Carbon Materials and Manufacturing
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Lecture - 27
Photolithography

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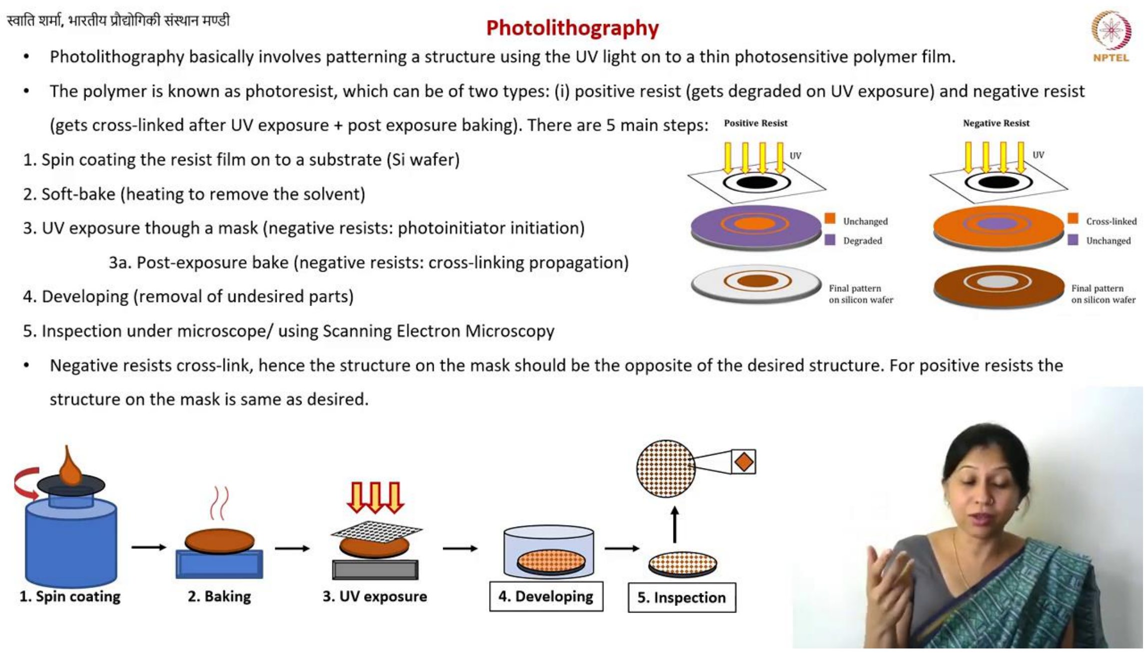

The first technique that we are going to learn is known as photolithography. This is one of the most commonly used techniques in microfabrication also. It is important because the polymers that are used in photolithography, they yield reasonable glassy carbon. Now, forget about glassy carbon for now. In this slide, I am going to tell you what is photolithography. This is a highly simplified version.

I am telling you some very fundamental steps of photolithography to give you an idea of what is done. But if you want to learn more about the optics of photolithography, then there are so many NPTEL lectures on Microfabrication. So, you can then refer to those lectures for further details.

So, photolithography involves UV light. Now, how does it involve? How do I use light as a tool? So, light can be used as a tool if the material that I am dealing with is sensitive to that light. You know that there are many materials that are photosensitive. You leave them in the sunlight and something bad will happen to them. It changes their chemical structure that is what is actually happening to them. So, you have photo-sensitive materials.

Now, photosensitive materials may be sensitive to different wavelengths of light. All materials do not have absorbance at the same wavelength. So, they may be different photosensitive materials that may be sensitive to different wavelengths of light. Now, in the case of photolithography, we are particularly using materials that are sensitive to UV light. And these materials are known as photoresists or commonly you just call them resists, but these are called photoresists.

Now what happens when they are exposed to UV light? Two things can happen; either they chemically degrade, or in some cases, you may even get larger molecules, they harden because they get cross-linked with their neighbors because of the UV light.

You get a larger chunk of material or your material completely degrades. So, these can be two possible effects of the UV light, and that is how you also then define your resist. Photoresist can be of two types; one is known as negative photoresist and the other one is known as positive photoresist.

And I will describe why would you call something negative and positive. The definition is that the positive resist would get degraded when it is exposed to the UV. And whatever gets cross-linked after the UV exposure, you will call them, those kinds of raw materials, negative resists. And there is a very minor difference in how you perform photolithography.

First let us talk about the five main steps of photolithography. What do you do? You take silicon wafer. Silicon wafers wafer looks like maybe in the next time, I will show you an image. So, a wafer as the name suggests, is very thin it is a wafer and its typically a circular wafer, you can also get square wafers that are used more in the case of solar cell fabrication. But for photolithography and so on, you will get these circular wafers. They are typically either 4 inches or 6 inches in diameter. And these are actually single crystals, you can draw really large crystals of silicon.

And then you can make wafers, you can slice them into thinner wafers. And then of course, you can also have p-doping in the wafers and n-doping in the wafer. You have a different crystal orientations in the wafers 1 0 0 or 1 1 1 plane. So, again that is the separate topic altogether.

But, you take a silicon wafer, now on top of that, you pour your photoresist. So, in this schematic I have shown, that the grey circular thing that is the silicon wafer. And the big drop orange colour drop that is your photoresist and the arrow indicates that this would rotate at very high rotations per minute.

You will have between 1000-5000 rpm, but typically you would have less than 3000 rpm. So, you pour a drop of your photoresist on top of the silicon wafer, the wafer should be clean. There is also wafer cleaning process and can be called the pre-step before spin coating. But assuming that the wafer is cleaned, then you spin coat your polymer on top of it.

And then this blue thing which you see in this schematic is something known as spin coater. So, basically it is the motor. And this motor has also a vacuum chuck which means that you can attach your wafer on top of it using vacuum. So, then this motor rotates and at whatever rpm you set, let us say 3000 °C and you rotate it, what will happen?

That liquid will convert into a film, now you will be working with this film, and the thickness of this film can be determined by setting the correct rotations per minute and also, of course, it will depend on the viscosity of your liquids.

If you have photoresist let us say if it is very viscous in that case you may require higher rpm to get a certain film thickness, and in the case of very less viscous materials. Then even at very low also you will get thinner or thicker film that can be optimized using the viscosity of the polymer, and then you will make a film. That is your step number 1, making a uniform film of polymer or resist on top of your cleaned silicon wafer.

Now, whatever polymer you use, may have certain solvent or may have some volatile things. So, you want to get rid of them, and that is why you will do certain baking. This baking is for most resist, done below 100 °C. So, 65 and 95, are the temperatures at which you will do the baking of the resist. So, you get rid of the solvent or at least the unnecessary solvent.

Now, you want to expose this entire thing to the UV light. Will you expose the entire structure to the UV light? Let us say I am using a negative photoresist here which means that the parts that are exposed will become crossed linked. If I expose the entire structure to the UV light, then the entire wafer the entire film will become cross-linked and that will become hard, we do not want that.

What I wanted, let us say I want certain square patterns on top of my silicon wafer. What I will do is, I will make something known as the mask. Mask is typically a glass or quartz, it should be UV transparent. So, you will have a transparent structure or a film, I mean substrate.

And on top of that, you will make some black structures show here, whatever you need or whatever patterns you want, you can have circles. You can have any complicated patterns. I can make my own picture, it does not matter because this has to be just printed on top of the mark, as long as you can print it on top of the mark which nowadays you would be using any CAD software.

It is not that you are using traditional printing technique. So, it is easy to make pretty much any structures and hundreds of such structures. So, for example, if I need one square pattern which is 5µm by 5µm or 20µm by 20µm square, I can make several such squares on top of a wafer which has 10cm diameter, so that would be then my one entire batch of structures.

So, I make these structures on top of a transparent material such as glass, it should be one transparent, and very flat because flatness is important. Now we are going to attach it on top of your silicon wafer.

It should be as closely attached to the silicon wafer as possible. Why, because the next step is that you expose this entire thing to the UV light. Now, UV light will go only in those regions where you have the transparent parts, where you have the black parts here or not black necessarily, but let us say a metal also can be used. But something that can block the light from going to your polymer. So, through the transparent parts, only the light will go.

However, where you have the edges of these transparent parts and non-transparent parts, there the light can get distracted. And that diffraction will actually lead to rough edges in your structure. And that diffraction is what you want to minimize and that is why you want to have as closely attached mask as possible, this is also one reason why we did the baking before.

Because if you attach the mask and let us say your material still has some solvent. It is soft in that case what will happen? It will damage your mask. And these masks are reasonably expensive, especially as the structure size goes down, the smaller the feature the more expensive your mask is, because let us say for up to 25μm structures, you can slightly modified inks not the traditional inks.

But still you can use these glass or quartz substrates, and you can do the printing. You can use certain types of printing techniques. But when you want to make structures which are like smaller than 5μm in dimensions, in that case you need to use very sophisticated techniques. And you need to do this printing of mask using certain metals, you use things like electron beam lithographic just to make the mask.

When you use metals like chrome for making the mask as the inks. Now, the mask itself can be really expensive. And it is not just about expensive the fact that you want to utilize it for several batches, you want to have the exact same structures for several batches. So, you do not want to damage your mask and that is why the baking step was also important.

Now, you did the UV exposure. Now, will you have any dose of UV? No, you need to optimize the dose of UV light, because now your material can crosslink or degrade when it is exposed to the UV light. If the film is too thick, and it is not exposed for long enough duration to the UV light, then maybe only the top part will get cross-linked. Or if I overexposed it, then it might happen that the top part will give me T like shapes. You have straight walls, but on top of that, there are too many cross linking, this is called T topping in fact.

So, overexposure and underexposure both are bad for the structure. So, you will optimize for every photoresist typically the manufacturer will give you the instruction – what film thickness requires, what dose of the UV light, and then accordingly you can adjust the intensity of your lamp UV lamp. You have a machine which has you have something called a mask aligner, which can align your mask on top of your wafer.

So, your mask aligner or your simple UV lamp whatever you have, the intensity of lamp you need to know, and accordingly you can calculate for how long do you want to expose your samples of UV light. So, this is kind of the most important step, and that is step number 3.

I have written 3a here. It is done only for negative resist which crosslink when exposed to the UV light. But crosslinking is initiated by the UV light, but you may not get complete crosslinking. For that, you need to heat it. So, actually crosslinking propagates during this other baking step which is known as the post-exposure bake, so that is only done for negative photoresist, and then you develop these structures.

So, what is develop developing of the structures? You put it inside a chemical. Now, that chemical will selectively wash away the degraded part in the case of positive resist or the uncross linked parts in the case of negative resist. So, now, you have a certain chemical which is especially dissolving one type of the of the polymer.

So, what will happen now? Here is the picture. So, you basically put your entire wafer inside this structure, and then some parts selectively will get removed and the other parts will remain, and that is how you have your structure. You will typically have a lot of structures on one wafer, and then you will do the inspection that you are able to get what you made then you can do further processing with these structures.

In our case when you want to make glassy carbon structures, now you are going to take either the entire wafer or you can cut it into smaller pieces. If it is a batch fabrication technique, put it inside the furnace, and make sure it is in a tube furnace and you have an inert environment.

And then heat it up to what temperature now? Well, 900 °C can already give you a reasonable carbon if the structure size is small enough. If it is in the microdomain typically 900 °C gives you reasonable glassy carbon.

Now, there have also been a question about whether or not this material should be called glassy carbon. Because traditionally glassy carbon is prepared at 3000 °C. And many people still believe that it is not just about the removal of the impurity, it is also about the kinetics of carbonization and graphitization, which may not be possible at temperatures as low as 900 °C.

But here is the thing the material that we obtained at 900 °C. It has properties very similar to glassy carbon. For example, number 1; it is prepared by coking. So, it has flat surface that is something which is very important for us. In fact, in this case, the surface is even very uniform and flat because you prepared it by spin coating. So, using this photolithography technique, you already prepared an extremely flat film.

And all your structures are film-based structures, they already have a flat surface. You are working with liquids from the beginning, even the resins are not solid, you are working with liquid. So, you already have a very flat structure. Because if you have a phenol-formaldehyde resin which undergoes coking, then in that case you will get very nicely atomically flat surface.

Other things such as electrical conductivity that is also within the same range as what you have for large-scale structures. Young's modulus is also in the same range. So, most of the properties are similar to the commercial glass-like carbons, when you get glass-like carbon from a photolithographically patterned structure. Now, specifically in this particular case, I would like to mention the commercial name, I do not like to use commercial names, but there is a type of photoresist which is known as SU-8. I am using this name because this is the polymer that gives you a good quality glass-like carbon. It is known to give you a good quality glass-like carbon, or the carbon that is very similar to properties of commercial glassy carbons.

However, having said that there are other polymers that have also been tried out for giving for whether or not they yield glass-like carbon. You can read, there are several papers. The point is that the material should undergo coking and in the case of microfabrication, sometimes you do not know what is the exact chemical structure of a resist.

In the case of SU-8, we know it is a type of phenol-formaldehyde resin because these resins are traditionally used for making glass-like carbon structures. So, it was already expected that this will give similar material at microscale as well, and that is why this resist became very popular for yielding glass-like carbon. But there are also other polymers, if you do not know their chemical structure exactly, then what you can also do is you can.

For example, you can perform certain experiments, you can make structures that are very sharp. Let us say conical structures and when you see how much does the tip bend on carbonization. That means the material is going through coking. But at the same time, it might be going through so much coking that you are losing shape.

You can do multiple experiments. You can take the tip and keep it upside down. And see if it elongates? The best case scenario is that when your material goes through a semi-solid phase, but not so liquid-like phase that it loses its shape. And phenol-formaldehyde resins are traditionally used for this glassy carbon precursors for a very long time.

These are the five steps of photolithography. As I said that this was a very general idea of the technique. There are a lot of things involved. When you are doing the UV exposure for example, then you can also make multi-layer structure. You make one layer, you make certain let us say the square pattern, and on top of that you want to make something else In that case, you will require these machines known as the mask aligner. When you making the second the structures, the second layer of your structure, need to be aligned very well with the first layer because otherwise you may end up having certain offset, that is very undesirable.

You cannot really see through the naked eyes these micro scale structures. And for alignment you need these microscopes and that is why you have this overall setup. You also have UV exposure, you can perform using this masks. You also have something known as a maskless lithography center where you do not have a physical printed mask.

But you design it in certain software, and then through that, you expose the UV light. There are many variations and there are many advancements that have already taken place in the case of these UV exposed exposure step. Most importantly, you can make very small structures and different types of mask fabrication techniques are also available.

Also the optics of these instruments is also very interesting. You can have complete contact of your mask, sometimes there is some proximity, your mask is in the proximity of your wafer, but not completely touching that you would do that in the case of a polymer where you cannot avoid certain liquid part or in the polymer does not become hard before the exposure.

So, you do not want to attach the mask to it. So, there are many other things, there are many other techniques. But in the end, what you are getting is these kinds of structures on top of your silicon wafer.

Here one more small thing that I would like to mention about negative and positive resist. Why the terms negative and positive are used? Because you see in these images, you will see that if you have a positive resist, positive resist means this will degrade on the UV exposure.

So, you will have the same structure on your mask. Because whatever is not that structured, you want it to get degraded and washed away with the developer. In that case, you have sort of the same structure, so you call it positive, you have the positive structure on the mask also.

In the case of negative resist, you have the opposite structure because the parts now that are exposed to the UV light will stay there because they become cross-linked. And the uncrosslinked parts washed away with the developer.

So, in that case, you will have the negative of your axial structure on top of your mask, and that is why the name negative and positive terms are used.

Now what is the next step? You have a photoresist, you perform photolithography, you get some micro-scale structures. And now you take your entire silicon wafer or the pieces put it inside the furnace heat it at 900 °C. Now, why 900 °C? There is one more important thing.

Why do not we go to 3000 °C? Why cannot we make better carbon? We know that if we increase the temperature, it will increase the cost of the overall process that is true. It is energy-consuming and so on. But at the same time, you may get higher graphitization, higher graphitization means higher order.

This glass-like carbon is a non-graphitising carbon. So, it will never convert into polycrystalline graphite, keep that in mind because you always have these curved carbon structures. You always have these fullerene-like structures that are not going to give you 100 percent graphite. You are not going to get even polycrystalline graphite that is why they are called non-graphitising.

But then why do we talk about graphitic content in them? Well, some parts do have graphitic ordering. They may not have the AB AB A arrangement, they may not have the exact graphite like crystal structure, hexagonal crystal structure. But they do have these graphitic sheets on top of each other, they may be randomly oriented; random orientation is known as turbostratic arrangements.

So, these are turbo strategically arranged carbon structures that also contain some curved carbon structures. Now, you can also think of the modules that we had discussed.

There is a coexistence of curved carbon structures along with these larger sheets which have turbostatically arranged carbon sheets. And in some cases, if you keep on heating it let us say if I heat it to 3000 °C, these turbostratic sheets, not the curved carbon parts, but the turbostratic part does have possibility to convert into graphite or to become more graphitic which will give you slightly higher electrical conductivity, may be also better mechanical properties.

But why do not we do? Is it worth it? It depends on our application; how high you want to go with electrical conductivity? But even let us say electrical connectivity was very important to us, and if we heated the device that would be better for us.

Still, the problem here is that you have a silicon wafer. You need to also make sure that your wafer ,your substrate does not melt and does not get deformed, even does not get deformed by thermal fatigue.

The melting point of silicon is 410 °C. But when you are performing the heat treatment operation, then you are heating it very slowly, you are heating it at like 5 °C. 5 °C per minute that is your ramp rate.

So, you have this process goes on for several hours, and also when you have the highest pyrolysis temperature or carbonization temperature, for example 900 °C then you would keep your material at 900 °C at least for an hour. And then you may also have a nice ramp rate for the cooling because cooling does make a difference to the microstructure of your carbon.

So, this may lead to certain thermal fatigue. That basically means your silicon wafer may even melt or at least slightly deform at a slightly lower temperature. So, to be on the safer side, you would never go above 1200 °C in the case of microfabrication. You can also use other substrates which are high temperature withstanding substrates.

People have used for example steel substrates, people have used also sapphire and quartz substrates, not all of them can go to higher temperatures. So, depending upon your application, you can choose the right substrate. Silicon-based technology is very widely available because also this is used in the IC industry.

The thin-film technology for silicon wafers is sort of already available. These spin coating techniques with all these machines are easily commercially available, so that is why we use silicon, and also the best thing about silicon in general is the fact that you can grow films on top of it, silicon oxide films or silicon nitride films. Silicon oxide can be easily grown just by keeping the silicon wafer inside an oxidation furnace.

So, you have oxygen there and high temperature, so the top layer of silicon itself converts into silicon oxide. The interesting part is that this oxide layer is electrically insulating. And sometimes you can create certain windows in this layer also by using lithographic techniques and then etch the oxide through that window. So, you can selectively get parts of your wafer that are electrically conductive, and parts that are not.

Also, by changing the doping conditions of silicon, you can have different types electrical conductivity and under what conditions that can also be controlled. So, silicon wafer has already been used a lot in electronic devices and semiconductor devices that is why typically that is what is used.

But if you want to just make a carbon structure where you do not really care about the properties of the substrate, then you can also use other substrates, or even when you care about the properties of substrate.

You can even choose the glassy carbon substrates. If you remember I had shown you this film of glassy carbon, a plate of glassy carbon, you can even use that as a substrate for your entire pattern. In that case, you can go to higher pyrolysis temperatures and higher carbonization temperatures. So, you can play with all of these parameters and then you can come up with the devices. The most common parameters that are used for glassy carbon-based microfabrication, are number 1 – you use silicon wafers with or without oxide films depending upon your application. Number 2 – you use this photoresist, which is the phenol-formaldehyde resin ,which is a negative resist SU8, and it is available different viscosity. You use 900 °C pyrolysis temperature ramp rate of less than 5 °C per minute. And you use the inert environment for pyrolysis. And now you get your carbon structures.

Remember that these structures will be dimensionally smaller, they will be shrunk that is the same problem we have in large-scale manufacturing. You end up losing some material because it becomes smaller. But here you can even utilize that fact because smaller structures will have a higher surface area.

So, smaller the better in the case of micro nanofabrication, so you can even sometimes carbonize micro-scale structures, and now you get nanoscale structures. You did not really have to use a fabrication technique that was usable for nanoscale. You could just convert your micro scale structures into nano. So, even that can be used as an advantage the wastage of materials. It is not that big a problem in the case of micro-scale because overall the usage of materials is less, much less compared to what you have in the large scale structures.