


Microscale Transport Processes
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Lecture No. #07
Photolithography (Contd.)

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Wet etching

- Subjecting parts of an object to chemical reactions and subsequent dissolution.
- The other parts are protected by a mask.
- Technique is used in fifteenth century to decorate armours. Wax is used as a mask. Wax on parts, identified for etching is cut out. Dipping into reactive bath for a period of time ensures chemical etching / hollowed out pattern in places, not covered by wax. Wax is removed by heating later.
- Rate of etching follows Arrhenius expression, and is strong function of temperature, unlike solubilisation of resist.



This, welcome to this class of micro scale transport process; what we are discussing is various micro fabrication techniques in particular photolithography. And we have already discussed how to transfer a pattern using a mask and a mask aligner, and what is the use of photoresist, how this photo resist is coated on a silicon substrate, these points we have already discussed. We start this class with a discussion on with etching. I must point out to you that the etching process that we discussed before, the etching involves dipping this, I mean what I mentioned before is that etching involves dipping the substrate which has already been exposed, and the polymer has already been solubilised.

After this exposure and after this development, after putting this substrate in into the developing solution, after all this process is done a way, then you take this substrate and put into the etching solution. And etching involves etching - involves reaction of silicon with the etching chemical and by that way, the product that forms goes to the

solution and silicon is gradually etched or a groove or a channel forms on the exposed part of the substrate.

So, the etching can be of two types, one is referred as wet etching, where the silicon substrate after exposure and after development through after solubilising the relevant resist part. This either it could be dipped in an etching solution which is a chemical solution or it could be done by a process which goes by the name dry etching. So, etching could be of two types, one is wet etching; the other could be dry etching. Wet etching refers to dipping the substrate into a chemical and conducting a chemical attack, but that is through a liquid phase; so that is what we refer here as wet etching. So, what we have here is wet etching involves subjecting parts of an object to chemical reactions and subsequent dissolution. So keep in mind, there is another process which goes by the name dry etching. Here we focus first in this slide, the wet etching process.


So, wet etching involves subjecting part of an object to chemical reactions and subsequent dissolution; so that a channel or a groove forms on the exposed part of silicon substrate. The other part, I mean depending on whether you are using positive resist or a negative resist, the other part which has not been solubilised with the resist, the other part where the polymer the photo resist has not been solubilised. So, the other parts are protected by a mask. This technique is used in 15th century to decorate armours. Wax is used as a mask there, wax on parts identified for etching is cut out; so that means, on a metal plate wax is deposited and depositing wax is no big deal, you understand how wax is? You have seen a candle and how wax melts.

So, the wax is deposited on the metal plate and the parts that are identified for etching those are cut out; that means, in those places the wax is taken away. Then these metal plate is dipped into reactive bath, for a period of time that ensures chemical etching or hollowed out pattern in places. So, the places where there is where the wax is taken out, in those places the etching is possible, chemical attack is possible, the chemical can access the metal plate and there a hollowed out pattern results; in places where which places that are not covered by wax. Later, wax is removed by heating this metal plate. Now, rate of etching follows Arrhenius expression, you must understand one fact there is that you have earlier dipped the substrate into a developing solution.

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Typical Protocol

- Immerse the wafer in acetone in an ultrasonic bath to dissolve organic residue and then drying.
- Repeat the previous step with alcohol.
- Dehydrate on a hot plate at 120°C for 5 minutes
- The first three steps, above ensure removal of contaminant from the wafer.
- The wafer is coated with photoresist in spin-coater.
- System is heated to 65°C for one minute, and 95°C for three minutes to ensure hardening of photoresist.
- Exposure.
- The wafer is post-baked to 65°C for one minute, and 95°C for two minutes to ensure progressive rearrangement of material during thermal deformation.
- The system dipped in developing solution for 3 minutes.
- The system is rinsed with alcohol, and dried with nitrogen.
- The system is heated to 200°C for two hours.




If we go back to our previous discussion, in a in the typical protocol that we discussed, there near the end you can see, we have mentioned that the system is dipped in developing solution for three minutes. This developing solution is primarily to dissolve the photoresist material; this is just a solubilisation process. So, these does not involve Arrhenius dependence, Arrhenius type dependence on temperature; however, this etching is etching for etching is a reaction etching is a reaction of silicon with the dipping solution. So, this rate follows Arrhenius expression and is a strong function of temperature unlike solubilisation of resist. So, this is a very important point you should note down that rate of etching is a strong function of temperature. So, when you calculate how long you should keep the substrate in the etching bath that time you calculate or when you consider the rate at which the etching will take place that would be a strong function of temperature, unlike the solubilisation of photoresist.

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Anisotropic etching

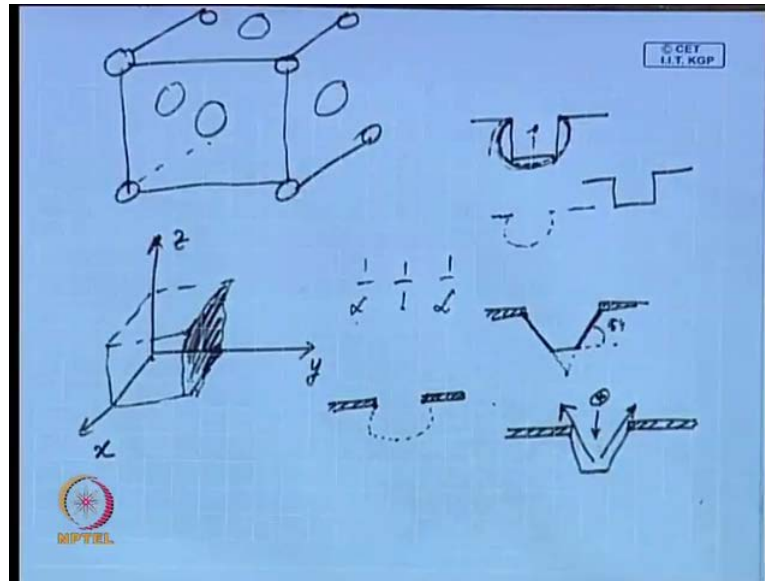
- $\langle 111 \rangle$ planes of silicon are highly packed with atoms.
- Velocity of etching is slow along planes $\langle 111 \rangle$ and fast along $\langle 100 \rangle$ or $\langle 110 \rangle$.
- Typical etching speed with KOH along $\langle 111 \rangle$ plane is $13 \mu\text{m}/\text{hour}$.
- The etching speed is 60 times faster in other orientations.



Now, I must point out here, when it comes to wet etching, there are two types of etching possible. One is anisotropic etching and other is isotropic. Isotropic means, it is identical in all directions; anisotropic means, it has some preference; it has a preferential etching in one particular direction. Now, here I would like to point out once again that this 111 planes of silicon are highly packed with atoms. Let me revise once again this, what this 111 plane is. Silicon crystal is made of it is basically silicon follows a crystalline structure; it has the atoms are arranged in a particular manner.

It is not like glass, which is amorphous and there is no particular arrangement. So, in silicon crystal the atoms are arranged in a particular manner and that manner is that it is face centred cubic lattice, inter penetrating network of face centred cubic lattice. Face centred means, you have a cubic lattice; that means, a cube that means, atoms are placed on all corners of a cube. Face centred cubic lattice means, over and above of these atoms, there are further there are more atoms at the centre of each face. So, other than the atoms in a corner, there are atoms at the centre of the face.

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So that it means you had these are the atoms. So, this is a cubic lattice and you have the atoms at atoms are in place. So, these are the atoms, now over and above these atoms, you have atoms at the centre of each face there are atoms. Now this is one face centred, this is a face centred cubic lattice structure. Now, I said inter penetrating network of face centred cubic lattice; that means, you have one such cubic cube. You place another cube on top and then move that cube by a distance as I pointed out in the last class one fourth, one fourth, one fourth, in x, y, and z direction.

So in that case, whatever structure that results that would be considered is inter penetrating network of face centred cubic lattice structure, which is basically the crystalline structure of silicon. So, because of this structure, you have 1 1 1 planes of silicon, which are highly packed; this 1 1 1, this refers to the miller index. In the last class, we have discussed what miller index is and you have to look into these, how this 1 1 1 how these are defined.

So, velocity of etching is slow along planes 1 1 1 and fast along 1 0 0 or 1 1 0. Let me point out once again very quickly what this 1 1 1 plane is. As per the miller indices, if I look at a cube, I find one plane; it is making intercept to the x, y, and z axis. What is the value of that intercept? So, I will have intercept for the x axis, I will have another intercept for the y axis, another intercept for the z axis for each plane. And that intercept value reciprocal of that intercept; these are these numbers that I have here.

So, this as far as this plane is concerned, this has an intercept on y at a unit distance away from the centre. So, it is making an intercept at one, as far as this y direction is concerned, but when it comes to the directions x and z, these plane does not intercept at all or in other words it intercepts at infinity. So, when I look at 1 by 1, 1 by infinity, and 1 by infinity; what I get is $0 \ 1 \ 0$. So that is what this plane refers to. Similarly, you can come up with a plane $1 \ 1 \ 1$. So that is what we are referring here that in silicon crystal, $1 \ 1 \ 1$ planes are highly packed with atoms compared to $1 \ 0 \ 0$ or $1 \ 1 \ 0$, these are the planes.

And when it comes to etching that means that silicon this atom is reacting with etching chemical; so, the etching process will be slower in $1 \ 1 \ 1$ plane and etching process would be faster in other planes. So, there would be a preferential etching in one direction that is what I am trying to get to. So, typical etching speed with cube is along $1 \ 1 \ 1$ plane is 13 micro metre per hour, the etching speed is 60 times faster in other orientations. So, when you dip this substrate in the etching chemical, you will see the cutting of that crystal in one particular plane. It is not that it is uniformly been cut that groove is formed the depth, it is not uniformly picked up rather it would be cut in a particular direction.

Can you tell me what would be a uniform etching? If it would have been anisotropic etching, how would it look? Suppose, this part is protected by mask and only this portion is the, only this portion is exposed, I mean this portion etching can take place. Now, if it would have been an isotropic etching; for example, if we if you have glass, glass does not have a crystalline structure, it is the amorphous material. So, amorphous material means these are the chains are dangling, here I mean the atoms are random. So you can you tell me how would the, how would be the shape of isotropic etching process. If it would have if the etching would have been taking place uniformly in all directions, then it will not be this; this does not mean it is uniform in all direction, what it means, uniform should be these.


Think of it, this is the point throughout which the etching is taking place and you should be, you should form a circle uniform in all directions. So, gradually this would be changing because the etching centre would change; so, this is called isotropic etching. So, isotropic etching does not mean this, this is not isotropic etching either. Isotropic etching means this is isotropic etching.

Now, this is what we have in silicon is an anisotropic etching, which is which I have already pointed out in this slide; that the etching speed is 60 times faster in other orientations and etching speed in $1\ 1\ 1$ plane is 13 micro metre per hour. So, this gives you some feel 13 micro metre per hour. So, how long you have to keep this substrate into the, I mean immersed in the etching solution; so, this gives you an idea in that respect.

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Anisotropic etching ...contd.

- Etching happens preferentially along a crystallographic plane.
- The crystal will make the cut-out forms appear spontaneously along the planes where the etching is slowest.
- This form of etching makes possible cavities with facets, which can be useful.
- This type of etching is not possible in amorphous solid, e.g., glass.



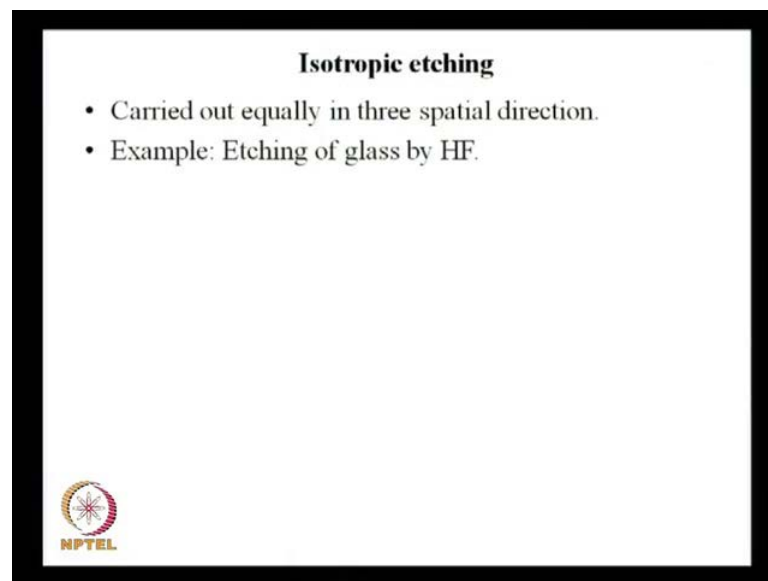
Now etching, So therefore, you must agree that etching happens preferentially along a crystallographic plane, we all agree to that. The crystal will make the cut out forms appear spontaneously along the planes, where the etching is slowest. So, there would be cut out form, which appear spontaneously along the planes, where the etching is slowest. This form of etching makes possible, cavities with facets which can be useful. What that means is that, if somebody wants see this is $1\ 1\ 1$ plane, this plane is $1\ 1\ 1$ plane, this plane is $1\ 1\ 1$ plane; and these makes an angle of 54 degree that we already pointed out.

You remember in previous slide, the highest density planes form an angle of 54.74 degree to $1\ 0\ 0$ plane. So, this is the angle of this is that angle. So, the groove that is been form. So, this part is protected by mask, this part is protected by mask and you are trying to create a channel on silicon substrate. And when you try to do that, what you end up with is a, what you what I say here is this form of etching makes possible cavities with facets. So, you have an inclined face here, it is not a straight channel. So, this is what you are going to form, when you when you go for a wet etching.

Now, if this is something which you want perfect, but there is a short coming to it; is that if you want to make a deep hole or a deep channel for some reason. If the channel that you want make is deep channel, in that case what you end up with is beyond some point; suppose this if they you continue doing the etching, then it will end up here; beyond this point you cannot etch anymore. So, suppose you want to make a deep channel or if you want to make a through hole. So, you have to be careful, I mean there is a limited there I mean up to certain point you can do, beyond certain depth probably you cannot.

So, this point is there; however, in many situations, you want the channel to be this way and then this anisotropic etching is perfect. This type of etching is not possible in amorphous solids such as glass; that I already pointed out, because in glass what you will have is what we refer as isotropic etching. So, this isotropic etching is carried out equally in three spatial direction. So, it does not have any preference for any particular plane. So, this etching would be, if this is the area protected by mask. If this is the area protected by mask, you end up forming a channel which takes this kind of shape.

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This is a good example of isotropic etching; example is etching of glass by hydrofluoric acid.

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Dry etching of silicon

- Attack of a substrate by an ionic species, contained in gaseous or plasma phase.
- Isotropy or anisotropy controlled by the etching process, and not by crystalline structure.
- Types of dry etching:
 - Physical etching (sputtering, ion-beam etching, ion milling)
 - Chemical etching
 - Physico-chemical etching (RIE)
 - Physico-chemical etching with inhibitors (DRIE)



Now, as I said the etching could be of two types, one was the wet etching; that means, you are conducting the etching by dipping the substrate in a liquid. Instead of that there could be a process which goes by the name dry etching of silicon. Dry etching means, it has it does not involve any liquid; it is done using energised ionic species; attack of a substrate by an ionic species contained in gaseous or plasma phase that is how dry etching is done. So, what you do here is you have, suppose this is the portion which is protected by mask. Now, what you are doing is you are exposed this portion is exposed. So, it is bear silicon, it is actually having bear silicon is little difficult, because moment you keep it in oxygen, there would be a very thin layer of silicon dioxide forms on this layer, but this can be etched out fast, there would be a very thin layer of SiO_2 .

Now, that is probably not the point what I make here is what you have is, this is bear silicon. Now you have some ion, suppose this is a plus ion and these ion is coming this ion is bombarding the substrate. So, this ion is energized. How do you energize these ion? First of all you apply a voltage, pretty high voltage and then you apply vacuum as well. So, these medium is vacuum, you have certain selected gas, which can be ionized and then apply a voltage. These ions are energized and these ions are pretty much they are ballistic. So, they bombard the surface of the substrate and then, there is a reflection also going on in this direction. So, automatically the plane that you cut, it has a layer like this; it forms, because when the reflection takes place that reflection that we will chip away the silicon material, so automatically you develop anisotropy.


But mind it, this anisotropy is not caused by the crystal, crystalline structure, this anisotropy is caused by the system itself. You have chosen your system that way, I mean this ions are bombarded and the path the ions are taking automatically, I mean the ions are routed that way that it makes anisotropic. I mean it does anisotropic etching. So, attack of a substrate by an ionic species contained in gaseous or plasma phase. Isotropy or anisotropy controlled by etching process and not by crystalline structure. In wet etching, this anisotropy was controlled by a crystalline structure, but that is not the case for dry etching and there are various forms of dry etching possible.

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Physical etching

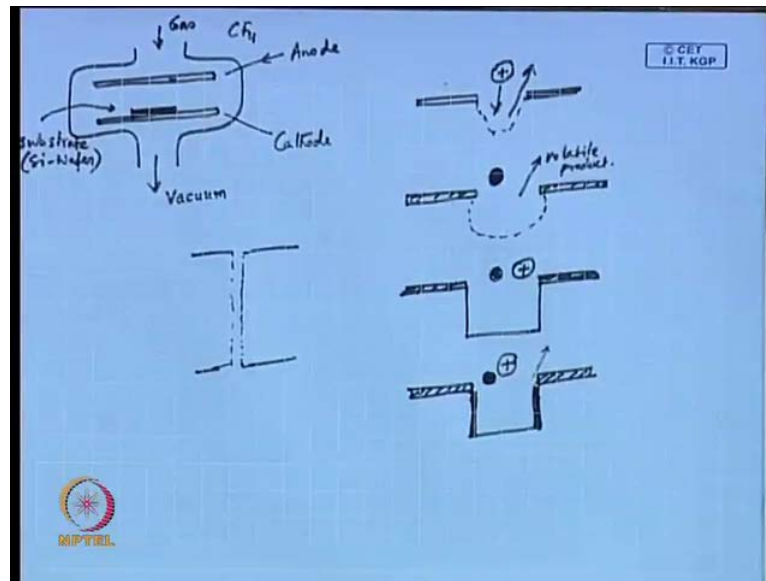
- Ions are accelerated in an electric field (10 eV to 5000 eV generated between two electrodes).
- Ions bombard the surface of a target.
- Low pressure (~ mTorr) helps in making the ion ballistic.
- Use of CF_4 gas is common in ionization.
- The method is inherently anisotropic because of the pathway taken by the reflected ions.
- Selectivity (about the portions of the substrate to be etched) is poor.

Etching rate 0.6 $\mu\text{m}/\text{hour}$ to 18 $\mu\text{m}/\text{hour}$ for most materials.



First of all, one is the first one is physical etching, which goes by other names as well sputtering ion beam etching ion milling. So these are all the same, I mean they refer to the same etching process. The second method is chemical etching. Third one physico-chemical etching, it is also goes by the name reactive ion etching, in short form RIE. And the fourth one is physico-chemical etching with inhibitors, which goes by the name deep reactive ion heating DRIE. Now, let us focus on first what the physical etching is. Physical etching or which goes by the name sputtering ion beam etching or ion milling, these involve a chamber.

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You apply vacuum here and you introduce some gas here, a common gas could be CF_4 , which can be ionized. CF_4 , CCL_4 is carbon tetrachloride; CCL_4 is used for certain form of chemical etching, this I mentioned about those four methods. The fourth one DRIE that use CCL_4 , physical etching it is done by CF_4 , this CF_4 would be ionized. Now, here you have an anode and cathode. So, this is the anode, the upper one is the anode and a lower one is the cathode and here lies the substrate, this dark one, this dark one is the substrate. This is that silicon wafer substrate what I should write it as silicon wafer, so this is the silicon wafer. This silicon wafer is placed on the cathode and you have this anode and these ions are accelerated in an electric field.

So, let me go back to the, let me look at the slide here, ions are accelerated in an electric field 10 electron volt to 5000 electron volt generated between two electrodes. So, ions bombard the surface of a target. So, ions are accelerated in an electric field. How are the ions formed? You introduce the gas, you create a vacuum and by vacuum, I mean it is low pressure. A low pressure helps in making the ions ballistic, why do you have vacuum in the system? This chamber, because this will help making the ions ballistic. You know what ballistic means, it will be easy for the ion, I mean you will give more energy, you will put more velocity more momentum to the ions. So, low pressure of the order of millitorr, what is one torr? One torr involves one millimeter of mercury, the pressure equivalent to one millimeter of mercury, this is a very small pressure as such and you are talking about one millitorr.

So the, so you maintain a low pressure inside the chamber; and this low pressure helps in making the ions ballistic. So you apply, you put anode and cathode, put the silicon wafer on the cathode, introduce a gas, which can be ionized, the typical example is CF_4 . You apply vacuum, so that pressure inside the chamber is low and you apply an electric field 10 electron volt to 5000 electron volt. Use of CF_4 gas is common in ionization, the method is inherently anisotropic, because of the path way taken by the reflected ions that is exactly what I pointed out, just in the previous note. That you have, if this portion is masked and if you have these portion exposed and if this is the ion that is coming from anode to cathode, because this silicon wafer is sitting on the cathode.


So, plus ion is coming, it is attracted towards the cathode, so this is coming down; and then it is chipping away silicon, but chipping away and when it is reflected because of the path way taken by the reflected ions, because of the path way taken by the reflected ions, the method is inherently anisotropic. So, it does not depend on whether you have items packed in 1 1 1 plane or not. If you bring in some other material, which does not follow a crystal line structure or does not or is not packed in 1 1 1 plane, still you see this anisotropic that is what I want to point out. However, one negative aspect of this physical etching selectivity about of the portion of substrate to be etched is poor.

You need precisely, this is the place where I want to etch, I need a précised groove formed at that place and this is this physical etching process is less selective. Etching rate is 0.6 micrometer hour to 18 micrometer per hour for most materials. So, etching rate can be, etching rate will vary you must understand, etching rate would be a function of how ballistic the ions are, what are the conditions prevailing. So, etching rate typically changes from 0.6 micrometer per hour to 18 micrometer per hour. And these etching rate defines, how long you have to keep this silicon wafer in this chamber; if you want to create a channel of certain depth.

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Chemical etching

- Chemical species (neutral) migrate towards the target by diffusion.
- Chemical reaction occurs on the surface of the target.
 2XeF_2 (sublimated) + Si \rightarrow 2 Xe + SiF₄ (volatile)
- Both the products desorb and diffuse back.
- Chemical species not accelerated by application of voltage.



The next technique that I have here goes by the name chemical etching. Physical etching is where the ions are bombarded and ions are physically chipping away the silicon from the surface. In chemical etching, a chemical species which is neutral species that migrates, chemical species migrate towards a target by diffusion. That means, this was if this was example of physical etching, I have a similar situation the silicon wafer a portion of it is masked and the other portion is open for exposure. Now, I am exposing this to a chemical etching process. So, here we have a neutral species, it is not a charged ion.

So, you have to mind one thing in chemical etching process, you do not have any anode or cathode, you do not have any voltage applied it is just a neutral species. What is the example of neutral species? I have gives it in the second point the reaction here. Chemical reaction occurs on the surface of the target, here you have XeF₂. XeF₂ is sublimated; sublimated means it was in solid phase and it was brought from solid phase to gaseous phase inside the chamber. So, XeF₂ in gaseous phase diffuses. So, colored sphere that I have here this dark colored sphere, this is XeF₂ in sublimated state. Sublimated means XeF₂, a solid XeF₂ was somewhere there nearby and that XeF₂ has been sublimated; that it has taken from solid phase to the gas phase. And one gas molecule XeF₂ is just its floating around it; it has a high diffusibility, you know gas molecules can diffuse easily.

So, it is getting in contact to the exposed surface that is what we have, this XeF₂ reacts with silicon, silicon in silicon wafer. This XeF₂ reacts with silicon to form Xe and SiF₄; and

these Xe and SiF₄ is SiF₄ is volatile. So, SiF₄ is volatile what does that mean, product is SiF₄. So, Si is eaten away, Si is taken away. So, silicon is taken away from the surface of the silicon wafer and it is making a product, which is not a solid; so, which is not sitting on the silicon wafer rather it's volatile, so it is going out. So, what you have here is a volatile product goes out. So here this ion this is not a ballistic ion, I mean this process does not involve any ions which are bombarding the surface.

So, how is this XeF₂ how it is coming in contact? Suppose, I have etched some portion; now, how is suppose I have formed cavity already, but I am making it more deep. So, how is this XeF₂ getting into that cavity for further etching, it is by diffusion only. A gas molecule diffuses; you know what a diffusion process is? I mean it is a very simple process, you do not need to energize or anything; of course, molecule has its own energy, but it is like you have created a smell here and somebody of that there in the corner of that room, he can smell it, is that that form of diffusion we are talking about.


So that diffusion should be uniform in all direction. These molecule will come in contact with silicon in all direction uniformly. So, what you expect is an isotropic etching happening, because it is governed the axis of this, the movement of this XeF₂ molecule to into the inside the group is purely controlled by diffusion. And diffusion should be isotropic in all direction; it does not have any preference. It is not that this is bombarded and then, it is reflecting and it is the angle of inclination what matters, it is not that way. It is simply, it is diffusing in a very gentle mode and then it is going and accessing the silicon mode surface, having the reaction; and once the reaction is done, the product itself is volatile, so product leaves the surface.

So, this is what is chemical etching. So, both the products dissolve and diffuse back. Both the products that means, Xe and SiF₄ both of them desorbed, they do not adsorb to the surface; they desorb and diffuse back to the bulk, so they go back to the, they go back to the bulk. So, you form an isotropic etching from this process. Chemical species not accelerated by application of voltage. So, if somebody asks you, what is the difference between physical etching and a chemical etching, now you know that.

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Chemical etching ... contd.

- Volatile products are not reflected.
- Movement is diffusive, and not ballistic.
- Mostly isotropic etching.
- Etching rate $\approx \mu\text{m}/\text{min}$.
- Etched surface is rough.
- Pressure is maintained at 0.1 Torr to 1 Torr.




The other points that need to be noted here is volatile products here are not reflected, I pointed out this it is not like ions, which has an angle of inclination and reflection. Movement is diffusive and not ballistic, so mostly isotropic etching will result. Etching rate is micrometer per minute. However, the etched surface is rough that is the people who are practicing it, that is what they said. Pressure is maintained at 0.1 torr to 1 torr. You may ask me why it should be why the pressure is still low. If you have a low pressure, you can have probably a higher mean free path of molecules and which you are trying to utilize here, because the molecule has to penetrate into the groove. So, probably something of that is happening there. It is pressure is maintained at 0.1 torr to 1 torr. Of course, the level of vacuum is not that much as it was in physical etching.

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**Physicochemical dry etching
(Reactive ion etching: RIE)**

- Combined effect of physical and chemical etching.
- Commonly used in microfabrication.
- Target is placed on the cathode.
- Cold plasma breaks down CF_4 to $\text{CF}_3^+ + \text{F}^-$ and makes the ion ballistic at low pressure.
- Anisotropic; Etch rate 10 times that of physical etching.
- Good in etching SiO_2 (wet etching of SiO_2 takes time) from the surface of Si wafer.



Physico-chemical dry etching, now I at the very outside I pointed out that there are four types of dry etching possible. Here we are not talking about dry etching, and not wet etching, which we discussed before, putting the silicon wafer in a liquid. And the etching takes place in the liquid phase that was wet etching, this is dry etching. And in under dry etching, we have four categories physical etching, which goes by other names as well and probably the other names are more common, you might have heard of I have gone for, I mean this material has undergone ion mill, etcetera. So, we have discussed already the physical etching and chemical etching, the first two categories.

When we come to the third category, physico-chemical etching or physico-chemical etching with inhibitor, you want to get the benefit of both. Physical etching process as well as chemical etching process, so that is what is referred as physico-chemical etching, take the benefit of both the processes. This physico-chemical dry etching that also goes by the name reactive ion etching RIE; this is combined effect of physical and chemical etching. So, what that means? These means that you have as before, you have a masked portion, and you have a portion of the wafer, which is exposed which is open for exposure. Here you have a neutral species as it is in chemical etching and also you have a ion, as it is in physical etching and both are doing the etching.

Both are doing the etching and incidentally, I mean I can tell you how the shape would look like, I mean it will be interesting, because one isotropic and another is anisotropic. What I find is that the shape would be something like this. So, this is what you have. You have both volatile products coming out; so it is it will not be entirely depending on physical etching. So, the reflection of ion would be less, but still it is not isotropic. It is basically you are merging the two schemes. So, you can expect it would be half between the two and that is probably what has happened here, so that I how the shape would look like.

And this shape by the way is not anisotropic one, this is what is isotropic etching, this is still anisotropic, but it is not forming a surface of acid, forming a slanted surface. So, here this is a, this reactive ion etching is commonly used in micro fabrication, it is a more common method, this reactive ion etching than other techniques. It is a combined effect of physical and chemical etching. Here the target is placed on the cathode, we already discussed how the physical etching was taking place? You remember that you have an anode, you have a cathode, and you have the silicon wafer sitting in the cathode. So here also the same thing is happening, you have because you will have this gas, you will have target place on the cathode, cold plasma breaks down CF_4 to CF_3 plus F^- and makes the ion ballistic at low pressure.

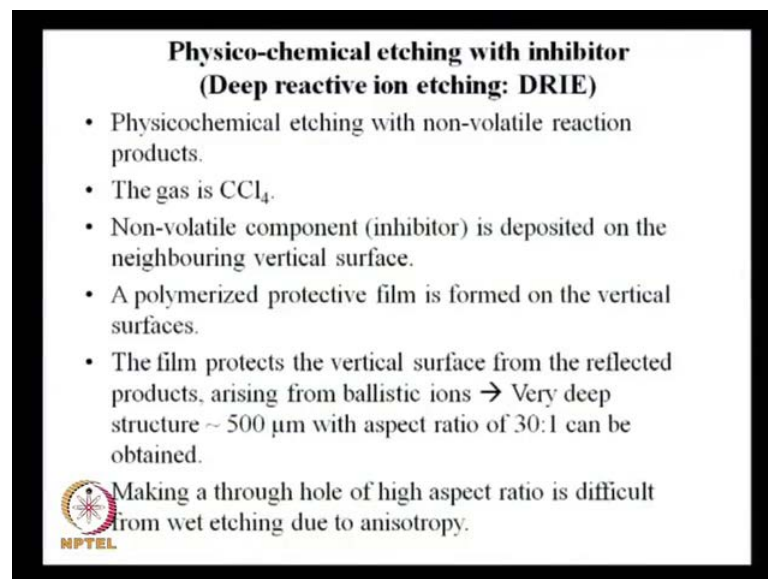
So, this is having an etch rate 10 times that of physical etching. So, these etching process here, the etching rate is 10 times that of physical etching. And good in etching silicon dioxide, wet etching of silicon dioxide takes time from the surface of silicon wafer. This so what is essentially the last two points, what they mean is that physico-chemical dry etching is good to etch silicon dioxide. Silicon dioxide, as I said silicon dioxide will form automatically, if you leave a bare silicon in atmosphere, the oxygen is there that oxygen will react and it will form a nanometer scale layer of silicon dioxide, it will form automatically and that has to be etched so. So any etching you start, the moment you start the process, you have to first etch silicon dioxide and then etch silicon.

And etching silicon dioxide is not that it is more difficult than etching silicon. And in some cases, you intentionally give a silicon dioxide cover. On silicon surface, if you heat silicon wafer to say 600, 700 degree centigrade in oxygen in air, automatically you will form a silicon dioxide layer, which is much thicker. And that breaking that silicon dioxide layer would be difficult breaking, that silicon dioxide layer simply by the by wet etching

is difficult. Typically this dry etching process is good to chip away that silicon dioxide layer. And more importantly, this physico-chemical dry etching, since it is ten times faster than physical etching, this method is further, I mean it is preferred to etch silicon dioxide layer.


So, if you have a question in your mind, why do I etch silicon dioxide, because I was working with silicon wafer, you said it is mono crystalline, you have all kinds of things phase centered cubic lattice, etcetera. Why am I getting into silicon dioxide, because this is because silicon dioxide automatically forms, if you leave it in atmosphere and at times you can have silicon dioxide as a mask, it intentionally made on silicon wafer. And you have to etch that silicon dioxide first, you have to remove that layer, then only you can get in contact with the bare silicon. So, etching that layer is this method of physico-chemical dry etching is good.

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**Physico-chemical etching with inhibitor
(Deep reactive ion etching: DRIE)**

- Physicochemical etching with non-volatile reaction products.
- The gas is CCl_4 .
- Non-volatile component (inhibitor) is deposited on the neighbouring vertical surface.
- A polymerized protective film is formed on the vertical surfaces.
- The film protects the vertical surface from the reflected products, arising from ballistic ions → Very deep structure ~ 500 μm with aspect ratio of 30:1 can be obtained.

 Making a through hole of high aspect ratio is difficult from wet etching due to anisotropy.

The fourth method, as I said it you are taking benefit of both physical etching and chemical etching, on top of that you have another addition to it, which is physico-chemical etching with inhibitor. Inhibitor is a new item here inhibitor. This method also goes by the name deep reactive ion etching DRIE and this is very common, I mean if somebody is making a through hole in a silicon wafer; that means, you have a silicon wafer which has a thickness of 500 micrometer and you want to make a through hole and that hole diameter has to be very small.

So, you are creating a hole which has a very high aspect ratio. That means, what you mean by what I mean by aspect ratio? I have a silicon wafer, this is the wafer, this is the wafer and I want to make a through hole like this, through the wafer. This will not be very easy, if you are going by wet etching, it would be anywhere slanted, so beyond a distance you cannot etch. If you are doing a physical etching, you will end up with anisotropy some kind of anisotropy, because of this bombardment and reflection of ions, so at one point, you will it is not possible. This thickness of a silicon wafer, I said is 500 micron and if this diameter of the hole is less, say we are talking about say 10 micron or 20 micron.

So, you can think of the aspect ratio of this and how will you etch this; so that is an issue here. And this deep reactive ion etching is very popular technique for doing this job. The way it works here is that physico, it is a basically a physico-chemical etching; however, the reaction products, in case of a chemical etching I said, it is the reaction product the product that is formed is volatile. So, it does it dissolves from the surface and diffuses back to the bulk. But there, the product that is formed, I mean so you are tailoring this process such in such a way; so that the product that is formed it is non-volatile, the reaction product is non-volatile.

You can achieve this by choosing the gas, carbon tetra chloride instead of CF_4 , you can you need to use CCl_4 . So, non-volatile component, which we are referring here as inhibitor, is deposited on the neighbouring vertical surface. What does that mean? You have this portion masked and you have this portion is exposed as before the silicon substrate here. And then you are forming, you have introduced one; it is basically physico-chemical etching, so you have a neutral species and you have a ion and both are doing the job. Now, the product that is formed, it is neither it is the chemical, see the ion what whichever is reflected it will go out.

However this chemical entity that is there the product that is formed, that is not diffusing out rather that is non-volatile product. So, what will happen is that will stick to the surface. So, what you end up with is, you will have a coating forming, this inhibitor will form this will form a coating, this is the layer. A coating would be formed in the vertical wall. A coating will be formed; this coating is made of product of this chemical etching process. In a chemical etching process, the product is volatile, so it can diffuse back to the surface. Here the product is not volatile, so it will deposited next door.


So, next door is basically the vertical surface. Because this product is trying to raise up, but since it is not volatile, it has to stay there itself. So, what you end up with is a polymerized protective film, formed on the vertical surfaces. So, it your choice of the chemical that you have, which is making this protective film. So, I repeat once again physico-chemical etching with non-volatile reaction products, the gas here is CCl_4 . Non-volatile component, which is referred as inhibitor is deposited on the neighbouring vertical surface, a polymerized protective film is formed on the vertical surface. Now, this film protects the vertical surface from the reflected products.

So, ions are reflected back and on the way, it is it creates the anisotropy that is how physical etching was happening. Here this protective cover will ensure that no more chipping takes place from the vertical surface. So the film protects the vertical surface from the reflected products, arising from ballistic ion, because you had ballistic ions as well as chemical species, both present there. So therefore, very deep structure of the order of 500 micrometer with aspect ratio of thirty is to one. Thirty is to one means, one is a diameter of that hole and thirty is a depth of that hole, that kind of aspect ratio is achievable. So, this DRIE method is truly very popular method, if some wants to make a through hole in a silicon wafer, many occasions that is required and through hole with aspect ratio. So, 500 micrometer means, it is palpable 500 micrometer I can see on a ruler, but as I said 10 micrometer, the aspect ratio creating that aspect ratio this method is very popular. And making a through hole of high aspect ratio is difficult from wet etching due to anisotropy, this you already have appreciated.

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Deposition on silicon and glass

- Deposition is required to form electrode, catalyst, thermal or electrical insulation, adsorbent, optical elements on the wall of the channel.
- Physical vapor deposition
Certain species from the holding gas is adsorbed on the surface of the target. Two types are thermal evaporation and sputtering.
- Chemical vapor deposition
Certain species from the holding gas reacts with the target forming compounds that are chemically bonded to the target.



So, we have already discussed how to do the etching. We have so you have to, we have a process which goes by the name spin coating, which was used to coat the coat the substrate by photoresist material, then we have a aligner to set a mask on top of that. Then we have a light source and we illuminate, we change, we have chosen the photoresist material, which has certain photo solubility properties and we by that method, we have created an exposed part and an unexposed part; and then we have after we have done that we have gone for the etching process. Etching can be of two types, it could be wet etching or it could be dry etching. And this wet etching and dry etching processes, I have already discussed, I mean you, by now you should get a get an over view of how these systems work.

Now, once you have created the channel; so, what you have done? You on have taken a silicon wafer 500 micrometer thick other dimension is 4 inch, 4 inches; and you taken you have taken that wafer and you have created a channel. You have, you if you somebody wants to get T joint, you can do that. So, you have engraved a channel on that substrate that part is done. Next, what needs to be done? If you are creating a micro fluidic or micro scale structure. On that channel there needs to be a deposition of other material.

And once the deposition is done, probably you have to put a lid on top of this. So, you have to take another wafer and put it as a lid and then bond it; and then you have and

you have to make some external port, you have to put some external ports; so that these bonded the two layers, the sandwich that you form, then that has some connection with external world. So that when you are putting the fluid, putting the sample, it can you can put it; so, you need some connection, some inlet outlet ports in that micro structure device and you are done. So, what you have done? You have taken a silicon wafer, you have created a channel; created one channel, multiple channels, whatever you want.

Now, within that channel you will have catalyses happening, within that channel you have reaction happening, within that channel you will have electrodes, within that channel you will have separation, so everything will happen there inside the channel. Channel can be, will have a circular geometry that is that depends on how you designed your mask and how you transferred the pattern. Once you have done the channel, then the other thing that you need to do is you may have to do deposit some other material inside the channel that is the possibility. And then at the end of it, you have to put another take another wafer and put it on top and then bond it, so that this whole system becomes water tight.

You put a sample and the sample should not leak from the side, so you have to make truly strong water tight structure and then you make inlet outlet ports. So that the structure can interact with external world and then you are ready; that is what you microstructure device is. So once we are done with this, so we can say that this is my, this is the microstructure device I have and it will start you can start the play with that instrument. So, we have already talked about how to make the channel, now we are getting into this deposition on silicon and glass. Deposition is required to form electrode, catalyst, thermal or electrical insulation, adsorbent, optical elements on the wall of the channel; so, for these reasons you need to deposit the material inside the channel.

So, deposition could be you are making, you are probably forming an electrode at one end of the channel, not over the entire channel, only one portion after this sample mixes with the reagent and they flow, then they undergo passive mixing, then they undergo some operation; and then they it has to be you may be looking into this electrical field flow fractionation by in where, you are basically putting them in banded in layers using two electrodes. So, electrode has to be placed on the channel, one anode one cathode should be there on the wall of the channel.

So, how will you deposit this material on the channel? There are two ways it is possible; one is one goes by the name physical vapor deposition and other goes by the name chemical vapor deposition. Here, we are talking about deposition, I mean a last, earlier we have talked about physical etching and chemical etching, they are our objective is to etch away, take away the silicon from the substrate, so that you can form a groove. Here, the idea is to deposit another material, on that groove and that deposition is possible by physical method or chemical method. In physical vapor deposition, certain species from the holding gas is adsorbed on the surface of the target **certain species from the holding gas is adsorbed on the surface of the target.**

Two types are thermal evaporation and sputtering; there are two types physical vapor depositions possible, one goes by the name thermal evaporation and the other goes by the name sputtering; I will discuss this in the next class, how what this thermal evaporation is sputtering, what are these? The other deposition method is chemical vapor deposition, this is the short form is CVD and it is again a very popular technique. Here certain species from the holding gas reacts with the target forming compounds that are chemically bonded to the target.

So, you have a chemical reaction happening, you have chemical vapor deposition and when it is done just by a physical adsorption method, it would be physical vapor deposition. You can of course; there is a deposition you can always go for an electrolytic method for deposition. You have already studied what this method is, how to make a electrolytic deposition; you put it in a electrolytic bath in from a liquid form, you can make a deposition. Of course, you may say that it is you can even do a precipitation; you can have that material precipitated on the surface. However, one thing I would like to tell you at the very outside that why people are going through this route, why they are going for deposition from vapor phase, I mean deposition on silicon and glass, but nobody is talking about deposition in the form of precipitation or things like that. Here you are talking about deposition from the vapor phase.

The advantage here is that when you are in vapor phase, the diffusivity of the molecules are or the molecules can access the substrate, can access the surface much easily. So, if a crystalline structure forms, that crystalline structure would be, it would be more

homogenous. But if it is deposition from a liquid phase, then there would be mass transfer limitations coming into play. You know the diffusivity in a liquid phase and diffusivity in a gas phase, they are different; they are their orders of magnitude different. So, there could be mass transfer limitations, just you think about it, I mean what how this, what could be this show this problem would be.

Of course this chemical, in the next class, I will discuss what this physical vapor deposition and chemical vapor deposition are, but this deposition from the liquid phase from a liquid bath is also very popular by the way. However, these vapor phase depositions are a little costly, and it is they have definitely some advantage to offset the cost, that is why the people are, that is why still this methods are also popular that you have to bear in mind. So in the next class, I will discuss this physical vapor deposition and chemical vapor deposition, thank you.