

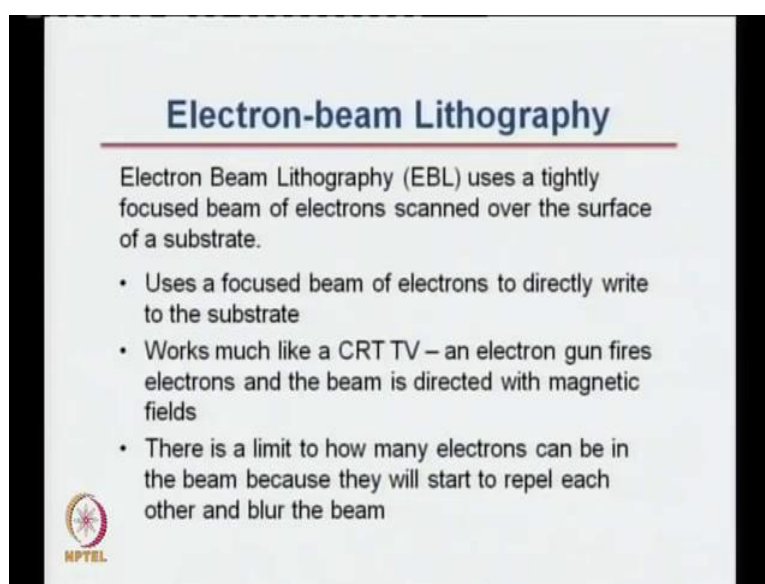
Nano structured Materials-Synthesis, Properties Self Assembly and Applications
Prof. Ashok. K. Ganguli
Department of Chemistry
Indian Institute of Technology, Delhi

Module - 2
Lecture - 14
Lithography-II

Welcome back to this course on nano structured materials, synthesis, properties, self-assembly and applications. We are today in the twelfth lecture of module 2 and this is the second lecture on lithography. In the last lecture, which was lithography part one. We had discussed what is lithography, which means to write on stone. Here modern day lithography we discussed how you can write very small nano structures on the basis of photolithography that is using light or x ray lithography using x rays.

Today we will carry on that discussion into other forms of writing or designing patterns on surfaces based on several other techniques other than light, which is photolithography or x rays, which is x ray lithography, which we discussed in our previous lecture, the lecture eleven of module two. So, today the second part and the final part of lithography we will be first discussing on the electron beam lithography.


(Refer Slide Time: 01:53)



Electron-beam Lithography

Electron Beam Lithography (EBL) uses a tightly focused beam of electrons scanned over the surface of a substrate.

- Uses a focused beam of electrons to directly write to the substrate
- Works much like a CRT TV – an electron gun fires electrons and the beam is directed with magnetic fields
- There is a limit to how many electrons can be in the beam because they will start to repel each other and blur the beam

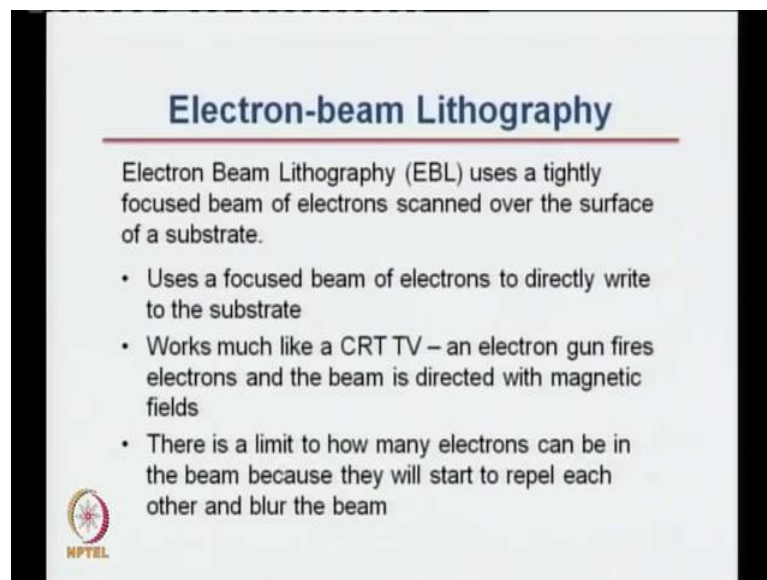
 NPTEL

From the term electron beam Lithography, you can make out that you are going to use an electron beam to make patterns on surfaces. So, the electron beam lithography will use a

very focused beam of electrons. This focused beam of electrons can be scanned over the surface of any material, which we call a substrate. So, we can directly write on a substrate using a very focused or a fine beam of electrons.

It is similar to like in cathode ray tubes, which you have in your television, where you have any electron gun which is the source of electrons and electrons come out from this source or the electron gun. This beam of electrons is kind of directed or guided using magnetic fields or electromagnets in the inbuilt, which will allow the beam to be focused.


(Refer Slide Time: 03:02)



Electron-beam Lithography

Electron Beam Lithography (EBL) uses a tightly focused beam of electrons scanned over the surface of a substrate.

- Uses a focused beam of electrons to directly write to the substrate
- Works much like a CRT TV – an electron gun fires electrons and the beam is directed with magnetic fields
- There is a limit to how many electrons can be in the beam because they will start to repel each other and blur the beam

 NPTEL

That will be used to make patterns on a substrate. So, this beam works very much the electron beam can be thought of which ordinary cathode ray tube, but which will be focused on a point using electromagnetic fields. There is a the number density of electron, that is how many electrons can be in the beam, there is a limitation because if you have too many number of electrons because electrons as you know are same charge, they have a negative charge they will start to repel each other.

If they start to repel each other that means you will broaden the beam. So, the beam diameter will become large and that will not create a sharp or focused electron beam. That blurring will not allow you to make very nice patterns or very sharp patterns of small dimensions. So, it is very important to control the electrons within a small diameter

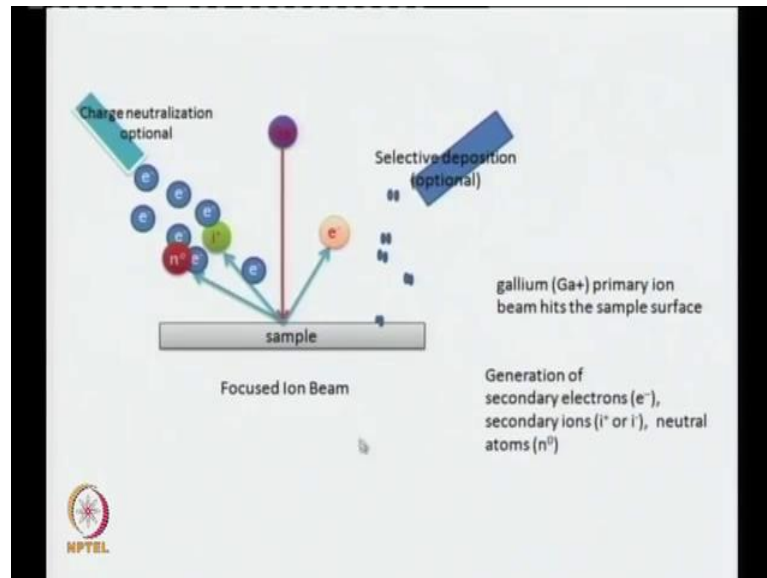
that means you have to focus the electrons in the beam. If you have too many electrons then that can be a problem.

So, you need a concentrated charged stream of electrons which is generated from an electron gun. These beams can be pulsed that means you have an electron beam for a short burst of time may be few microseconds, few milliseconds and then it will stop and again it will start. So, this is called a pulsed electron beam. It can also be a continuous electron beam. So, we can have both pulsed electron beams and continuous electron beams and they can be used for writing patterns on surfaces.

We can make very small structures or very small designs or objects by focusing these beams. So, you can fabricate very small sized objects using the highly focused electron beams. Now, diffraction normally limits the spot size and. So, smaller the wavelength smaller is the spot size, that is the size of the electron beam which falls on the substrate. So, this is something you have to take care. So, to make the electron beam very small you have to use very small size of the wavelength.

The wavelength should be very small. To have very small wavelength the electron that means has to have high energy because the wavelength is inversely proportion to the energy. So, when you create the electron, then it can be generated at a certain energy using a certain potential. So, you can vary the potential to generate different energies of electrons and which you can control and hence you can control the wavelength of the electrons. Hence you can control the spot size of the electron beam. So, this is a typical diagram.

(Refer Slide Time: 06:24)



A schematic diagram of what happens in a typical focused ion beam. So, you have here you can what we generated here is the electron beam, but you can also have particles like gallium ions.

(Refer Slide Time: 06:43)

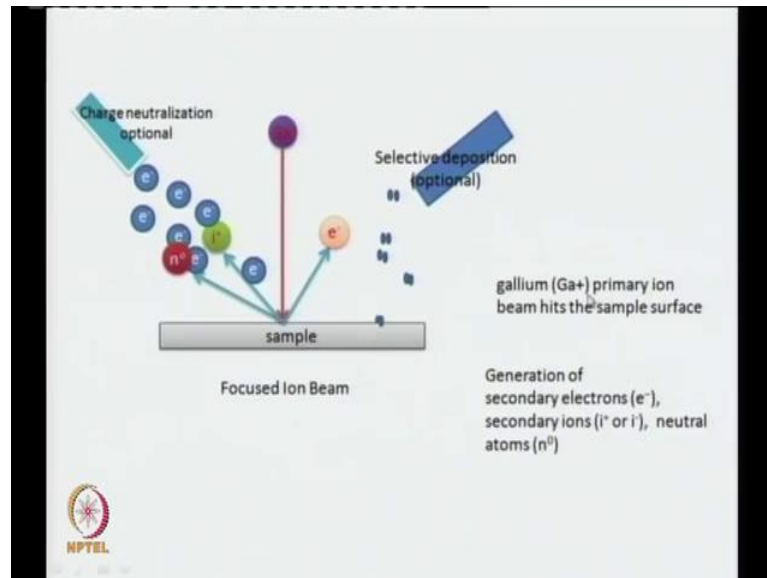
Electron Beam

- The beam, a concentrated, highly charged stream of electrons, is generated by the acceleration and conversion of electricity.
- Beams are either pulsed or continuous.
- Fabricate small objects by strongly focused particle beam
- Diffraction limits the spot size
- Smaller the wavelength smaller the spot size

The NPTEL logo is located in the bottom left corner of the slide.

So you are having here gallium ions which impinge on a sample.

(Refer Slide Time: 06:48)

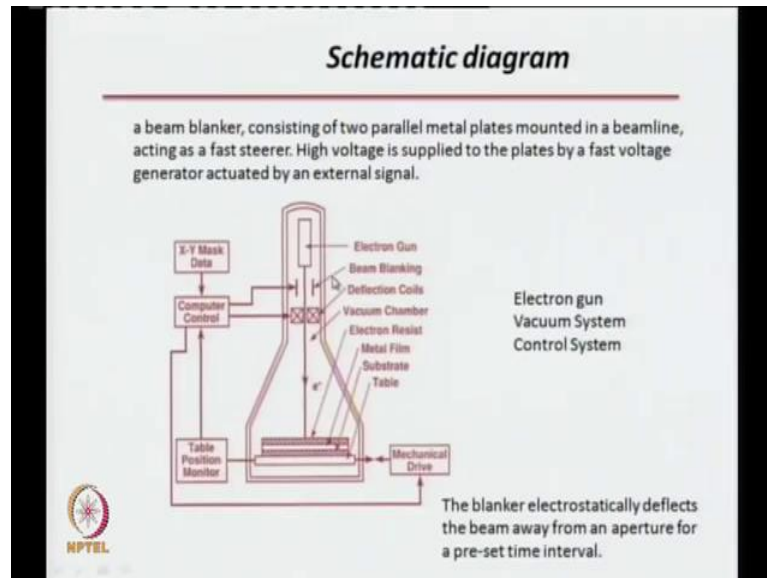


So, gallium ion is the primary ion beam which hits the sample. In this focused ion beam case you can have this beam falling on the sample and creating what are called secondary electrons. Then these secondary electrons can be used you can neutralize them if you want or you can additionally deposit something else, that is called selective deposition which is an optional aspect of this focused ion beam technique.

So, basically here there are a certain ions which are used very commonly and gallium ion is one of those ions which is used very commonly in a focused ion beam study. So, you can have an electron beam lithography or you can have using ion beams also you can have a lithography. So, if when you have this ion beam falling on the sample you generate this secondary electrons. These secondary electrons or secondary ions or neutral atoms can be generated. The neutral atoms can be generated when you neutralize these ions i plus with some charge negative charge then you will get neutral atoms.

So, you can have neutral atoms electrons positively charged ions coming out of the sample using a gallium ion source. So, this is called a focused ion beam arrangement. So, you can have a focused electron beam or you can have a focused ion beam to fall on a substrate.

(Refer Slide Time: 08:31)

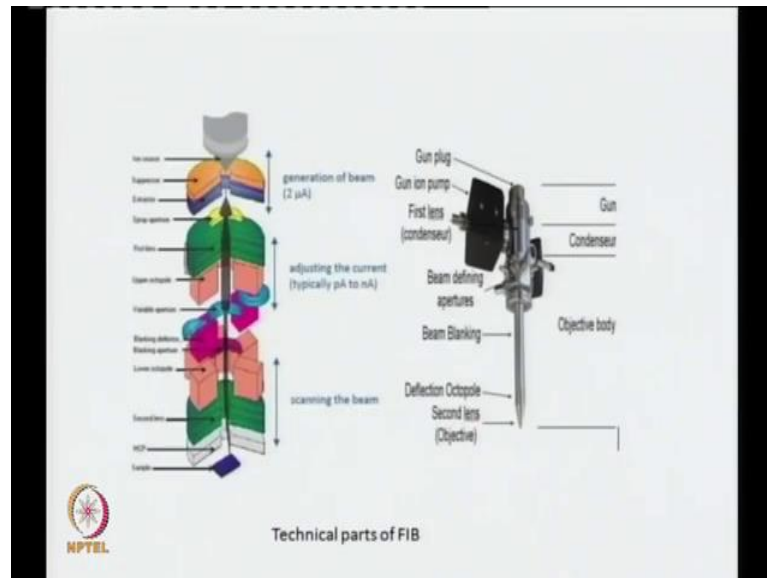


Now, another schematic diagram of this process of how electrons are focused is you have this chamber which is an electron gun. So, in this electron gun electrons are generated because you apply a very high potential here. It is like a cathode ray tube you have a cathode a metal foil from which you can get electrons. These electrons traverse this region where you have something called beam blanking.

The beam blanking basically electrostatically deflects the beam away from an aperture for a preset time interval. So, the beam blanking is important for guiding the electron beam which is coming out of this electron gun. So, you generate electrons here, then you have pass through these where you have these electrodes. Then you further control these electrons as they are passing through, which are called deflection coils. This allows you to focus the electrons.

Ultimately it falls on the sample where you want to make a pattern and this whole thing is then a system which is generating an electron focused electron beam on a sample. So, you can have a focused ion beam as I showed in the previous slide using gallium ions which is called a FIB and you can also have electron beam focused on this sample.

(Refer Slide Time: 10:15)



Now, if you that is a schematic diagram if you want to look at this focused ion beam equipment, the cross section or if a view inside it has got many parts. So, at the top in this focused ion beam system, you must have a source for ions because that is going to be the source for if you are going to use gallium ions, this is going to produce gallium ions. So, that is your ion source.

Then you have several basically electromagnets which control your ion beam. So, they are having different names which are called suppressor, extractor etcetera, but basically this part is involved with generation of the ion beam. So, this part is actually not very far off the distance between the ion beam source and this is around 2. Here the current, which we are using is typically 2 microamperes.

So, this closely spaced electromagnets which is of the close to the ion gun is, which is called a suppressor and then you have a extractor. This produces an electron beam, here you put a current which is approximately of the order of 2 microamperes. When you bring the beam further where you have these lenses which control the ion beam, then you have further electrodes. You have an upper electrode, you have which is like an octopole it is called an octopole like you have dipole, quadrupole this is an octopole.

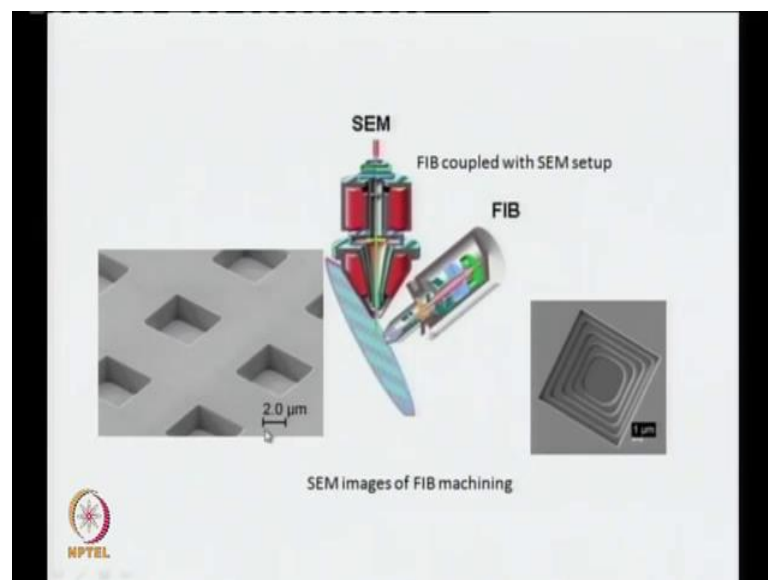
It helps in focusing the electron beam. Here the current is typically adjusted to much smaller current. So, in the order of Pico amperes to nano amperes. So, here you had in

microamperes. Now, in this range you have much smaller current it is of the order of Pico amperes to nano amperes.

Further, you have other systems like shown earlier, you have this blanking deflector which keeps the beam or which will help you scan the beam. So, if you want to turn the beam to scan to a particular point or to this point, these further octopole will help you in scanning the beam. So, this part the lower part of the FIB system helps you move this focused beam.

The beam is focused, but if you want to move this point throughout the sample, then you may you have to deflect the beam. So, you must be able to deflect the beam without increasing the radius of ion beam. So, it should be focused properly. Now, this is a kind of a cross sectional view and this is how a real a FIB looks like. Again the parts of the same this is where the gun is there and the ion is generated. This is basically contains the material which will pump the ions and then you have a condenser and then apertures and then beam blanking and then you have the octopole and then you have the objective just before the sample. Using this using this FIB, you can make this kind of structures.

(Refer Slide Time: 14:00)

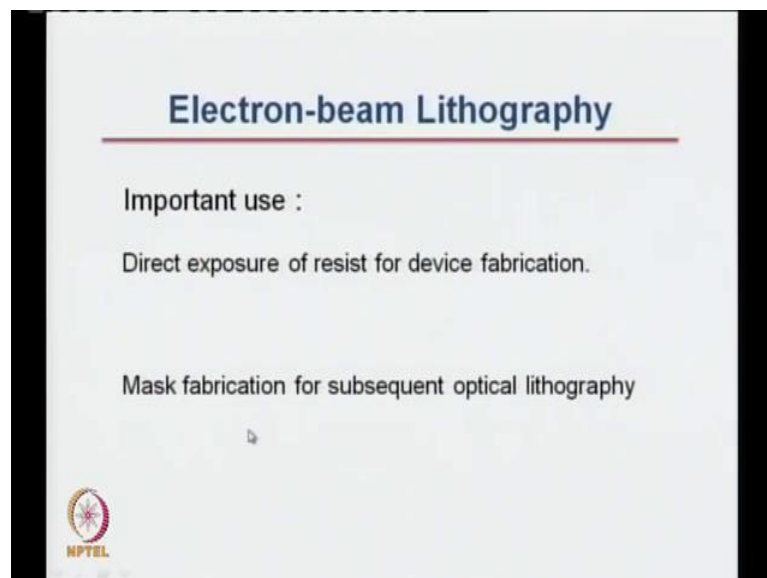


So, using this focused ion beam, you can make this kind of structures as you see that these are of the order of 4 microns across. These structures can be seen using a SEM. So, always a FIB is coupled to an SEM. So, FIB coupled with SEM has both the scanning electron microscope as well as the focused ion beam arrangement in the same machine.

So, that when you make a structure like this using the ion beam you make this structure then you want to see this structure. So, how do you see this structure is you must have a scanning electron microscope aligned such that these structures are visible.

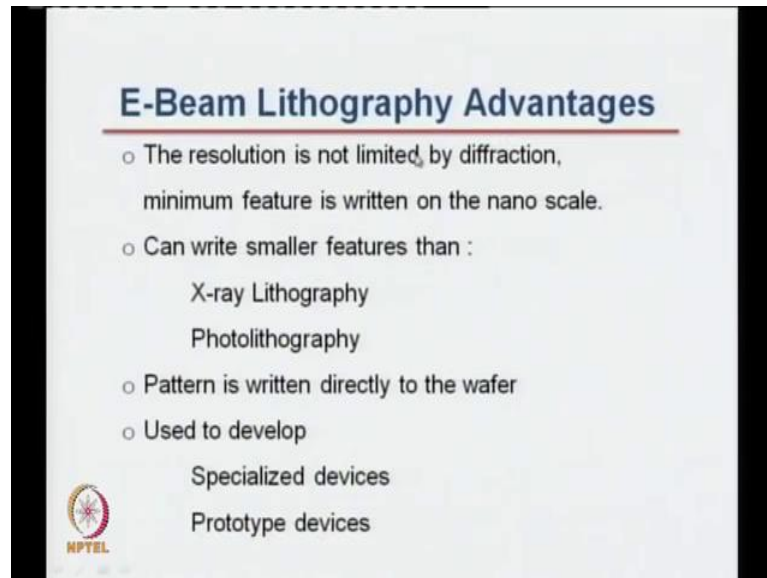
So, this is a typical setup for what today we call the FESEM FIB system. So, which has got a field emission scanning electron microscope. So, that is why we called it a FE SEM and a FIB which is called a focused ion beam setup. These can make structures either remove patterns like this from this part or remove patterns from the sides to create this kind of a square spiral like a structure. So, these are typically how you do lithography using a focused ion beams in a FIB FESEM system.

(Refer Slide Time: 15:30)




Now, the use of these kind of ion beams or electron beam lithography, is that you can directly expose the resist for device fabrication. We discussed what are resists in our previous lecture. Here you can directly use the electron beam to make devices. You can also make masks based on electron beam lithography, which can subsequently be used for optical lithography.

(Refer Slide Time: 16:03)



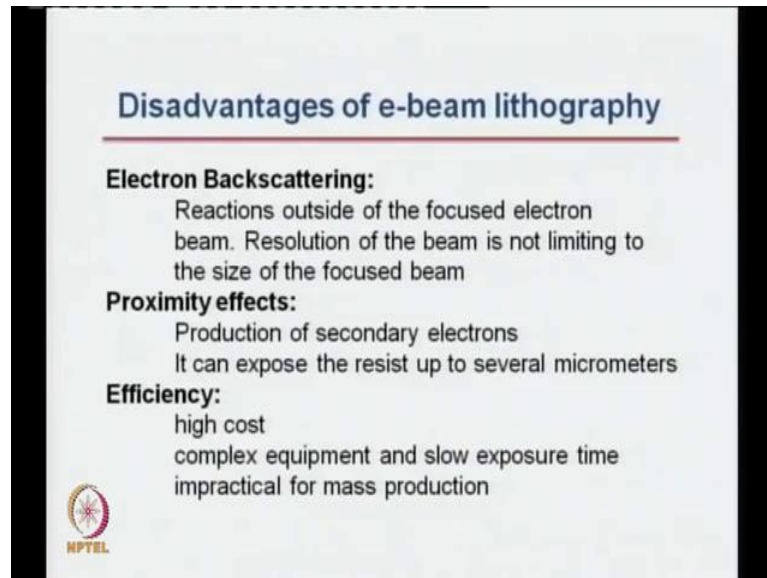
E-Beam Lithography Advantages

- The resolution is not limited by diffraction, minimum feature is written on the nano scale.
- Can write smaller features than :
 - X-ray Lithography
 - Photolithography
- Pattern is written directly to the wafer
- Used to develop
 - Specialized devices
 - Prototype devices

 NPTEL

The electron beam lithography has many advantages. The resolution is not limited by diffraction, the minimum feature is written on the nano scale. So, you there is something called diffraction limited which you have with light. There the resolution is related to this diffraction limit. Here the resolution is not limited by the fraction. The minimum feature size you can really bring it down to the nanoscale. You can write or make patterns, which are much smaller than what you can do in the techniques that we discussed in the previous lecture. That is using x ray lithography and photolithography. So, electron beam lithography has an advantage that you can make much finer much smaller structures using the electron beam. The pattern is directly written on the wafer.

(Refer Slide Time: 17:00)




Disadvantages of e-beam lithography

Electron Backscattering:
Reactions outside of the focused electron beam. Resolution of the beam is not limiting to the size of the focused beam

Proximity effects:
Production of secondary electrons
It can expose the resist up to several micrometers

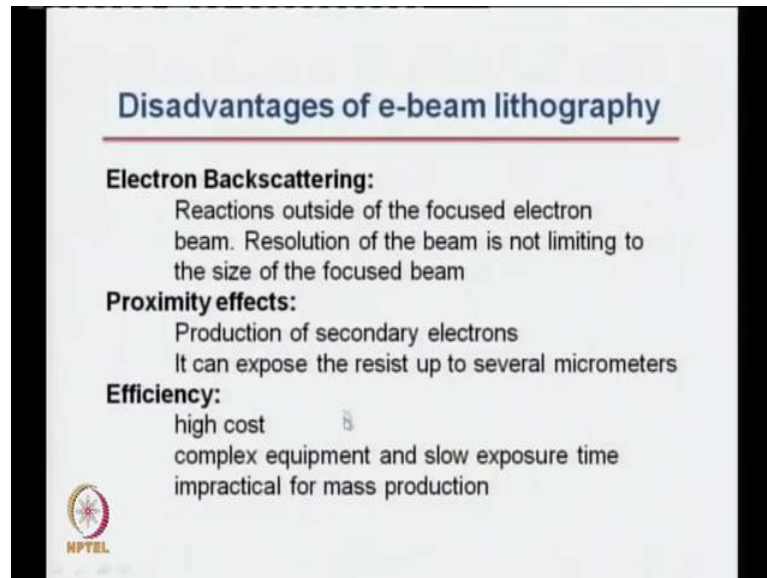
Efficiency:
high cost
complex equipment and slow exposure time
impractical for mass production

 NPTEL

This e beam lithography can be used to develop specialized devices and prototype devices. The disadvantages of e beam lithography. There are couple of disadvantages for example, when you use an electron beam, there can be electrons which are backscattered like in an SEM you can always have electrons which are backscattered. Those electrons can give rise to reactions, which are outside of the focused electron beam.

So, you want to make some structures within where you focus the electron beam, but if you have electrons which are hitting places away from that, then you are going to make some patterns elsewhere also, which can happen using the back backscattered electrons. So, those are not the electrons which we are focusing on the substrate. So, that is one disadvantage of the electron beam lithography.

(Refer Slide Time: 17:58)




Disadvantages of e-beam lithography

Electron Backscattering:
Reactions outside of the focused electron beam. Resolution of the beam is not limiting to the size of the focused beam

Proximity effects:
Production of secondary electrons
It can expose the resist up to several micrometers

Efficiency:
high cost
complex equipment and slow exposure time
impractical for mass production



The resolution of the beam is not limiting to the size of the focused beam. The resolution has something else also it is not only that the size of the focused beam is important. Then there are proximity effects that means, you as we mentioned that you can have secondary electrons. You use an electron beam and secondary electrons are generated from the materials, which are on the substrate and then they can have additional effects. These secondary electrons or a reactions outside the focused electron beam can expose the resist to several microns.

So, ideally you are making focusing the electron beam to work within a submicron region or few nanometer region. However, these proximity effects make you make the resist to be exposed or structures to be made over several micrometer. So, that is the much larger area which you do not want actually to be patterned, but can get patterned unless you take special care.


(Refer Slide Time: 19:06)

Disadvantages of e-beam lithography

Electron Backscattering:
Reactions outside of the focused electron beam. Resolution of the beam is not limiting to the size of the focused beam

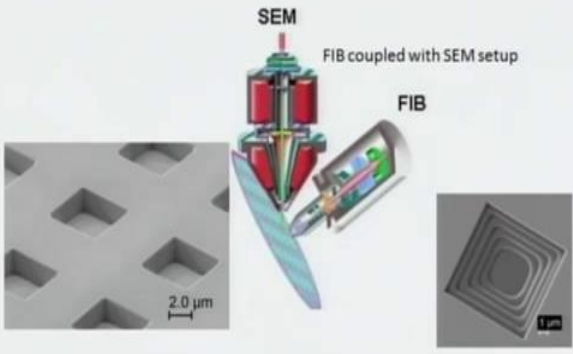
Proximity effects:
Production of secondary electrons
It can expose the resist up to several micrometers

Efficiency:
high cost
complex equipment and slow exposure time
impractical for mass production



The third thing is this e beam techniques are quite expensive, because they involve complex equipment and they have slow exposure time.

(Refer Slide Time: 19:23)




SEM
FIB coupled with SEM setup
FIB

2.0 μm

1 μm

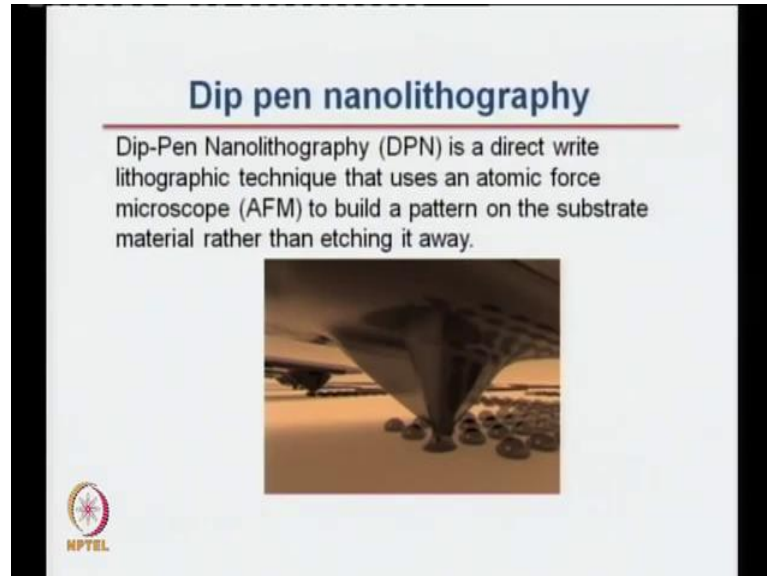
SEM images of FIB machining



It is impractical for mass production it has high cost. As you see the equipment is quite complex because we have several lenses apertures and blanking devices within this chamber. You have detectors for SEM and again several lens as electromagnetic lens is built in the SEM. So, this whole equipment becomes very expensive for making patterns

on substrates. Now, we discussed the advantages as well as the disadvantages of e beam lithography.

(Refer Slide Time: 20:00)

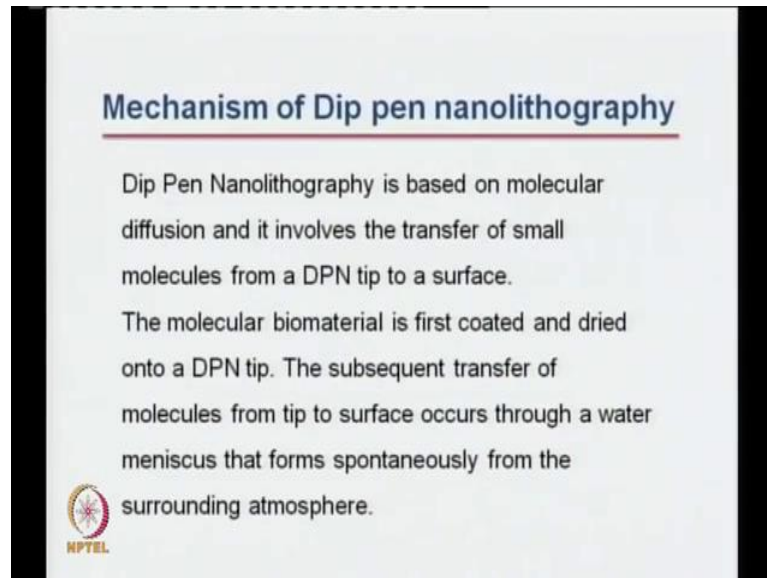


Now, move to another technique, which is a low cost technique, which is called dip pen nanolithography. So, if you go by the term dip pen, it is like you are having a pen and you are dipping it in an ink to write. So, it is this term dip pen nanolithography has emerged from that idea, that you have a probe which dips into a solution which contains some molecules, which you want to pattern on another surface.

So, typically it is a direct write lithographic technique, that uses an atomic force microscope. So, the probe that is the atomic force microscope as you know has a probe. That probe is used to build a pattern on the substrate. Here you are adding something on the substrate.

So, your writing means you are putting some ink on the substrate you are not removing anything from the substrate, you are not etching anything away from the substrate like you were doing in the ion beam or the electron beam techniques. So, this is your building there you have a flat clean substrate and you are making a pattern by adding some molecules on top of the substrate using an AFM tip.


(Refer Slide Time: 21:27)



Mechanism of Dip pen nanolithography

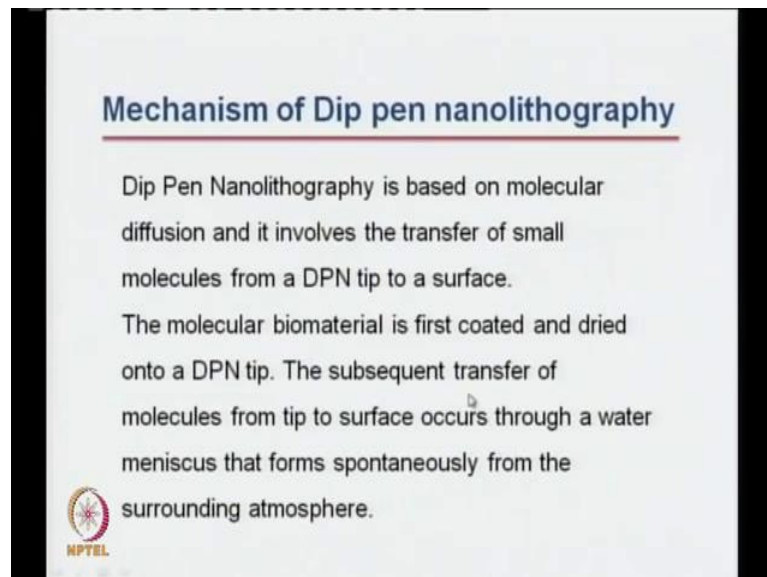
Dip Pen Nanolithography is based on molecular diffusion and it involves the transfer of small molecules from a DPN tip to a surface.

The molecular biomaterial is first coated and dried onto a DPN tip. The subsequent transfer of molecules from tip to surface occurs through a water meniscus that forms spontaneously from the surrounding atmosphere.



So, this is the dip pen nanolithography is based on molecular diffusion. It involves the transfer of molecules from the tip of the dip pen, which is typically an AFM tip on to the surface. How you do it is, first you take the molecular biomaterial. Normally, it is used a lot for bio nanotechnology or bio sensing etcetera.


(Refer Slide Time: 22:02)



Mechanism of Dip pen nanolithography

Dip Pen Nanolithography is based on molecular diffusion and it involves the transfer of small molecules from a DPN tip to a surface.

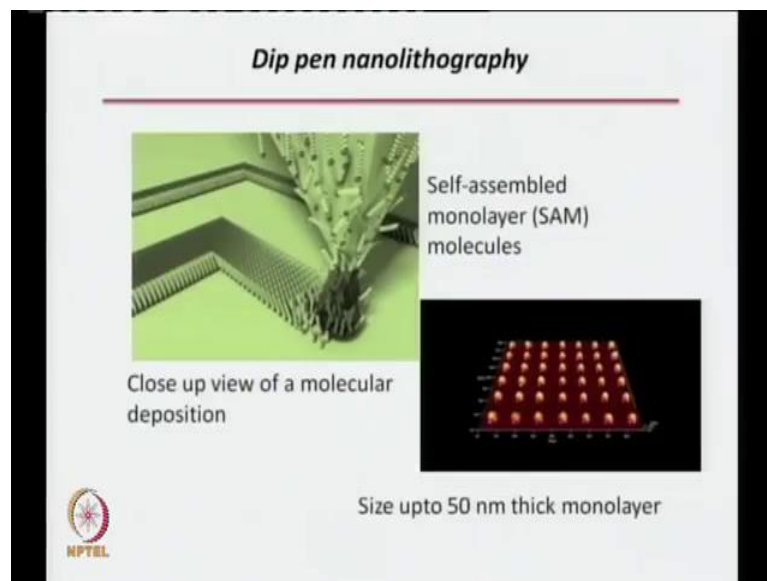
The molecular biomaterial is first coated and dried onto a DPN tip. The subsequent transfer of molecules from tip to surface occurs through a water meniscus that forms spontaneously from the surrounding atmosphere.



The molecular material is first coated and dried on the tip of AFM. So, you have this dried material on the tip of the AFM and then this material is transferred, that is the molecules are transferred from the tip to the surface of the substrate through a water

meniscus. which forms spontaneously from the surrounding atmosphere. So, you have this tip of the AFM on the outside there is a dried layer of molecules and when it comes into surrounding with some moisture then that moisture droplet takes those molecules within the droplet. Then wherever you place the tip that droplet will be placed at that position. So, that is how you pattern a surface using a dip pen lithography. So, this is a picture.

(Refer Slide Time: 22:59)

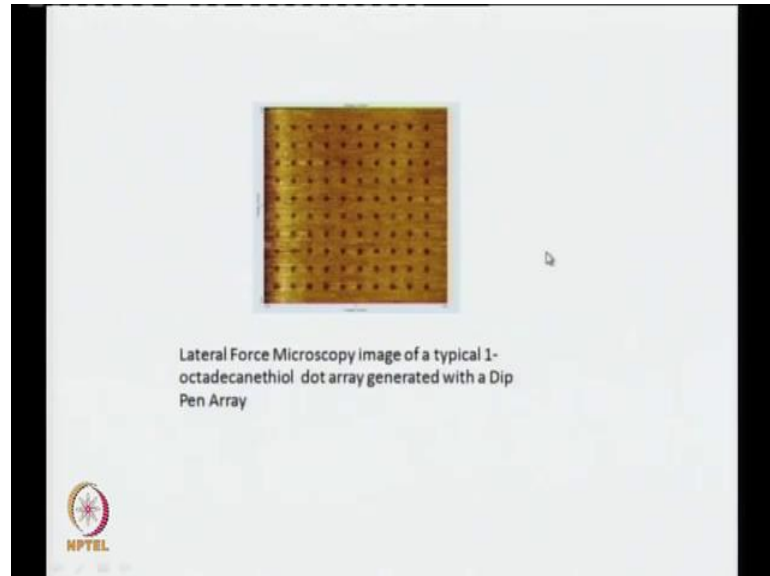


So, you have here the AFM tip which you can see the sharp tip of the AFM. Schematically you are been shown that there are several molecules which are on the surface of the tip. These are assume to be dried the molecules are sticking onto the surface. Then when you have a droplet formation, because of moisture or some other solvent, then these molecules from the tip get into the droplet and wherever now you take this tip the molecules will be transferred on the surface.

So, if you move this tip like in this manner. So, the molecules are getting patterned on the surface in this manner. So, this is typically a dip pen nanolithography by which you can generate self-assembled monolayer which are called SAM's. This is a typical picture an AFM picture of these molecules, which are like fifty nanometer thick monolayer of molecules which is assembled on the surface. This is called self-assembled monolayers used in dip pen nanolithography basically using an AFM tip to place the molecules at precise positions on the substrate, without using etching or any technique. This is going

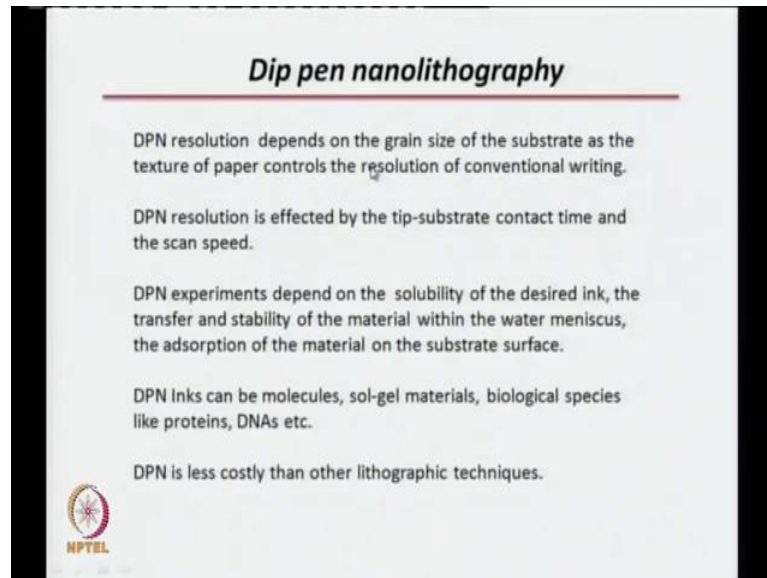
to form on top of the surface. So, this is another image of such array of assembled molecules.

(Refer Slide Time: 24:46)



This is octadecanethiol molecules, which are arranged in regular fashion using a dip pen nanolithography. This is an AFM image it is a kind of AFM image called specifically LFM, which is lateral force microscopy. This will be taken up in a different case where a different types of AFM microscopy is being discussed. So, it is a kind of AFM which is called the lateral force microscopy, where basically you are trying to measure the lateral forces not the vertical forces. By which you are transferring the information which you get from the forces which are generated in the layer in the x y's direction onto a map and hence you are getting a map of the molecule. So, what are the things that we do in a dip pen nano lithographic technique. We basically put molecules in a particular pattern using an AFM tip.

(Refer Slide Time: 26:03)



Dip pen nanolithography


DPN resolution depends on the grain size of the substrate as the texture of paper controls the resolution of conventional writing.

DPN resolution is effected by the tip-substrate contact time and the scan speed.

DPN experiments depend on the solubility of the desired ink, the transfer and stability of the material within the water meniscus, the adsorption of the material on the substrate surface.

DPN Inks can be molecules, sol-gel materials, biological species like proteins, DNAs etc.

DPN is less costly than other lithographic techniques.



The resolution of the technique depends on the grain size of the substrate. So, if your substrate is very fine grained. Like if you write with ink on a paper if the paper has small grains which is very fine, then it will control the resolution of your writing. Similarly, if the substrate on which you are doing dip pen nanolithography, if that has very fine grains then your resolution will be high, but if you have very large grains then you will have very low resolution.

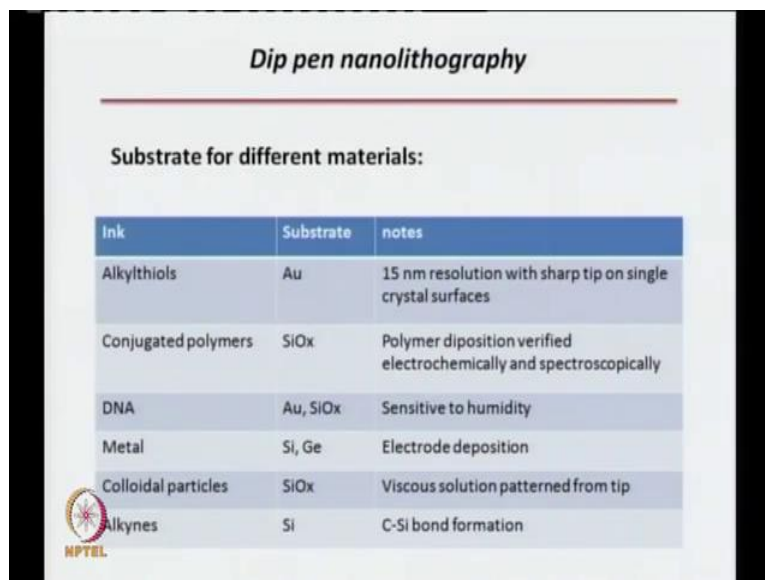
The other thing is that, the resolution is controlled by how much time the tip on which these molecules are there and the substrate come into contact because to make the droplet sit on the surface, you have to bring the tip close to the surface. There is some contact between the droplet and the surface. So, what is the contact time before you lift the tip and take it to another position. So, this contact time is very important which controls the resolution.

Also the scan speed how fast are you moving in the x y direction, you are AFM tip which has the molecules which you want to put on the surface on the outside of the AFM tip. So, the tip substrate contact time and the scan speed both affect the resolution of this lithographic technique. The experiments of course, will depend on the type of ink that you use. That is what is the ability of the molecules and a stability of the molecules within the solvent, which may be water in most cases. So, what is this stability and transferability of the molecules onto the water droplet.

The second most important thing is what is the adherability, that is the absorption of the material. when you put the droplet on the surface of the substrate how good is the absorption of the molecules on the substrate surface. So, this is also very important. What are these inks that we are talking about in dip pen nano lithography. These can be molecules these can be sol gel type of molecules like some kind of alkoxides, these can be bio molecules they can be thiols which are to be a bound to gold particles. They can be bio molecules like proteins or DNA, etcetera.

So, several types of inks can be used and these inks will transfer the molecules of interest on the substrate this technique is much less costlier than many other techniques that we have discussed. Higher the resolution may be less than in many techniques like e beam lithography etcetera. So, it is low cost technique, good for many applications especially in the chemical biochemical pharmaceutical bio sensing kind of industry. It can be used very easily with the resolution, which it can afford. So, if you want high resolutions, then you have to use other techniques like x ray lithography or e beam lithography. So, the substrate.


(Refer Slide Time: 29:30)



Dip pen nanolithography

Substrate for different materials:

Ink	Substrate	notes
Alkylthiols	Au	15 nm resolution with sharp tip on single crystal surfaces
Conjugated polymers	SiOx	Polymer diposition verified electrochemically and spectroscopically
DNA	Au, SiOx	Sensitive to humidity
Metal	Si, Ge	Electrode deposition
Colloidal particles	SiOx	Viscous solution patterned from tip
Alkynes	Si	C-Si bond formation

 NPTEL

So, we discussed the inks, now the substrates for different materials. For example, you want to put thiols onto. So, your molecule is thiol, which you want to transfer on to a substrate typically you will use gold as a substrate. Here you can have resolution with like fifteen twenty nanometers with a sharp tip on single crystal surfaces. So, if you have

single crystals of gold surface, then you can have fifteen nanometer resolution, then if your ink is some polymer.

Then you take some silica as a substrate and this deposition can be verified electrochemically or by using spectroscopy. If you want to deposit DNA, you can use either of these 2 substrates whether gold or silica type of substrate and DNA, this can be sensitive to humidity. So, you have to control the humidity in the chamber where you are doing this kind of lithography.


If you want to deposit metal, then you choose a substrate like silicon. This was silica related this is silicon and or germanium. So, these are available silicon and germanium substrates and you can deposit metal on them. This can be done which is using what is called electrode deposition. Then if you want to use some colloidal particles you can use silica as a substrate and you use. Basically you will get a viscous solution at that tip and then you can pattern using that droplet which is forming at the tip.

In many cases you have to deposit some kind of carbon triple bond, compounds like alkynes. In that case people use something like silicon because you can generate carbon silicon bond formation in those systems. So, these are different choices of substrates depending on the kind of material you want to deposit. Now, if you have, you can apply to many bio sensing applications. This is one of the most important applications using dip pen lithography.

(Refer Slide Time: 31:50)


Biosensor Functionalization by Dip Pen lithography

AFM cantilever is used as sensor to detect miniscule quantities of biomolecules



AFM cantilever Fluorescent tagged protein pattern on the cantilever

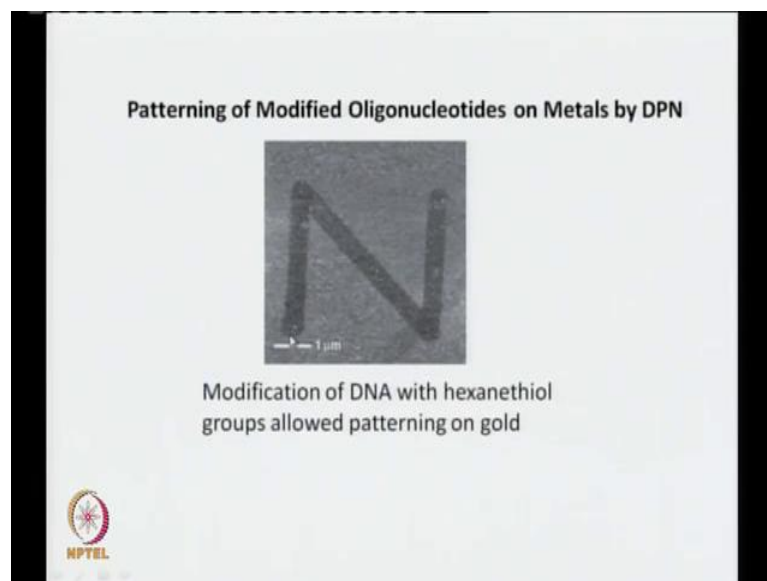
Binding of the target molecules to the cantilever affects the change in cantilever dynamics (stress, resonance, deflection)



So, this is an example. So, you have an AFM cantilever as your tip or a probe and you are going to use it as a sensor to detect small quantities of biomolecules. So, in this cantilever, this AFM cantilever you can have fluorescent tagged protein on the cantilever. If you bring it close to a surface, which the protein will bind. Then you can study this as a change of the fluorescence. So, actually binding will cause change in the cantilever dynamics like in AFM, you have this cantilever which basically measure the force of the cantilever in the presence of a surface.

Now, you can modify whenever this kind of binding will happen the stress or the resonance or the deflection of the cantilever will change. You can monitor that and if you have fluorescent tagged protein you can monitor that using fluorescence. So, this is a very important application. I think the most important application where dip pen lithography has been useful and will be useful in basically sensing biomolecules.

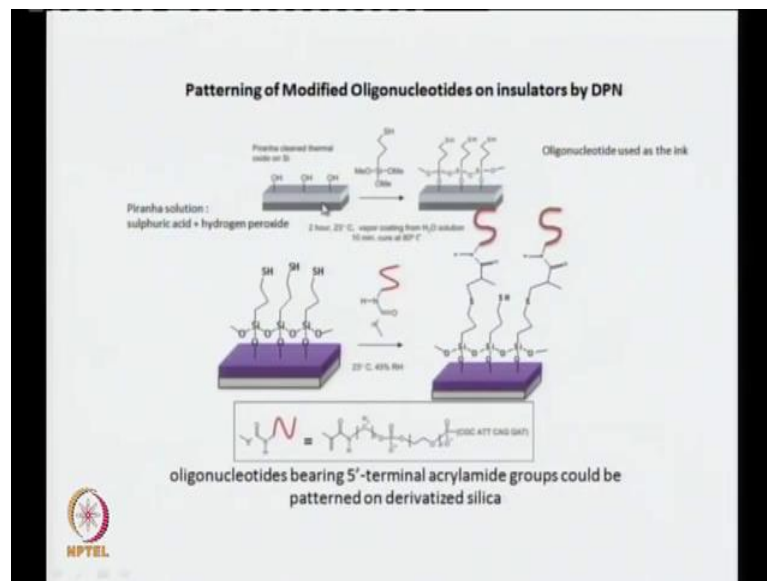
(Refer Slide Time: 33:10)



Now, this is a pattern of some oligonucleotides on a metal surface. So, you have a metal surface on which you have a pattern, which is made up of some molecules which are some kind of nucleotides. So, basically you can use DNA with hexane thiol which you pattern on gold. So, the more detailed methodology is shown in this slide. That you take a substrate, which is your say your gold or silicon here it is silicon. So, you clean the silicon surface with what is called a piranha solution.

The piranha solution is a very kind of corrosive solution, which is a mixture of sulphuric acid and hydrogen peroxide and it is used to clean silicon surfaces. So, once you clean silicon surfaces, you also generate hydroxyl groups on the surface. So, the piranha solution is useful because it not only cleans the surfaces, it also generates hydroxyl groups on the surfaces. Now, when you generate this hydroxyl group on the surface and you ultimately want to attach these oligonucleotides. So, first what you use is you use a thiol. So, this thiol is based on some silicon compound.

(Refer Slide Time: 34:42)



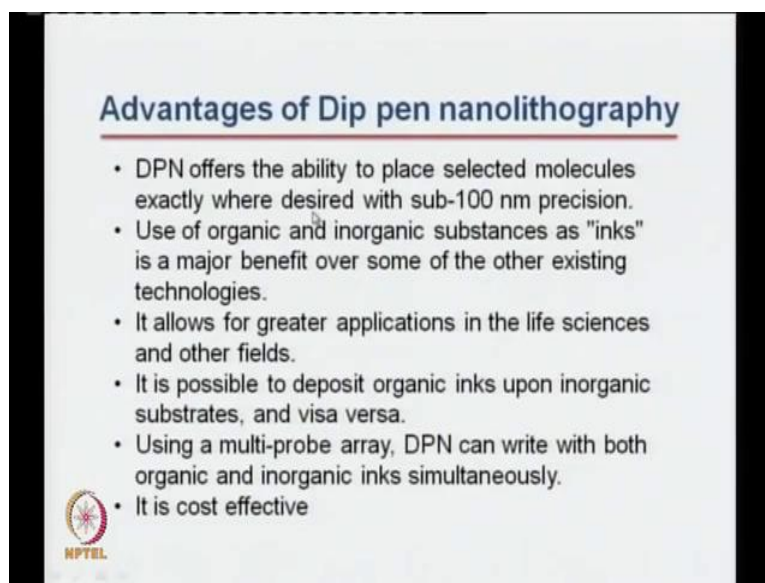
So, you have these alkoxy groups which are methoxy groups and on one side. So, silicon has tetravalency. So, you have 3 bonds with alkoxy groups here methoxy groups the fourth one is related is connected to a thiol group. Now, when you react this surface with thiol groups will come and bind the silicon group will come and bind here. So, you will have this oxygen groups will react with the alcoholic groups and you will get loss of water molecule and you will have this molecule with a thiol a dangling outwards.

So, you are your converted an alcoholic group on the surface to a surface which now has got dangling thiol groups. Next, you use this and react it with the nucleotide of your interest. So, here the nucleotide is something like that which has got a kind of this oligonucleotide which is a 5 prime terminal acrylamide groups are there. This thing can react with your thiol groups.

So, here you see this carbon will react with this thiol group and will bind to this molecule. So, you started with an alcoholic group on the surface. Then you generate a silent thiol group on the surface, then when you react with this nucleotide of this particular composition. These are the bases as you know and then you get this final layer which has got this nucleotide dangling on top of the surface. So, you now have functionalized the surface with a nucleotide of a particular type, which you wanted of a particular sequence that you wanted.

So, this is a very important application using dip pen nanolithography where you can use a surface and this technique to pattern oligonucleotides and other biomolecules. Then this can be used as a sensor for molecules, which can be selectively recognized by these nucleotides.

(Refer Slide Time: 37:10)



So, the advantages of dip pen nanolithography, it has the ability to place selected molecules exactly where desired, but with the precision of around somewhat close to hundred nanometers or slightly less than hundred nanometers. You can use both organic and inorganic substances as inks. This is a major difference compared to other existing technologies. It allows for greater applications in the life sciences and other fields. It is possible to deposit organic inks upon inorganic substrates and vice versa.

Using a multi probe array you can write both with organic and inorganic inks. So, both can be done simultaneously and it is cost effective. So, the precision is not as great as

you will get in e beam lithography or ion beam techniques or x ray lithography, but you can do several patterns, several modifications easily at low cost with bio molecules with this technique.


(Refer Slide Time: 38:32)

Scanning Probe Lithography

Probe:
STM, AFM

Techniques:

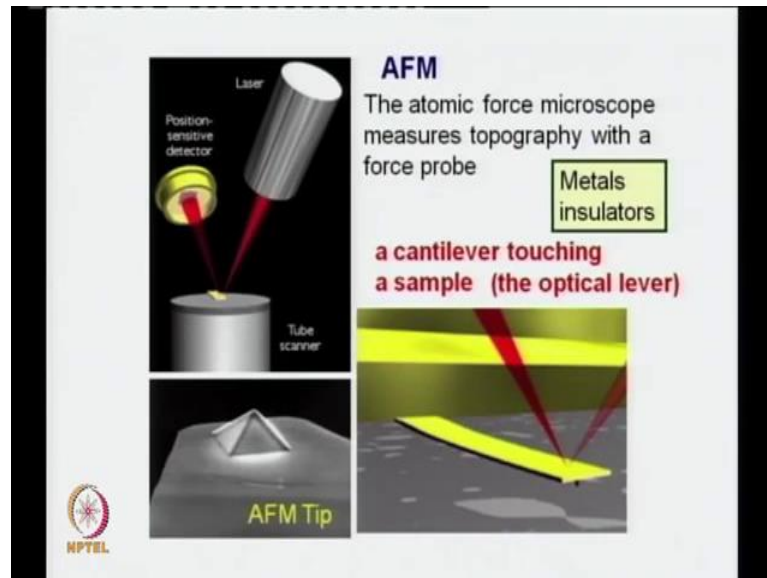
- Voltage pulse (AFM)
- CVD (STM/AFM)
- Local electrodeposition
(substrate in solution and tip as local counter electrode. Example
Co on Au) (AFM)
- Dip-pen (AFM)

 NPTEL

Now, the other technique which we are going to discuss today is the scanning probe lithography. Scanning probe microscopy involves AFM STM and all those kind of technologies which have been developed from AFM and STM. Basically scanning probe means you scan a surface using a tip which is the probe. Now, instead of doing microscopy which is the most common term scanning probe microscopy people discuss quite often, which involves looking at a surface using AFM or STM. Here what you are going to do is you are going to write using those techniques.

Not just see the surface, but you are going to change or pattern the surface using the same techniques of STM and AFM. So, STM and AFM today can be changed to several types. So, modifications are there. So, there are techniques like the voltage pulse method or you have the CVD method or local electro deposition, where the substrate is in solution and the tip as a local counter electrode. An example of that is cobalt on gold using an AFM tip or using a dip pen lithography using again an AFM tip. So, basically scanning probe lithography is using scanning probe techniques like AFM STM to write patterns or draw patterns on surfaces. Whereas, scanning probe microscopy is using those techniques to look at the surface to see the surface.

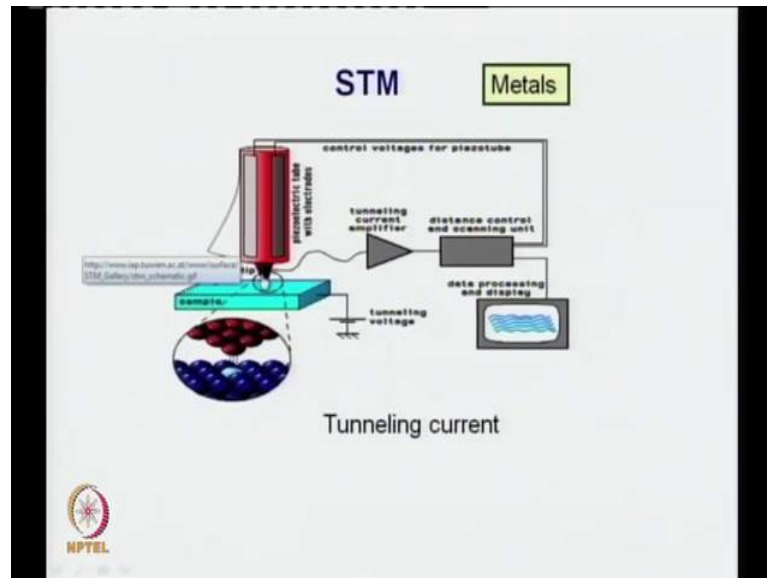
(Refer Slide Time: 40:19)



Here we are trying to make patterns on the surface. Basically an AFM all of you know that involves a cantilever and a typically you shine a laser on the cantilever. The cantilever if it has a deflection because of the surface will show up in the detector because the laser beam will move its position. From that you can calculate the force between the cantilever and the surface.

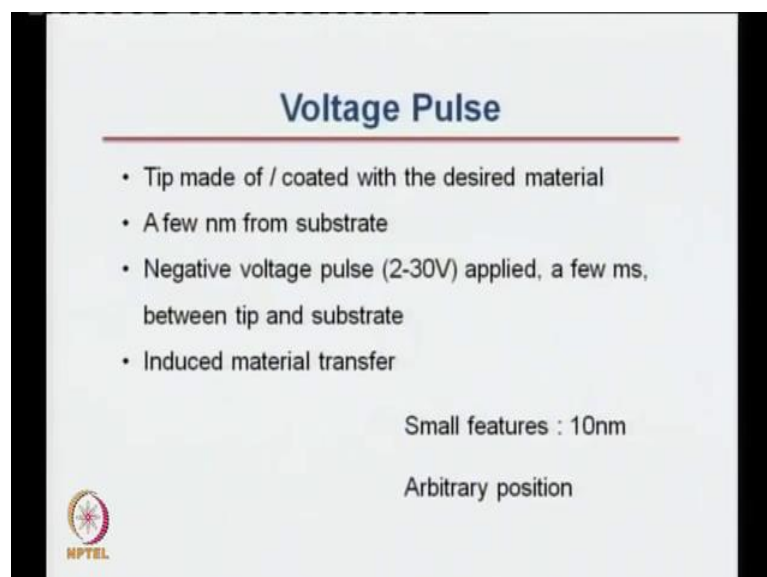
This is the typical method how you measure or look at the surface topography using a force probe. Hence this is called automatic force microscope. This is a more broadened view of the cantilever, which has a tip at the base. So, this is the cantilever and this is the tip, this is the AFM tip which is at a pointed. So, you on that surface to probe any surface to look at a surface you basically look at the changes in the forces at different positions on the surface and you draw a topography map. Now, you are going to use the same probe, but you are not going to look at the surface. You are going to make patterns on the surface using the AFM.

(Refer Slide Time: 41:35)



The STM again has a tip, but now you do not measure forces, you measure tunneling current on the forces right. This allows you to understand the topography of the surface. This is a typical scanning tunneling microscopy, where you measure the tunneling current and understand the topography of the surface. However now you are going to use the same tip of the scanning tunneling microscope and we are going to measure. You are going to make patterns on the surface.

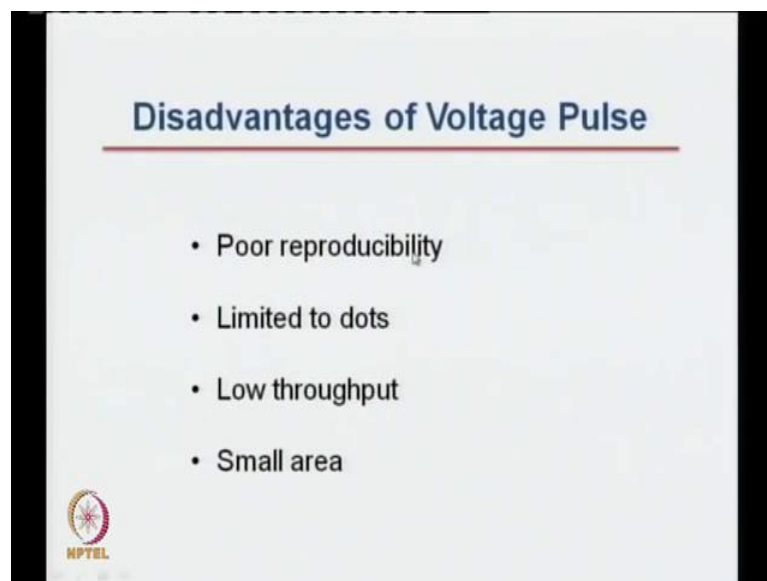
(Refer Slide Time: 42:10)



So, what is the voltage pulse technique. In the voltage pulse technique you make your coat the desired material which you want to pattern on a tip right. It can be made of the tip or it can be coated on the tip and it has to be brought close to the substrate. So, a few nanometers from the substrate. Then you apply a negative voltage pulse, say of the order of 2 to 30 volts and for a small time of few milliseconds between the tip and the substrate.

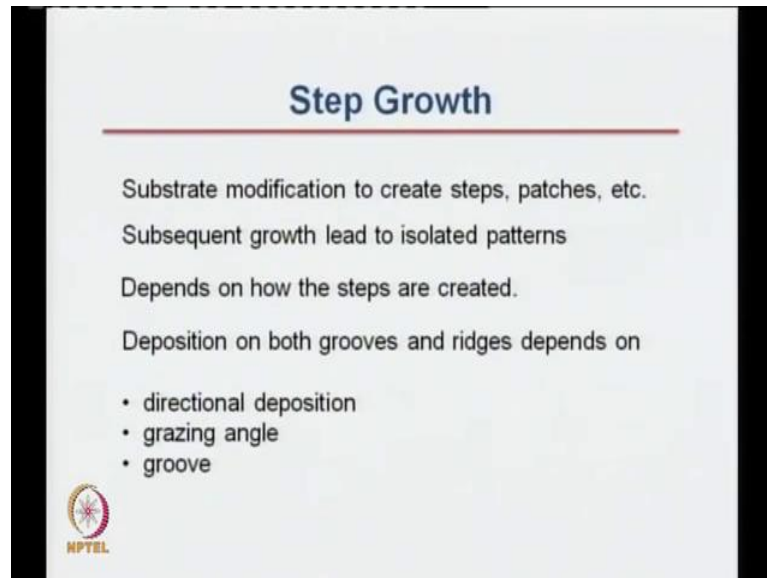
When you apply this voltage for a small time, there is transfer of material from the tip to the substrate. So, using a voltage pulse you are patterning your transferring the material which is coated on the tip onto the substrate. So, by this technique you can make small features of around 10 nanometers. You can go to some arbitrary position. The position is not very, very precise of course. The disadvantage of voltage pulse technique is poor reproducibility because every time you cannot go to the same position.

(Refer Slide Time: 43:23)



The same position it is limited to dots. So, you cannot make too many different types of patterns you can make dots and it is low throughput methodology. So, you cannot do large scale patterning a large scale not many size many number of patterns you cannot do using the technique of this particular voltage pulse, scanning probe lithography. You are normally using a small area. You cannot also do this kind of lithography on a large surface. You can have modification to this. You can have what is called the step growth in the step growth you must have a substrate which is modified to have steps or patches.


(Refer Slide Time: 44:17)



Step Growth

Substrate modification to create steps, patches, etc.
Subsequent growth lead to isolated patterns
Depends on how the steps are created.
Deposition on both grooves and ridges depends on

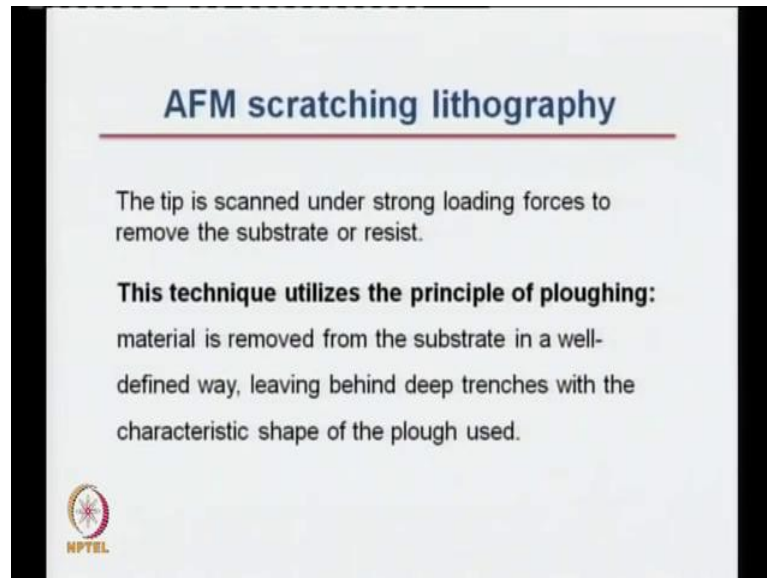
- directional deposition
- grazing angle
- groove



Subsequently, you can grow molecules to lead to isolated patterns. This will depend on of course, how you make the steps. So, the first step that you have to create steps or patches that will ultimately lead to the type of pattern you will get. So, it depends on how the steps are created then you can do deposition on both the grooves and the ridges that is between the steps. That depends on how you bring in your probe.

So, you can do directional deposition or grazing angle or there is a groove method, how to pattern the surface. So, that will depend on the technique that you apply you can do all the three. You can have directional deposition, you can do grazing angle deposition or you can deposit on the grooves.


(Refer Slide Time: 45:11)



AFM scratching lithography

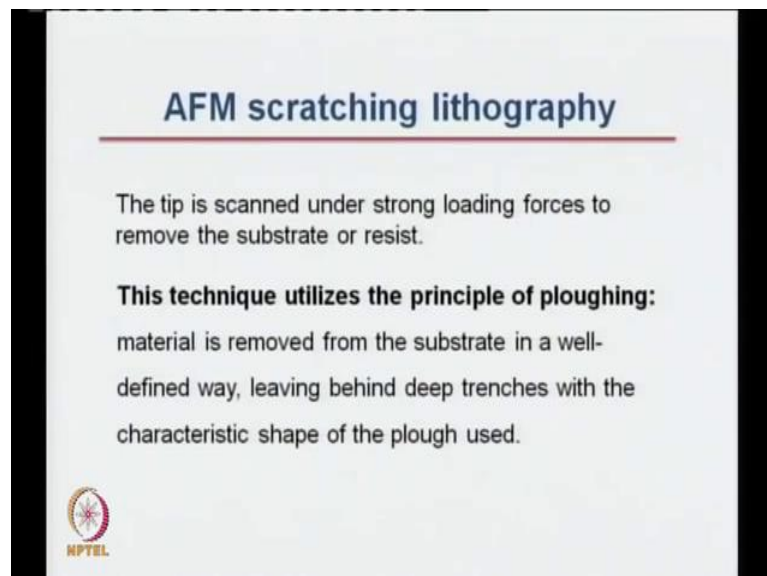
The tip is scanned under strong loading forces to remove the substrate or resist.

This technique utilizes the principle of ploughing:
material is removed from the substrate in a well-defined way, leaving behind deep trenches with the characteristic shape of the plough used.



So, for this the most important thing is the substrate has to be modified to create the steps or the patches where you want the pattern to grow. Now, you can also use a scanning probe technique to make patterns by removing atoms from the surface. It is like etching away from the surface the term we are calling it as scratching. AFM scratching lithography that means you remove the atoms from the surface. So, the tip is brought on top of a surface at particular point where you want.


(Refer Slide Time: 45:50)



AFM scratching lithography

The tip is scanned under strong loading forces to remove the substrate or resist.

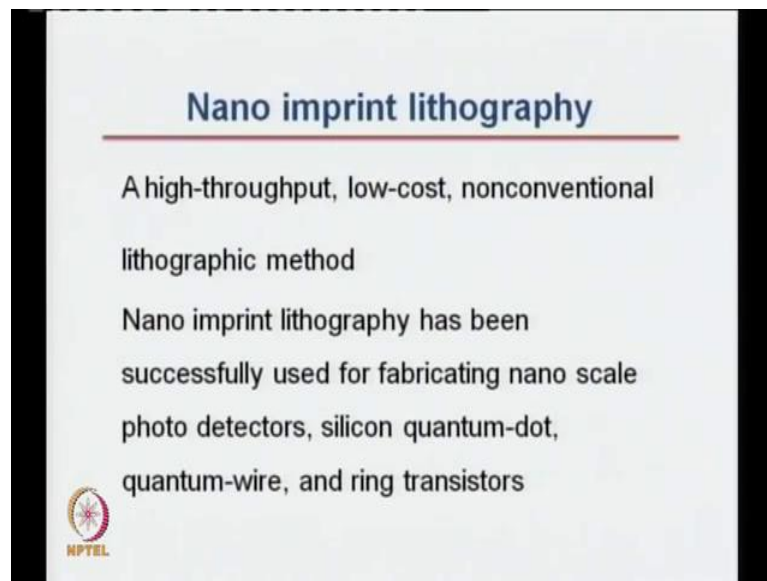
This technique utilizes the principle of ploughing:
material is removed from the substrate in a well-defined way, leaving behind deep trenches with the characteristic shape of the plough used.



A very strong force is applied strong loading force is applied to remove the substrate or the resist which is on top of the substrate. That will remove some substrate atoms or molecules. This technique is like ploughing, like in a field in agricultural land we have seen how people plough on the field and you leave patterns on the ground. This is typically like that. So, you have an AFM tip and you bring it with lot of force. So, lot of load on the surface and then you move the tip.

So, it will leave behind a kind of a ridge, that is you will make a kind of remove atoms and so there will be deep trenches and depending on the type of plough you have used. If you have AFM, which has got 2 tips, then at the same time you can make 2 trench using that particular AFM. So, nowadays you can design AFM's with several tips. So, at the same instant if you have say 5 tips like your 5 fingers which are scratching the surface. You will leave behind 5 lines or 5 trenches. Now, how much deep can you go that and all you can control using the type of probe that you are using.

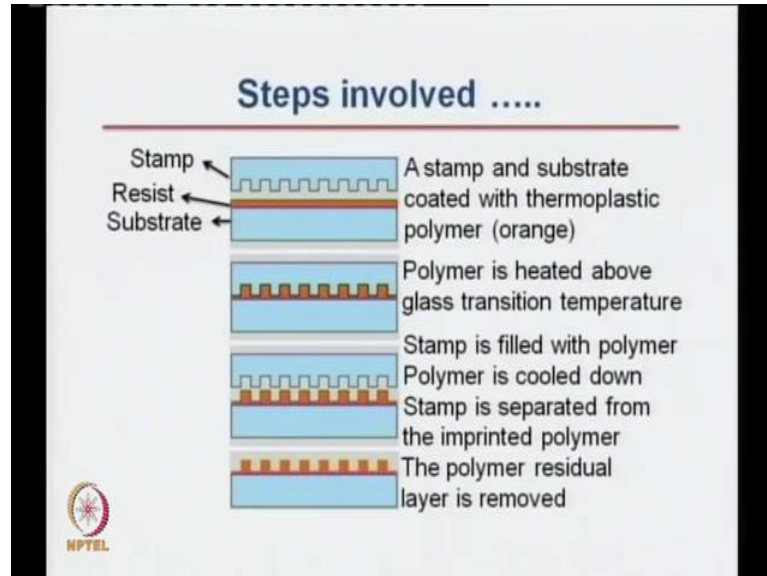
(Refer Slide Time: 47:20)



Now next you can come to what is called another technology, which is nano imprint technology or nano imprint lithography. From the term imprint you can make out that this is like a stamp. You have a stamp you put it on an ink and then you stamp it this is one method like it is called stamping method. This slightly different nano imprint lithography, but has lot of similarities to the stamping technique. A high throughput and

low cost technique. This is a high throughput that means you can do lot of nano or submicron structures using this technique.

(Refer Slide Time: 48:07)



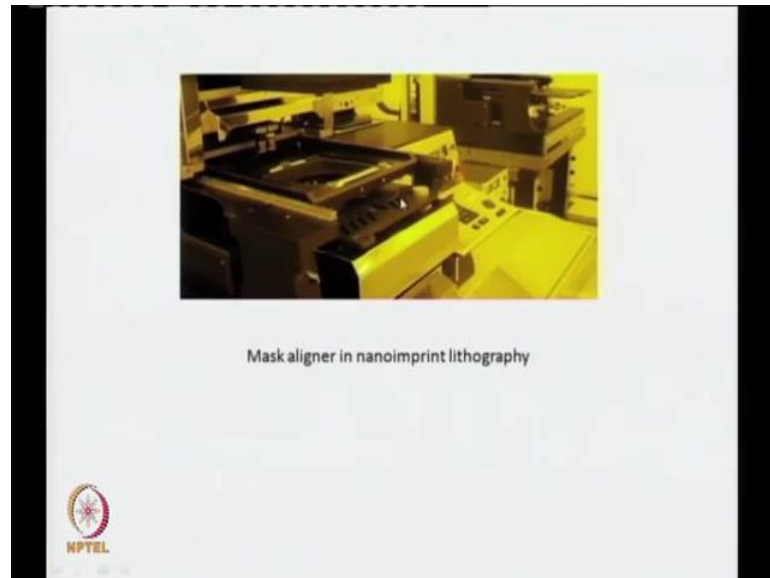
This is being used in large scale you can use it in large scale for fabricating nano scale photo detectors putting making quantum dots, quantum wires and ring transistors etcetera. So, typically what you have is, suppose this is your substrate and then on top you have this resist. So, the substrate is coated with a resist and you bring in a stamp. The stamp is going to leave an imprint on the resist. So, the stamp has some kind of a structure which will be imprinted on the resist. So, this resist is typically a polymer.

So, you bring the stamp, you heat the polymer little bit and this temperature at which the polymer melts is called the glass transition temperature. So, different polymers have different glass transition temperatures. So, once you heat the polymer above the glass transition temperature and you bring the stamp closer on top, then the stamp will be filled by this polymer because the polymer is now a liquid above the glass transition temperature.

So, this polymer liquid will flow in these gaps. So, it will take that shape and then you cool the whole thing. Once it is cooled down then you can remove the stamp out. So, what it will leave behind is this kind of structures on the resist. Then you can remove whatever is in between also you can remove the polymer layer. So, only this part, this particular shape will remain after you remove or etch away the polymer which is present

in this small fashion. So, this is typically nano imprinting technique. You can do large scale imprinting it is low cost and easy to do. Now, how to arrange where the mask will come that means where the stamp will be positioned exactly, how you want to do.

(Refer Slide Time: 50:20)



For that many times you use what is called a mask aligner it brings the stamp exactly at the place, where you want it to come on top of the substrate of the resist. So, this is a picture of a mask aligner in nano imprint lithography.

(Refer Slide Time: 50:30)

Nano imprint lithography

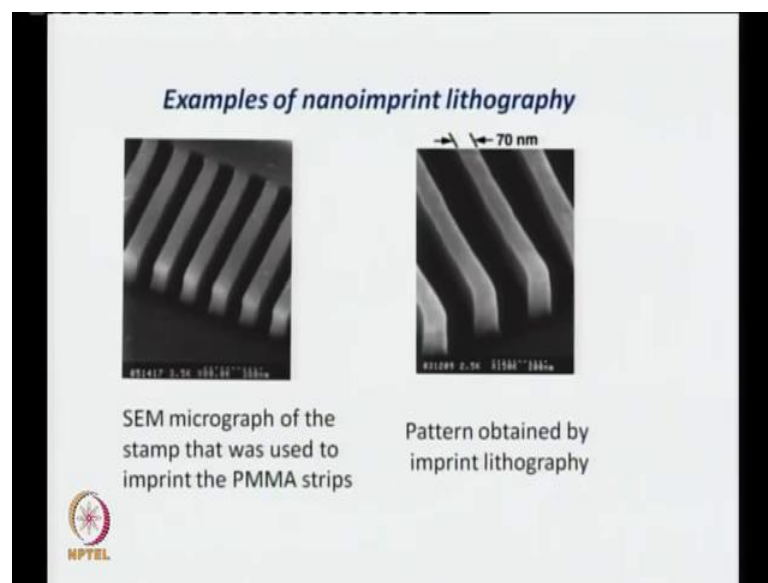
Advantages :

- Up to 25 nm feature size can be obtained
- 70 nm pitch, vertical and smooth sidewalls
nearly 90° corners
- Uniformity can be obtained over an area of
15 mm by 18 mm in a single imprint

NPTEL

So, advantage of using a nano imprint lithography is, you can use up to 25 nanometer feature size it can be obtained with some 70 nanometer pitch with vertical and very smooth sidewalls. So, you can get 90 degrees corner that means absolutely. So, you have a wall and then you have the horizontal floor and it is exactly at 90 degree. So, you can get very perfect corners and you can have uniformity over a large area. So, you area is in millimeters this is the largest size we have. So far discussed we have been discussing everything in microns or nanometers, but here the scale is very large. You can imprint over a range of like 15 to 18 millimeters.

(Refer Slide Time: 51:18)



This is an example of nano imprint lithography. So, on the left this is the stamp and this was used to make an imprint on poly PMMA which is well known polymer, which is poly methyl methacrylate. If you use this stamp on that you get this kind of pattern. So, using this stamp you have got this kind of pattern. So, this is like 70 millimeters here and this is an SEM picture of the stamp and this is an SEM picture of the imprint.

So, you can see the imprint comes on the resist, on the polymer which you have used using this stamp and you can reuse this stamp many times. So, with that we kind of come to the end of today's lecture is also the end of module 2. In which we had 12 lectures and we will start our first lecture of module 3 next time that we meet.

Thank you.