VLSI Technology

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

Lecture - 25
Wet Chemical Etching

We have discussed about lithography. So, you know, by lithography we have transferred the mask pattern on to the silicon wafer. Now, usually the next step after lithography will be etching, right and most often you will find that we will protect some regions on silicon by silicon dioxide and after the lithography, we will etch the silicon dioxide from the unwanted portions, so that silicon is exposed and when you are doing this etching, I think I have mentioned it time and again, that silicon dioxide is etched by using dilute hydrofluoric acid solution. That is you mix hydrofluoric acid with deionized water and then you can etch it. In fact you use a buffered hydrofluoric acid solution, where you use measured quantity of ammonium fluoride and hydrofluoric acid, so that it gives you a controlled etch rate of 1000 Angstrom per minute.

Anyway the point ….. is that after or at the end of lithography what we do is we subject the silicon wafer to an etching step and most often in the lab you will find that we are going to use some kind of an etchant solution. For example, if I am etching silicon dioxide it will be a hydrofluoric acid solution; if I am etching aluminum for example, let us say, I have a metal pattern and you want to etch that metal pattern, then you will be using an aluminum etching solution. If you want to etch gold, you will be using a gold etching solution or sometimes you may even have to etch silicon, for various specific applications.

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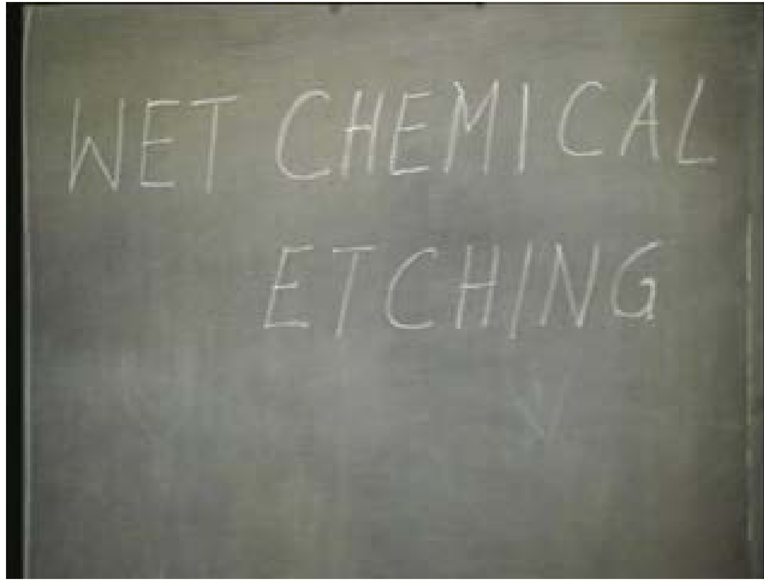

For all these we generally use some etching solution and this process of etching is called wet chemical etching or sometimes simply wet etching. The name is self-explanatory, right, wet chemical etching that is etching takes place in a solution medium. That is why it is wet. You use some kind of a solution and chemical etching, because there is some etching reaction that is taking place. The substrate material, I mean whatever you want to etch that is reacting with the etchant solution; some chemical reaction is taking place as a result of which some soluble products are being generated and that is how etching is taking place, right. So, this is the significance of the term wet chemical etching. By implication obviously, I imply that there is a dry etching as well, otherwise why should I call it wet chemical etching. But, we will talk about dry etching later; what is dry etching, why is dry etching necessary? This class, let us focus on the topic of wet etching, wet chemical etching.

So, what do you do? You put your substrate material into the etchant solution, right and what are the things that is going to happen inside? First of all you have some etchant material in the solution, right; for example, hydrofluoric acid in your HF solution. You want this hydrofluoric acid to be made available to the silicon dioxide with which it is going to react, right.

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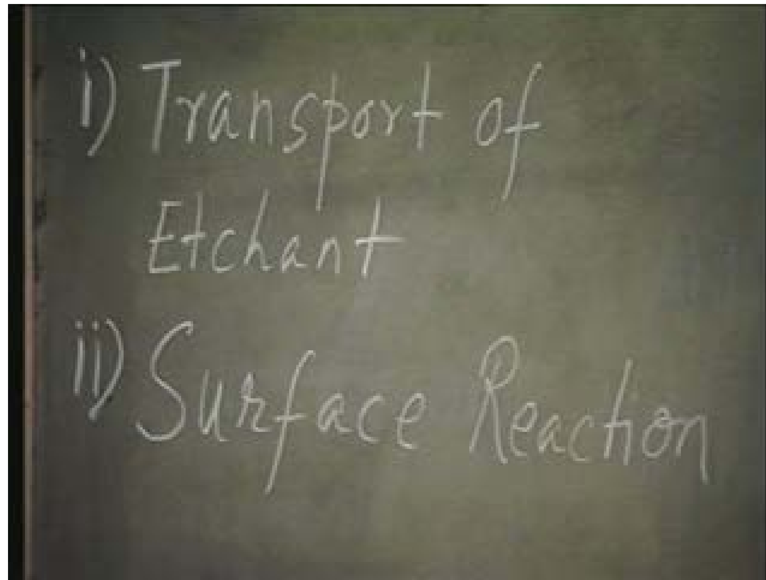

So, that is the first step, transport of the etchant material to the surface of the material that is to be etched; transport of etchant from the solution to the surface that is to be etched. What is step number 2? This etchant must react with the surface that is to be etched. That is the second step is surface reaction, right. I mean finally after this reaction, the reaction product must be removed from the reaction site, right. So the final step is transport of reaction product from the surface.

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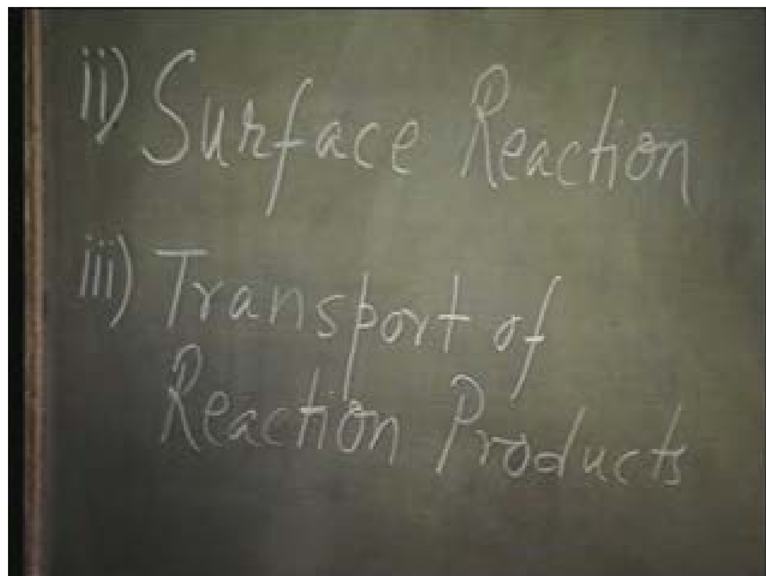

Let us inspect each one of these steps more closely. First step I said is transport of etchant. The etchants are in the solution. Now, imagine your sample is immersed in the etchant solution. So, the solution layer immediately adjacent to the surface that is the stagnant layer and that will get depleted of the reacting species. For example let us say, my silicon dioxide surface is immersed in the hydrofluoric acid solution. So, what is happening? Hydrofluoric, HF is reacting with silicon dioxide. So, if there is no fresh supply of HF, then the solution which is immediately adjacent, immediately surrounding the silicon dioxide surface that has got depleted, HF supply from there, agreed.

So, in order to, the etching reaction, in order for the etching reaction to progress I must have a fresh supply of the etchant material and how will it come? This etchant material is present in all the rest of the solution, where it still has not reacted with the surface to be etched. So, again you see, I have set up a concentration gradient. The concentration of the etchant is not exactly the same everywhere, right. So, it is going to diffuse through the stagnant layer just adjacent to the surface to be etched and the first criterion is satisfied. I have the transport of the etchant, diffusion of etchant through this stagnant layer, so that they can come to the surface that is to be etched, agreed. So, I have a possible bottle neck here. This etching process may be limited by the diffusion of the reacting species through the stagnant layer. This is a possible bottle neck that the etching reaction, I mean the total process of etching may be dominated by how fast this etchant material is diffusing through the stagnant layer.

Of course, if the etching reaction is such that there is an evolution of gas, then the stagnant layer will be broken; there will be no problem for the reacting species to come and meet the surface. Otherwise if I have a stagnant layer, it may mean that the etching process will be diffusion limited, diffusion of the reacting species. Then of course, once the reacting species have come to the surface, I come to step 2 that is that of surface reaction and here you can very easily understand that if the etching process is going to be reaction rate limited it is going to depend on crystal orientation, provided I am etching a crystalline material, right. If it is reaction rate limited it will depend on which face of the crystal I am seeing; is it 1 0 0 or is it 1 1 1 and that can affect the etching process.

Therefore, we say in general for a crystalline material the etching may be anisotropic; it may be isotropic that is it may be same in all direction, but it may be anisotropic when the etching process is dominated by the reaction rate, right and then finally, I come to the third step that is the transport of the reaction product.

Why is it important? You know very well from the law of mass action that unless the reaction products are removed from the site, the reaction will stop. So, if you want the etching process to progress, you must have some means of relieving the reaction products from the site. This can be facilitated by stirring. That is why we often say when you are doing a wet etching please stir the etching solution to achieve uniformity of etching. Stirring is going to serve both first and third purpose. That is it is going to facilitate diffusion of reacting species and it is also going to cart away your reaction products from the reaction site. So, going by these three steps now, we can say that etching of crystalline material can be isotropic or it can be anisotropic. It will be anisotropic when it is reaction rate limited; it will be isotropic when it is not reaction rate limited that is when most probably the first factor that is the diffusion of reacting species is going to govern the etching process and of course if you have an amorphous or polycrystalline material, then etching is going to be uniform; it is going to be isotropic.

Now, to talk about the etching process, let us take a few common materials which are to be etched in VLSI technology. First of all, let us talk about etching of silicon. Etching of silicon is a fairly difficult proposition. The etching of silicon is done by a sort of two-step process. That is in the first step you convert the silicon into silicon dioxide and in the second step, you etch that silicon dioxide. So, the first step in the silicon etching is going to be oxidation which is analogous to your anodic oxidation reaction and the second step is going to be etching of oxide. So, invariably we will find that the silicon etchant has more than one component, more than one material in it. One is for oxidation; one is for etching of that oxide.

Now, as I said the oxidation reaction is analogous to that of the anodic oxidation.

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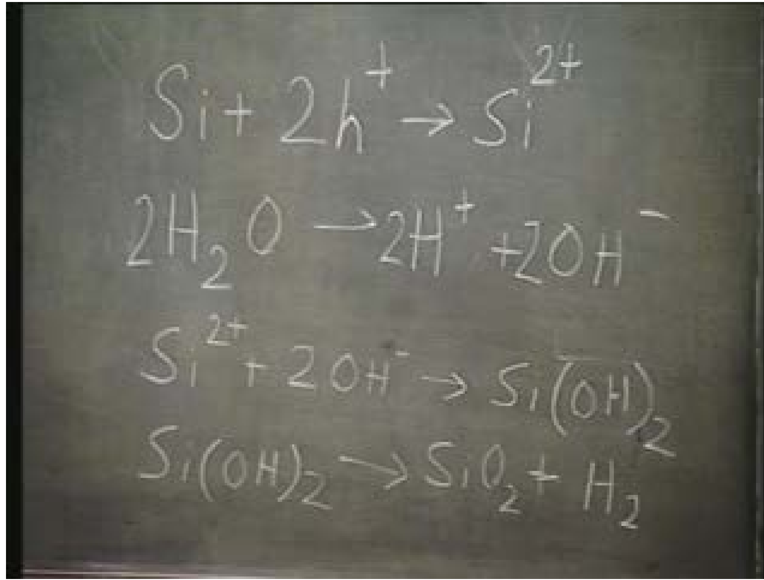

That is silicon it finds holes to form Si 2+. This is a basic anodic oxidation reaction; silicon with two holes forming Si 2+ and water electrolysing into H plus and OH minus and then, Si 2+ reacting with OH minus to form an intermediate compound of Si OH whole 2, which finally gives you silicon dioxide and hydrogen. So, this is our basic anodic oxidation reaction. The only difference in this case is that I do not have a well-defined anode or a cathode. Remember, in case of anodic oxidation, silicon was always used as the anode. I supplied the voltage, so that silicon is always the anode and the other electrode is always the cathode.

In this case I am not supplying any voltage. It is not electrochemical etching; it is chemical etching. So, you do not have a specified anode or cathode. A point on the silicon surface can behave either as anode or as cathode and if this point behaves as anode and cathode for approximately same period of time, equal period of time, then your etching will be uniform; if not you will have preferential etching. Now, whether a point will behave equally like an anode or cathode or it will behave preferentially will depend on various factors; for example surface defects, for example etchant temperature, for example adsorption process at the etchant semiconductor interface. All this will play a very crucial role to determine whether a point is going to be anode and cathode for

approximately the same period of time or not. If more or less the amount of time is equal, then you are going to have uniform etching, otherwise you will have selective etching.

So, what actually do I mean that it will behave like a localized anode or a localized cathode? Obviously, if it is a localized anode that means this reaction will dominate; it is the same point.

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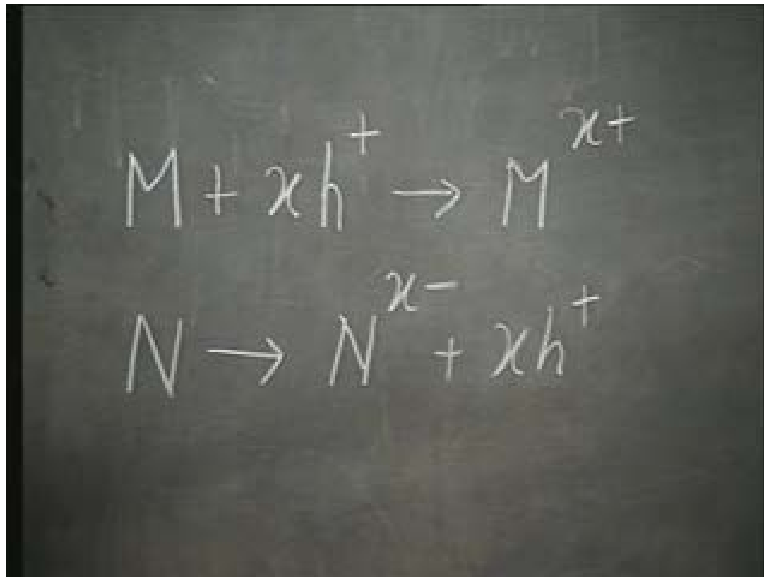

If I take the point as M, point on the material, if it is behaving like a localized anode, then this neutral M is going to react with x number of holes to give me ….., which is analogous to this reaction, right. This is where I forced silicon to be a anode. In the case of the chemical etching, this is a localized anode. While this is behaving liking an anode, this reaction is taking place and when this is behaving like a localized cathode, then what do I have? I have just the reverse reaction that is I have a neutral point which is going to give me ……, right. So, this is a localized anode reaction; this is a localized cathode reaction.

Now as I said, we will always find in a silicon etchant, we have more than one constituent. A very common silicon etchant is called HNA. H stands for hydrofluoric, N

stands for nitric and A stands for either acetic acid or aqua that is water; hydrofluoric, nitric and acetic acid or aqua.

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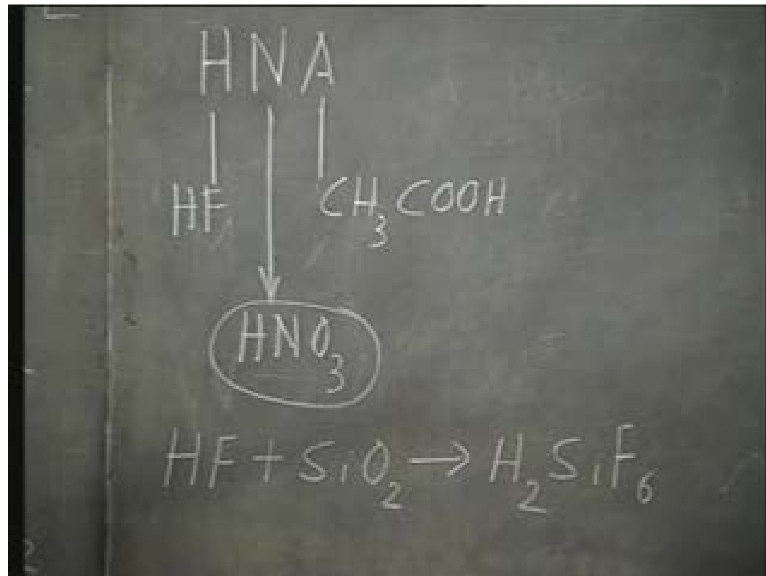

How does the etching reaction actually take place inside this? As I told you, first silicon is converted into oxide and this is the oxidizing agent; primarily this is the oxidizing agent. So, the purpose of the having nitric acid in the etchant solution is to oxidize silicon and then, this oxide is going to react with hydrofluoric acid to give a reaction product which is H 2 Si F 6, which will be dissolved. You can stir to remove this from the reaction site, right. So, let us concentrate on how does the nitric acid converts silicon into silicon dioxide? First of all, in this nitric acid we have a small amount of HNO 2, which occurs naturally by breaking nitric acid.

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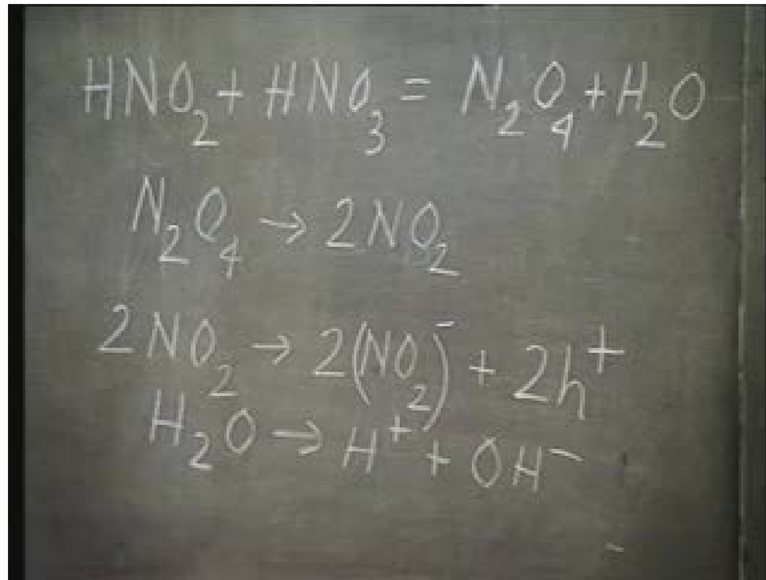

So, it will have a small amount of HNO 2 and that is going to be very crucial for the reaction. So, this is going to give me the hole generating species. See, for the anodic reaction to progress, I must have a supply of holes. So, in this entire reaction the presence of HNO 2 is crucial, because that is going to give me N 2 O 4, which is going to give rise NO 2 and which is finally going to give my holes. Now, silicon is getting supply of holes and the anodic oxidation reaction can progress. On the other hand, you know, next step is going to be water breaking into H plus plus OH minus and then the positively charged silicon reacting with the negatively charged hydroxyl ions, etc. But, I also have another thing.

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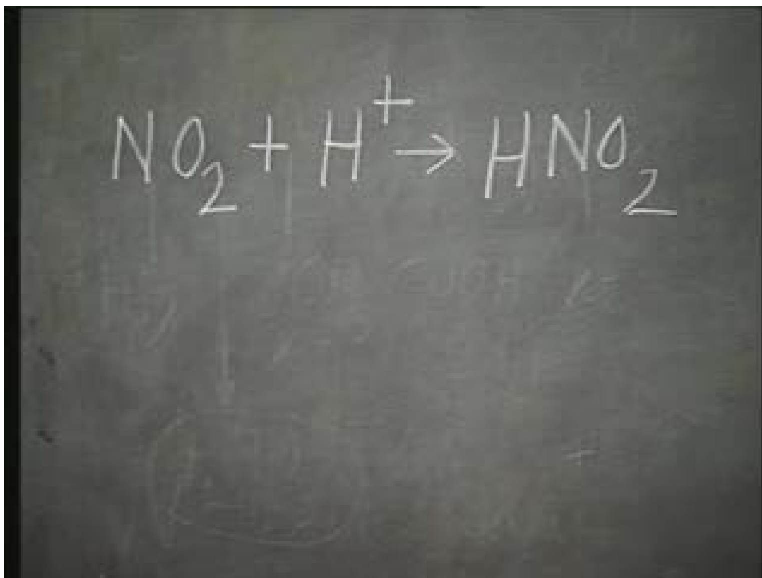

So, you see, HNO 2 is getting regenerated in the reaction. Do you see this? To begin with, I needed HNO 2 to initiate this reaction process; I needed HNO 2 for this first reaction, which is a very crucial reaction. I needed this to generate N 2 O 4 and subsequently NO 2 and which finally gave me my NO 2 minus and holes and I needed these holes to follow the anodic oxidation path, which you have already seen. At the same time, this NO 2 minus, it reacts with the H plus ions and it gives back HNO 2. So, you could say that HNO 2 even though it is crucial for the reaction, it is not actually getting consumed. So, we call this kind of a reaction an auto catalytic reaction. That is HNO 2, you know what a catalyst is, right; it does not really take part in the reaction, but it facilitates the reaction.

So, this HNO 2 is the auto catalytic agent; it is getting regenerated in the process. But remember, the initial supply of HNO 2 is very crucial for the oxidation reaction to start. Once it starts, ok, you can get a replenished supply of HNO 2. But to begin with, you must have some HNO 2 to start this reaction. That is why this first reaction is called the rate limiting reaction. That is the most crucial reaction, the rate limiting reaction and sometimes to facilitate this, ammonium nitride is deliberately added, so that you have a supply of HNO 2. In addition to nitric acid, ammonium nitride is deliberately added to

the etchant solution, so that you have an enhanced supply of HNO 2. So, this is what is going on inside the etchant solution when you use the hydrofluoric, nitric and acetic acid path. For various other applications, one uses various other silicon etchants.

Now the question is of course, what are these applications? Today one of the major reasons for silicon etching is in micromachining. You know what micromachining is? In this, see, silicon is not just a very good semiconductor; it has also excellent mechanical properties. So, what is happening? This is the era of miniaturization. So, previously we had for any control circuitry, for any control this thing, you had a sensor somewhere, sensor somewhere right at the spot and you had some control circuitry; sensors and actuators. Now, what we want is we want to integrate the sensor and its controlling circuitry in the same chip that is we want to have smart sensors. Sensors which will not only sense a catastrophe, but it will also take actions to prevent it. So, these are smart sensors.

So, for that what you do is you already have a very developed silicon technology. So, putting the controlling circuitry on a silicon chip is not a problem at all and in the same chip that is in the same silicon substrate, you want to have a sensor device. That is you want to use silicon also for sensing. Now, let us take a very simple sensor element, let us say a pressure sensor. What is the most common form of a pressure sensor? I have a thin membrane of silicon. Whenever there is a pressure, it moves. I can measure that movement electrically, my measuring the variation of capacitance, right. You know capacitor. Capacitance is going to be dependent on the separation between two plates. If this thin member is one plate, then when I apply a pressure, the distance is going to be less, therefore capacitance is going to increase and all I have to do is to sense this change in capacitor and my actuator circuitry can actually trigger on that; as soon as this capacitor exceeds a critical value, it takes some action.

So, for this kind of application, it is very important to have a thin membrane of silicon, right, which whenever we apply a pressure will move, will bend. How do you get this silicon membrane? By etching of course; so, we use silicon etching. See, that is, that is

actually a good thing, because silicon technology is so developed; all that we know in VLSI can be readily adopted for this kind of micromachining approach. So, this can be used. This is actually a very important area today, a very hot area one can say, silicon micromachining, because silicon has excellent mechanical properties as well. It is not just a good semiconductor, it has excellent mechanical properties and that can be used in making the sensors.

So, there our requirements can be various, like for example you want a controlled etching, right. So, you may want to have anisotropic etching. That is let us say I want the etching to the stopped automatically. Do you understand? What I am trying to say is suppose I have this full silicon wafer, which is say 500 micron thick. I want to have finally a 5 micron thin membrane. That means I want to etch off 495 microns and keep only the remaining 5 microns. How do I ascertain, how do I control the etching that I stop exactly after 495 microns are etched? You understand the degree of accuracy you need, 5 micron in 500 micron? One way of doing that is by providing a suitable etch stopped layer. There are various ways of doing it. I am just giving you some very simple examples. For example let us say, I have an 1 0 0 silicon wafer.

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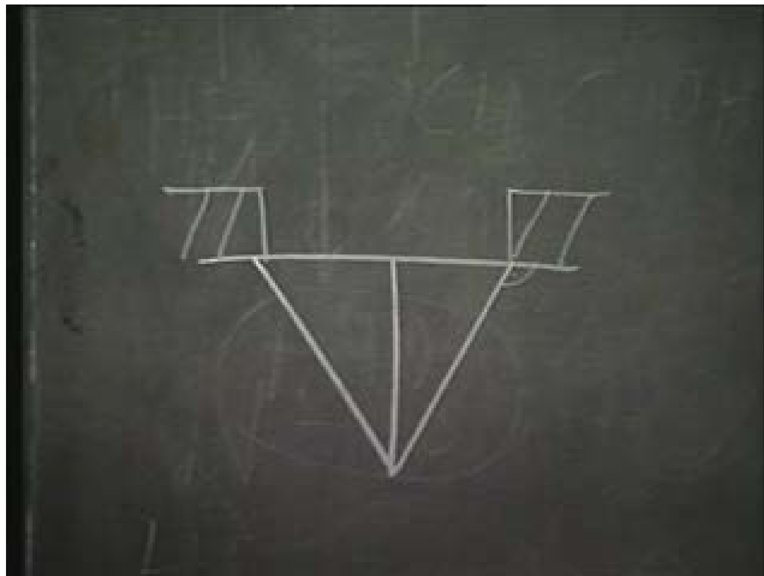

Now, if I have an 1 0 0 silicon wafer, this portion is say, protected, masked by certain material and I subject it to anisotropic etching, anisotropic etching such that the etchant etches 1 0 0 planes, but it does not etch the 1 1 1 plane. You remember, it is most difficult to etch 1 1 1 plane, right. So, I have an anisotropic etchant, which is actually a, one such etchant is available; it is called EPD, ethylene diamine pyro catechol and water; EPD or EPW it is called. So, this will etch 1 0 0 planes; 1 1 0 planes will also get etched at a comparable rate, but when it comes to 1 1 1, the etching will be virtually stopped. So, if I subject my wafer to such an anisotropic etchant what will be the etch profile like?

V shaped, very good; so, I have a…. Do you see the advantage now? This is self-limiting, right. This will go, get merged here. So once I, this is of course you know, you know the angle, you know this angle, 54. You know this angle. So you see, this height is therefore a function of this window and that angle. That angle is constant. You play with the window size and you can stop it wherever you want it. So, this is one very simple way of controlling your etching, right. Using an anisotropic etchant, because you know the etch process is going to be self-limiting, it is going to end here and by controlling the window size I can stop the etching where I want to.

Another way of doing the same is by controlling the doping of the substrate material. See, the doping of the substrate also plays a crucial role in determining the etch rate. So, you can have solutions, etchant solutions which will say etch a moderately doped layer very fast, but it will stop at a heavily doped layer. All you have to do is to dope up to a depth of 5 micron. The doping concentration should be very high in that region and then you subject it to the etching. Everything else will get etched except that heavily doped region. So, you can control the depth of that heavily doped region and realize your membrane thickness.

Similarly another way will be to use a pn junction. You can have etchant which will etch say, p-type region more compared to the n-region. So, these are all ways and means of controlling the etching. You can use an anisotropic etchant or you could use special etch stop layers. Those layers are called etch stop layers, where the etching is effectively

stopped. So, you can have a heavily doped region in order to stop the etching or you can have a different doping n-type versus p-type of the bulk material, so that will automatically control your etching. So, this is about silicon etching.

Of course, the other very important material which you may want to etch is silicon dioxide, sometimes silicon nitride. In these cases you have to remember a few things. That is you know silicon dioxide can be etched using hydrofluoric acid. That is not my problem. My problem is I may have silicon dioxide grown or deposited by a variety of technique. You must remember that the etching is going to depend critically on the actual processing and in this case I will tell you some of the basic, certain guidelines. First of all film will etch much faster than the bulk material. Why am I saying that? Silicon dioxide, even a quartz piece which is silicon dioxide and the silicon dioxide grown on silicon sample is also silicon dioxide. But, if you try to calibrate your etching solution, if you try to get the value of etch rate by etching quartz in it, you will definitely have a much slower rate than when you are trying to etch the silicon dioxide film. It is much easier to etch films than a bulk material.

Similarly films which are irradiated, they tend to etch faster; they get sort of weakened and they etch faster. But, there is one notable exception. That is when photoresist is irradiated, it gets hardened. Negative photoresist, once it is irradiated it is very difficult to remove. Otherwise, generally films when they are irradiated, they etch faster. Then of course, if you have films with poor microstructure or with a lot of stress in it, then they will etch faster. Then remember one more thing. If your film is non-stoichiometric, which is the case when you deposit silicon nitride by plasma deposition technique, we will discuss the plasma deposition technique little later; you know, normally silicon nitride, it has a chemical formula of Si_3N_4 that is the stoichiometric composition. But by plasma deposition, you do not get this exact stoichiometric composition, you have SiN_x and that film will etch much faster than a stoichiometric Si_3N_4 and of course, if you have a mixed film, like you have mixture of oxide and nitride, silicon oxy nitride for example, that will etch much faster or if you have a phosphosilicate glass, P_2O_5 and SiO_2 or if

you have a borosilicate glass, then they will tent to etch faster. So, normally for etching silicon dioxide we use a hydrofluoric acid based solution.

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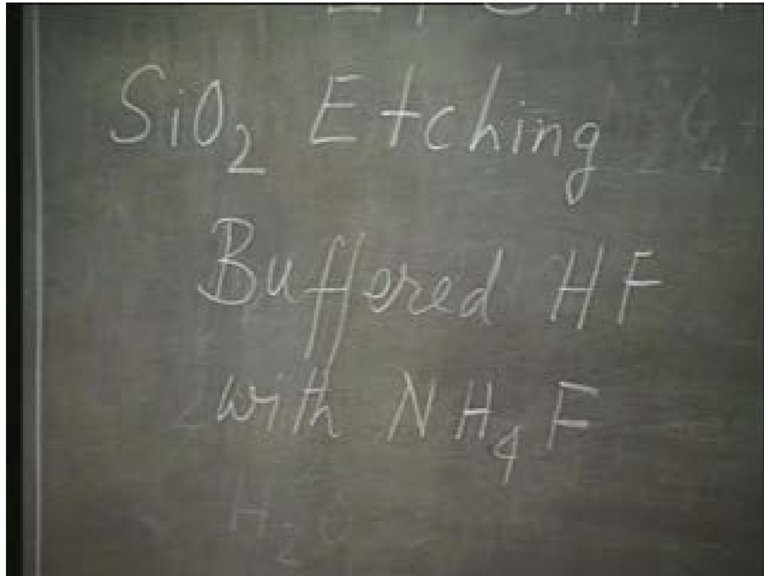

Most common etchant is buffered hydrofluoric acid where hydrofluoric acid is buffered with ammonium fluoride; hydrofluoric acid is buffered with ammonium fluoride. The other important material that you will want to etch is metal films. Normally what we do is you know, we deposit metal all over the silicon and then using your final contact metal mask, you remove the metal from unwanted portions and keep it only on the contact windows. That is what is done. Now, when you are etching this metal, the two most common metals we use are aluminum and gold. Etching aluminum is actually very simple. Aluminum is quite simple to remove.

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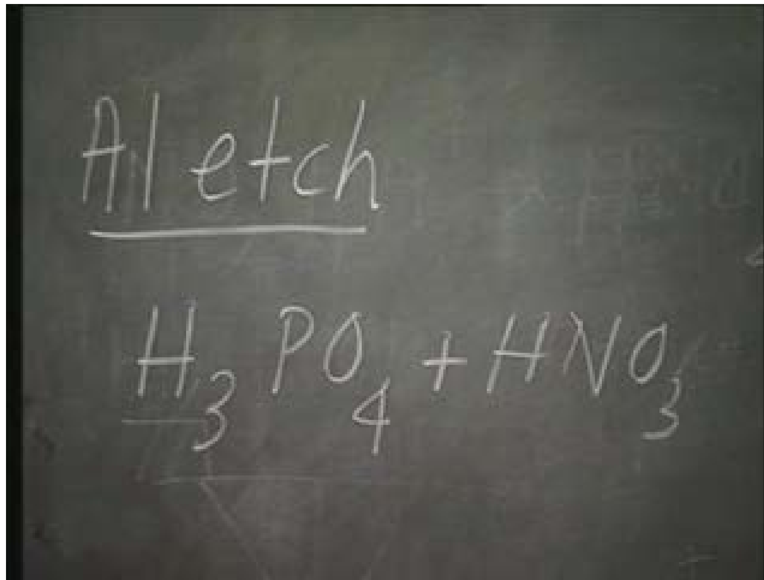

You use a mixture of orthophosphoric acid and nitric acid, H 3 P O 4 plus HNO 3; heat it slightly and aluminum gets etched. But remember, you cannot use it with all kind of substrates. For example, if you happen to work with gallium arsenide, you cannot use orthophosphoric acid. That will attack gallium arsenide.

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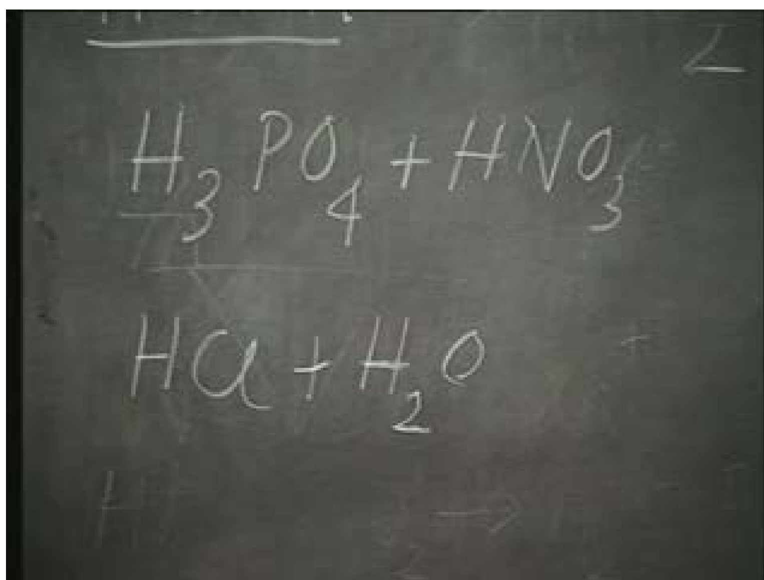

So, for that you have to go for an alternate solution. That is using diluted HCl. Like I said it is very simple to remove aluminum. You have to choose an etchant material depending on your substrate, which can withstand this. Let me throw a question at you. The other important material that I want to etch is gold. How does one remove gold? If you have not forgotten your high school chemistry, then you will tell me how does one remove gold? How can, yes, aqua regia. Unfortunately, if I subject semiconductor material to aqua regia, that will also go. So, I cannot use aqua regia for etching gold in VLSI technology, right which is a very critical point. Remember, you cannot use aqua regia to remove gold.

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You have to go for an alternative solution, which is a mixture of potassium iodide and iodine and water; very difficult to etch unless you use this particular solution. But, even this solution has a problem. You know, iodine has a dark colour, so your solution will be totally opaque. You cannot make out whether gold has got removed or not. You have to take it out of the solution, wash it and only then you can make out whether gold has been removed. That is why, that is why we do not normally go for gold etching if we can help it. For aluminum, this is the common practice. You evaporate aluminum all over the material and then you etch aluminum from the unwanted region.

For gold, that is why we try to use a different technique, which is called the lift-off technique, which we will discuss when I am discussing the metallization process. In that case, ok, let me briefly tell you what we do. You first put the pattern on the semiconductor.

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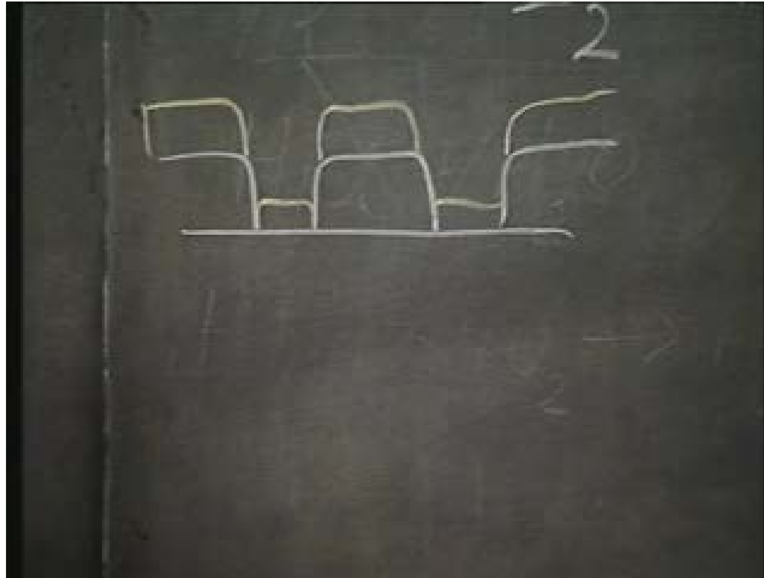

So what you have is this is your semiconductor and you have a pattern with photoresist. Let us say, this is my pattern. These are the portions which are protected with photoresist and then you deposit gold all over. So, what do you have? You have gold sitting here and you have gold sitting here and gold here and gold here and gold here. Now you put it in acetone. You know that positive photoresist is dissolved in acetone. So, what will happen? These are the portions, where I have gold sitting on photoresist.

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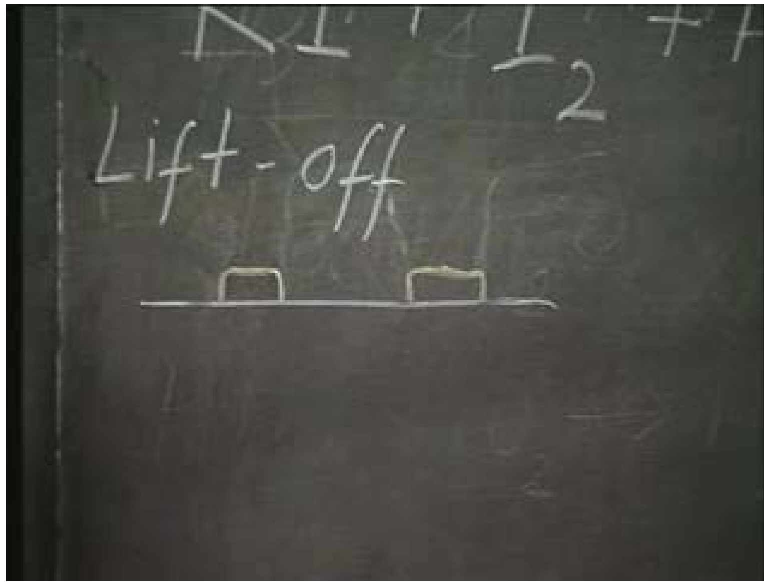

So, photoresist will get dissolved, taking the gold also along with it. Similarly from here, photoresist will go taking the gold along with it and from here also the same thing will happen, leaving gold only in these two regions where I wanted it. So, you see, I did not have to etch gold. So, whenever you have to use gold as a metal, you try not to go for gold etching. That is you do not want to put gold all over and then etch it from the remaining portion. What you try to do is go for a lift-off technique. It is called a lift-off technique. Of course, this lift-off technique also has a lot of intricacies, which we probably will discuss later, when we are discussing the metallization problem. But this I just wanted to mention in passing, because etching gold is so very difficult.

Anyway, what we have seen today is how the most common materials we encounter in VLSI technology can be etched by the wet chemical etching technique. I will just leave you with something to think about. Remember, all the etching processes I have discussed here, they are all based on chemical reaction. The etchant material reacts with the substrate material, in order to etch. Now, consider the following problem.

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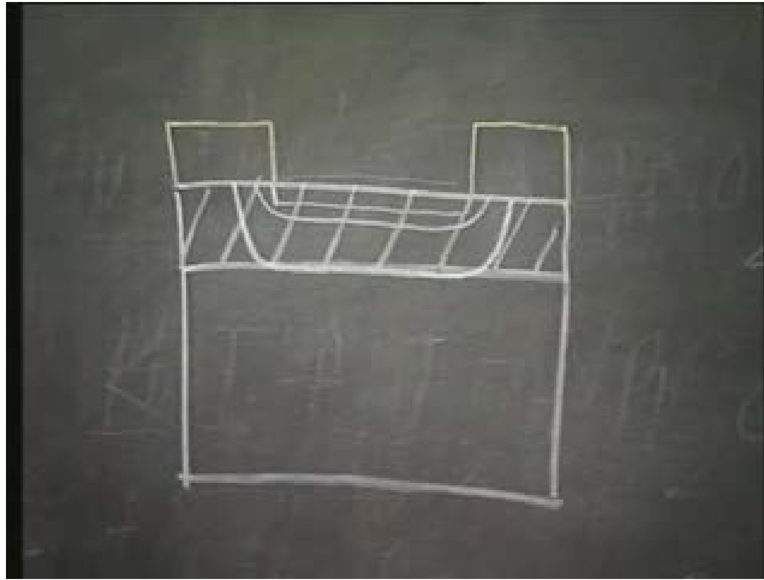

I have to etch this shaded region. It may be oxide, it may be anything. I have used a mask and I am subjecting it to the chemical etching, the wet chemical etching. Because it is a chemical etching, for the etchant material, this surface, first it etches like this. Then, it sees this surface that is the side wall as well as the bottom. As far as the etchant material is concerned, there is no difference between these two materials; the side wall is also silicon dioxide the bottom is also silicon dioxide. So, it reacts with both the side wall as well as the bottom surface. So, the side wall also gets etched and the bottom also gets etched and this process continues till I have etched the entire region.

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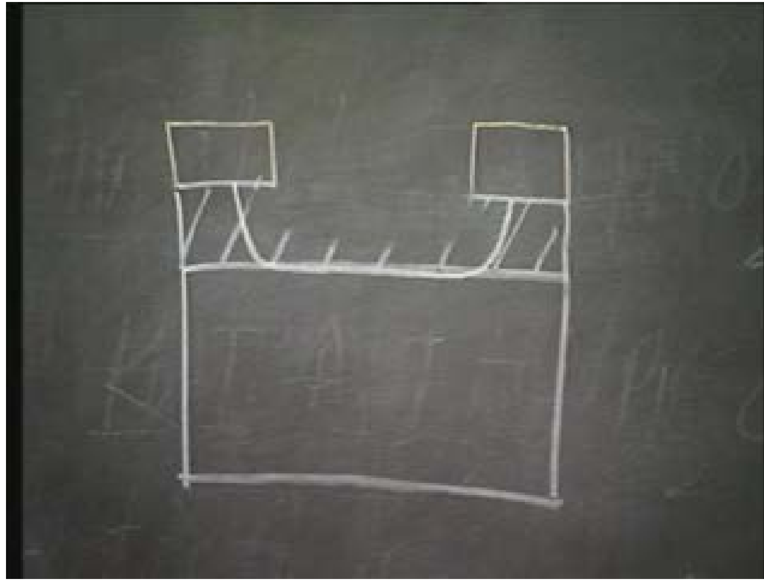

This is what my etching profile is going to look like. I have what is called an under-cut, under the mask.

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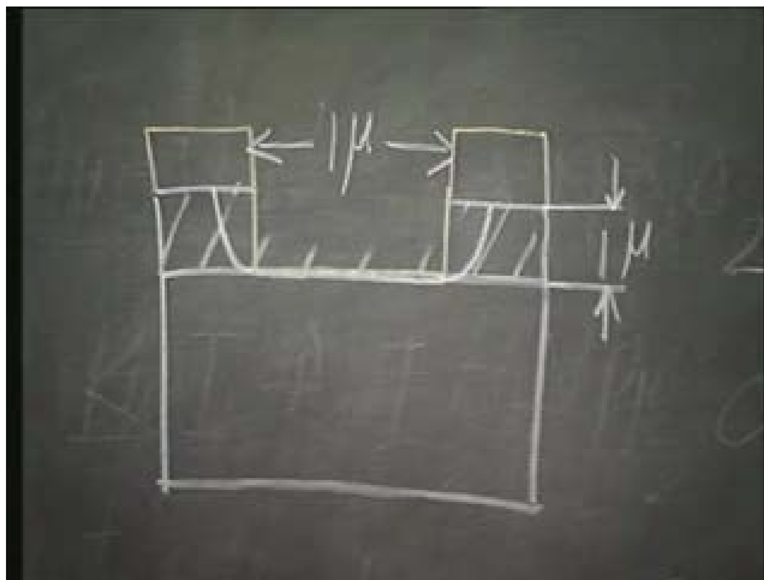

Ideally my etching should have been, etching profile should have been like this. But, since the etchant cannot distinguish between the side wall and the bottom surface, it has gone under the mask on both the sides and I have a profile like this. Now, if my window

is 1 micron, because now the device dimension is shrinking if my window is 1 micron, if the height of this is also 1 micron and if I consider that the etching is perfectly isotropic that is it cannot at all distinguish between the vertical and the horizontal walls, that is the etching in the vertical as well as the horizontal direction is identical, then even though I have 1 micron window, my final feature size is going to be 3 micron, which is intolerable. I cannot have such a tolerance. What do I do?

This is the question we are going to take up in the next class.