Bio - Microelectromechanical systems

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Module No. # 01

Lecture No. # 38

Hello and welcome back to this 38th lecture on Bio-microelectromechanical systems. Let us quickly preview what we did last time.

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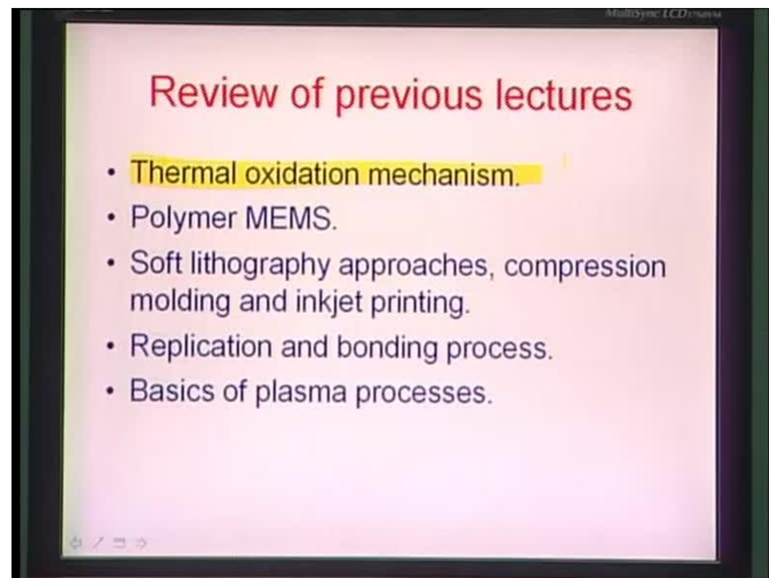

We talked about thermal oxidation mechanisms, particularly Deal Grove kind of modeling systems, where wet and dry oxides could be possible thermally at the expense of consuming silicon from a surface and it is a diffusion driven process. We talked about some polymer MEMS and partly covered different techniques like soft lithography, approaches compression molding, inkjet printing, so on and so forth.

We started with replication and bounding processors and then molding processes. Basically, investigated what kind of wafer bonding schemes are really available for plasma or for polymer related processes or polymer MEMS; we use this very commonly

available technique for surface modification or energy wherein, a surface is actually brought to a high energy, lower energy by exposing it to gas plasmas.

In this context, we were evaluating some of the plasma systems and possessives. We started with a DC glow discharge, talking about how plasma can be formulated, how it can be used towards machining. We found out the mechanisms, where a diatomic gas would actually ionize or excite and create different kind of free radicals, ions, electrons, other species, and so on so forth.

Then, we also found out that we can actually drive in these ions onto substrate, which are kept on the cathodic side or the Crooke's dark space to do fabrication. The serve state nature sometimes being insulating in case of polymers may extinguish the plasma which is otherwise a self-sustaining process. Therefore, we need an RF frequency sometimes to actuate polymer mechanisms. We talked about RF discharges in the way they are made and also discuss briefly about, what is an impedance matching network.

If you may remember, we need to use the maximum power transfer theorem for ensuring that the power which is pumped out of the RF generator is 100 percent coupled to the system. For proper power coupling, it is important that the impedance of the plasma system is same as the impedance of the source resistance or impedance. For the very fact that the plasma system being non-homogeneous material with different dielectric constants.

You never know, how the impedance would vary and therefore, you have to always have some kind of a matching network in series. So that the overall impedance can actually be made equal to the sources resistance, so that you could pump out maximum power from it without getting things reflecting off at the source resistance end.

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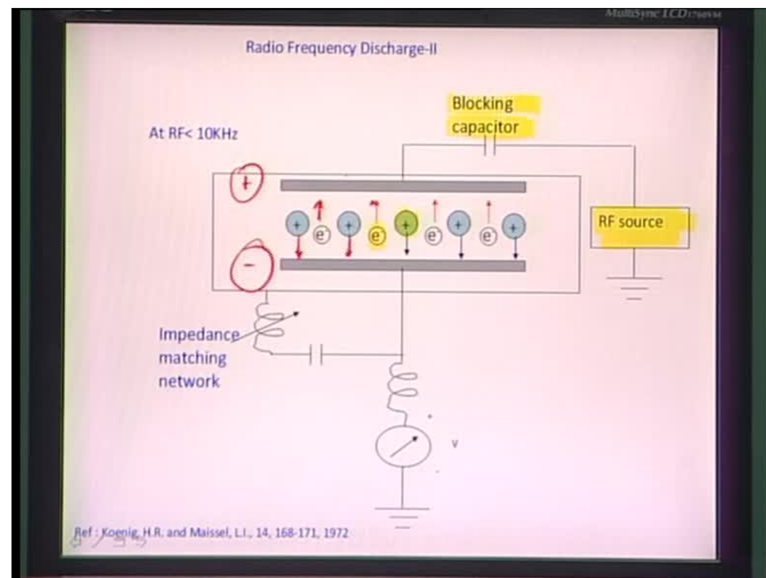

Now, let us look at how this RF plasma is created, generated and sustained. What are the basic differences in this case, than the earlier used DC glow discharges. As I told you before, this blocking capacitor ensures that the RF source 100 percent feeds the voltage supply onto this parallel plate system. Here, you have these ions and electrons as you are seeing as species, which are made within the plasma chamber. Now, if you actually go ahead and produce or couple the RF source onto the plates, there is almost always a change in polarity with RF signals. For half cycles this plate may be positive and this may be negative and for the other half of the cycle, this may be the opposite behavior.

Assuming for the first half cycle, you will have the ions moving downwards and the electrons going upwards, because the anode is up here. The next half cycle exactly this other sequence will be repeated, because now this will be the negative end and this will be positive end. The positive ions would go towards the negative plate and electron opposite. So, really as the frequencies kind of switch, you have the ions and electrons kind of alternating between the two plates as you can see in this particular illustration (Refer Slide Time: 04:15).

One more important factor is that beyond a certain frequency, which is typically about 10 kilo hertz or so, the behaviour of the ions change slightly. Below 10 kilo hertz, it is almost always the ions and electrons move parallel. They go towards the opposite plate and as you change the polarity they would also change the direction of their motion but,

above 10 kilo hertz the field is too fast for the heavily moving ions to follow the field. As a result of which it is only the electrons which go around and ions kind of remain static within the bulk of the plasma. Due to which sometimes the plasma plates in such an RF discharge at above a certain frequency above 10 kilo hertz at a negative charge in comparison to the bulk of the plasma, which is otherwise positive because of the accumulation of the ionic species within the bulk of the plasma.

RF systems typically have Crooke's dark space in both the areas, both the plates. Essentially, the problem of polymers or insulating materials being exposed and the plasma self-sustenance not able to happen is kind of taken care of by mechanisms wherein, the other plate which is not covered by the insulating material is used in an electron generation mechanism, because both the plates are negatively charged with respect to the bulk of the plasma. So that is what radio frequency discharge really is; as you see here, in the frequency range above 10 kilo hertz, only the electrons are the one species, which move and the ions remains stationary.

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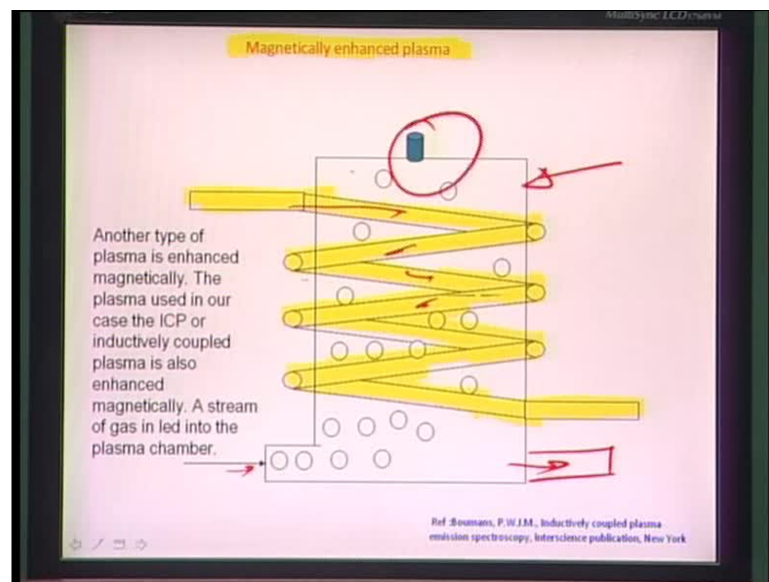

Let us now look into another aspect of how plasma can be created and that is essentially, magnetically enhanced plasma systems. Another mechanism of producing these plasmas particular high density plasma, this is also the magnetically enhanced plasma systems as you can see here. In this particular plasma system and essentially inductively, we also call it inductive coupling of the plasma in this particular behavior. Mostly, this is used

for the bonding mechanisms within two or more wafers were surface energy is used. So, either RF frequencies used or magnetically enhanced plasma systems are used for this kind of bonding mechanisms. We call it inductively coupled plasma and the way this system works is very unique and simple. There is a coil as you are seeing here, which is placed around the chamber containing the gracious species (Refer Slide Time: 07:03). So, this coil is actually the RF coil and it has the radio frequency.

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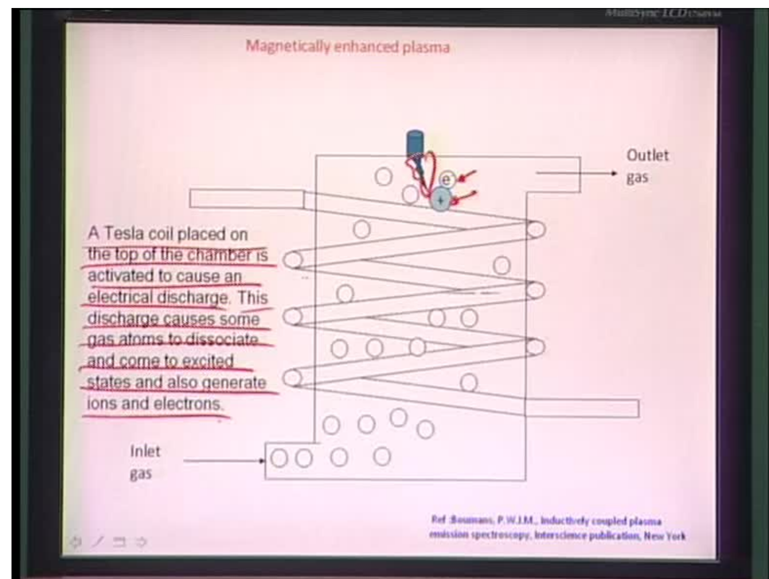

Let us suppose that we have at one point of time a current across this coil which goes in this direction. As if, with using the right handgrip rule, if the coil kind of the current goes in this clock wise sense the magnetic field will be pointing downwards. Then, if the current is reversed back the magnetic field should be pointing towards the direction of the thumb that is upwards.

You have bidirectional magnetic field frequently oscillating in the plasma systems, just by coupling this current across the coil around this plasma chamber here, which has the gaseous species in it. The gaseous species flown in typically and flown out or there is a flow out mechanism let say, in this particular area. You create constant pressure and a constant flow rate of a certain diatomic gas. Essentially, what you do is, you first now create through a testla coil, which is actually placed here, a small spark which excites a few atoms and makes them ions and electrons around the coil area.

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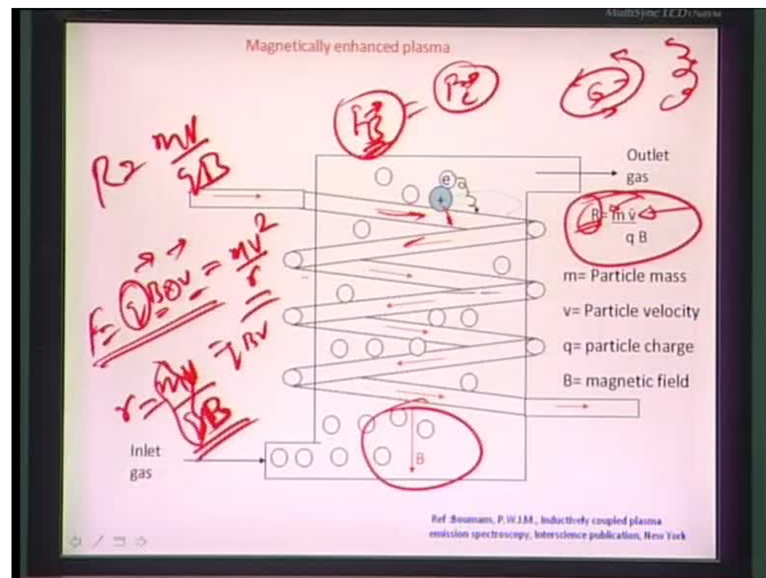

Now, you have highly moving or high velocity ions and electrons, which have suddenly come out of the localized domain, where the tesla coil had given its one firing and essentially are sparking. Therefore, these ions and electrons can be further driven by using Lawrence forces by the magnetic fields which are kind of coupled.

A tesla coil on the top of the chamber is activated to causes an electrical discharge. This discharge causes some gas atoms to dissociate and come to excited states also generate ions and electrons. Finally, these ions and electrons are moved around by means of this coupling magnetic field. As I told you, if the current is in the clockwise sense, the magnetic field is in the downward direction, as you can see here in this particular illustration (Refer Slide Time: 09:19).

This is the magnetic fields direction and this being the direction of the current across therefore, this magnetic field is able to cause both the ions and electrons to experience forces. This forces Lawrence forces, which are also given by F equal q B cross v, where B is basically the magnetic field, v is the velocity of the moving ion and q is the charge on the moving ion or the charge species, which may be an electron.

We can really balance this force as you can see here in a manner, so that you can equate this to the centrifugal forces or the centripetal forces mv square by r of an ionic system. We are talking about situation wherein, we are balancing the magnetic force; the Lawrence force F B with respect to the centrifugal force on charge species. We are

letting them to execute circular motion as you can see of different radii here. So, there are different circular motions that are generated from different species.

Essentially, the R vector here is nothing but mv by qB, this equal to qvB assuming that the v and B are always perpendicular to each other and sign 90 is 1. We can actually make the magnetic field or the way that the tesla fire is the charge into the medium be always perpendicular to the direction of the magnetic field. Essentially, the idea is that the radius of motion that will be generated in that case will be simply mv by qB. So, this is the mass per unit charge and this is the velocity per unit magnetic field.

We can really create this kind of a condition by placing the tesla coil on a magnetic fields value in a manner that you have ions to move along in small radii. Now, I would like to bring to your radius, one important thing that the ions are very heavy in this particular case. Therefore, they would execute larger radii from this particular equation whereas, electrons are not so heavy, they are comparatively much lighter and they would be executing much smaller radii. This makes an ion or a diatomic species dragged along with the ion to collide with multiple electrons as these small circles and big circles intersect.

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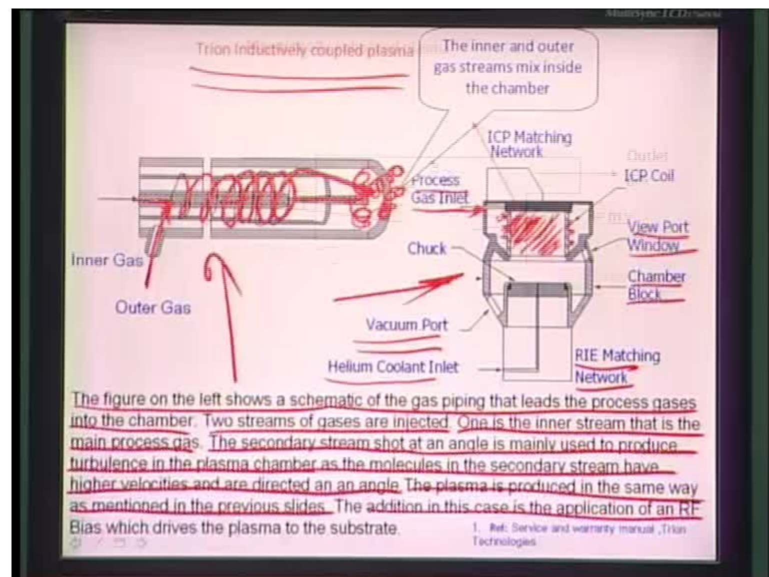

The small circular path of the electron and the big circular path of the big heavier ion intersects and that causes higher and higher density of the plasma systems. You have more electrons, more ionization which is generated and then we can actually keep on

building the energy this way, so that you can have a localized high density plasma system. Inductively coupled plasma really produces a lot of situations, where the density attainable of the gas plasma is probably the highest and that is how these kind of plasma systems operate.

Let us look at into a very practical example, of such inductively coupled plasma system and also known as Trion Inductively coupled plasma system. Trion is an info company it is based in dallas texas. Essentially, they are making these clusters with 5 or more chambers of inductively coupled plasma chambers, whose cross section has been illustrated here (Refer Slide Time: 13:00).

As you can see here, there is this gas chamber which is actually evacuated using set of turbo pumps to a very low active or to a very high vacuum level. Then, there is a gas flow maintains inside at certain flow rate terms of SCCM - Standard Cubic Centimeters per Meter and process inlet gas typically goes from this direction. There is always a catch to how the process inlet can be sent in and I am going to illustrate that little bit.

This is the ICP coil as you can see, this coils are actually placed around the chamber and is used for generating magnetic field. This is the viewport window through which you can see whether the plasma has been created, the chamber block which is used which is perforated. There is cooling mechanism which would give continuous cooling to the metal of this particular plasma and then there is a vacuum port here and helium coolant inlet, which actually tries to go and take off the heat from the metal.

Plasma again is a high radiation intensive process and metal containers may get heated up with that radiation, so you need active cooling effectively. Essentially, there is RI matching network some were the bottom here, we should be able to give maximum power transfer from the RF generator onto the plasma system, once the plasma system has been created using magnetically enhanced plasma mechanisms.

In this case, the plasma I would like to recall, the plasma is created using coupling magnetic fields but the plasma can be driven using RF. Therefore, this can be also effectively used as exposing insulating surfaces, which is normally done by using an RF bias to such systems. One problem here though which is very important is the fact that you have to somehow intuited velocity in the flowing ions or species, so that the term B

cross v really gets effective. There is a finite amount of force which is generated because of that.

In order to do that you create two capillaries of a streams of air: One stream as you seeing is going in this direction, there is an outer gas, which kind of revolves here throughout the chamber and goes into this main chamber. Then, there is an inner gas which goes from the inlet stream and then they makes and creates a lot of turbulence in this particular zone, which causes the mixture of inner and outer gases and to generate even a denser plasma.

So, as v is more at the turbulence factor is more, local turbulence is more and there is always a tendency of more and more collisions between the ions and the electrons based on theories formulated earlier. This flow rates can be controlled in a manner, so that the inlet process gas results in some kind of a density of states of the plasma system.

The figure on the left here shows a schematic of the gas piping that leads the process gases into the chamber. Two streams of gases are injected. One is the inner stream that is in a main process gas and then there is a secondary stream shorted in angle; it is mainly used to produce turbulence in the plasma chamber as the molecules in the secondary stream have higher velocities and are directed an angle (Refer Slide Time: 16:00).

The plasma is produced in the same way as mentioned in the previous slides and much denser system can be produced by changing the velocities of the secondary and the primary streams and mixing and matching is applicable. The addition in this case is the application of an RF bias, which actually typically drives the plasma to go work on the substrate as you can imagine in this particular case.

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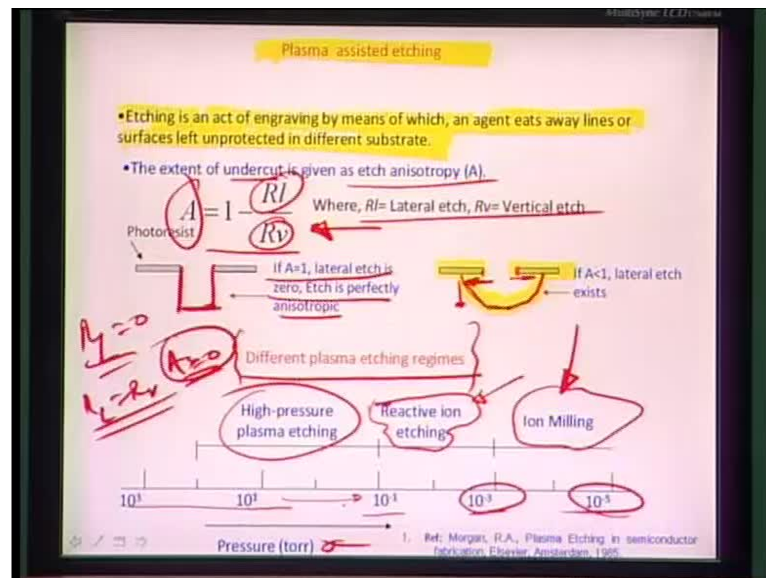

Having said that let us see what plasma processes can really do. Basically, one of the purposes of plasma is to etch surfaces and essentially, if you look at the definition of etching it is really as have been illustrating before, it is an act of engraving in which, an agent eats away lines or surfaces left unprotected in different substrates. Here, also just analogous to what happens of the wet etching case there is an undercut problem.

If you have a masking layer like this as you seeing here, there is a tendency of the whole profile to kind of eat away into the masking layer as you can say in both this directions. Therefore, the overall opening size is more than the opening provided by the mask, so that is actually undercut. The extent of undercut is again given by this formulation here and essentially, it is known as the mathematical terms etch anisotropy (Refer Slide Time: 17:23).

The anisotropy of etch is essentially 1 minus the lateral etch divided by the vertical etch R l by R v. If A is 1 it means that R l and R v, R l is the lateral etch is 0, so the channel is perfectly straight face, which happens normally in dry another mechanisms. If the lateral etches equal to the vertical etch the anisotropy is 0, which means that is a perfectly isotropic etch.

Therefore, the lateral etch rate is pretty much similar to what the vertical etch rate is, you end up in to getting some kind of a hemisphere of etching. Based on the different pressures where the gas plasma is formulated in, you can divide into different etching

regimes, one where if the pressure is too high and mean free path is too low. You call this just the surface based high pressure plasma etching, which causes a surface place modification the chemical modification of a small atomic layer on the surface. You go a little bit lower on the pressure let us say, from 10 to the power 3 to 10 to the power 1 torr all the way to about 10 to the power minus 1 torr 10 to the power minus 3 torr.

In this particular pressure regime, again you have another technique reactive ion etching which I have described in details before during micro fabrication processes. Here, there is a removal mechanism and also there is a chemical change both followed, so it is a physicochemical process of etching. If you go further down on the pressure to as low as about 10 to the power minus 3 to minus 5 torr, you get what you call ion meaning is simply ablation of material mechanical removal, wherein the plasma has a high enough impact to cause the material to get the graded or a blatted of the surface that is called the ion milling. You have three different regimes of plasma etching based on what are the operating pressures that somebody would have.

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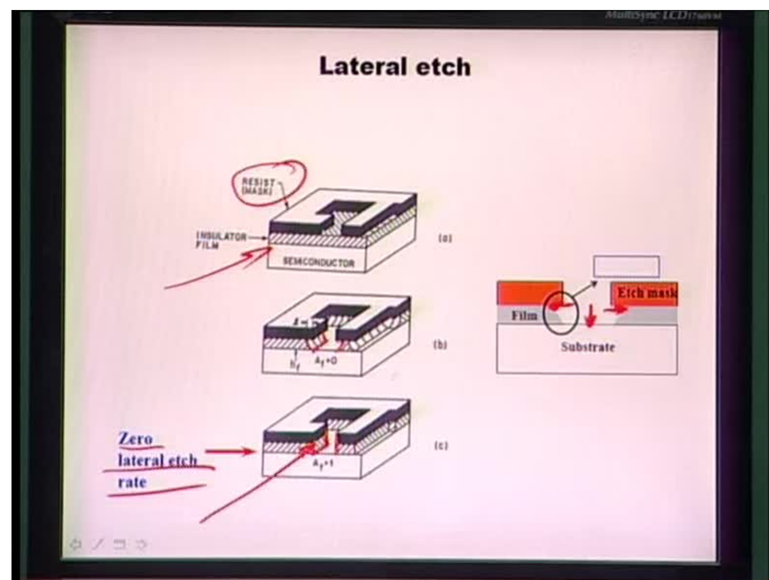

The lateral etch again is the amount of etch in the lateral direction, so here for instance this is the vertical direction of the etching and this is the lateral direction of the etching in both directions. Essentially, 0 lateral etches something which can be represented by this kind of trench you can see the mask and the layer below it are more or less same. If you have a positive lateral etch, you have almost an undercut below the masking or the

sacrificial layer. You start with this which is by depositing some kind of resist mask or sacrificial layer on the top here (Refer Slide Time: 20:17).

If you want to avoid this problem you can actually use low pressure plasma regime wherein, the ions have sufficient momentum and direction to cause vertical etches; vertical structures etch through the photo resist mask is thus causing 0 lateral etch rate.

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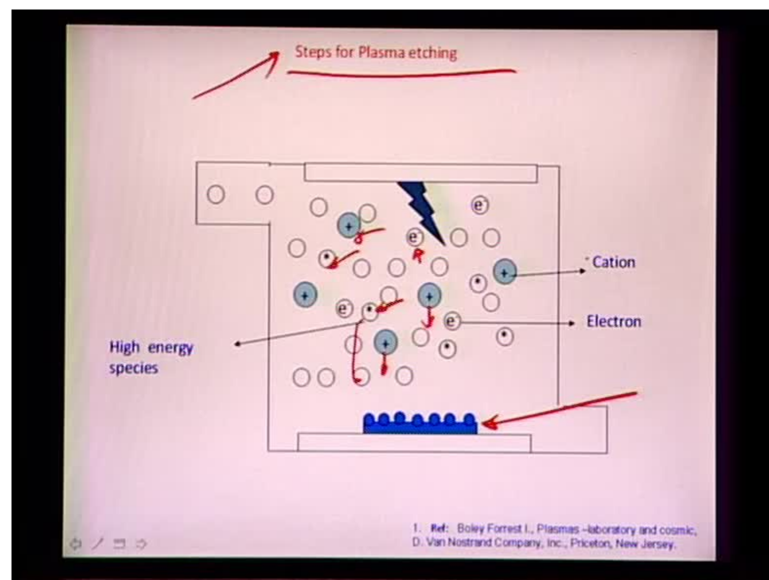

Let us look into another aspect of plasma etching and how we can have different steps or different face of this whole etching process. So really, it is all about generation of positive ions or electrons or free radicals, which are represented by this high energy state here of materials that a plasma system really comprises of.

Now, we will basically keep the substrate somewhere here and put a site bias voltage also, that this ions hit the substrate with certain momentum and also the free radicals go towards the particular substrate. The way it would happen is that one of the free radicals finally, goes all the way down from this chamber atmosphere sits on over the surface atoms let us say, these dots here are the surface atoms. The free radical rolls and tries to find out an atom where it can really form some kind of a chemical bond with; so the free radical is a high energy species it looks for its partner, which is essentially a dangling bond on the surface which may have been left over because of some other ionic impact, which has been a preceding process from this process of free radical movement on the surface.

You get a conjugate or create a conjugate there is a chemical reaction which happens between the two and this is one integral species now and this can be taken away easily into the atmosphere and can be pumped out of the system (Refer Slide Time: 22:34). The way that you remove surface atoms really is based on four process steps, so a five process steps rather, you generate the free radical within the plasma of the free radical observes onto the surface number two.

Number three is the free radical rolls over the surface to find out dangling bonds or sites are active sites, where it can form some kind of a coupling or a reaction once the site is approached a number five. In step number four it forms chemical reaction, so the free radical actually develop some kind of compound species with the metal atom of the surface thus reducing it or thus removing it from its interstitial site. In the fifth step, it gets carried away into the atmosphere as a gaseous species, which is now sent out of the vacuum chamber from the outlet side.

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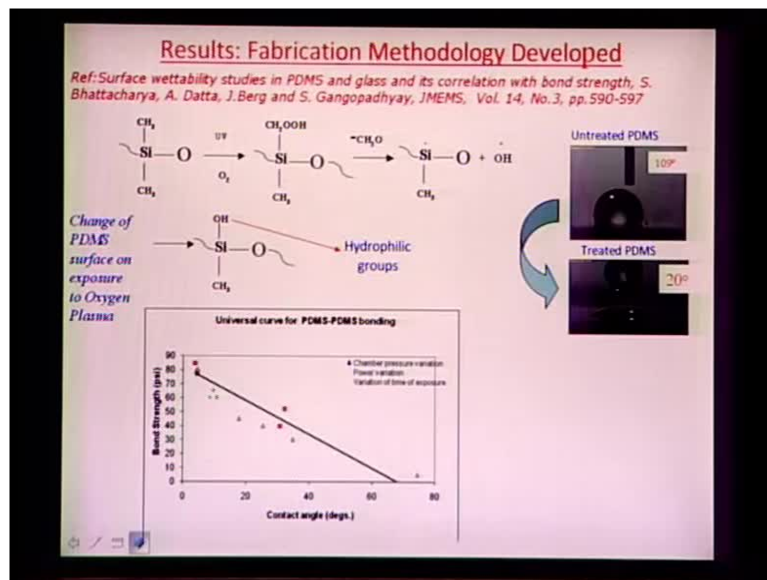

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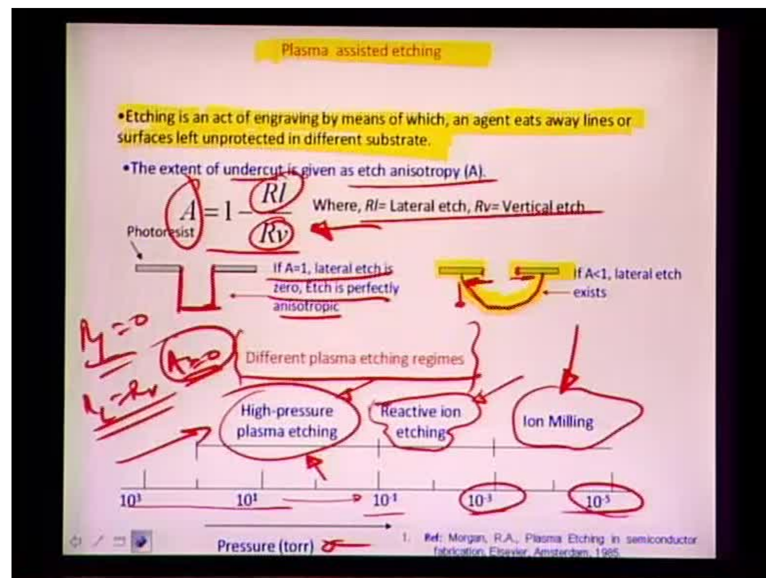

Thus you can have atoms of the surface etched of using this chemical reaction of the free radical and it can be used for a substantial material removal. We could mask the layer to prevent erosion over the entire surface and to direct their erosion only on specific areas of the surface and thus you can develop features and structures using this particular methodology. Having said that let us look at some of the results and discuss, what really happens in case of the high pressure etching regime.

As you know, we had started this topic or started the discussion primarily because we wanted to bond between two surfaces, which were essentially polymers in nature. As we said that we use a clean bonding protocol using oxygen plasma. Some other process where some high energy species changes the energy of the polymer from low state to a higher energy state, it becomes more hydrophilic in nature.

As a result of which develops some silanol kind of linkages which can condense to each other to formulate a Si O Si bond and water molecule comes out. This technique is really some kind of a surface chemical modification and as pointed out here in the different pressure regimes, it happens towards the high pressure plasma etching regime, because the idea is to be able to just etch away a small portion of the surface chemically removing the backbone really intact that is the whole purpose.

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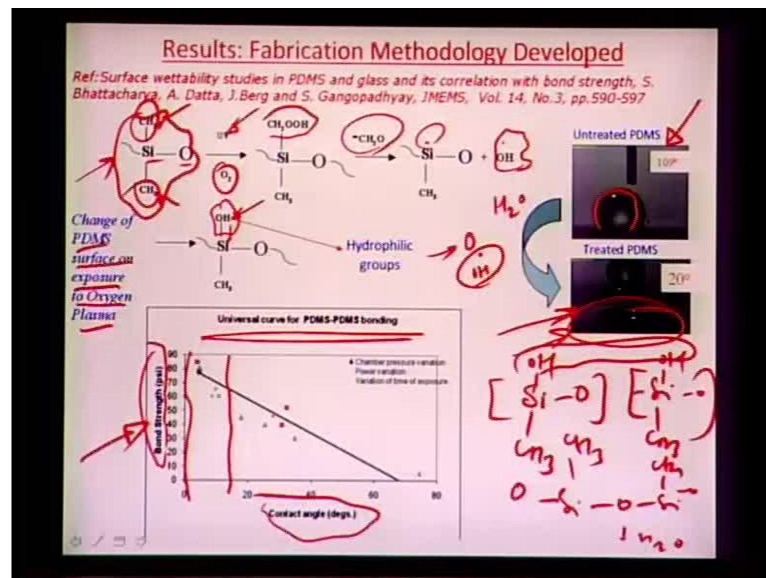

What really happens in terms of removal? Let us talk about this model system of PDMS polydimethylsiloxane, which is used in most of the cases for application in molding techniques. Then later on plasma bonding, a clean bonding is use for forming multiple layers of stacks and close chambers and features. This is essentially the PDMS species with a double metal group as you can see here on the Si O bond (Refer Slide Time: 25:26).

So, use UV excitation and oxygen plasma and create a CH 2 OOH group on the surface here, you actually take of the CH 2 O group of the surface and it reduces into some kind of a free radical species is a dangling bond of silicon, which is left over. There is a lot of OH within the plasma you have oxygen species; let say you have created an oxygen plasma and we are trying to expose the surface of oxygen species, oxygen free radicals which would react with water vapour and equilibrate with that to formulate a lot of OH with dangling bonds. This would essentially come and sit on the top therefore, the methylated surface here of the PDMS really changes to a hydroxylated surface as you can see here.

The effect can be very beautifully observed in terms of a change in, what do you call in an advancing contact angle. If you put a droplet of liquid over such a surface which is highly methylated, there is always it bears like a lotus leaf; it almost always beats up the water into a small football kind of a mechanism with a very high contact angle about 108

degrees about 110 degrees close to that. Now, if you have expose this surface to oxygen plasma and you have hydroxylated the surface is going to be a lot polar moieties on the surface and therefore, the effect is almost immediately visible. The water droplet here is now kind of no longer beading, it is trying to wet of spread around on the surface. So, it shows that the surface as gained energy, it has definitely changed or modified chemically.

Therefore, the indication of OH is really made by looking at indication of the concentration of the OH is really made by looking at the contact angle of the surface. Now, my supposition here is that if suppose, let us say, you have two such species which are formulated this hydroxyl moieties over the surface and you bring them in close proximity with each other there is almost a tendency of Si O Si linkage to be formulated and H 2 group being generated. So, this is the way things bond together chemically irreversibly.

Therefore, if you expose to pieces which are metal rich polymer pieces and then bring it closer to each other, there is a tendency of an irreversible silanol Si O Si kind of linkage to be developed. Now, assuming that is true the bond strength really then would be a function of how many hydroxyl groups are there on the surface. If you have number and higher density of the hydroxyl groups there is almost always a better bondage in terms of sticking to one another at several active sites in comparison to one where the hydroxyls are the concentration is depleted or limited.

Here the idea is that, can I really develop a common scale of reference to certain my plasma treatment or level of plasma treatment, where I can find out or correlate, what would be the best possible plasma parameters used for the maximum bond strength? This is essentially something that our group has reported earlier, where we talk about a universal curve for PDMS or PDMS glass bonding. Here, as you are seeing to measure the bond strengths of several such surfaces after we have exposed them to oxygen plasma and also parallelly measure there contact angle.

We are very amaze to see that the bond strengths falling in a regime less than 10 degree contact angle on the surface of the maximum. So, may be the number of hydroxyl groups on the surface which causes this, what kind of spread around and wet the surface increase very prominently.

Resulting in actually a zone here as you can see, which is a relatively very high bond strength area. So, all it needs is to kind of investigate different plasma parameters experimentally and check the contact angle every time and then alter the parameter in a manner the contact angle can go below 10 degrees or so.

You are mostly asserted that there is a 100 percent bonding mechanism carried on between the two wafer surfaces, if you could actually take it below 10 degrees or so. This is the very interesting observation that one has from such references.

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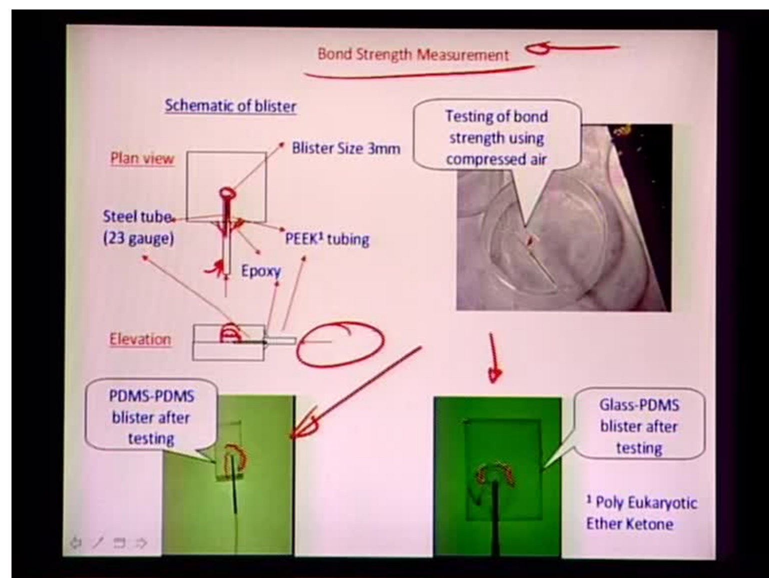

The way the bond strength can be measured and that is actually we did in this experiment on this paper was reported back in 2005 in general of micro electromechanical systems. Here as you see, you have a PDMS blister which is failed because of the pressure, so blister essentially is a small embedded chamber inside the two pieces of bonded PDMS with a supply point, which is covered with this peak tubing a steel gauge, which takes all the air inside this chamber and epoxied at the corner here, so this is a total system. The epoxy used in these cases is a quick setting less than 5 minutes epoxy and it creates sufficient bond strength between the epoxy and the peak on one side and epoxy on the PDMS on the other side, which avoids any kind of failures etcetera.

Then, what we do is we supply compressed air inside at a controlled rate thus manually observing the pressure level. This compressed air goes into this blister and starts expanding the blister till and until we see a separation starting to happen on the edge like

this (Refer Slide Time: 31:13). So, there is a separation which is started to happen. This separation is essentially determined by a microscope and then the moment this suppression starts taking place, reading is noted on the compressed air, the gauge for the compressed air.

A pressure level is found out in terms of p s i, which has caused or initiated the separation to happen. It is a very quick process and this particular p s i level is essentially the internal pressure of the blister, we can calculate what is the pressure on the outside of the blister it is basically by Pascal's law it is distributed and we assume them to be equalized.

The pressure that you read out on the regulator of the compressed air is also the failure pressure for the blister to be disintegrated and the PDMS to be separated from the PDMS; we consider that to be the bond strength. We consider the amount of pressure at which the blister separation takes place to be a function of the bond strength of the material. If you assume that we can find out really that the bond strength is really a function of the several different parameters like time of exposure, plasma pressure, the flow rates so on, so forth and the RI power that is being used.

Typically, we find out that the most favorable systems are also the high pressure low power kind of systems, where there is just a small layer of chemical change, which is made on the surface without really going into the siloxane backbone of the material, they really going into the Si O backbone of the material. Therefore, it is very desirable to operate the plasma system in a manner that you have an extremely high pressure, low mean free path and low power given on. The idea is to just be able to modify that small metal layer and create several dangling bond, so that you have interlayer bonding between the two expose surfaces, once they keep together after this exposure is over.

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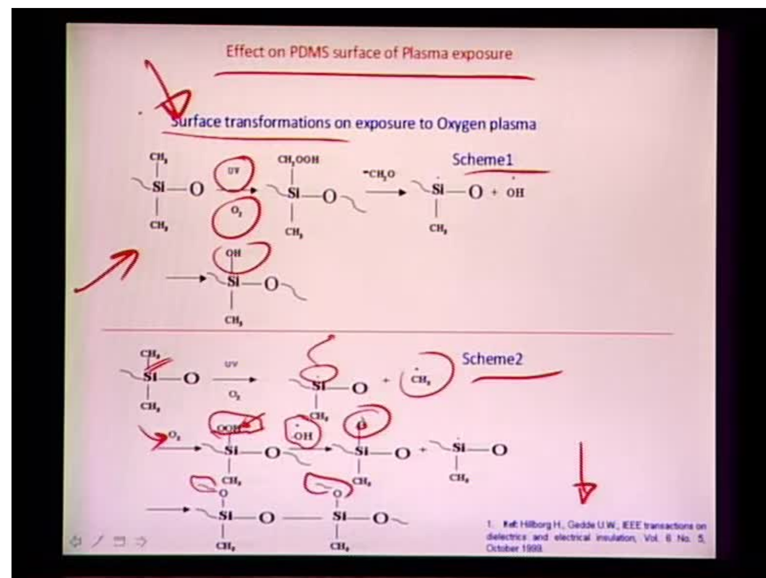

There are several effects that PDMS surface would have on plasma exposure. People have reported this often on in several times, materials or several literature sources is time and again. In one illustration here, in the surface transformation takes place due the UV of the plasma and generating silanol. In other illustration, you can see there is a different scheme of mechanisms which is happening here, you have metal and you have for the metal going out on a dangling bond which is created.

Then, you have again absorption of OOH from the oxygen; hydrogen is picked up from the water vapour of the atmosphere. Then, you have OH free radical going out now and then you have a o free radical species generated in a Si. Finally, you have this O available for any kind of bonded. There are different schemes by which you can illustrate, what kind of surface transformations would take place. This is basically done on real time base is using spectra metric studies inside the plasma chamber on a real time basis.

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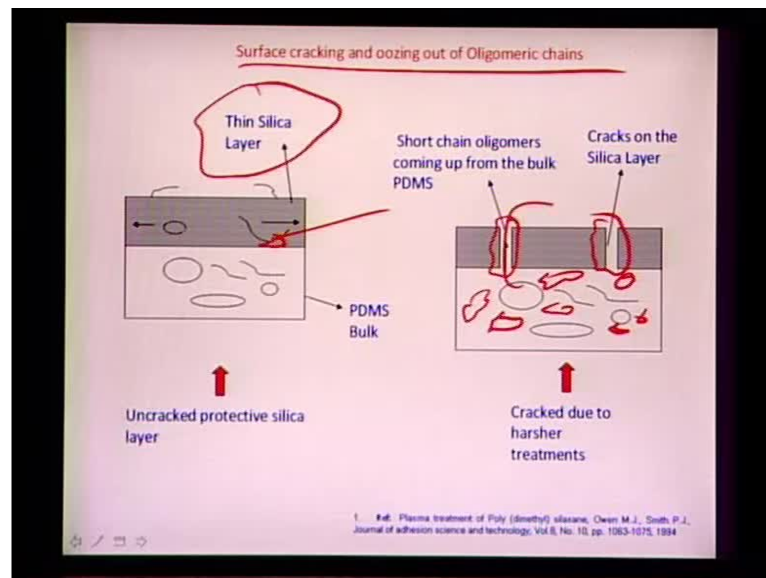

You insert a probe and see, what exactly are the transformations, what are the kind of signals which are given and correlate the bond energies to see what are the intermediate states which are formulated in the plasma as it has been generated and you are working on a striking it onto a surface. What is also a very important for me to tell you is that surfaces of polymers normally crack specially on exposing to this kind of high energy radiations of plasma or ionic gases. It is very natural to assume that the crack because of the kind of ionic momentum delivery that you give onto the surface.

Now, assuming that there is a silicon layer which is formulated by exposure at the first site and this is the thin silicon layer. You have already formulated cracks here (Refer Slide Time: 35:10) and you know that the internal structure of a polymer is highly dynamic and there is always a circulation and movement of oligomeric changes inside the network. It is almost always kind of logical to assume that some oozing out of these chains will take place on the surface.

With time if I live an expose surface, it should again try to get back its hydrophobicity by these materials trying to ooze out continuously from the crack and going and spreading all over the hydroxylated surface and covering another layer of metal on the top of the surface. These are oozing chains, which are actually going out; the polymer structure itself in its depth is very highly dynamic in nature with things floating around.

That is how the polymers are made of, they have extremely high energies in terms of chain flexibility, the elasticity etcetera. If you assume that is the case especially the cracks are more prominent if the plasma treatment is harsher, it means if you have high powered lower pressure side the cracks are more promulgated essentially. So, there would be a severe tendency of surface recovery.

The surface energy which has been had by the exposure would slowly lowered out with time, just because of this oozing out action and covering of the surface from the internal structure from the oozing out of the internal structure of the polymer onto the surface. So, assuming that happens, can we really characterize it? The question is that if you use a contact angle you may be able to find out some explanation.

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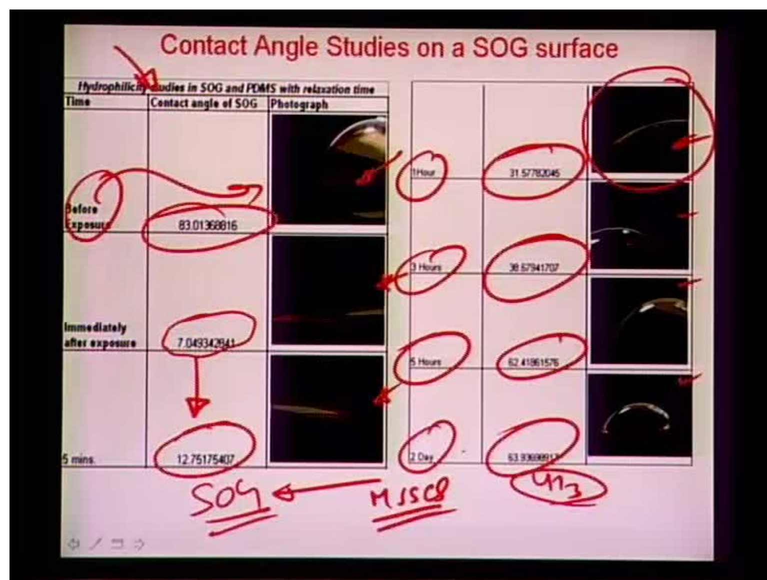

These here points out or indicates studies made on another kind of methylated polymer called spin on glass which is MSS key or methyl silsesquioxane, where there is also a lot of methyl rich surface that we have to consider . This right here is an illustration of what the contact angle really is before the exposure to oxygen plasma; it is about 83 degree celsius. Essentially, you try to find out what is the state of contact angle at each time of post exposure recovery by exposing all these pieces together.

Then, covering the others in vacuum sealed environment and immediately measuring after exposure the contact angle, it comes down to as you see 7.04 degrees. Then, the other sample which was actually expose parallel with this sample and was kept in

vacuum is evaluated after about 5 minutes and the contact angle comes out to be about 12.75.

So, there is a slight increase that means surfaces trying to recover it now changes after 1 hour. This is the third sample, which was actually expose simultaneously with the sample and kept in vacuum. Now, after 1 hour we evaluate the contact angle to be 31.57 and after 3 hours this is 38.67, after 5 hours it is 62 and after 2 days it is about 63, so you are seeing that the surface contact angle has been recovered to almost close to about two third or 66 percent of the initial value of 80, which is amazing actually 75 percent I am sorry of the initial value of 80, which is amazing.

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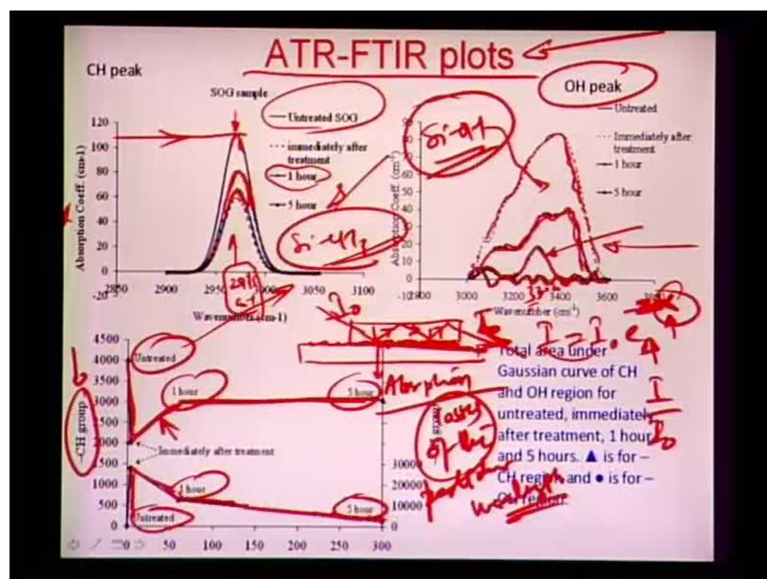

Therefore, there is almost 75 percent recovery of the surface by means of this oozing action of the dynamic chains within the polymeric network which try to just look for this cracks on the surface and ooze out and form a monolayer on the net surface. This can also be illustrated separately and scan on the ATR-FTIR. ATR-FTIR is essentially again nothing but Attenuated Total Reflection Fourier Transform Infrared Spectroscopy. So, this right here indicates some of the plots on the ATR-FTIR as you are seeing here, this is essentially corresponding about 2975 centimeter inverse wave number this is essentially the Si CH 3 bond.

Let me explain how an ATR actually works or an FTR are actually works. Now, FTIR is nothing but, a Fourier Transform Infrared Spectroscopy. What it means it is essentially

that you have an infrared wavelength, which goes into a sample and couples in terms of photon to phonon converge in terms of bond vibration.

The way that this FTIR works is that as I told you, it is essentially a translation of photon to phonon. You are coupling light infrared radiation into a medium on the bonds of the medium are continuously vibrating because of this light coupling action. Essentially, once you basically do this kind of coupling there is absorption of certain energy at a certain frequency or c by lambda that means a certain wave number, 1 by lambda is actually wave number that is how you treat.

Wave number based absorption in certain wave numbers happen, because coupling of light to certain bonds, which have certain vibration frequencies. You can characterize the different types of molecular bonds or environments, based on what frequency or what wave number gets coupled to that particular bond.

Here, for instance this is Si CH 3 bond, your coupling light at 29 35 centimeter or 25 75 centimeters inverse wavelength. It is giving out a signature of the species that what kind of bond it is, here it is Si CH 3 bond, it is a signature of Si CH 3 bond which happens at lambda inverse equal to 29 35 centimeter inverse. Here, you are seeing that the untreated SOG is actually having a pretty high absorption coefficient, which is also dependent on the particular wavelength that you are measuring.

These are all done at same wavelengths, because the absorption coefficient changes with wave length. In this case, the maximum absorption coefficient that you can get in comparison to the different wavelengths that are available for finding out this absorption rate. The untreated is at the very top which indicates that the absorption coefficient is the highest and therefore, highest amount of Si CH 3 bonds are present really in this particular point. Immediately after treatment, it falls down to this area here, as you are seeing this is the dotted line. So, this is immediately after treatment it falls down; the absorption coefficient falls down.

Then 1 hour after the recovery is done, again you find out there is a slow increase in the methylation. Here, 1 hour a plot is essentially this plot. From the doted plot to this continues plot here in 1 hour you see there is a slight increase in the methylation peak, for 5 hours again there is a much higher increase in the methylation peak. Slowly this methyl peak is growing with time which is also an indication of what is happening on an

actual scale. So, ATR and I forgot to mention this is basically attenuated total reflection mode (Refer Slide Time: 41:48).

What happens here is that you have a crystal and this crystal is actually close to the surface in questions, so this is a surface you are planning to investigate but this with the crystal. Then, you couple light from outside within the crystal and in a manner that it gets totally internally reflected and comes out like this. You have this light totally internally reflected and you can actually do the reflective index variation accordingly. Now, here essentially whatever light falls on this interface between the film and the crystal is responsible for causing absorption losses of the particular wavelength.

Let me write this down a little clearly, absorption losses of the particular wavelength is almost an immediate effect which comes out. Therefore, this right here is an illustration of that the absorption is increasing, which means that more and more methyl is generating on this interface, which is causing more and more absorption of the light. The outlet frequency here or outlet intensity here is not really equal to the initial intensity, so it is equal to I 0 e to the power of minus z times of the depth of penetration sorry alpha times of minus of z by the (()) slope of absorption this is the depth of penetration; z is the depth of penetration, depth of coupling into this particular medium.

If alpha is investigated it gives an indication or it is basically a direct indication of what is the intensity change. We are calculating I by I 0 ratios, where this is I 0 and this is I essentially. This side here is I, so we are calculating the I by I 0 ratio and trying to find out, what this alpha value is and absorption coefficient is and that you do over different wavelengths because absorption coefficient also is the function of wavelength (Refer Slide Time: 44:07).

ATR-FTIR, we can actually get feeling of how the methyl peak is varying, it is growing certainly, it was initially very high, came down to all time low and then certainly growing. Similarly, if I look at the other end that is Si OH peak formulation and we are looking here at 300 3300 centimeter inverse roughly, which is also a good estimate of the Si OH peak in the FTIR scan. You can find out that immediately after treatment, the untreated sample here has a very low methyl content it is at the bottom here and it does not have it hardly has any symbol. These are all kind of normalized over a particular

wave number values and that is how you actually calculate the absorption coefficient here.

When immediately after the treatment is done, this dotted line becomes the new description of the Si OH, which means that there is the really a growth you see the area under the curve here, it is a real growth in the SI OH the amount of bonds which are available here is very high. About 1 hour again, as you are seeing that slowly the methyl is trying to go on the surface and cover the surface there is a slow decrease in the hydroxylation of the peak because this ATR here actually is giving a surface effect, what is going on in the surface.

The surface shows that there is tendency of decrease of the hydroxylation, which means that has been covered continuously by the oozing out molecules on the diffusion process along the surface. Then, again after about 5 hours it further comes down to an all-time low of the hydroxyl peak. So, hydroxyl peak is continuously coming down, methyl peak is going up and if I actually try to see the area under the curve here.

Here essentially, these are some arbitrary units in which you plotting the CH group on this side and may be the OH group on the other side. So, this curve here really indicates the area under the curve for the different samples like untreated 1 hour and 5 hour and this curve here really relates to the area under the curve of the CH group that is for untreated to 1 hour to 5 hour.

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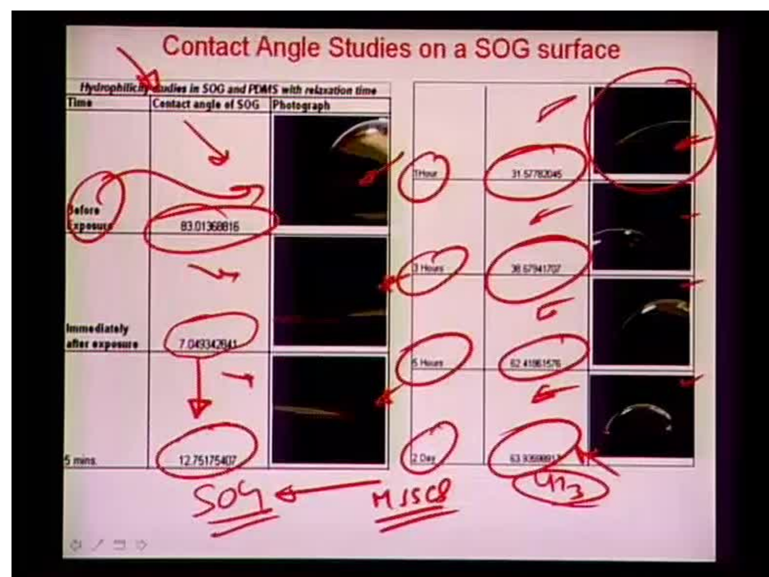

As you see here, the cumulative growth of these areas or the methyl area is an indication of what is the increase in contact angle simultaneously. The cumulative decrease in the hydroxyl peak is also kind of giving ratio of the contact angle. If you may remember the contact angles were earlier illustrated here by these different values. So, the ratio of the areas under the peaks also a clear cut indication of the ratios of the various contact angles with respect to the different time points that has been used for taking this particular data.

This kind is an exactly a very nicely made estimation of what really goes on the polymer surface and it is a wonderful characterization technique, which tells us the basic sciences which is going on is essentially a slow or gradual methylation and simultaneous dehydroxylation in parallel to each other, which makes the surface recover hydrophobicity with time.

Now incidentally, this surfaces can be used for a lot of the biological entities, because biological entities itself would tend to deadhere more to the surface if it is hydrophobic in nature. Of course, there will be non-specific absorption problem, which can be passivated by using some other components like bias etcetera, but such kind of films is excellent, we have seen and studied as I will be demonstrating later in the final lecture of this series. This hydrophobic recovery of the surface is very positive for the miniscule DNA levels also even getting amplified.

Essentially, you need to coat the whole chambers, inner walls or interiors with this kind of a film and expose it to plasma and keep it in an open so it, self recovers. You see that as low as a few nanograms per milliliter or picograms per femtograms per milliliter of DNA solution taken AB initio can also get amplified with PCR or other protocols especially the microchip level just by using this 1 sole coating.

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Differences between various etch regimes

S.N.	High Pressure Etching	Ion Milling	Reactive Ion Etching
1	Mean free path of the species is much less than chamber size	Mean free path is comparable to chamber size because of low pressures	Moderate mean free path of the species.
2	The plasma is used to start and stop chemical reactions	The plasma is used to abrade the substrate by sputtering out material	Processing is primarily chemical transformation of the surface
3	Ion impact energy is low .	Ion impact energy is high	Moderate impact energy
4	The plasma is homogeneous and isotropic	It has a high directionality.	The degree of anisotropy is higher

1. Ref: Spitzer Lyman, Jr., Physics of fully ionized gases, Interscience Publishers, New York, 1962

We will discuss some of these illustrations probably towards the last lecture of this particular series. Now, I would just like to summarize the various differences between the etch regimes that we have talked about, so high pressure etching, ion milling and reactive ion etching of the three different pressure regimes over which this different kind of etching mechanisms happen.

High pressure means mean free path of a much smaller size much lesser than the chamber size. The plasma essentially in this case is used to start and stop chemical reactions. The basic mechanism is by which etching takes place is just chemical, you have low ion impact energy again, because the amount of free distance available for the ions to move in between before the first collision or second collision is very low.

The plasma is homogeneous and isotropic in this particular illustration whereas, ion milling were the mean free path is comparable to the size of the chamber of low pressures and the plasma is used to ablate the substrate by sputtering out the material. So, essentially it is a physical ablation of the material which is happening in ion cleaning.

Ion impact energy is extremely high and it has a high directionality, so you have chance of a cutting very narrow trench; high aspect ratios trench with straight walls in this particular illustration. Reactive and etching is somewhere in between both the ion milling and high pressure etching in terms of pressure ranges, so you have a moderate mean free path of the species. Processing is primarily the transformation of the surface and you

have moderate impact energy of the ions. Degree of an isotropy is definitely higher than the isotropic nature of the high pressure etching, but then is not as high as ion milling, it is somewhere in the center.

This in a nutshell is the various differences for the different etch regimes that happen then we believe it is very important for basic understanding of all plasma processes in the field of MEMS a MEMS device. I would like to go into different regime of MEMS processing call additive techniques.

Here essentially, you are talking about things like chemical vapor deposition to make thin material films on the substrate. You have a gas face and you create a reaction in that gas face and whatever is precipitated is actually captured on the top of a surface. The gas phase can make Si O 2, it can make silicon nitride, it can make silicon carbide and then you can capture these moieties from the gas phase onto the surface in question. That way you can develop thin films and such reactors are also known as CVD or Chemical Vapour Deposition reactors.

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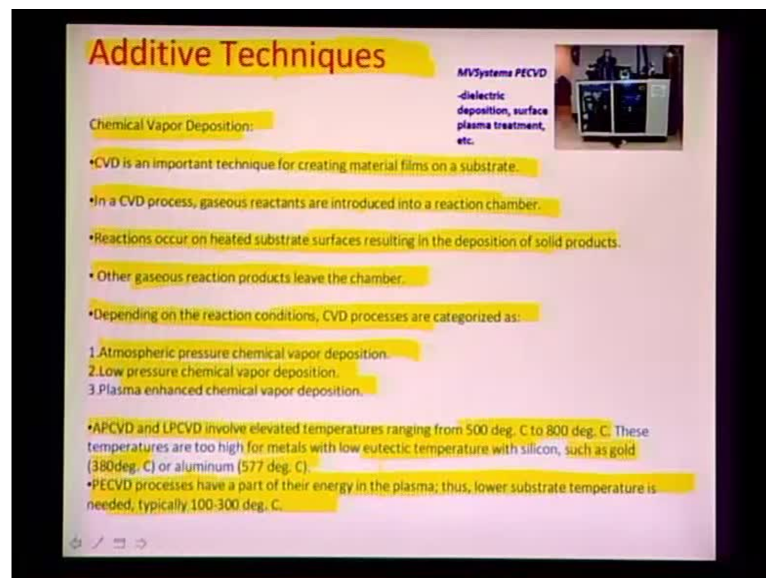

Essentially there is a material created inside reaction, inside the gaseous system and that is captured over the surface in question. It is an important technique for creating material films. In the CVD process the gaseous reactants are introduced into a reaction chamber first.

The reactions occur on heated surface in the deposition of solid products. Other gaseous reaction products leave the chamber typically depending on the reaction conditions. CVD processes now can be really categorized as: atmospheric pressure CVD - APCVD, low pressure CVD - LPCVD and plasma enhanced chemical vapor deposition - PCVD.

Typically, the low and the atmospheric pressure CVD is involve elevated temperatures about the 500 degrees to 800 degrees for the reactions to be used for depositing films on the substrates. By temperature we mean that the substrate, I mean that the substrate is heated to this particular temperature. So that whatever is happening in the gas phase interacts with a vibrating lattice on the top of a silicon substrate and becomes one integral with it and start spalding it. Diffuses through sometimes, the particular silicon species and makes a thick layer of the particular material that you want to deposit.

For metals through sometimes with low eutectic temperatures let us say, gold etcetera, these temperature are pretty high metals would melt as low as 308 degrees specially in thin gold films or aluminum films melt all the way, it may go out to our last up to about 577 degrees, but certainly it cannot take the additional temperature, which is used for LP or APCVD processes.

There is a cold plasma process for that kind of a situation, which is normally used wherein, instead of this high temperature Lattice vibration affects, you use plasma to create ionic momentum. So that you can deliver what is happening in the gas face simultaneously by creating a plasma phase over this whole substrate and let the ionic momentum take care of the embedment of the gaseous product being made onto the surface in question.

It is actually a cold system, where with lower substrate temperatures typically about 100 to 300 degree celsius you can still get thin oxides of nitrate formulated. Now, this is the very interesting and important process because in microelectronics are in MEMS, we almost always need to cover material electrodes of metal electrodes with this insulating layers, because you have to have separation between the different levels of the architecture. You have to provide adequate insulation between the different levels of the architecture. Therefore, one layer of conduits may not be connected to the next layer of conduit which is over it.

So, in order to prevent such steps or processes, you have to use some material or some process wherein, there is no evaporation issue with the metal conduits which are formulated.

If you have a case, where you know at a colder temperature you are able to generate this oxide insulation over the top of this electrode material that is probably the best that microelectronics, micro fabrication could offer to MEMS industry. Therefore, most of the insulating layers on electrodes especially multilevel architecture, whether it is microelectronics or MEMS is done using PCVD methods of Plasma Enhanced Chemical Vapour Deposition Method.

This right here is such a system, it is a PCVD brought from mv systems and it is used for a lot of dielectric deposition, surface plasma treatment and other associated processes to see that chamber in this particular region here. The associated vacuum pumps of the power sources the RF signal sources etcetera, the gases are actually supplied on to the system externally there are special piping, which are meant for evacuating the chamber, so there is a separate vacuum circuitry.

There are piping which are meant for flowing different gases, there are mass flow controllers which can control very accurately how many SCM or Standard Cubic Centimeters per minute of flow is essentially in leaded or put into the chamber or made inlet to the chamber. Also, the whole system has an upper gene mechanism, where you can easily control the vacuum at the time of loading or unloading the substrate wafer of the substrate material. So, this is a very nice additive technique.

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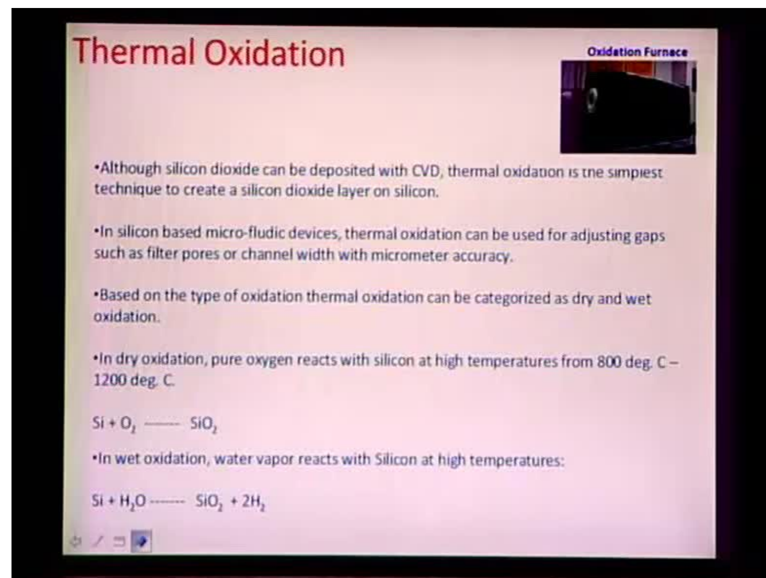

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Thickness of Oxide Layer of Thermal Oxidation

The density of silicon and silicon dioxide are 2,330 Kg/ m³ and 2,200 kg/ m³ , respectively. Molecular masses of silicon and xoygen are 28.09 kg/kmol and 15.99 kg/kmol, respectively. Determine the consumed silicon thickness for a silicon dioxide film of thickness 'd'.

For 1 kmol silicon, one will get 1 kmol silicon dioxide. For the same surface area, the ratio of the thicknesses is equal to the ratio of volume:

$$\frac{d_{Si}}{d_{SiO_2}} = \frac{V_{Si}}{V_{SiO_2}} = \frac{M_{Si}/\rho_{Si}}{M_{SiO_2}/\rho_{SiO_2}} = \frac{28.09/2330}{\frac{(28.09+2\times15.99)}{2200}}$$

$$= 0.44$$

Thus, for growing an oxide film of thickness 'd', a silicon layer of 0.44×d is consumed.

Another important technique I have already mentioned is thermal oxidation, I am not going to go through this. Let us actually do a small example problem for understanding the thermal oxidation process here, as you see the density of silicon and silicon dioxide are 2330 kg per meter cube and 2200 kg per meter cube respectively. Molecular masses of silicon and oxygen about 28.09 kg per kilo mole and 15.99 kg per kilo mole respectively. We want to determine the consumed silicon thickness for the silicon dioxide film of thickness d.

We assume if the oxide thickness is d by elipsometric measurements etcetera, what is a consumed thickness in turn of the silicon? I just want to recall that this thermal oxidation is the diffuse of driven process, where there is a tendency of the oxygen atom to come within the lattice and set and make the oxide layer. We can solve this by saying that a for a 1 kilo mole silicon, 1 will get about 1 kilo mole of silicon dioxide.

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Thermal Oxidation

Oxidation Furnace

•Although silicon dioxide can be deposited with CVD, thermal oxidation is the simplest technique to create a silicon dioxide layer on silicon.

•In silicon based micro-fludic devices, thermal oxidation can be used for adjusting gaps such as filter pores or channel width with micrometer accuracy.

•Based on the type of oxidation thermal oxidation can be categorized as dry and wet oxidation.

•In dry oxidation, pure oxygen reacts with silicon at high temperatures from 800 deg. C – 1200 deg. C.

$Si + O_2$ ------- SiO_2

•In wet oxidation, water vapor reacts with Silicon at high temperatures:

$Si + H_2O$ ------- $SiO_2 + 2H_2$

That is how this reaction works in, so you have a unimolar composition of this reaction 1 mole of silicon reacting with 1 mole of oxygen to produce 1 mole of silicon dioxide. So, if this is a kilo mole the yield will be a kilo mole.

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Now, assuming that to be true and we also assume that we are actually having the same surface area to grow the silicon dioxide as you are having the available surface area for silicon, so the area is same. Essentially, the volume of silicon that can be found out by multiplying the density of silicon therefore, if you compare the densities between the silicon and silicon dioxide it is essentially, so we can say that the densities are mentioned here as 2330 kg per meter cube for silicon and 2200 kg per meter cube for silicon dioxide.

Now, we may assume that the area on which the silicon dioxide is growing is essentially same as the area of which the silicon is consumed, so these areas are same. Assuming that to happen, the thickness of the silicon per unit thickness of silicon dioxide is also same as the volume ratio, because the area are same in both cases they are all same in both cases. The volume of silicon to silicon dioxide really determines the thickness of silicon to silicon dioxide.

Now, I know that this is d, that is what the questions says that you have consumed thickness of silicon which is d. Therefore, you can say that the volume here is nothing but the mass per unit density of silicon and mass per unit density of silicon dioxide. Once we do that, we can find out the mass of silicon dioxide from the values of silicon and oxygen independently which is given here (Refer Slide Time: 59:02).

There are twice oxygen plus silicon, so this many kgs per kilo mole and this divided by the density would give the volume of silicon dioxide similarly, the total amount of mass of silicon is about 28; molecular mass is 28.09 kg per kilo mole. This divided by the density of silicon 2330 kg per meter cube would give the total volume of silicon in this particular case. The volume ratio is same as this ratio here, as you can see which comes out to be about 0.44. Therefore, the total amount of thickness of silicon which is consumed is about 44 percent of the thickness of silicon dioxide which is created.

That is essentially what the question was that how much was the consumed silicon thickness. With this, I would tend to close these areas of micro fabrication. The next lecture will be talking on a very interesting area of how this we can integrate these all techniques together to build real biochips or real systems, thank you.