Advanced Machining Processes
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Week - 10
Lecture – 27
Polymer Processing

Welcome back. So, today we would be talking on this polymer processing with some details of how polymers are fabricated. And this would be followed by again some basics of gas plasmas and how you can use gas plasmas to fabricate microsystems. So, let us do a quick recap of what we did in the last lecture. We talked about various etchants and isotropic or homogeneous etching technique. We mentioned about etch selectivity and selective layers.

We also briefly talked about physical dry etching, chemical dry etching, physicochemical dry etching where use of plasmas would enhance the directionality on an isotropic velocity of the etching process. We also described photolithography, the basic process of mask aligning with the wafer which is coated with the photoresist. And then we described there in different types of lithography like contact, proximity, and projection lithography processes. We discussed about positive and negative tone photoresists and how they would cross bond in one case, in the case of negative and de-bond in the case of positive to basically create features and structures on the surface.

We also described polymer MEMS and then talked about systems like soft lithography, compression molding, inkjet printing so on so forth. And then we had just about started with replication and molding process which we kind of illustrated as the mother process for all these soft lithography techniques. So, we will now start with some other soft lithography techniques which come from the same replication and molding technique. And so, first technique which is of lot of prominence is microcontact printing. Now, here the basic process is somewhat similar to inking or stamping.

So in a stamp typically what happens is that there is a sheet of paper and then you have a stamp pad, and you have a rubber stamp. So, you basically take the stamp and take the ink from the stamp pad and print it on to the surface in question. While printing what happens is that the capillary action of the paper drives the ink from the surface of the stamp on to the paper itself. So, this is the normal stamping process. If I can actually miniaturize this whole activity on to a scale where we are talking only about a few micron by few micron, let us say 10 micron by 10-micron features.

And then instead of ink we have a way to print molecules, then this can also be a very important basis of making diagnostic assays like protein microarrays or DNA arrays. And let us look at this very important technique of microcontact printing which can be used for making or realizing such prints or stamps and stamping process there in. So, the process starts with step A here, where you can see that this is a piece of PDMS which has been replicated and molded. So, with the power of photolithography you can go very very small up to 10 micron into 10-micron size features can be produced in the PDMS. And then this PDMS surface is actually inked up and this ink can be something like a self-assembled monolayer, alkyl thiols, proteins, DNA so on so forth.
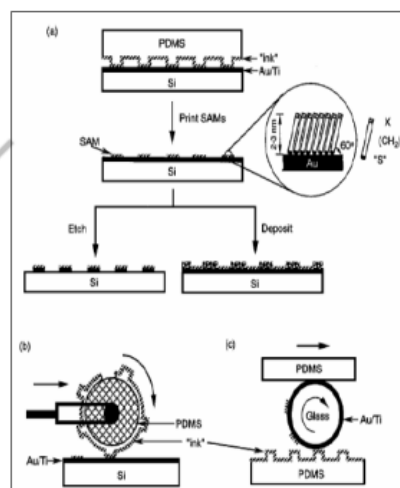
So, whatever molecule you would like to ink on you first ink on the PDMS surface. So, once this is inked up the PDMS surface can be pressed and held against a layer which is actually the layer which is the receiver layer like just like the photo just like the paper in case of stamping example. So, in this particular case let us say you have a gold titanium layer which is the receiving layer. So, there is a transfer layer which is represented by this hatched lines which is actually the layer of the molecules and then there is a receiving layer at the bottom here which is a gold titanium-made layer at the bottom. So, the idea is that the stamp is made in contact with the receiver layer and there is sufficient amount of time you know which is given for the reaction kinetics to happen and the molecules transfer from the PDMS surface onto this gold surface by virtue of adsorption kinetics.

So, if sufficient time can be allowed here the rate of kinetics the rate kinetics driven absorption of the molecules would happen and molecules get subsequently transferred from the PDMS stamp onto this thin layer or thin film. So, you can look at these for example, alkyl thiols self-assembled

monolayers being transferred from the stamp as small heaps or small places the blow-up view of this is here and you can see that these are about close to 2.3 millimeters in height it is an angle of 60 degrees, and you know it is a sort of self-assembled monolayer. So, there is an assembly regular assembly of these structures is stated here. So, therefore, this is a transfer technique of SAMs on to the gold layer.

You could actually again you know selectively etch out on this layer or even deposit on this layer selectively. So, that you have various orientations where in this particular case you may have etch off the gold films at the places where the SAMs are not sticking. So, the SAMs can be made as a etch protective layer here and the remaining portion of the gold film can be exposed to an etchant. The etchant does not affect the gold layer underneath the SAM and wherever the SAM is present it gets protected. So, you have you know steps of gold or heaps of gold protected by the SAMs, and the remaining gold which was exposed earlier taken off.

Simultaneously you can also deposit layers on the top of this and the idea is that the SAMs can be removed later on. So, therefore, whatever you know it is a sacrificial mask of SAMs on the top of this gold layer and the remaining portion you deposit and remove the SAMs later on. So, that you have only selective areas which are coated with the deposit. So, you can use them as various masking strategies and steps for masking at the nanoscale. So, basically, this process has been linearized process, but then many intelligent modifications have been made.

For example, in this particular case, the throughput of a process can be increased by coating the SAMs in a circular cylinder rather than a straight surface and then rotating the cylinder every time. So, that it walks over this wafer containing the gold titanium film and it creeps on creating a big array of these molecules and the molecules can be fed every time it moves through or rotates through the gold titanium layer. Similarly, you can also have another you know transfer of layer of molecule from this PDMS1 here to the PDMS2 surface by means of a suitably rotating glass cylinders which takes up the molecule from this PDMS layer and transfers it to this PDMS layer. So, you can use these intelligent techniques for high throughput patterning of various layers using this microcontact printing. So, typically you know it can be performed on both flat and curved surface as has been illustrated in these examples B and C.

So, that is another very high utility process called micro contact printing which is used for you know it is one of the soft lithography techniques for printing of molecules at a very high resolution. The other process that I would be interested is basically you know another replication and molding technique where you can actually make a hybrid bio device. So, for example, in this particular case you can see there is a PDMS first layer which has been deposited on the top of this silanized silicon mold and then you have a Teflon tubing which has been inserted in covering a certain region of

this particular you know PDMS coated silanized silicon mold. And then there is another layer of PDMS, second layer of PDMS which is actually poured on the top of this layer of Teflon mounted over the lower layer of PDMS first layer. And then when you remove this Teflon tubing out you are left with a cavity which you can suitably filled with PDMS again.

And so, you can have a chamber you know illustrated in this manner. You can also have vertical channels which can be drilled through by using Teflon tubing again suitably and then you can actually have a interconnect between these chambers and channels and these can be very good basis. So, the silicon can also be even patterned and etched selectively. So, it can formulate a hybrid multi-layered bio device where one layer is silicon which is patterned, another layer is PDMS first layer and then second layer, and subsequently many layers which you can you know coat on the top of each other. So, then you can connect the tubing's, and this can be the source of a microfluidic device.

PDMS glass silicon hybrid biochip
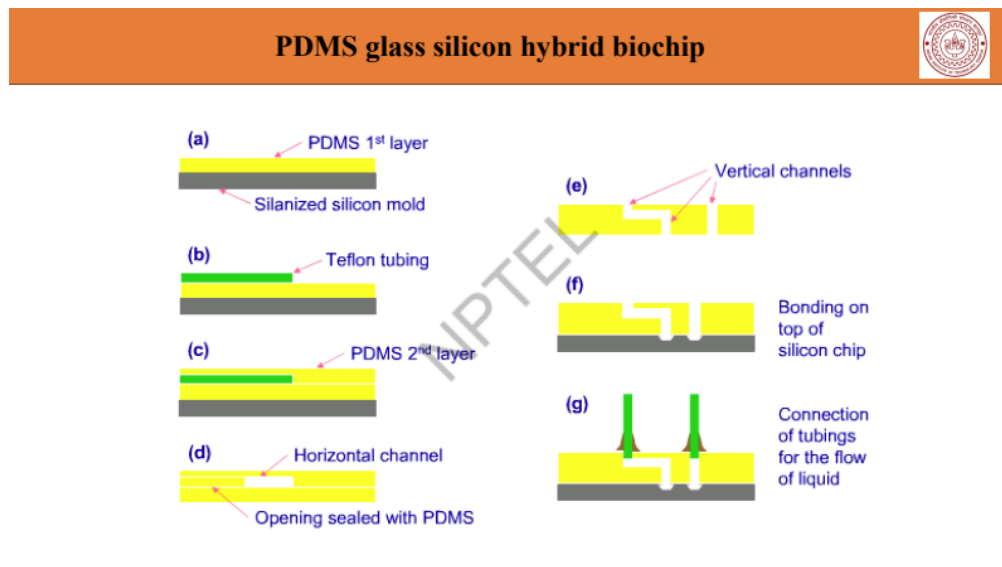
So, again silicon hybrid you know PDMS glass silicon hybrid biochips are very commonplace these days it is done by using again fundamentals of replication process in unison with some other steps. And just like hybrid machining, this is a hybrid processing which would work for you know formulating these microchannels of features onto the surface. There is another very interesting example of what replication can do and typically prior to this as almost everybody knows replication was on a 2 and half d basis you know. So, it is basically on a on just on a flat surface and you had the luxury of printing in the x y plane and all the patterns all things would be in the x y plane. Nobody really thought of what would happen if the replication can be taken from a surface onto the bulk volume of the PDMS.
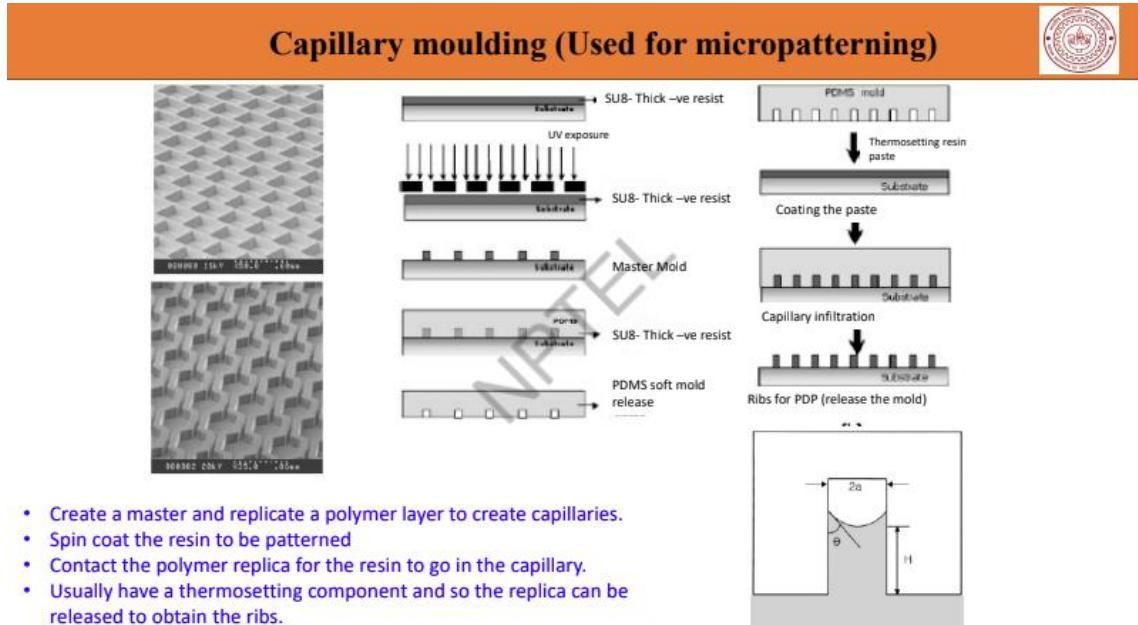
So, there is an illustration of this available in literature where you can make microchannel arrays by etching off materials from the PDMS surface. So, here for example, is a PDMS slab and basically what you are doing here is you are suitably sizing copper wires into different sizes and shapes and these wires are knitted into the plastic into a plastic box which is thereby drilled an array of holes are drilled in this plastic box and the copper wires are kind of knitted as an array a dense array as you can see in this illustration here. And then once these are knitted these are well knitted this these wires are replicated. So, you pour liquid PDMS over these wires and then you know you can actually cure the PDMS. So, that the PDMS forms hard solid rubbery membrane and then you can swell the PDMS matrix.
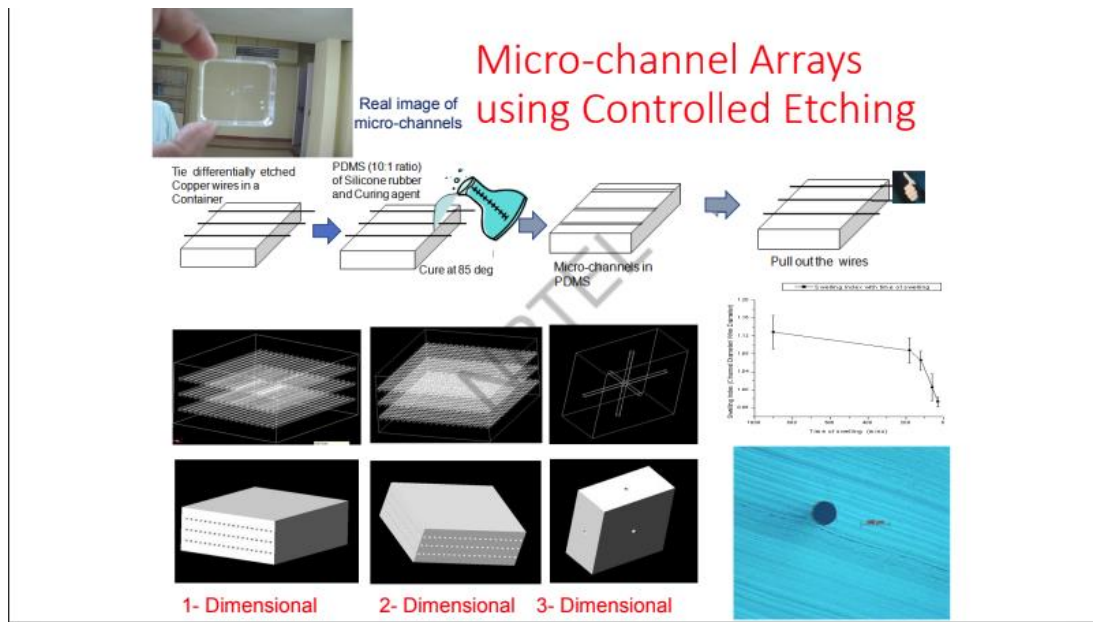
So, that you can individually pull the air the wires out and that results in your microchannels. So, you can have microchannels not only on a surface by using two and half D lithography, but also in the bulk or the volume as you can see in some of these illustrations where you can see how the channels have been created. If you look at this particular figure closely you will see a crisscross channel created within the volume of the block there is one channel in this direction there is another channel in this direction if you look at it very very closely. So, the only issue which comes here is in terms of swelling the PDMS matrix and shrinking it back and so we have seen that while doing it the circularity of such a channel is very well retained and you use a solvent to typically expand this PDMS. And then you know if you evaporated the solvent goes away and it's kind of de-swells back and while de-swelling it kind of maintains the aspect ratio of the structures and features.

So, it is a very important technique for realizing arrays of micro-channels in the bulk volume of the PDMS matrix. So, this is another extension of replication and molding in the third dimension. A very interesting process which is sometimes used for display technologies is capillary molding

used for micropatterning. And here typically the process starts with a thick SU8 negative tone resist coated onto a surface which is UV exposed selectively. So, that you have cross-bonded areas remaining as pillars on to the surface of the wafer.

Capillary moulding (Used for micropatterning)

- Create a master and replicate a polymer layer to create capillaries.
- Spin coat the resin to be patterned
- Contact the polymer replica for the resin to go in the capillary.
- Usually have a thermosetting component and so the replica can be released to obtain the ribs.

And basically, what you do is you take this mold and create negative replica by using PDMS and create a replica of small cavities on the lower surface like this to add resolution achieved by SU8, PDMS and the UV exposure-driven photolithography. So, once this mold is realized this is actually a PDMS soft mold and this would be used for molding thermosetting plastic paste or resin paste which is you know coated onto some hard substrate. So, for example, in this particular case as this mold has been realized you can use this mold to try to create features or imprints on a thermosetting resin paste which is coated onto a substrate. And here for example, when you pressurize this PDMS mold on the top of this thermosetting resin, the resin would go inside these cavities and fill up although they may not fill up completely there is a downside to this process and I will illustrate a little bit later. But the idea is that when these capillaries are sort of molding the thermosetting resin paste and then temperature is taken up.

So, the T is increased at this particular step. So, these polymers which are actually molded into the capillaries are set they are thermoset and resulting in basically very hard-natured thermosetting resin sitting on the top of this wafer. And then you can remove the PDMS away whereas, the resin would not go anywhere because it has already set on the top of the substrate. And so, you can have a very dense array of micropillars by using this very beautiful strategy of using a alternate PDMS mold to create this kind of a pillar array.   The only downside to the process is of course, surface tension because as you know that there is always in a capillary a contact angle which is established by the meniscus which flows into the capillary, and it is really a function of the forces

of cohesion and adhesion between the resin and the surface and the resin and resin itself.
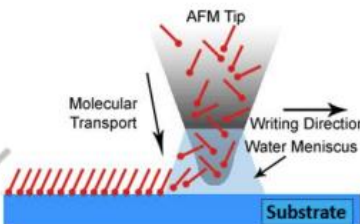
So, it is a three-phase interface air on one side, the PDMS on another and the third itself is the resin and this angle really depends on the interplay between the PDMS resin and air at this triple point or this point of interface. And so, if there is a contact angle which is formulated in this capillaries you can safely estimate that the capillary will not be totally filled and there would always be gap in the capillary end when this resin occupies a portion of the capillary. And this can be a reason of inaccuracy of these pillars when you talk many such pillars and arrays of pillars. And so, therefore, this allowance has to be taken into picture beforehand. So, that you can have a proper accurate imprinting of these ribs of the thermosetting plastic material.

So, this is capillary molding used for micropatterning of substances. So, this is one very interesting soft lithography example. The other very important and essential technique which people use nowadays most often is the dip pen lithography. So, the other process of good importance is this dip pen lithography, and this is also another process of writing molecules and the way that this goes. In fact, it was developed by Shad Merkin's group up at Northwestern who used an STM pen an AFM you know tip or tip of an AFM to write the molecules.
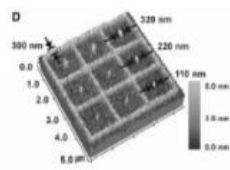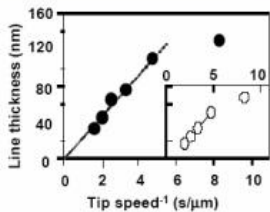
The way it goes is that you basically create you know an ideal condition of humidity and temperature and vary it in a manner. So, that you have a thin film or thin layer of water around this tip you know this AFM tip. On this water may be just a few monolayers thick. So, just a few atoms it is just a small layer. This layer is used for transporting molecules which you can deliver micro fluidically on to the surface of this AFM tip and it flows by virtue of electric field or some other

you know and then once it goes into this small water meniscus it automatically gets transported and can get imprinted or deposited on the on the substrate.

So, the condition that is created here really is that the forces of cohesion between the water and the substrate is probably forces of adhesion I am sorry between the water and the substrate is probably lesser in comparison to the adhesion between the water and the tip and so, therefore, this water meniscus can move along with the tip as a brush thus coating or delivering the molecules on to the substrate from place to place. So, typically there is a company called Nano Inc. Incorporated which had actually made this process happen and when it started it was actually a serial process, but then there have been initiatives where you can actually make this process parallel with multiple tips writing bunch of different molecules. So, you can actually use this to write self-assembled monolayers again DNA, proteins etcetera. So, this example here actually illustrates a protein microarray where you can see you know it is a basically almost 5 micron by 5-micron surface that you are investigating and each of these is a protein molecule.

So, therefore, there are these different protein molecules placed by this powerful technique dip and lithography and you can create microarrays separated by a resolution about almost 200, 300 nanometers. So, that is the power of this process. So, typically if you look at the some of the characteristics of the line thickness and by line thickness, we mean the line of molecules that would be deposited onto the substrate by virtue of this transport. So, the line thickness is actually directly proportional to the inverse of the tip speed meaning thereby if the speed is lower if the tip speed goes down line thickness would go up for obvious reasons that there is more amount of dwell time of the tip at a certain particular place. So, that is what is this fascinating process of dip and lithography it is again another soft lithography technique because it can write soft molecules onto the surface using an STM pen.
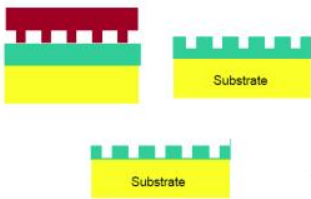
Let us now look into some of the other techniques apart from soft lithography that are available for the purpose of polymer MEMS and so, one technique which comes to the mind almost immediately is compression molding. So, as mechanical engineers, some people would already be aware of what compression molding really means essentially it means that there is a mold which is hard and can withstand temperature and pressure and then there is a thermoplastic polymer which is deposited on the top of a substrate and basically apply heat and pressure on to this mold to imprint this mold on to this thermoplastic material and the idea is that once this material is set at a certain temperature value the mold can be withdrawn back and that is how you can actually make the pattern transferred on to this substrate. So, that is what compression molding is. Another very interesting process is injection molding, and this is illustrated in this figure here where you can see the feed of the polymeric material happen through this lead screw which pushes the polymer melt. So, in this region there are heater bands which would melt the polymer and the polymer melt is pushed forward into this die cavity and the die cavity has some release agents on both sides.

So, that the idea is that you can separate whatever is formulated here. So, whenever the polymer melt goes into this area is a low-temperature zone it immediately solidifies and thins the shape of the die. So, these days there is an increasing amount of use or application of these techniques for creating CD-ROMs and features down to almost 0.1 microns deep and 0.6 microns in wide or width I mean features separated by this kind of a distance scale and easily be you know made by this process for developing CDRs.
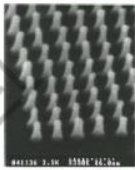
So, some of these processes like I already mentioned about this immunochip film clara technologies are actually made using compression molding process. So, if you can actually take this down to the nanoscale a very interesting process develops out of it which is called nanoimprint lithography,

Nano imprint lithography

Imprint mold with 10 nm diameter pillars

10 nm diameter holes imprinted in PMMA

10 nm diameter metal dots

Substrate

Substrate

- Nano-scale extension of hot
- embossing
- Need a nano-scale master mold
- Added to ITRS Roadmap

and it is a nanoscale extension of hot embossing or compression molding as I illustrated in the slide before. So, here for example, is a very you know interesting example of nanoimprint lithography.

So, what you do is you take a PMMA or polymethyl methacrylate and then use E-beam lithography to drill these holes which are all at a distance of about 10 nanometers and they are having diameters of about 10 nanometers also. So, the power of the electron beam you can actually do this lithography and drill it you know make a through hole in it using this E-beam lithography.

So, this can be used as a shadow mask typically for depositing material. So, let us say if you use this PMMA as a shadow mask you can deposit 10 nanometer metal dots separated by about 10 to 20 nanometer distance as you can see in this particular illustration here. And this metal dot-coated substrate can further be used as the mold the hard mold to pattern polymers. So, you can actually make a patterning of these 10-nanometer diameter pillars with these dots shadow graft or shadow deposited on the top of this silicon using this PMMA. So, the power of electron beam is translated in terms of resolution of these dots is further translated in terms of the formulation of this micro this is this nanopillars at a   scale which is very very small and minuscule.

So, typically this nanoimprint lithography is such an important technique now that it has been added to the ITRS road map, particularly for end of the device end of the road devices. And these days there is an increasing use of nanoimprint lithography in microelectronics for depositing you know gate dielectrics or even sometimes metal insulators. So, metal gates so on so forth. So, that is a very important process than nanoimprint lithography. So, we come to almost the closure of polymer MEMS here and some of the very interesting techniques which are available would once again go back to photolithography and would like to illustrate some of the experiments that you do for the photolithography process.

Process Steps for Photolithography

PR spin coating

Soft baking

Alignment and exposure

So, this for example, is the spin coating of the polymer resist. As I mentioned photolithography has a very important process step of coating a thin layer of resist material onto the wafer surface. This for example, is actually the wafer surface when you are applying the resist on the top and this is the spin coater. So, it would spin at a certain controlled rpm, and you can spin thicknesses defined by spin speeds onto the top of this wafer. Once it is spin coated you can heat and soft bake the resist.

So, that whatever liquid is available here for carrying the resin material is all evaporated and the resin is all set. And the next process of course, is this photolithography where you align and expose this wafer with   respect to a mask and you can actually imprint the pattern onto the resist through the mask using this alignment and exposure tool. So, this is these are some of the processes associated with photolithography. Of course, you will have to do the mask alignment by using these microscope objectives and microscope eyepieces where the objectives are in this particular region, and you can actually see visible differences in terms of alignment of the wafer and the mask. So, typically it is a sequential process you can have multi-level masking technologies where you know more than one level of mask is needed to fabricate MEMS structures.

And therefore, alignment between the two different levels also sometimes becomes very very critical and for that some very well-engineered and designed alignment marks are given on the CAD file. So, that it can be replicated onto the hard mask. So, that between step 1 and step 2 there is always a well-aligned domain and there is no chance of a dimensional inconsistency between the various layers of lithography. So, these are the 3 steps of photolithography.
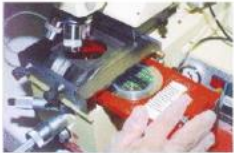

Process Steps for Photolithography

Mask loading

Alignment

Wafer loading

Exposure

So, once you have exposed the resist then you have. So, before exposing you basically do the mask loading. So, the wafer loading and the alignment these are all represented here. So, the alignment can typically be done by set screws which are to you know give rotation to the stage or given x and y movement. And there is also a z movement of the stage which can take the resist-coated wafer close to you know the surface of the mask.

So, that you can have contact lithography. And then you do the exposure where you can pre-set the intensity dosage as well as the time of exposure. And then following this you do the development where you know whatever resist has been exposed let us say if it is a positive tone resist in the developer solution the areas or regions which are exposed would come out and then you would have vias and trenches in those places. And after doing this the resist can be made as a sacrificial mask where wherever the vias and trenches have been opened can be etched off or etched out using the etchant solution. So, that you have a pattern etch on the surface of the silicon wafer. So, these are the various steps of photolithography than in a laboratory. So, typically in high throughput processes sometimes there is a nozzle to do spray development of the resist.

Process Steps for Photolithography

Mask loading   Alignment

Wafer loading   Exposure

And then you can have big transfer lines where you can have these different processes of substrate cleaning, resist coating, heating, pre-baking of the resist, exposure and development all automated in a particular manner. So, that you can have high throughput production of these wafers. So, that is a kind of practical demonstration of how photolithography can be done. Let us now understand a little bit about what are the changes or what are the chemical changes which would result when you actually bring in photoresist.

So, why is it that exposing the photoresist to a beam of light would actually make a chemical change happen on the top of the resist surface. So, here is again an example illustrated where we

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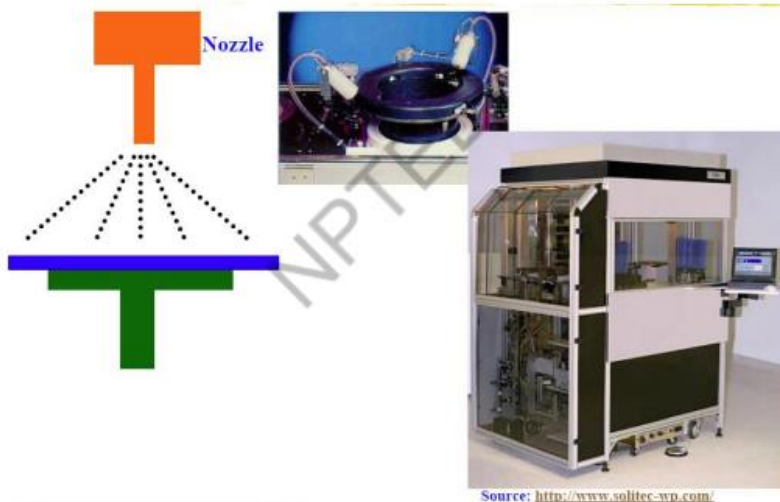
are talking about negative tone resist SU8. So, SU8 is a grade of resist available from a commercial manufacturer called Micro Chem and they are available at different viscosities and varying from 2005, 2010, 2025 as you go along the higher grade of the resist the more thick and more viscous the resist actually becomes. And so, you can have a thicker film spun or thicker features which are realized with the higher grade of the resist and thinner features when you go towards the lower grade of the resist. So, what is the constituent of SU8? So, basically SU8 primarily is an epoxy with a structure like this and this is a CO-C bond which typically looks like the epoxy group, and you can see here that this is actually the SU8 molecule with these epoxy rings at both ends.
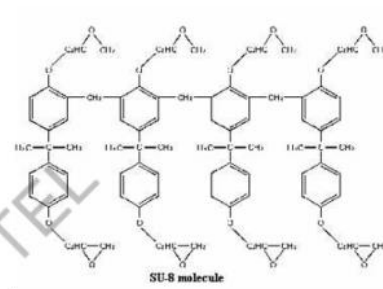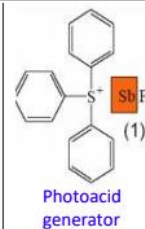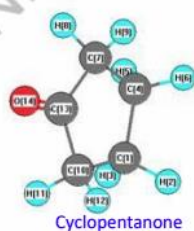
-ve tone photoresist SU8

- **SU8 is primarily an epoxy with structure**

$$-CH_2C-CH_2$$
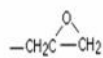
Epoxy

- It is primarily a mix of three compounds viz.

(a) An Epoxy Resin. [defined as a molecule containing one or more epoxy group]

(b) A solvent Cyclopentanone.

(c) And a photoacid generator

SU-8 molecule

Cyclopentanone

Photoacid generator

So, there are various rings at both flanks of the molecule and somehow, we will have to do some you know chemical modification of this ring. So, that they can cross bond and that cross bonding should only be on exposure to light. So, what all are the other constituents? So, you have an epoxy resin already defined molecule and then you have a solvent to carry the resin around. So, that if when you do spin coating or a process like spin coating there is a solvent which carries the epoxy all through the surface. So, you have to dissolve it to change the thickness into a you know a thinner level and that solvent needs to be as a carrier fluid incorporated there.
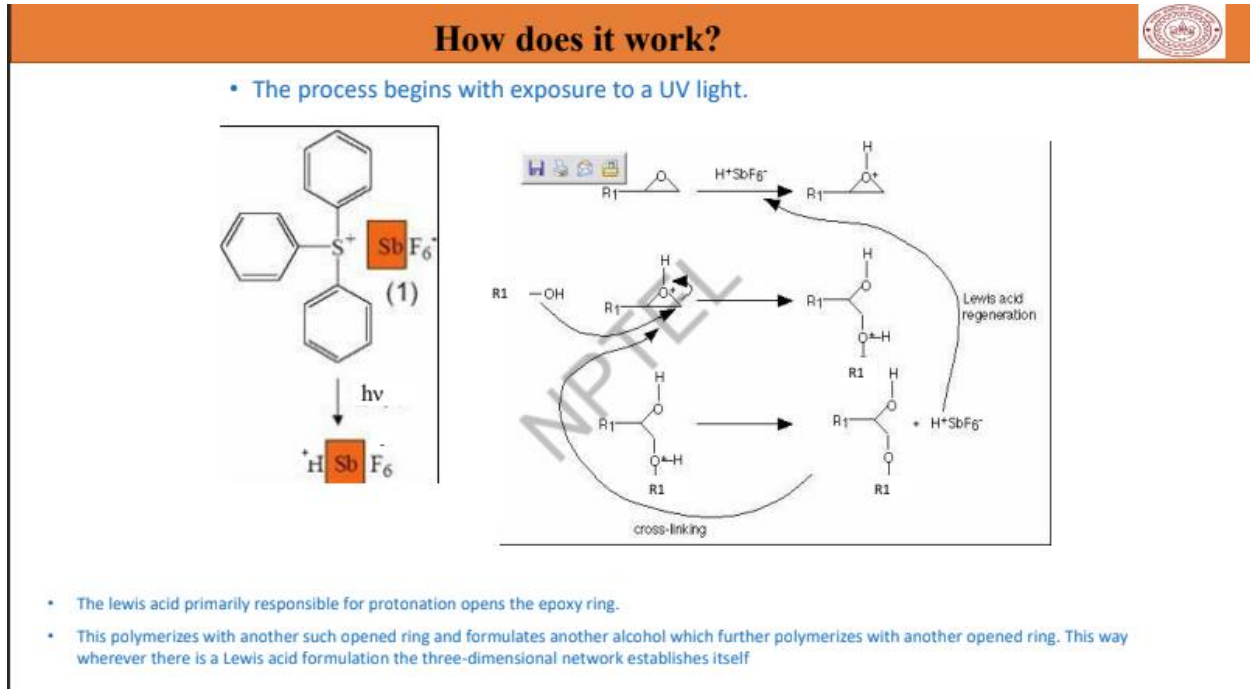
And then there is a photo acid generator. So, you have a mixture of the epoxy resin solvent in this case it is cyclopentanone and a photo acid generator and what this photo acid generator does is basically it produces it is a weak acid, it is a Lewis acid, it will produce a H plus ion or a hydrogen ion or a proton on exposure to light. The moment this H plus is created there is a chain of reaction which happens into the zone where this H plus is released and what happens is that the epoxy group on the photoresist actually opens up in this manner. So, you have the H bonded to O and giving a plus charge on the O and then you have again a similar kind of bondage you know from another R1 OH which is already present. And so, you can actually club both these R1 O   plus H and R1 O plus H in this particular manner and once this is done the hydrogen kind of gets off and you are left with this moiety here and hydrogen plus is generated back.

So, it acts as a catalyst, and it joins the photo acid generator group. So, you have an opening of the epoxy ring which causes more than two molecules to kind of play with each other, and you know develop bondage and it goes out the hydrogen ion goes out and joins the photo acid group here.

So, you have a cross-linked network of polymers in this manner wherever there is this H plus ion or hydrogen ion or proton which is generated which means that wherever there is an exposure to light thus generating the H plus out of the photo acid you would have a cross-linking which would cross-link the matrix of the polymer and make it solid. So, that is how with UV light or UV exposure the cross-linking of SU8 negative tone photoresist works. So, protonation and opening of the epoxy ring and cross-linking these are the three steps which polymerizes the resist in those areas where it gets exposed to the light. So, now let us talk about some tricky processing issues like what would happen when the resist is either overexposed or underexposed or as a matter of fact underdeveloped or overdeveloped.

So, as you know that there is a release of a H plus you know or a proton hydrogen ion which causes the epoxy ring to open. So, that you can have cross-bonding bonding it is very natural to assume that this H plus and the way it reaches is a diffusion-limited process. And therefore, if the right amount of exposure time right amount of H plus is not released then it probably is not sufficient to make the resist cross bond in the manner that we wanted to. And therefore, if you underexpose the resist let us say for example, this is a very nice illustration of what happens if you change the time of exposure. So, this is 30 seconds is about 50 seconds, 100 seconds and then 150 seconds and then you know 200 seconds.
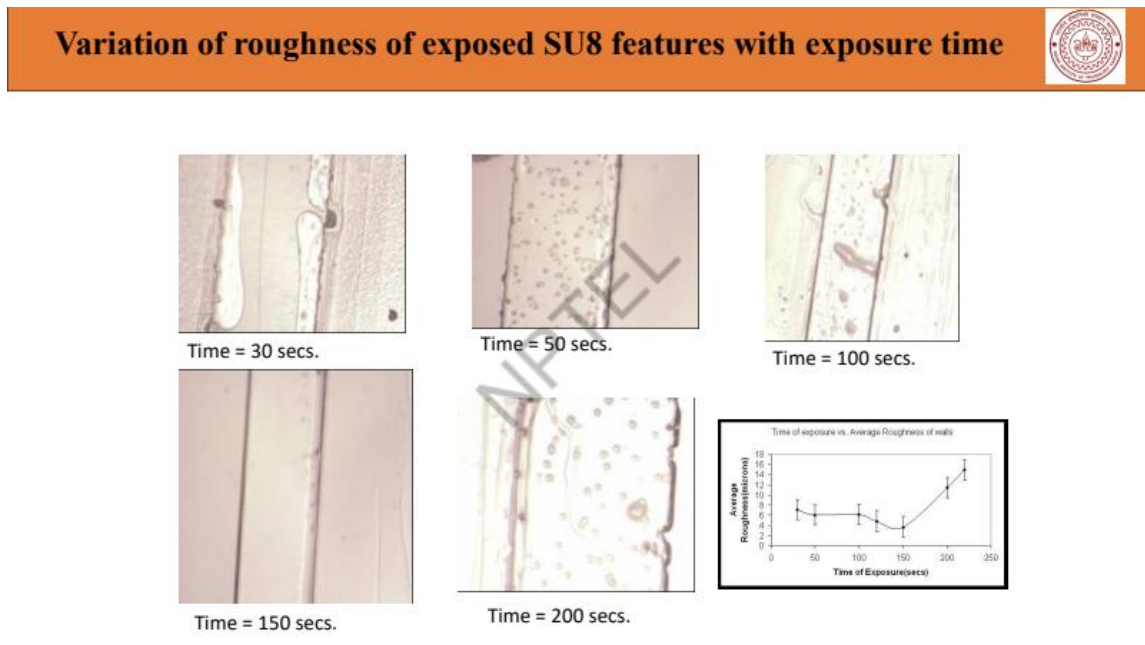
So, you are seeing here that the edges of the resist are very very rough when you talk about let us say smaller exposure time. And this particular illustration here the resist is having a very perfect edge because of the right time of exposure of this particular resist. So, therefore, you have to do studies like these to find out what you know would give you a good feature or good you know consistent you know consistently developed feature on microfeature on the top of the surface in question. And so, time of exposure is a very critical thing to be balanced when you talk about

resist. Here for example, is a case where it has been overexposed and as you are seeing there is a first of all there is a change in the dimension of the resist and number 2 is that the edges are not very smooth because now excess hydrogen ions have been produced and those create cross bonding away from the actual size or window of the mask that was available.

So, you have bigger feature sizes and more rough sizes because of this time of exposure. So, you will have to balance out the time of exposure every time which is very very critical for the purpose of development of the resist. So, we refer to bulk micromachining you can combine two or more steps together to produce hybrid machining process where you can do the etching. For example, in this illustration as one can see we are doing photolithography with resist, and then with that resist you are patterning the resist and then with patterning.

So, you have a deposited film, and you want to etch it selectively. So, you have a photoresist, you have exposure, you have patterning. So, the resist is patterned here on the surface thus exposing these regions of the deposited film and then you can actually etch selectively because the photoresist may not be able to etch it is a sacrificial mask on the top. So, you etch selectively thus etching these portions of you know the where the resist was no longer there, or it did not protect and so you can have these blocks of the deposited film on the top of the surface as you remove this resist out using some other methodology. So, you can use a variety of these processes together to formulate micro features and micro patterns.
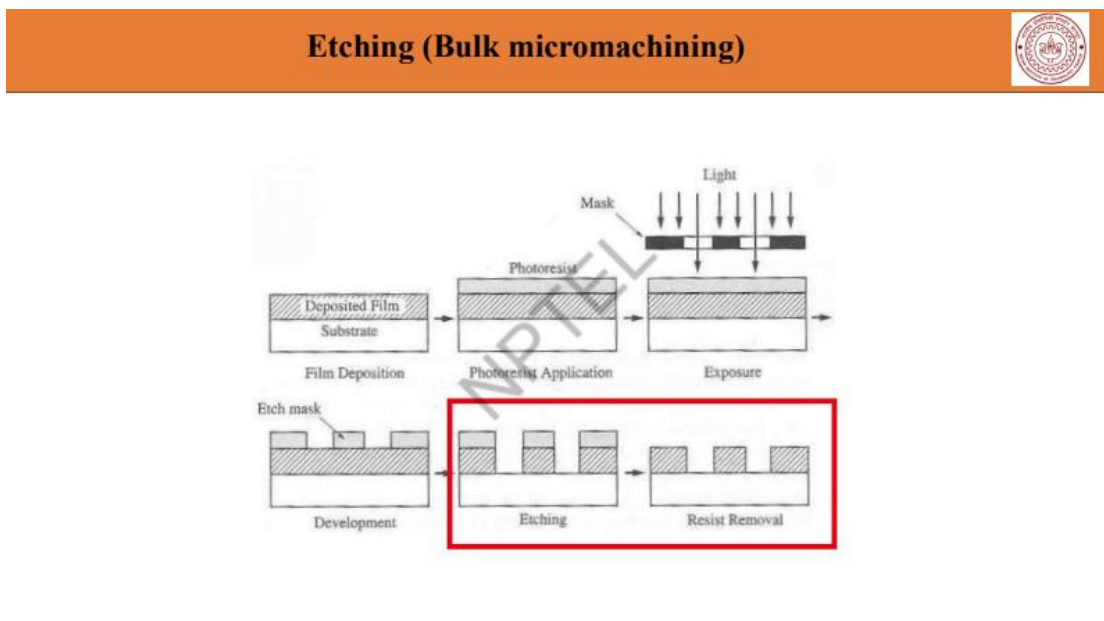
One more example is what you do with deposition and lift-off. Here, for example, you are actually exposing the resist to get a shape or feature through which you are doing some etching action. So, you are actually removing this grey layer here up till the green layer is probably the etch selective

layer.

Deposition and Liftoff

a) Expose Device Pattern
b) Develop photoresist (Shipley 352)
c) Etch sample (1 H₂SO₄ 8 H₂O₂ 100 H₂O)
d) Remove photoresist (acetone)
e) Metal deposition (e-beam)
f) Lift-off (acetone + ultrasound)
g) Final device
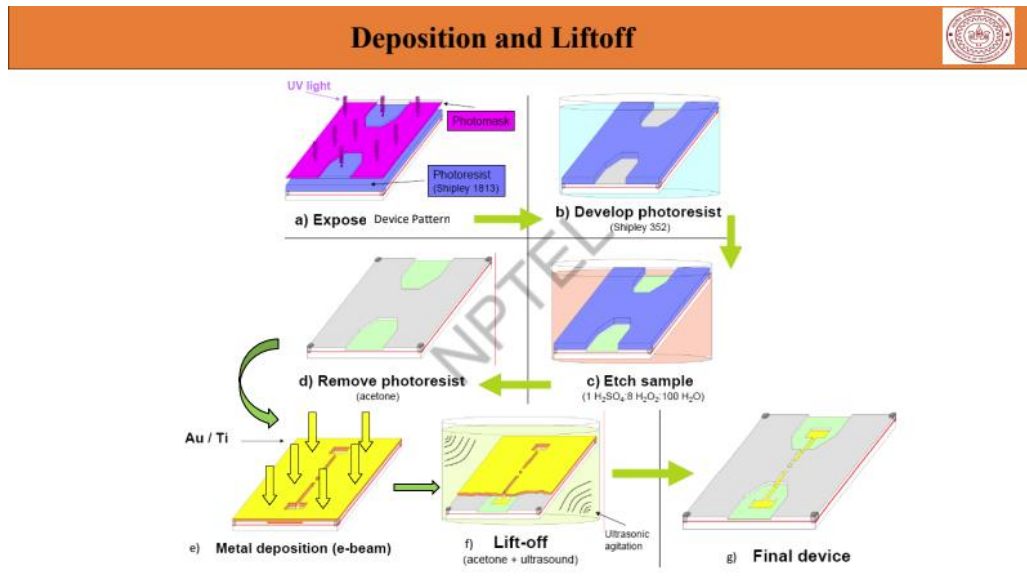
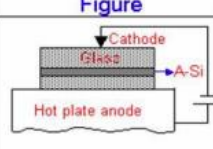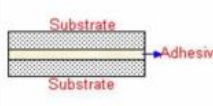tSo, it stops the etching stops here and then on this you are having another masking strategy and using this masking strategy you are basically trying to now deposit gold and titanium and then trying to remove the resists in these portions. So, that wherever the vias were open on the resist due to the second lithography step there would be a remnant film staying back because titanium is a very good agent which cross-bonds silicon oxide or dioxide to gold.

So, basically, it is a sort of adhesion layer or adhesion promotion layer. So, wherever there is a bare SiO2 which was exposed which was actually in this crevice here or in this crevice here the gold stayed, and it basically developed a bondage remaining film even if it went off because of development did not allow this portion of the film which was in that open area and crevice area to go away. So, that is how you actually realize microelectronic prints or circuits by using deposition and lift off. So, you are lifting off the resist in the undesired area and you are depositing in the desired area and that is why the processes deposition and lift off. So, these are some fundamental processes related to MEMS which are used in combination of variety of with combination with variety of other processes for realizing complex MEMS systems. It can be 7 layers, 8 layers, 9 layers different masks at each step, but then the idea is that you should be able to realize a microfeature with the accuracy that it is intended to using a combination of some of these processes.

Let us now look at a little different aspect of MEMS fabrication. So, once you are able to produce the microstructures and features in different layers the question of bonding between the layers comes into picture. For example, if you are developing a biochip and, in the silicon, base has carved-in channels and chambers we in the next step want to cover that with a glass plate. So, there is an issue of bonding which is involved between the different wafer level architectures and
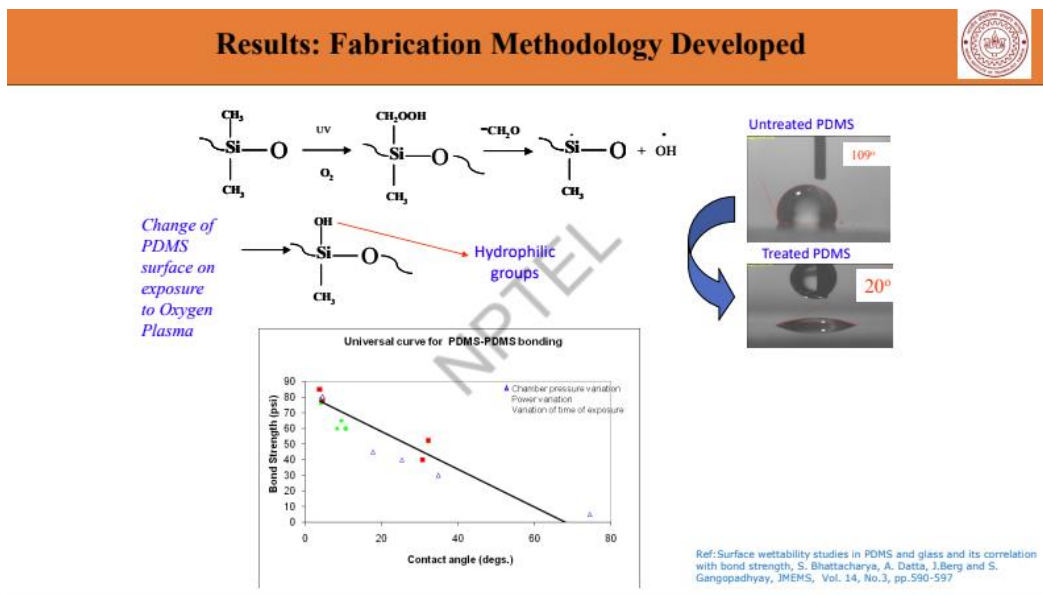
bonding plays a critical role in proper you know functioning of the MEMS system and although it comes as a part of packaging of the MEMS system, but then still the bonding is very very important because if suppose the bonding is not working properly then there may be leakages in microfluidic systems or dysfunctionality in terms of change in the inertness of the atmosphere which would have otherwise been needed for proper functioning of the device and therefore, bonding studies need to be done in great details. So, let us look at some of the basic bonding principles, wafer level bonding schemes which are available. So, the first scheme which comes into mind is field-assisted bonding which is basically you know bonding strategy driven by an electric field and here what happens is that if you have silicon oxide or on the surface of the silicon wafer on one hand and on another hand, you have let us say glass like soda lime glass.

Wafer level bonding schemes

S.N	Technique	Working principle	Figure
1	Field assisted bonding	Enhancement of ionic mobility from the surface resulting in creation of a strong field and bonding by fusion	
2	Bonding with an intermediate layer	Use of an intermediate adhesive layer to bond different layers	
3	Direct bonding	(1) Two substrates bonded to each other by thermal means (2) Low surface energy materials bonded to each other by use of Oxygen Plasma.	

Ref :.Langmuir I. and Mott-Smith H.M., Physics Review, 28, 727 (1926)

There is always a tendency of the sodium ions on the glass or the oxygen ions O minus 2 ions on the top of this SI surface to migrate towards each other. So, if I were to give a very very high field in such a situation with the glass slide or glass side being made the cathode and the silicon side being made the anode there is going to be a depletion layer which automatically comes up. So, the O minus which is there on the surface of the silicon would try to go towards the anode side and the Na plus which is already there in the glass would try to go towards the cathode side and this zone this grey zone here is the depletion layer which is created. So, once this depletion is created there are certain because of the certain absence of the sodium or the oxygen there is a lattice reformulation in that particular zone and because of that if you apply certain temperature there is a bonding of irreversible nature which happens between the lattice of glass and the lattice of silicon although glass is an amorphous solid it is a long range order solid, but the surface molecules of glass and the lattice of silicon because there is no field as such present it is a depletion region and there is no ionic interaction which is happening. So, this results in a permanent irreversible bond between the two and that is what is known by field assisted bonding or anodic bonding.

The other form of bonding which are used mostly in you know microelectronics and even MEMS is using an intermediate layer between the between the two wafers. For example, in this case let us say you have these two substrates to be bonded and you are using an intermediate adhesive layer to bond both the substrates, but mind you if there is a MEMS architecture which is available over one of these substrates unless it is you know well protected this kind of a bonding between the microstructure cannot take place because adhesive is a you know quite flowable material and it can flow into these features and structures and block them. So therefore, they are only used in illustrations where probably you need to have electrical interconnects or something in that order between the different layers and BCB in fact is you know a material which is used in bonding between different substrates in microelectronics of anon and so therefore, different layers can be bonded using BCB bonding technology. Apart from these two processes, the third MEMS bonding process which is of direct relevance to some of the polymer MEMS is direct bonding wherein either let us say in case of glass and silicon you can bond them to each other by thermal means by putting some pressure on the top of it and heating it to a temperature where lattice atoms kind of start vibrating and then they start diffusing into each other so that you can formulate the bonds. And in the other illustration you know you can somehow particularly in polymer MEMS case lower the surface energy of the material by exposure to variety of plasmas like argon plasma, oxygen plasma so on so forth.

Results: Fabrication Methodology Developed

Ref: Surface wettability studies in PDMS and glass and its correlation with bond strength, S. Bhattacharya, A. Datta, J.Berg and S. Gangopadhyay, JMEMS, Vol. 14, No.3, pp.590-597

So, once the surface energy of the material is lowered and it is made more hydrophilic there is automatic adsorption of OH or hydroxyl groups on the surface and the hydroxyl groups would kind of polycondense together to formulate a bond of irreversible kind between the different exposed layers of polymers. And so, this is a typically clean bonding recipe which is used in most of the polymer MEMS devices where polymers can be bonded to the glass or the silicon wafer very easily using this technique. So, for example, one of the very good examples of this bonding,

clean bonding procedure using oxygen plasma and the methodology involved has been reported in this paper of surface wettability studies in PDMS and glass. So, what is found out is that there is a series of reactions which happens on the surface of a PDMS by virtue of exposure to UV and exposure to oxygen plasma. And because of a series of reactions there is a formulation of this silanol group SiOH on the top of the PDMS surface at the cost of methyl groups.
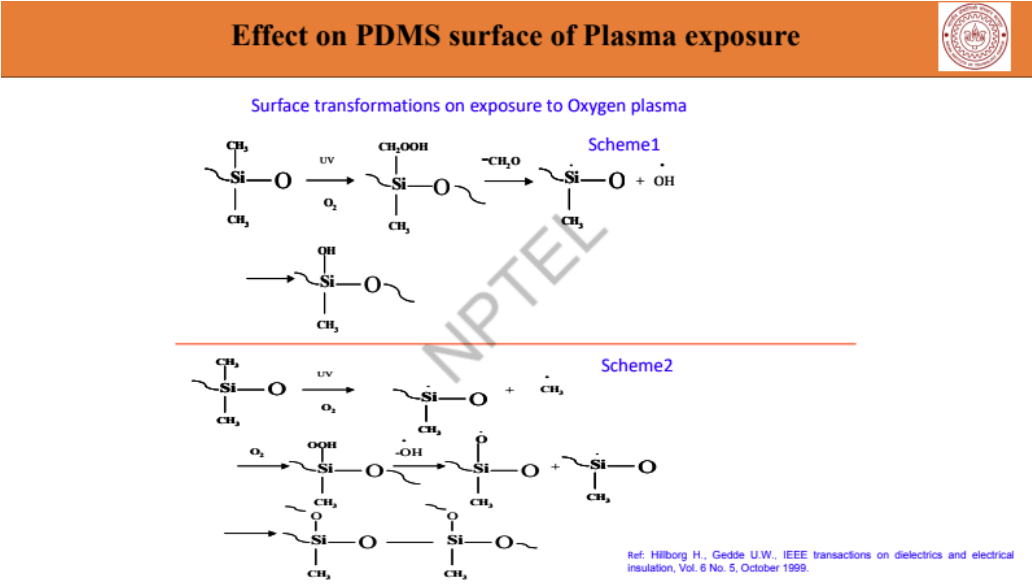
So, basically in oxygen plasma chamber methyl is kicked off and it replaced by hydroxyl OH. And one of the reasons why after immediately after the plasma exposure you find out that the surface becomes very hydrophilic. For example, you know in this particular illustration you can see the total contact angle about 109 degrees or so of this droplet has changed to almost 20 degrees by virtue of just plasma treatment. So, that is indicative of the fact that there is a lot of OH, lot of hydroxyl group on the top of the surface and which is resulting in a lower contact angle. So, in order to find out the bond strength you know the plasma parameters become very very critical because the idea here is that you should not be able to damage the backbone of this polymer molecule PDMS at the same time create enough surface reactions. So, that only at a very superficial level at the surface level there is a change or replacement of the methyl with the OH or hydroxyl groups.
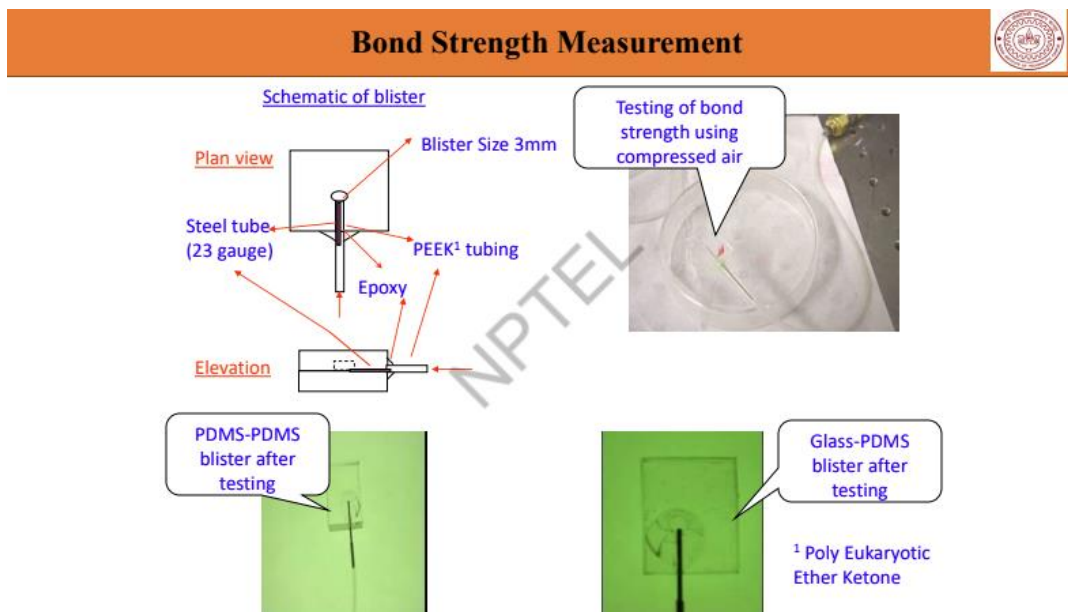
So, these authors here in this particular paper have developed a scale or strategy where they can have you know the measurement of bond strength on one side and contact angle and they have correlated very nicely that if the contact angle can be taken down below about 10 degrees or so, then the bond strengths actually become very high. And these bonds are because of the formulation of this SiOH and suppose there are two such surfaces which would form SiOH together there would be a polycondensation reaction H2O goes out and you are left with SiOSi you know linkages
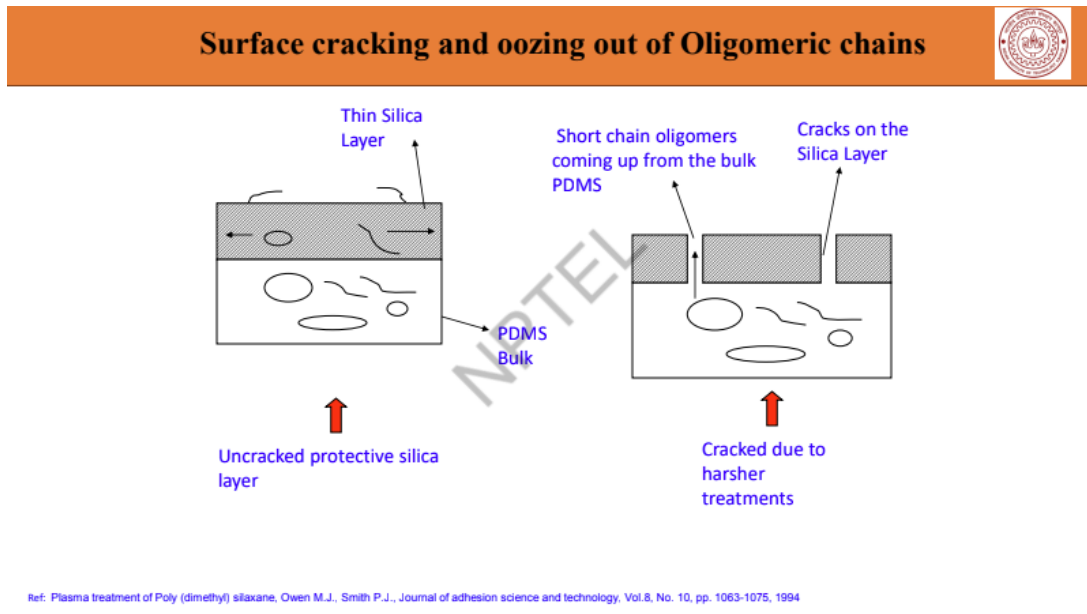
which is actually an irreversible bond in this particular case. So, the you know measurements of the bond strength in this particular example has been done by putting you know using lithography to develop this microchamber and this microchamber is again filled with air and for that mechanism you have a steel tubing and a peak tubing which is actually applied and epoxy is used for safeguarding any leakages from between the peak tubing and the PDMS and the peak tubing actually bites over the PDMS and creates a sort of reversible seal between it. So, therefore, there is a very less possibility of any air going out and so, what would happen is that if you control this air at a certain pressure there would be an expansion of this chamber till and until it actually formulates or develops a rupture and before developing a rupture even you can see under a microscope that the two layers are getting separated along the edges. So, that really is the basis for formulating the bond strength how much bond strength of this PDMS to PDMS would be is dependent on at what pressure or corresponding to what pressure these layers separate from each other.

So, you have these different cases where you can see finally, you know after the bonds get started to get separate they had rupture and you can have a critical value of pressure at which the bond starts to get separated. So, there are several transformations on the surface that have been reported by various groups working on PDMS. One of course, is the formulation of OH and another in scheme 2 there is always a series of steps of UV and O2 exposure which leads to again the formulation of SiO. So, there are different reactions which have been reported by various people working in this particular polymeric material PDMS as a basis of bonding scheme between the surfaces.

Effect on PDMS surface of Plasma exposure

Surface transformations on exposure to Oxygen plasma

Ref: Hillborg H., Gedde U.W., IEEE transactions on dielectrics and electrical insulation, Vol. 6 No. 5, October 1999.

There are also certain very important illustrations which come out for example, you know in case of PDMS if you keep it back in normal room temperature there is a hydrophobicity recovery of the surface and the way that it happens is that there are micro-cracks which are developed because of exposure to the plasma and there is always oozing out or you know coming out of the short

chain and long chain oligomers which are otherwise present within the small silica layer on the top of the PDMS formulated because of the oxygen plasma exposure.

Surface cracking and oozing out of Oligomeric chains

Ref: Plasma treatment of Poly (dimethyl) silaxane, Owen M.J., Smith P.J., Journal of adhesion science and technology, Vol.8, No. 10, pp. 1063-1075, 1994

And so, this oozes out and comes back to the surface thus changing the hydrophobicity of the surface almost immediately. So, the bonding between the surfaces is an immediate process. So, whenever you have both the you know OH groups just formulated on the surface on the silica layer immediately after the oxygen plasma exposure that is about the right time of bonding between the surfaces because if you delay or if you wait there is always a tendency of the hydrophobicity to recover back and lot of methyl groups to come and crowd the surface and that is actually going to ruin the bond strength. So, that is how polymeric bonding in MEMS can be realized and so, that brings us to the end of today's lecture. Thank you.