

Fundamentals of Micro and Nanofabrication
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Lecture – 30
Optical lithography basics: resist process-2

In this lecture, we will look at the kinetics of resist processing and how baking and development are going to help us achieve the three-dimensional structure.

In the last lecture, we looked at photosensitive material sensitive to a particular wavelength, and when exposed to that specific wavelength, how the solubility changes. Initially, the photosensitive is insoluble, but on illuminating, it becomes soluble. We control this illuminating region to define the pattern. We can either use a simple photoresist or a sophisticated chemically amplified resist, more efficient. Here instead of one photon de-linking a single polymer, it chemically amplifies the resist and de-link multiple chains. It allows using low illumination energy to achieve the same amount of de-linking as that achieved with a high power exposure, with regular standard resist. The kinetics of the process are important; absorption and how the sensitizers and the resins contribute to the absorption.

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The slide is titled "Kinetics" and features the IISc and CENSE logos in the top right corner. It contains the following text:

- Thermal annealing kinetics : Baking of the PR
 - Soft bake (before exposure) ✓
 - Post-exposure bake (after exposure) ✓
 - > Hard bake (after exposure) ✓
- Baking temperature and duration, before, after, atmosphere,..... All depend on the type of PR
- DUV PR as an example

Handwritten notes in red ink include "N₂, H₂O" next to the "atmosphere" underlined text.

There are three baking steps involved to supply thermal energy

1. Soft exposure bake: To remove the solvent from the resist and make it solid, before exposure.
2. Post-exposure bake: It is used to accelerate or arrest the reaction resulting from exposure. This baking is done after exposure.
3. Hard bake: This baking step is done depending on the subsequent processes. The hard bakes are used in special cases where you want to have a highly resistant photoresist for dry etching

The first two processes, the soft bake, and post-exposure bake, are typically used.

During baking, essential parameters to consider are temperature, bake duration, whether it is done before exposure after exposure, and baking atmosphere (inert or with water vapor). We will consider a typical example of DUV and try to understand how these processes are developed.

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Anneal/Baking condition

Type 1

- PR with low density
- Large free volume
- Acid diffusion is high

Type 2

- PR with high density
- Small free volume
- Low acid diffusion

Type 1 Pre-exposure bake Temperature < Glass transition temperature

Type 2 Pre-exposure bake Temperature ≥ Glass transition temperature

During annealing or baking important parameter to consider is the temperature. It depends on resist choose.

There are two types of photoresist, low-density photoresist called type 1 and high-density photoresist called type 2. Low-density photoresist has large free volumes; that means the


material is loose. At the same time, the high-density photoresist has a small free volume, with compact material packing.

When there is a large free volume, acid can diffuse quickly, but the diffusion of acids is low in high-density material; these acids originate from photosensitizers present in photoresist on photon illumination, called photo acid.

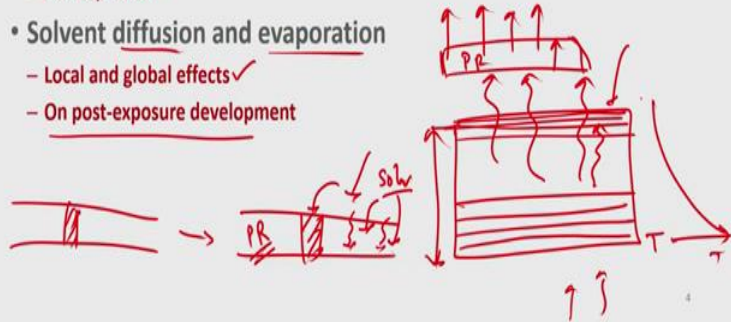
We choose the baking temperature depending on the diffusion of acid in type 1 and type 2 materials. For type 1 resist, low density resist, the baking temperature should be less than the glass transition temperature T_g , while for a type 2 photoresist temperature should be greater than you are T_g . This is the thumb rule used to choose the right temperature for baking. We have to understand the density of the material to select the right temperature. We choose the right temperature by seeing the datasheet provided along with the photoresist.

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Baking implications



- Sensitizer decomposition ✓
 - Temperature ✓
 - Atmosphere ✓
- Solvent diffusion and evaporation ✓
 - Local and global effects ✓
 - On post-exposure development

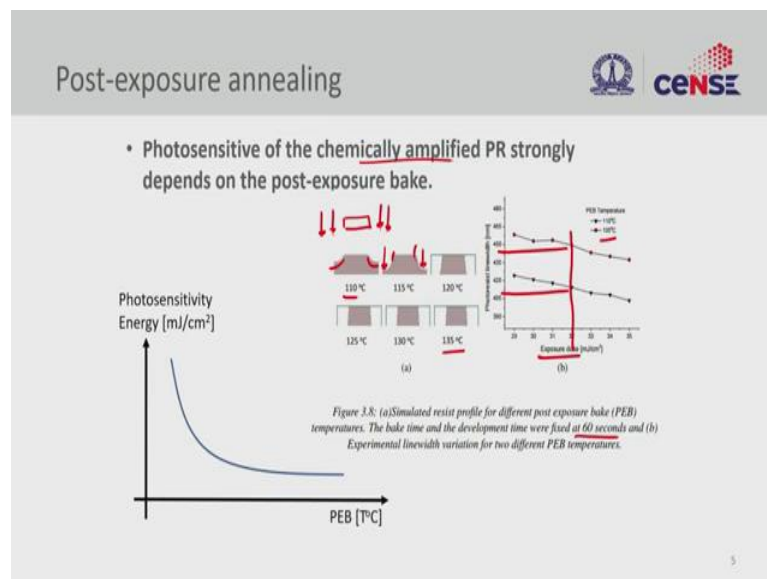


Temperature and atmosphere affects the sensitizer during baking. If the baking temperature is higher than required, it will decompose the sensitizer and lose the photosensitivity. Similarly, the atmosphere should not react with the sensitizer and decompose it. Hence choosing the right atmosphere and temperature is important so that the photosensitivity of the sensitizer is preserved.

The next point to consider is solvent diffusion and evaporation. A temperature gradient is developed in the photoresist during baking on a hotplate, with the bottom layer at a higher temperature. Hence the solvents start evaporating from the bottom, get hardened, and then the solvent present on the top will escape. But, on the other hand, if we are heating from the top, using lamp-type heaters or ovens, top solvents evaporate and solidify the top layer, which will make it difficult for the bottom solvent to escape.

After baking and exposure, we go for sample development using a solvent called developer. In this process, the solvent will attack the exposed region in case of positive resist part or unexposed region in case of negative resist. However, the solvent diffuses even into the resist regions that are not supposed to attack, so it is essential to understand and choose the right developer by looking at the photoresist sensitivity to the particular solvent, whether the solvent will diffuse into the photoresist or not. So, one should look at the datasheets before using a solvent to understand and avoid undesirable diffusion into the material.

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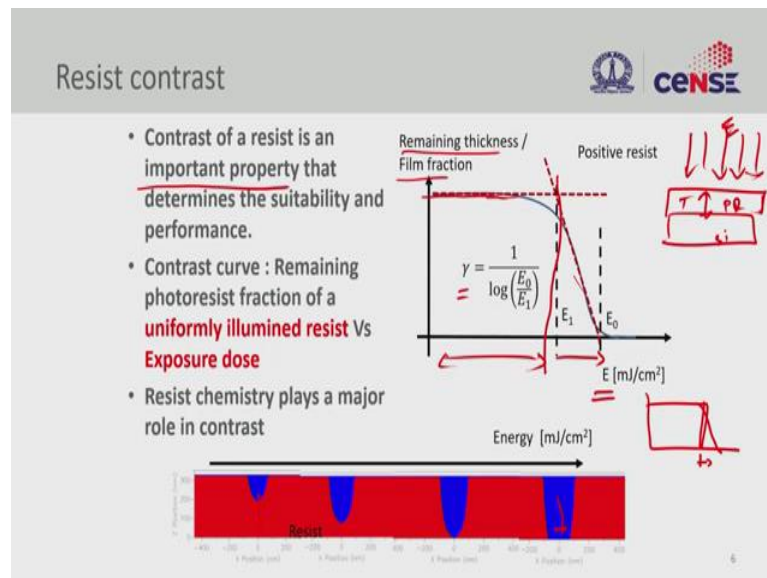


After exposure, the baking will accelerate the chemical reaction. The above slide shows features at different baking temperatures from 110 °C to 135 °C, baked for 1 minute. We can see with an increase in temperature; the patterns come out clearly.

At low temperature, say at 110 °C, heat is not sufficient to accelerate the reaction after the exposure, so the patterns will not develop properly. As we increase the temperature,

the reaction will accelerate, and a good profile is achieved. The photosensitivity can be accelerated by increasing the temperature, and dose. So, if we supply more energy, then it needs less heat to accelerate the reaction. For example, if we provide 32 mJ and bake at 110 °C, the line width of the developed sample is small compared to the one baked at a lower temperature. So, it is important to use the proper temperature to get the right dimension or line width. For example, 105 °C gives broader line width while at 110 °C and offers better CD, with just a 5 °C temperature difference. This tells us the importance of post-exposure bake for chemically amplified resist. This also applies to some unamplified resist where post-exposure bake is important to get the correct CD, particularly electron beam lithography.

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Next, we will see how much energy is required to expose the resist, i.e., the resist contrast. The above slide shows exposure energy vs. remaining uniformly illuminated photoresist thickness. Here they have a blanket illuminated with particular energy E photons on a photoresist and then measured the thickness of the remaining material. The graph shows that the material thickness does not change for all exposure dose below E_1 ; that means the energy is not enough to create any photochemical reaction. Beyond the threshold energy, E_1 , the material starts reacting, and then the remaining thickness starts reducing.

The resist contrast is given by



$$\gamma = \frac{1}{\log \frac{E_0}{E_1}}$$

Where E_1 is the exposure energy where material start getting removed and E_0 is the exposure energy where material is completely removed.

In the contrast graph, as we increase the energy, the material gets exposed and completely removed after crossing the threshold value. Ideally, we want it to step like curve, but it is very hard to get in the real world. So, the slope should be as steep as possible so that a small change in the exposure dose will give you complete removal of the photoresist.

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Development

- Following post-exposure bake the exposed(+ve) part of the resist is removed using a base-developer.
- In manufacturing, development is done in a spin stage.
- For small samples, dip development is sufficient.
- Final pattern depends on developer, development time, method used, etc...

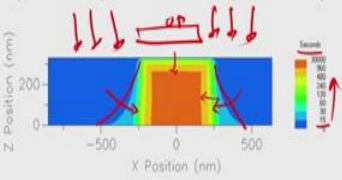
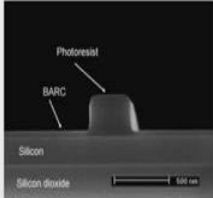



Figure 3.9: Simulated resist profile for different development time.

During development, we insert the exposed material into a solvent. The solvent will etch this or dissolve this exposed part or un-exposed part, depending on the tone of the resist. In the above slide, there is a opaque part and a transparent part. The colors shows how solvent diffuses into the material as a function of time to get the right profile.

At 15 seconds, there is a large foot in the profile; increasing the development time profile turns much steeper and consumes some resist thickness. There is always some baseline diffusion and erosion that will erode the resist during development.

So, we should be careful about the development time. After 1000 seconds, we do not see any difference in the profile, but the line width gets narrower. So, one should identify the right time, amount of exposure, development time to avoid resist erosion.

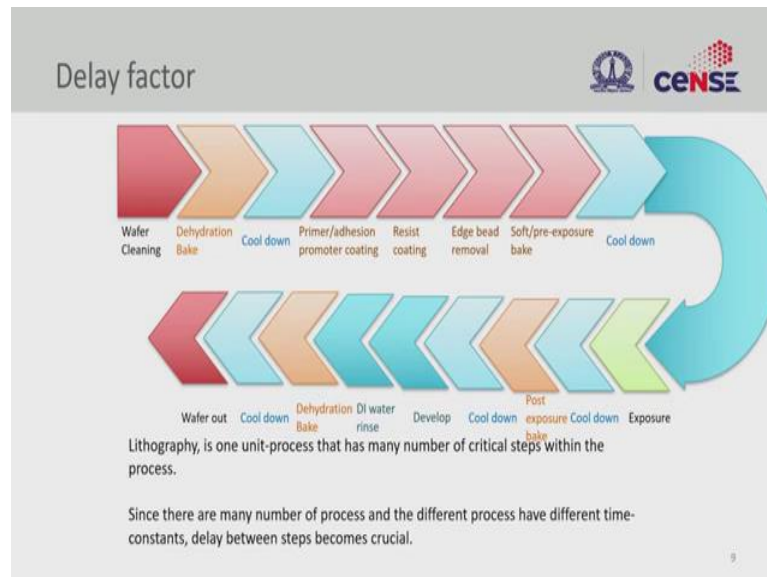
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Developer: Two Classes

Metal ion containing (MIC)	Metal ion free (MIF)
<ul style="list-style-type: none">• Made with NaOH/KOH• Cheaper ✓	<ul style="list-style-type: none">• Made with TMAH• Expensive ✓
<ul style="list-style-type: none">• BUT, Na/K contaminates device<ul style="list-style-type: none">– Especially bad for MOSFETs, diodes, etc.– Usually labeled as	<ul style="list-style-type: none">• Na or K free<ul style="list-style-type: none">– Can be safely used in CMOS and front-end process
<ul style="list-style-type: none">• Used in MEMS, developing photomasks	<ul style="list-style-type: none">• Used in electronic devices, photonics

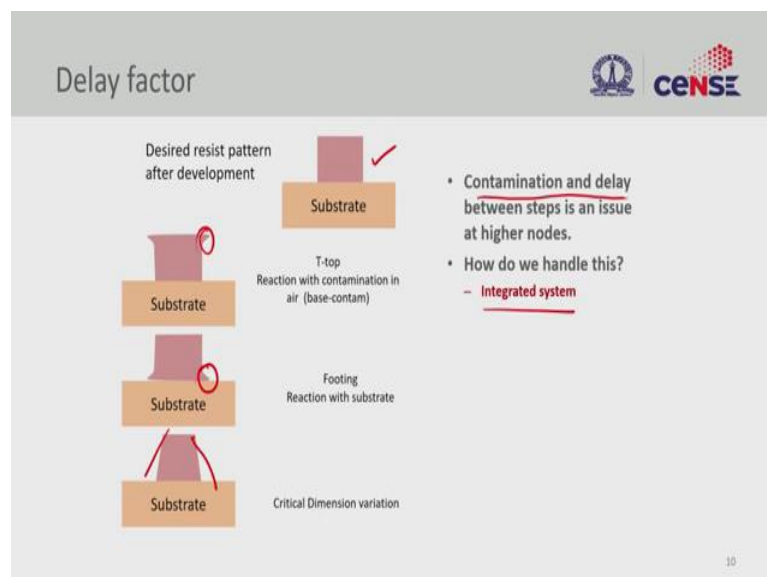
The developers are of two classes; one is a metal ion contaminated and metal ion free. This has a direct influence on the quality of silicon, depending on the application. Metal ions in the NaOH or KOH-based developer can diffuse into silicon or sit on silicon's surface, which is hard to remove. This will change the conductivity of the sample and effect the electrical properties of this device. For electronic device fabrication, one should use metal ion-free developers, tetramethyl ammonium hydroxide (TMAH) based. But these are expensive, while metal ion contaminated developers are cheap.

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The process flow in the above slide was discussed in the last lecture. During the chain of process, there must be no delays. Delay can cause some undesirable effects, and that should be addressed.

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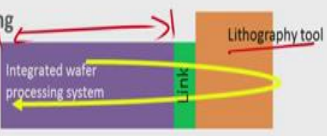
To address delay, all processes should happen in a coupled platform system; before that, we need to understand the cause of delays.

After development, instead of a sharp, vertical profile, we may get T top or footing or trapezoidal type of impairment in the structure. These are due to contamination and delays in the system. To avoid this, all processes should be carried out in an integrated



system, so that it happens automatically and quicker. Facilities in R&D lab may not have the expensive systems to carry out the automatic process, so the subsequent processes should be done quickly without delay.

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Integrated system



- Coating, baking, developing all done in one system
- Optimized process flow.
- Controlled environment
- Blanket wafer enters the system and comes out with the pattern (if integrated with the exposure tool)

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A track system is used in industries, where the lithography tool is one unit, and all wafer and the resist processing happens in a separate unit. All these processes coating, development, and baking take place in a controlled environment of pressure and humidity to yield high. If the integrated system is not affordable, we should make sure the subsequent litho processors happen without delay or with least delay in a controlled environment with maintained temperature and humidity in the lithography bay.

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Resist design



- Sensitivity ✓
- Viscosity ✓
- Adhesion
- Contrast
- Resolution
- Thermal stability
- Etch resistant
- Purity
- Charging
- Substrate compatibility - Si, SiO₂, InP, Metal
- Process compatibility →

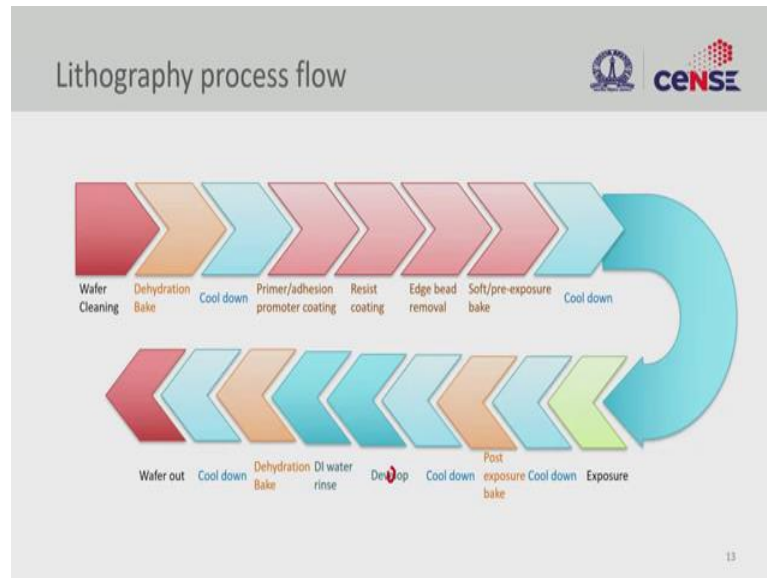
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In a resist design, all the properties of resist should be understood.

1. Sensitivity of the photoresist to the illuminating wavelength
2. The viscosity of the photoresist.
3. Adhesion of this photoresist to the substrate.
4. Resists contrast.
5. Resolution of the photoresist to the illumination.
6. Thermal stability, because we have multiple heating and cooling steps
7. Etch resistance; the resist should sustain the subsequent etch process
8. Resist purity; if the material is contaminated with ions or undesirable chemicals, it will affect the subsequent process and the substrate.
9. Resist charging. In electron beam lithography, charging is an important property that one should consider while choosing a resist. Charging has no impact on optical lithography.
10. Substrate compatibility; whether the resist can be used for various substrates like silicon or silicon dioxide or indium phosphide or metal.
11. Process compatibility; whether resist can be coated or can be used in plasma chamber for subsequent processing.

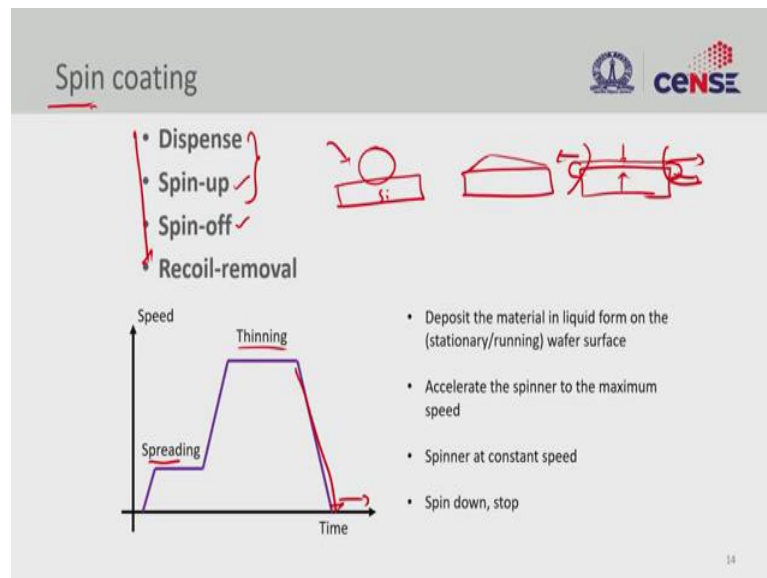
So, it is important to understand these properties before resist choosing and developing it.

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This lithography process flow was discussed in the last lecture; we should make sure that all these processes are followed properly.

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The photoresist is transferred to the substrate using the spin coating technique. It consists of four steps. The first one is dispensing the liquid photoresist onto the substrate. The second step is the spin-up; in this step, the material will spread onto this substrate, covering the substrate. The next step is a spin-off, where the material will spread to get

uniform thickness removing the excess material. The last step is recoil removal. The edge bead formed during the coating is removed in this step.

These steps are achieved by controlling the spin speed and time. The graph of speed vs resist thickness in the above slide shows the various regions of spin coating. The dispense and the spin-up step together comes under the spreading step of the graph. Then to achieve the right thickness of photoresist, thinning is done. And finally, the recoil removal step. After that, speed is reduced, and the wafer is taken out of the spin coater.

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Coating thickness

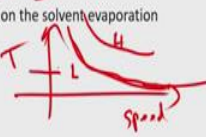



- Thickness of coating is directly proportional to the viscosity of the fluid and inversely related to the spin speed.

For a given viscosity, thickness (t) is related to spin speed(ω) as,

$$t \sim \frac{1}{\omega^{2/3}}$$

n depend on the solvent evaporation



$$t \sim \frac{1}{\omega^{\sqrt{T}}}$$

No evaporation during spinning

$$t \sim \frac{1}{\omega^{2/3}}$$

Constant evaporation

$$t \sim \frac{1}{\sqrt{\omega}}$$

Variable evaporation with spin

The final resist thickness depends on multiple factors; one of those is viscosity. For a given viscosity, the resist thickness (t) depends on spin speed(ω), and the relation is given by,

$$t \sim \frac{1}{\omega^n}$$

Here n depends on the solvent evaporation right. Based on solvent evaporation, resist final thickness will vary.

In case of no solvent evaporation during spinning, resist final thickness is given by,

$$t \sim \frac{1}{\omega^{\sqrt{T}}}$$

In case of constant evaporation with spin

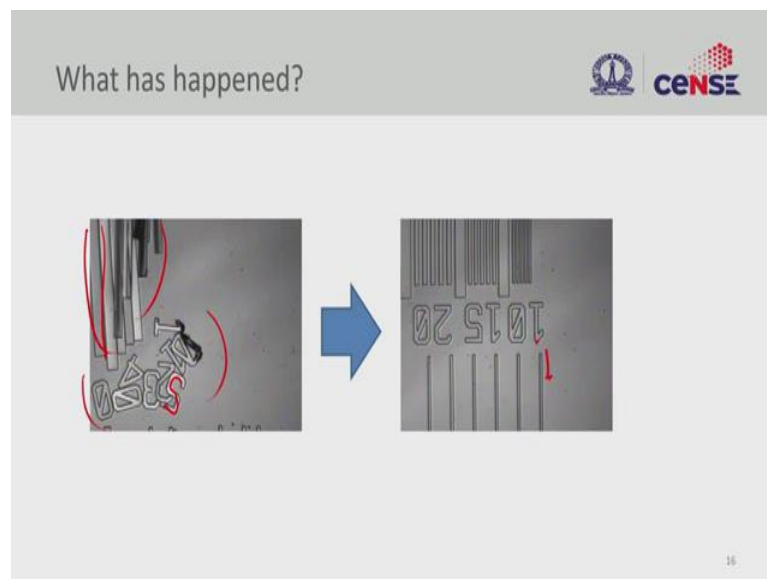
$$t \sim \frac{1}{\omega^{2/3}}$$

For variable evaporation with spin.

$$t \sim \frac{1}{\sqrt{\omega}}$$

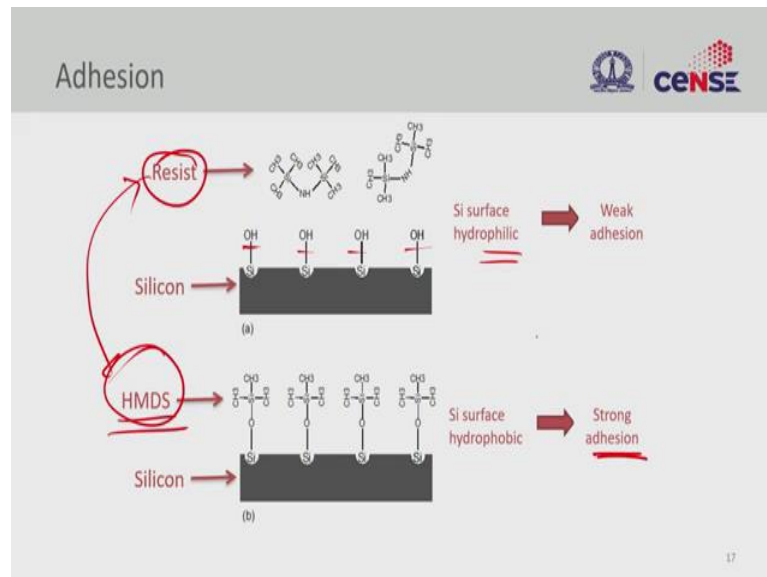
For a given viscosity, with an increase in spin speed, the resist thickness will reduce, and at higher speed, the thicknesses will saturate, and later on, resist thickness will not vary. If we consider high viscosity resist for the same spin speed, the resist thickness will be increased. We can take viscosity fluid or thin it down to achieve the desired thickness.

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The above slide shows a microscope image of 2 substrates, the left side shows nice features, but patterns all grouped in a space or all jumbled on top of each other, while on the right side, we see patterns sitting in the right place. The reason for this is the resist adhesion to the substrate. Along with patterning, adhesion is also an important factor during lithography.

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To address the adhesion problem, we need to understand the surface chemistry. A clean silicon wafer usually be OH terminated, a hydrophilic surface. This has weak adhesion with the resist. To achieve good adhesion, adhesion promoters are required. Adhesion promoters are essential to stick the resist onto the substrate and make sure structures stay on the wafer after patterning. These adhesion promoters chemically modify the substrate and create a hydrophobic surface, which has good adhesion to the polymers.

For every resist, there will be an adhesion promoter complement to it. They always go as pairs, while choosing a certain photoresist also choose the right adhesion promoter. The datasheet of the photoresist will have information on adhesion promoters that can be used. There are some generic adhesion promoters like HMDS; it is a commonly used adhesion promoter. It creates a polymer chain that promotes adhesion between the substrate and photoresist. The adhesion promoter assures that the resist will stick onto the wafer and patterns are nicely aligned.

To summarize, we learned photoresist kinetics, how photoresist evolve when heated, how reaction and development affect the profile, the effect of photoresist on the development process, and the effect of adhesion on photoresist process.

Not just choosing the right combination of wavelength and photoresist, it is also important to understand the photoresist process, what is the baking temperature, adhesion promoter one should use.