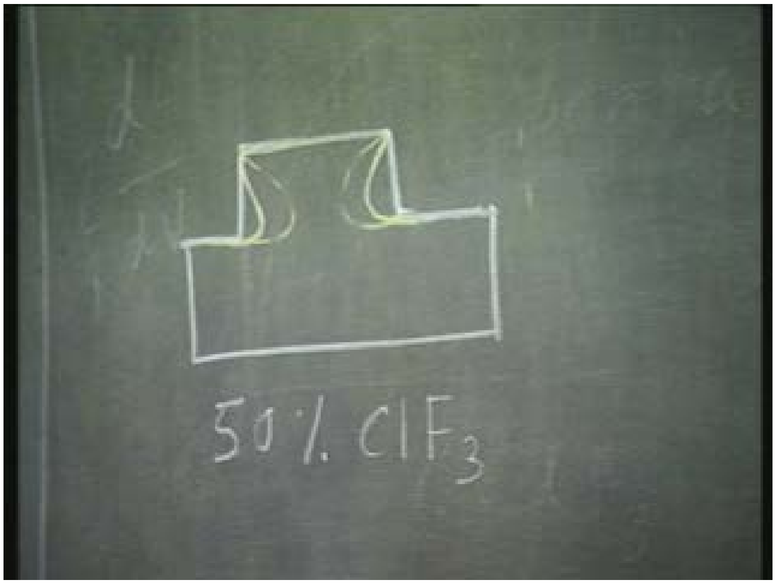

If I go even higher say 50%, so as I increase ClF 3 percentage, I am going to have more and more severe under-cut problem, because the etching is going to be isotropic. So, basically you see, silicon etching therefore you can do by using either chlorine or fluorine. Unless you are particular about the etch profile, CF 4 is most commonly used. If however you want to have good anisotropy, you have to use chlorine based etching or a combination of chlorine and fluorine based etching, because simple fluorine based etching can never give you an anisotropic etch profile, because of its spontaneous and vigorous reaction. Chlorine offers you more flexibility. There is possibility of energetic ion-enhanced reaction, as well as by suitably modifying the feed gas composition you can have inhibitor formation, so that also anisotropy is improved.

The other material that I want to etch is the metal aluminum. Now, aluminum does not get etched by fluorine at all. You know why, because aluminum fluoride is not volatile. Remember, for dry etching this is a prime concern, whether the reaction product is volatile. Unless the reaction product is volatile, it cannot be used for etching. So, aluminum is not etched by fluorine, because aluminum fluoride is not volatile. So, for etching aluminum, we again use chlorine. Chlorine can etch aluminum spontaneously; you can have isotropic etching. If you want to have anisotropic etching, then you should use an inhibitor forming substance in the feed gas. Also remember, like silicon, aluminum has a great affinity for oxygen. In fact, aluminum has a greater affinity for oxygen.

So aluminum, whenever you have aluminum film present, the surface is always covered with oxide and like silicon dioxide, aluminum oxide also cannot be etched by chlorine.

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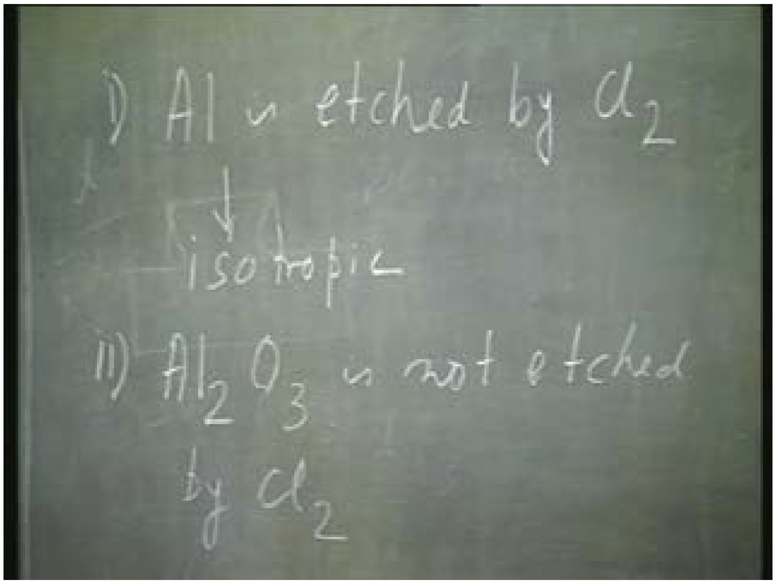

i) Al is etched by Cl_2

↓

isotropic

ii) Al_2O_3 is not etched by Cl_2

Aluminum is etched by chlorine, it is a spontaneous reaction; therefore the etch profile is isotropic. Aluminum oxide however, is not at all etched by chlorine. So, when you are etching aluminum, in practice, you must have a feed gas which will be able to etch not only aluminum, but also aluminum oxide. At the same time, if you want to have anisotropic etch profile, then your feed gas must contain an inhibitor forming substance, because otherwise it is going to be isotropic; the etch profile is going to be isotropic, right.

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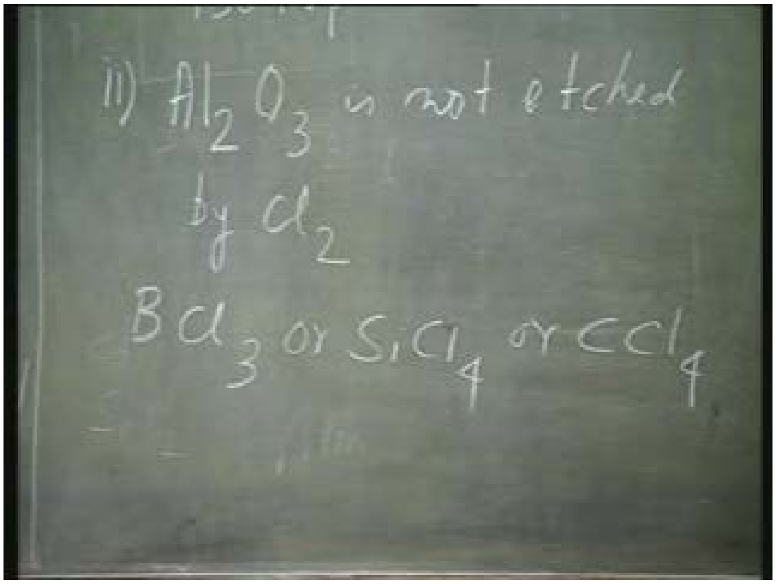

ii) Al_2O_3 is not etched by Cl_2

BCl_3 or $SiCl_4$ or CCl_4

This dual purpose is served mostly by using BCl 3 or SiCl 4 or sometimes even carbon tetrachloride. They serve the dual purpose. That is they etch the aluminum oxide as well as they form the inhibitor film to provide anisotropy. The other material that you are interested in removing is photoresist and I have already mentioned when we were talking about barrel reactor that photoresists can be very easily removed by simply burning it up in oxygen plasma. So, for photoresist removal, you do not need any of these fancy feed gases; all you need to have is oxygen plasma and photo resist can be ashed. That is called ashing of photoresist.

The other point that I want to mention is you know, we have talked about reaction rates, how the feed gas composition is going to affect the reaction rate and all that, but there is another factor which is also going to affect the reaction rate and that is called the loading effect. It is found that if you put too many samples inside the etching chamber, then the etch rate goes down. I put one sample, one wafer in the etching chamber and I measure the etch rate, after operation in a particular ambient condition. Then, keeping the ambient conditions identical, if I put 5 wafers, I find that the etch rate will become less; may be not 5 wafers, but if I put 50 wafers, I will definitely find that the etching rate is becoming less and this is called the loading effect; if you load the reactor chamber more, the etch rate is going to be less.

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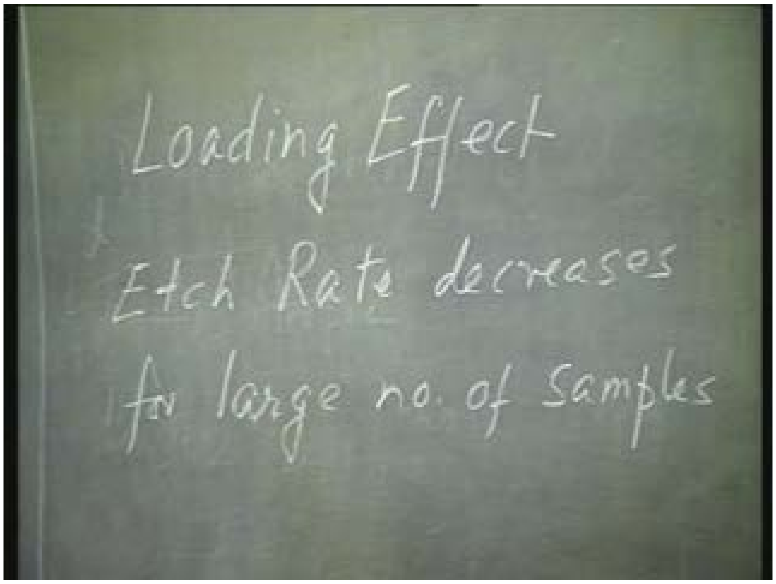

Loading Effect

Etch Rate decreases
for large no. of samples

Particularly when you have spontaneous, vigorous chemical reaction like fluorine based etching of silicon, this loading effect is quite a dominating factor. So, how to minimize the loading effect? Obviously, for mass production we would like to minimize the loading effect and this can be minimized simply by keeping the reactor area much larger compared to your total sample area.

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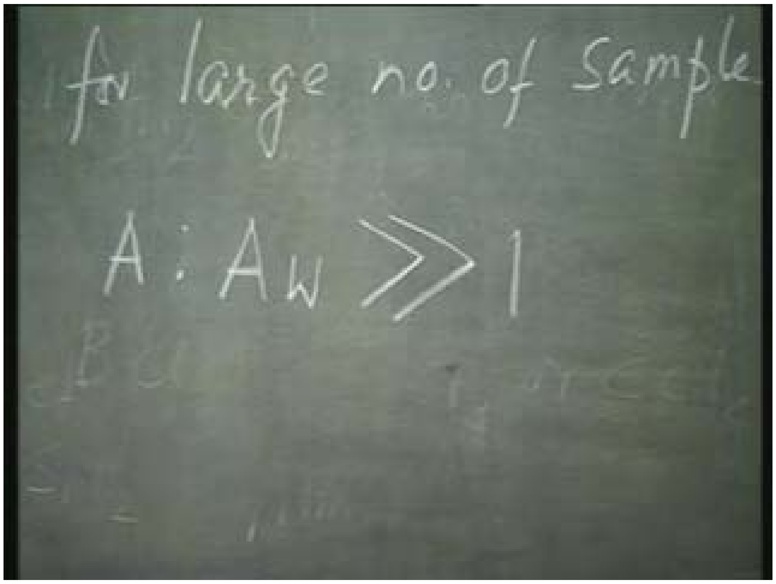

for large no. of Sample

$A : A_w \gg 1$

The ratio of reactor chamber area, A to the wafer sample surface area, Aw must be very large. That is in other words, you chamber should be big. The bigger your chamber, the less is the loading effect. So, the loading effect can be minimized by simply keeping the chamber area much larger. This is particularly important when you have a mass production …., where it is important that you can etch a large number of wafers, without having to sacrifice the etch rate. So there it is very important and the other factor of course, as I told you that loading effect is particularly dominating when we have a very spontaneous and very vigorous chemical reaction, for example fluorine based etching of silicon.

Now, so far we have talked about dry etching or in other words, you can also call it plasma assisted etching. So, dry etching or plasma assisted etching, they are almost synonymous. Now, plasma, in all these discussions, we have used plasma to etch the sample surface. Somehow the plasma has assisted either by generating the active chemical species or by energetic ion bombardment; somehow plasma has helped in the etching reaction. So, just as plasma can be used for etching reaction, plasma can also be used to do exactly the opposite. That is the plasma assisted deposition and the reactor designs are almost identical; if not identical, they are very similar.

You have the same two parallel electrodes; you have a chamber in which you produce the plasma. The only difference lies in the minute details. That is what should be the ion bombardment energy, what should be the sheath potential, what should be the pressure of the chamber. Except for these minute details, plasma etching chamber, plasma etching reactor is very similar to the plasma deposition chamber and plasma deposition is a process widely used today for deposition of dielectrics like silicon dioxide and silicon nitride. So, that is going to be our next topic of discussion.