# Instability and Patterning of Thin Polymer Films Prof. Rabibrata Mukherjee Department of Chemical Engineering Indian Institute of Technology, Kharagpur

## Lecture No. # 09 Photo Lithography- I

Welcome back, as promised we will now get started with some of the patterning techniques. In our pervious class, we discussed about the two basic paradigms of patterning at meso and nanoscale. If you can recall one of them was the so called top down method, and the other one was the bottom up or the self assembly methods.

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In this particular course, we will talk about a third paradigm, which is very close to the bottom up technique of self assembly, but not exactly similar and which we will term about as the SELF organization methods. So, this is something that not too many people really discuss, but we would like to sort of places at the third paradigm. And well, this is actually were the name of the course bridges the two. These type of self organization, we have actually few very carefully listen, we have talked about this type of self organization in one of our introductory classes.

And these self organization, we will talk about essentially is based on the instability of various sorts in ultra thin films. We have, I have given you one example one such example and that is based on what is known as the Dewetting; there will be some other settings also, where we will essentially show or our objective is to show that the self organization or the morphological evolution during the instability of an ultra thin film, particularly we will be talking about the polymer films. And why we will be talking about polymer films and not other generic liquids like water, or organic solvents will also I will make it clear to you, in course of due course of discussion. How this instability itself can sort of manifest as viable patterning technique.

So, we will see what are the forms of instability? One approach, scientific approach very significant very important from the standpoint of industry is to how this instability can be inhibited. So in order to achieve that all also, it is extremely important that you have a complete understanding of the instability process. But what we will show is that this these type of destructive instabilities which sort of leads to rupture or disintegration of a thin film. Many cases, it is a spontaneous rupture or spontaneous disintegration can also be sort of used as a viable patterning technique, but that, before that we will look into the conventional techniques particularly the top down techniques; and we get started with what we planned to discuss today that is photolithography.

Again, we have introduced to you, I have talked in the initial lectures that this is one technique on which the microelectronic industry significantly relies on and the phenomenal growth in the microelectronic industry in the form of faster computers, smaller laptops, high resolution display, large or high capacity memories, pretty much everywhere this particular technique has played a very significant role. So it is important, I mean people from electronics background, sort of have deeper understanding of this, this is interestingly one technique where lot of research high end active research goes on; and this is one research area where lot of findings almost every finding finds industrial application. Frankly speaking, photolithography itself can be one full course covering one entire duration.

So, you there are lots of integrity issues a lot of atomization automatic process that have now been incorporated, so all these things are there, but we will sort of talk about some very basic; so that you understand, what the process is? How it works? And what exactly is done in the microelectronic industry or how patterning is achieved. And then we will shift gears to the other lithographic techniques or areas where patterning is done.

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And so, which fall and which are more of polymer specific techniques, So which fall under the category of soft lithography; these methods we will talk in rather greater details including processes like Micro contact printing, Nano imprint lithography, and its variants capillary force lithography, Micro molding in capillaries etcetera, etcetera, But today, we will be discussing on photolithography.

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So, let us get started with what photolithography is, this a quick sort of recap of what we have already told that innovation in the field of integrated circuit is the main, photolithography is the main motive force for the tremendous advancement in the field of microelectronics. These are some numbers you may be interested, transistor was first invented in 1947, the first IC or the integrated circuit was built in 1960; at that time the line width and now, I hope you understand what exactly the line width means, it is the width of P or the N type domains was roughly five microns. So, first IBM PC was developed in 1981 with a 16 kilobyte memory, sounds childish now and a 4.77 megahertz clock speed. For a 40 GB D-RAM, around 1997, it was huge the line width was 350 nanometer; and as we have talked in one of our previous lecture, the line width is roughly around 30 to 35 nanometer for core I5 processors of Intel as of 2011. Now, closer is the packing, better is the performance of the circuit, higher number of transistors you can put so faster other things.

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So again here, it is more of the same things the, a brief history now pictorially, So 1971 Intel 4004 microprocessor; 1985 Intel 386 microprocessor, Pentium 2 around 1997, 2006 Core 2, now, 2011 we are talking about Core 5.

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Pretty much the same thing, this is what I was talking about the line width. So, you now understand that by line width, we are talking about the widths of the P type and N type domains. So, each one of the interfaces of the P type domain and N type domain acts as a transistor.

And what we have briefly discussed, and what we will take up in greater detail that you create these type of arrays of P and N type domains on a silicon wafer, which is the basic building block for the microelectronic industry; as of today is achieved or can be achieved by the method of photolithography. So, this advancement of how many transistors you can place inexpensively on an integrated circuit has given rise to the now famous, now very famous I would say Moore's law, which says that the number of transistors that can be placed in expensively on an integrated circuit doubles approximately every two years. So, what it means that this law predicts or that is how the advancements in the field of microelectronics has gone so far is that the narrow line width sort of becomes half of what has been achieved in a previous year or in exactly two years.

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So, this again a pictorial representation of Moore's law; so it is it shows, So let us say from 1990, where you had a transistor count of one million, it is a sort of looking into billions now. There are technical issues also which are coming up as a consequence of this, so, we will discuss some of these.

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Now, let us look into what photolithography is? This schematic actually captures rather nicely all the significant steps, but I am sure, if I show you this, it would not make much sense to you.

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Also we have a sort of a, we have an animation which will give you an idea about different steps of photolithography. At this point, I will request you to have a look at this one, without worrying too much about what is going on. So, the different steps surface preparation, deposition of the barrier layer, photo resist application, soft bake mask alignment, expose to UV, developing, hard bake, etch, resist strip, these are the different steps, I will give you an idea, what exactly you want to do. So, we will revisit this sort of animation as well as the schematic later, so you effectively understand what it is. So, let us look into it from a very simplistic standpoint.

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You all you essentially have is a surface of silicon, which is better known which comes in the form of wafer, wafer is a disc like material, which can be few hundred micron to about a millimeter thick. Now, you may also know that silicon is a crystalline material, and it is possible to create silicon with different orientations like 1 0 0, 1 1 0, 1 1 1. Now at the very outside, I have told you that we will be having a very, very simple understanding of photolithography, so we will avoid deliberately avoid a lot of integrate netegrities, and we will just have a gross idea about what is necessary to do.

Now it is, you may also know or it may be important to note that silicon has very high surface energy, this is number one. So, when you create fresh silicon or if you break silicon at a lattice plane, it exhibits a surface energy something in the range of 420 to 430 millijoule per meter square. Compare this to surface energy of water, which is roughly 72 degree 72.8 eight millijoule per meter square for water. So, if I now forget about patterning and everything and I ask you, that if I want to dispense some water on a silicon surface, what is going to happen? Most likely what is going to happen, you are going to see a complete wetting.

This is rather uncorrelated to what we are going to discuss today, but whatever we have discussed in this course so far based on that probably this concept should be clear to you now. Now the problem is, since this has a very high surface energy, it is rather unstable whenever it is exposed to atmosphere. And what happens is? As soon as a silicon freshly prepared silicon is exposed to atmosphere, which contains lot of oxygen, which is amongst oxygen and nitrogen more reactive species; that is immediately a surface reaction or there is an oxidation or you can say surface oxidation and what happens is? So if this, your silicon there is a very thin oxide layer or many times it is written as S i O x, because this can be non-stoichiometric oxides also. But important thing to know is that it can be that is will or will definitely be an oxide layer, which is known as the native oxide layer, and typically, this has a thickness of 1.5 to 2 nanometer.

If you have a good quality Ellipsometer, you can measure the thickness. Now, if you remember what we have discussed, we actually want to create this type of an array of P type and N type domains. What is typically done is that when for lithography purpose or fabrication of an IC, a silicon wafer is manufacture typically one type of doping is already given. So, instead of starting off with a bare silicon, which is undoped and then try to create some parts or dope some parts with P type and some parts with N type. Now, let me also tell you that we will skip all the details of, what exactly is necessary to be done to have P type doping or an N type doping, we will avoid the chemistry, but we will conceptually understand from an engineer's standpoint, what processes actually takes place. So, you typically get or get started with let us say a P type doped silicon wafer. So, you have a silicon wafer, which is already doped, let us say P type doped and also it has a 1.5 to 2 nanometer thick oxide layer. So, this is where you get started.

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Now, your essential objective is that if you have, let us say a P type doped wafer, you would like to create on its surface regular domains of N, so that as we have drawn in the previous slide, you actually have P N junction, so this is your object. So, what can be done? The best thing to do is you start off with a type doped wafer, and then somehow, cover it or cover parts of it with something, and then expose it to an environment where there is a reaction at the surface and there is N type doping. So, you have to cover parts of the wafer with something, as of now we are talking that to be a something, later we will talk to the details; so that the N type doping, the chemical which you are using for the N type doping, can have access to the wafer surface only at certain preferred or preferential locations and not everywhere.

So, ideally these are the areas; so, this is what you would like to achieve. So these are the areas, which sort of undergoes reaction and the doping becomes N type, the areas below this covered zones sort of remain P type. So, in other words, so these become N type, this remains P type. The important thing is that when you finally fabricate your I C chip, you also need to remove these covering things the things you have used for covering. But if you the one thing you must realize based on the understanding or thing we have discussed so far; that, if your N type dopant has to sort of have access to the wafer surface, you also need to get rid of the oxide layer.

Otherwise, what will happen? If you have a thin oxide layer, even over these zones, you it will act as a diffusion barrier and this chemical, which you want them to react on the surface of the wafer for the N type doping would not have direct access to the surface. But the other thing to sort of, consider is that if you can have these oxide layer; so, this is the wafer and here you have the oxide layer, if you can do something like you preferentially remove the oxide layer at these areas to have the desired opening; then itself, this oxide layer itself can act as that something what we talked here. Which is covering parts of the wafer, where the your the chemicals do not have access and they have direct access, because the oxide layer is now removed to these parts of the wafer.

But here is a problem, I mean when you are actually exposing your wafer to the environment, where N type doping reaction is about to take place; an oxide layer, if you remember what we talked a few minutes back, the oxide layer thickness of 1.5 to 2 nanometer is too low to sort of cause any significant barrier. So, the first thing we get started is to we deliberately grow on the wafer, the thickness of this oxide layer to few microns so that; and then, we do something to actually do this what we have discussed here. We create or preferentially strip off the oxide layer, according to the design which we want to create, so that when you have the N type doping, it has access to only this parts of the wafer surface.

So, the doping these areas become N type doped, the wafer remains P type doped so on the surface; you actually have now P N type junctions over here, here, here, and here. And then what you need to do is to remove the oxide layer; so that you have a wafer with which now has this P N junction. So, in a natural this is what we want to achieve. So from a flat p, you would like to go to this type of a structure and that is associated with these individual steps.

So now, if you relook into the animation we had seen a couple of minute back, I think some of the terms will now make sense to you; at least the term second term deposition of the barrier layer. So, this is essentially what we mean that on the wafer which we have taken, we now deliberately grow the oxide layer. So, it is this particular thing we are talking. So, the you essentially grow the oxide layer. And then, so if you relook at the animation now, so this, you should also understand now that you get started with a P type silicon substrate, then you grow the oxide layer on top of that. And then, subsequently what you would now try to do, I will come to what this photo resist and all these things or what the mask is doing and all these things.

But based on whatever little thing, we have discussed our final objective see what we actually want to do. We are, even if you are not understanding anything of these steps does not really matter, we will slowly make progress and we will understand each of the steps. But look at something that will make sense to you and it is this. So, this is something that should make sense to you now. So, you had taken an oxide layer, as we have discussed; and we have now created a pattern on the oxide layer, where you sort of see that the N type dopant which can be phosphorous has direct access only to the area over here to the surface of the P type doped silicon substrate or the silicon wafer over which the oxide layer has been preferentially removed. But now, as you see from point number two to this dopant stage there are lot of intermediate steps; so, definitely they will they sort of help in the achieving the process, so let us gradually discuss some of them.

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So, we get started with the process of wafer cleaning; of course, the wafers are chemically cleaned to remove any particulate matter on the surface, as well as any type of organic, inorganic or metallic impurities. This might sound rather simple, but reality is in a microelectronic industry, cleaning is a very, very significant business, because if your initial starting wafer is not cleaned, if there are any particulate matter or anything it is going to spoil your entire chip. Because of the simple fact that we talk that even in a Pentium 2 processor, in late nineties the line width was 350 nanometer. Now, in an I5 core processor the line width is roughly 30 nanometer.

Compared to this, the dimension of a typical dust particle, it is anything between 10 to 50 micron. A human hair, depending on the texture of individual persons here the width of a human hair is roughly 50 to 70 microns. So, you can understand that one dust particle sitting on the surface of a wafer is like mount everest sitting and every subsequent process gets completely distorted or damaged, because of the presence of dust particle. So, the first step is extremely important were you achieve the proper cleaning of the wafer. Now, this is what I told you, if I really want to wanted to give you a detailed description of how industrially it is achieved, there can be anything between 30 to 70 steps involving cleaning of different sorts, different solvent, different type of environment, etcetera, etcetera.

And in industrial scale, it is fully automatic; I mean, hardly a human hand intervention of any human being is sort of encouraged. Next thing, once you have the cleaned wafer, is of course, you understand that is to do the develop the barrier formation or essentially to grow the oxide layer to the desired surface, desired thickness. Oxide layer is very thin, so silica layers SiO 2 layer is grown on the wafer. At this stage, typically you place your wafer in an oxidizing furnace at high temperature, where there is a reaction of oxygen on the surface of the silicon and you can lead to the growth of the oxides here. (Refer Slide Time: 25:34)



So after this, you are in a stage like this, you reach this stage; so, you have the wafer and you have the oxide layer. Now, we have to introduce you, I have to introduce you to another very important term or any a very important item, that is necessary or used extensively in the photolithography industry, that is the photo resist.

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So, the next step is the photo resist application and the subsequent processes are known as the photo resist processing steps. And which essentially involve the primary steps of dehydration and priming, resist coating, soft baking, exposure, development and post development inspection. So, all these stages in photolithography or in the flow diagram or flow sheet of photolithography fall under the category of photo resist processing. Now, in order to understand this, the first thing you need to understand or know about what exactly is photo resist?

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Well, photo resist is nothing but a special class of photosensitive polymer and it has primarily two basic functions, it is the material that sort of helps in precise pattern formation. So, if you look here and you now try to get back and correlate to the animation what we saw, our intension is to create something like this. So, you essentially would like to create a sort of a patterned array of the oxide layer on your silicon wafer like this may be. So, these are the areas which remain exposed to that where the P type wafer is exposed to the N type dopant and other areas are covered with the oxide layer. However, these type of a pattering or a direct patterning of the oxide layer is not possible, direct patterning of layer is not possible.

However, what you can do or what is being done that you start up with a wafer have the oxide layer, apply this polymer, another thin film of this polymer photo resist. And this is the addition of knowledge at this stage, what you are going to have we will show you how it is done; it becomes possible to pattern or create regular structures on this photo resist layer. So, you start up with a uniform layer of photo resist and then you can do something. Again, I am using the word something a very vague word hardly should be

used in science, by which you can eventually create domains of the photo resist layer like this. So, these will be sort of strips of photo resist and you can do, so these areas, you have the oxide layer is now exposed. So, this is possible to achieve.

Now, if you look back at the animation again, probably you will understand our philosophy little more detail, as compared to what you understood so far. So, here you have the oxide layer, now you coat a layer of photo resist, so what is photo resist? And what exactly it does, we will see. Subsequently, this about this hardware element mask, I have not talked about yet. So, you place the mask and whatever these are processing steps, I have not, but these, whatever you are seeing falls under the photo resist processing steps, but what you now understand is that it becomes possible to create the structures in the photo resist layer.

So earlier, we expressed our desire or intension that you effectively want your wafer and on top that you want to have patterned oxide layer, but we then say that direct patterning of the oxide layer is not possible. So, what you actually, however what you can achieve is that you can take a photo resist layer a flat foot a uniform thick, uniform photo resist layer on the oxide layer; and then can create structures or patterns within that photo resist layer, above the oxide layer. So, this is what you are seeing here, that you now have a structured photo resist layer and then what you can subsequently do in one of the steps that is written here, we will discuss it when time comes. You can preferentially remove the oxide layer that is below the photo resist layer or the exposed part of the oxide layer. So, if you look at this hand drawn figure; so, you start off or let me draw it again. (Refer Slide Time: 31:33)



So, you sort of this is the wafer, this your oxide layer or the barrier what you have grown, you coat your photo resist, we will be using the (()) P R pretty routinely. Then, in the subsequent steps, you pattern your photo resist layer, you still have the oxide layer and you have the wafer, which is let us say P type doped, but subsequently, so this is PR the blocks or isolated patches of the photo resist. However, you now have direct access to the oxide layer or only a regular domain of oxide layer, which are covered by the photo resist layer and visible; so in the subsequent step, you may want to sort of strip off the oxide layer like this. So, this in principle gives you direct access to the wafer surface. Now, in the subsequent processing steps, of course, before you plug in your dopant chemical, which might actually react with the photo resist layer also, you would like to remove the photo resist layer and you probably how it is done and all that we will come.

So, you have the oxide layer and then you have pass the chemical for N type doping; so, these layers the these oxide layer which are now artificially made thick by growing the oxide layer act as barrier over these zones; however, the dopant attacks the surface over these areas and you get PN type junctions. So, I think schematically or conceptually is it, I hope the, what we desire to achieve is clear. So in order to achieve that, we need to have these photo resist layers, first it has to be coated. We also need to understand what exactly is photo resist? though we would not bother too much about its chemistry, we will learn or we will understand that there are two major types of photo resist; which are known as some of you might know, if you do a Wikipedia search or search the net you

immediately get lots of search results; one is known as the positive photo resist and the other one is known obviously, it is easy to guess now, negative resist.

Often, these positive and negative photo resist are also marked as the tone of the resist. So, we will understand what it all means, but then comes the question that you need to create these patterns in photo resist, it is easier said than done. Now, what exactly these patterns you are you are doing. So, if you remember that in our previous lecture, we talked about the regimes of top down techniques, where you start off with something larger and then at the macroscale may be you go to lathe machine and remove some of the materials or do some turning. So, the question to ask is that approach matches that you start off with a photo resist layer, which covers everything and then you create or take out the material, as you found is bound to get a feeling that well what ultimately have we done.

We have actually removed the materials over here; so that way, it is pretty similar sort of turning and operation. You start off with the larger material; you remove some of the materials preferentially and create your structures. But I think, I mentioned to you in the previous class that the biggest problem or the challenge now is that, if you remember that we talked about a talking about a line width, which is let us say thirty nanometer. So, actually what you are doing that you are taking off material of an area, which is only 30 nanometer wide, this cannot be achieved with any of your conventional techniques.

So, in order to achieve this and this is going to be very, very regular. So let us say, it is a few centimeter square area over which you are going to now have 30 nanometer lines like this. So, how do you do that? So, it turns out that this operations is done with the help of a hardware element; another hardware element, which you just saw in the in the animation that is known as the Mask. So, what you essentially try to do, this mask is like an original which you want to sort of Xerox. That is precisely, the concept that is applied here.

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So this photo resist, I will come to the detail, but let me just spend a couple minute to give you a very brief idea about the technique; as it turns out from the name that this is a special class of polymer of Photo Sensitive polymer. So, if you expose it to light, its property changes. We say changes, what does it mean? Well, it can actually sort of its property can improve or it can sort of crosslink or its property can degrade.

So this difference, whether this upon exposure the there is an enhancement of the property or the degradation of the property is actually taken care by the PR or the photo resist tones. So depending on, whether you have a positive photo resist or a negative photo resist, there will be a change of property. The details, I will come later at the appropriate moment, but at this time, let us sort of very simple try to explain what it is? So, if you take a photo resist layer on an oxide growth silicon or it can be any other material SIW, I will be using for (()) silicon wafer. And if you expose it to light, what type of light? Typically commercial photo resist work, ideally it can be any light, but these as we will show in one of our subsequent lecture that these resists sort of show a very preferential absorption peak towards ultraviolet light.

So, if you expose this resist to let us say an UV light, then what is going to happen is depending on its tone, there will be a uniform change in the photo resist property. So, suppose you a positive resist or a negative resist, I am still not covering that. So, suppose you have a resist, which has a property that upon exposure to light, it sort of degrades.

So, if you expose the photo resist film to UV light, then whole layer will degrade. In contrast, if you are using a photo resist, which has a property that upon exposure to light, its properties will enhance. Then what will happen? If you expose it to UV light, then the property of the whole layer will enhance. But now, if you can think of a mechanism, by which you preferentially expose some parts of this photo resist layer to light and you blind off or blank off some parts.

So, what can be a possible mechanism? Suppose, you use a hardware piece or hardware element like this, it can be simple slits. So, here you have a slit. So, these are some material is there and in which you have created some slits. This is just for an example, what I am giving, but this actually will give you a very nice idea about how a mask works. So, this is a piece of, let us say glass or metal or whatever it is and you have slits. So, if you now suppose, if you want to keep this on the surface of the photo resist layer. So, let us say the here is my photo resist coated wafer, and on top of that I place this particular block, which has let us say slits over here and I expose to UV light, what is going to happen? Let us say that these areas are opaque to UV light.

So in other words, the light sort of passes only over these areas and nowhere else. So, only over the slits the light passes, so what will be the consequence on the photo resist layer. The consequence will be, only over the areas where the light has passed; there will be change in photo resist properties. I hope the concept is clear. We talk about a photo resist layer; we understand that it is a special type of a chemical, which is photosensitive. So, if you expose it to light, which can be UV light; what happens is? There is a change in the property. Now, we have not talked about it in details yet, but there can be two types of photo resist tones, depending on whether it is a positive resist or a negative resist. If you expose the resist to light, the UV light there will be a change in the property.

So, if the whole photo resist coated film is exposed to UV light depending on the nature or the tone of the photo resist; either the whole layer will degrade or the whole layer there will be enhancement of properties. Now, what exactly is the enhancement or degradation we will come in to in greater detail. But if you expose, here is the important thing, if you expose your photo resist layer to UV light, then whatever is the change in the optical property that will occur across the entire zone or the entire film. Now, if you take a simple hardware piece, a commercial mask is not exactly like this, but for our understanding, let us say that we take a piece of opaque material and we create slits, opaque to UV light or the light you are exposing for photolithography. So these areas, it is opaque; and the other areas, it is transparent.

So, if you now place this hardware piece between your UV light source and the photo resist layer, then what is going to happen, is that UV light can pass only over these areas, and it cannot pass over these areas. So, it is going to sort of have some hindrance in its path and the photo resist layer, below which can be placed right on the photo resist film; the photo resist layer below this hardware piece will get exposed, but only these areas which were below each one of these slits will be exposed to UV and undergo a change in the property. So now, even on the uniform photo resist layer, there will be domains which now have different chemical property different property. And this difference is property; difference in property is due to preferential exposure to light or UV. So, this is important and for all practical purpose, this hardware piece is what is known as the photolithography mask.

So, here we add a little more to the story now, you have photo resist coated layer, then what you do? You place a mask. So, this is the mask. Let us say these are the opaque domains and these are the transparent domains. Now, you expose light, expose it to UV light. So, what is going to happen? These areas of the photo resist layer, which fall below the transparent domain, will undergo some change in their optical properties or will undergo some change due to their exposure to UV light. And you know these are photo resist, so these are photosensitive material. So, because of that photosensitivity there will be some change. And now, when you remove the mask, you still have an intact photo resist layer on an oxide layer, but you already have created domains within that photo resist layer, which are exhibiting different property as compared to other areas; or you have domains corresponding to the design of the mask and which has been subjected to UV light. So, essentially you create your original pattern on the mask and that preferentially gets transferred onto the photo resist layer

So, before I stop this class, let us have a quick look again at the animation. So, this you understand now oxide layer, this you also understand we now apply a photo resist layer. We now understand this. We have a mask here and this mask has a special feature. So, let us say, it allows transferring of light only over these areas, and other areas its opaque or it can be opaque over these areas, and other areas it is transparent. You place this

mask on the photo resist layer, and now you expose it with UV. So, depending on the type of mask, the areas which were sort of transparent, there is a change in the property of the photo resist layer. We will pick up the story from on further discussion on photolithography, from this point in our next class.