

Fundamentals of Micro and Nanofabrication
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Lecture - 49
Dry Etch: Etch mechanism

In this lecture on Dry Etching, we will look at the mechanism that determines the combination of gases used to remove material. Because plasma can also be used to deposit material, the suitable condition for the precursor gases must be known so that the material is removed instead of depositing. Though deposition instead of removal is the worst possible case, not removing anything is also undesirable. So, let us look at how these mechanisms are studied and what we need to make these radicals etch the material.

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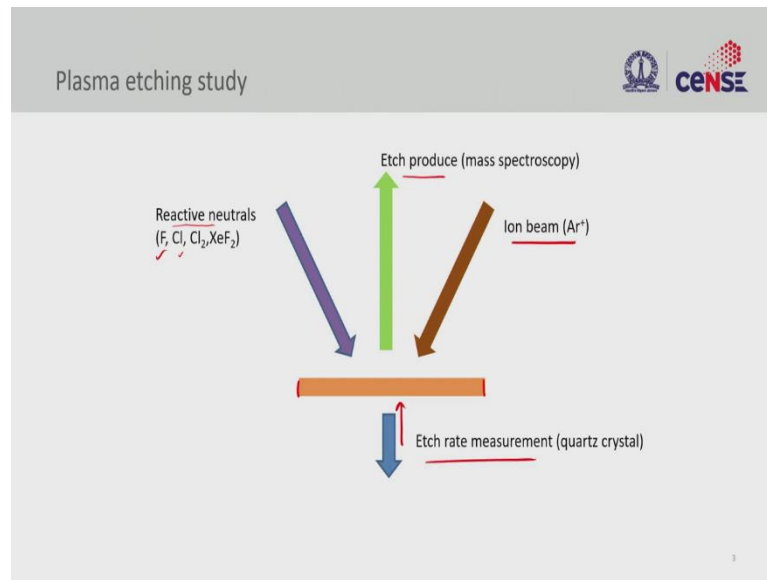
Etch mechanism

- Create reactive species in the system
- Create volatile produce of the substance that you want etch
- Remove the produce from the system

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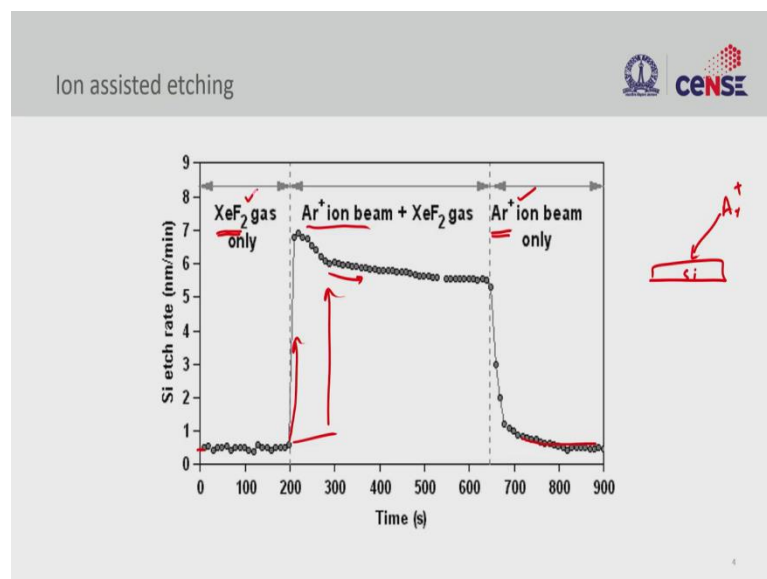
So, to etch a material, we need to create reactive species in the system, meaning the plasma, the wafer and the chamber. Those reactive species should react with the substrate and create a volatile product. If a non-volatile product is created, it becomes deposition. So, here we need to create a volatile product that should be removable outside the system. These are the three primary requirements.

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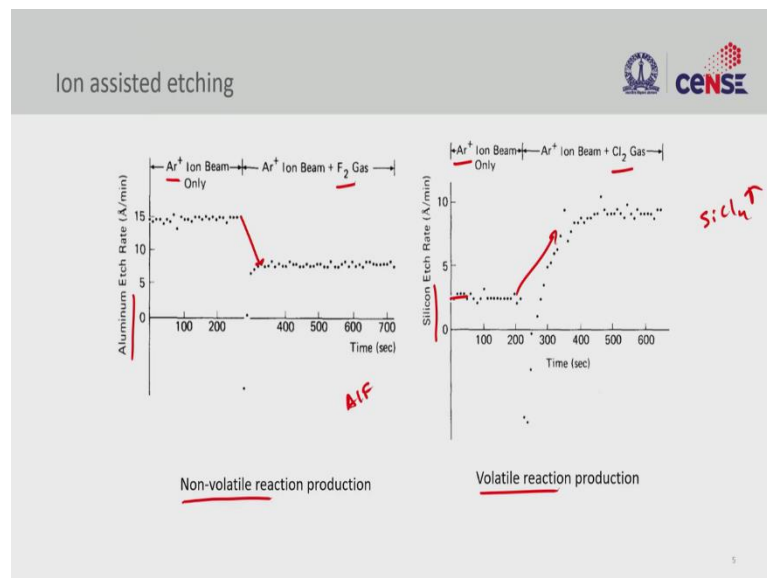
A simple system to study the plasma etching is described here. We look at the etching mechanism, the contribution of reactive neutrals and the ions to the etching. Beams of ion and reactive neutrals are shot on the thin sheet of material to be etched. The by-products of etching are sent to a mass spectrometer to study their chemical nature. At the same time, the etch rate is monitored by looking at the thickness using quartz crystal; the thickness is found by measuring the quartz crystal frequency. So, all these things are done simultaneously in order to understand the mechanism.

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In the previous lecture, we saw the relation between ion flux, ion energy, and the etch processes. Now, let us look at the contribution of ions in etching. Here, is a classic experiment that was done to explain the importance of ion. In this case, silicon is etched using xenon fluoride gas. When we flow xenon fluoride on silicon, the etch rate is negligible. But as the beam of argon ion is shot along with xenon fluoride, the etch rate shoots up and reaches a plateau. So, the etch rate increases in the presence of ions. However, the moment we remove xenon fluoride from the system and allow only the argon ions, etch rate falls; so, argon ion alone cannot etch silicon. In conclusion, we need both the etching gas and ions to etch.

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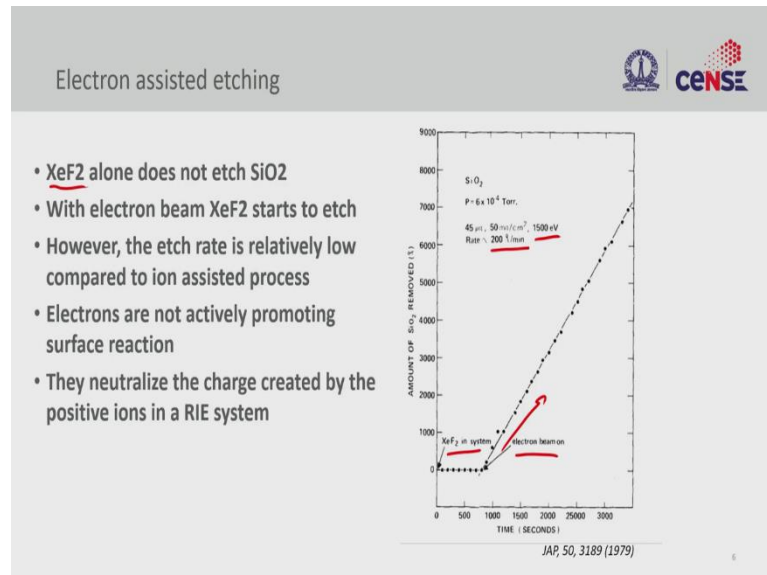


Here is again an example of ion-assisted reactions. In this case, some interesting experiments were done with halide and argon to show two reaction pathways; one includes etching while the other leads to deposition. So, the left graph shows the etch rate of aluminum. When aluminum is exposed to argon ion, the etch rate is about 15 angstrom per minute. The moment fluorine is passed along with argon ions, the etch rate goes down. So, though fluorine is known to be a radical, it is reducing the etch rate. On the other hand, when silicon is exposed to argon, low etch rate of 2 or 3 angstroms per minute is observed. However, the addition of chlorine increases the etch rate.

The difference observed is due to the creation of non-volatile products and volatile products. In silicon, SiCl₄ generated is a gas, while in aluminum, aluminum fluoride is

formed, a non-volatile substance that creates a coating preventing the argon atoms from etching. So, the ions are not the only deciding factors in the reaction paths but also the gas fed into the system.

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Having understood the importance of ions and neutral gases, we now look at the contribution of electrons. The following experiment was conducted to validate the contribution of electrons.

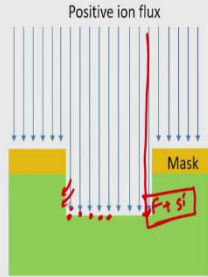
When xenon fluoride is passed on to silicon dioxide, no etching is observed. Then, we start seeing some etching on exposing the material to the electron beam, indicating that electrons can enable this etching. The problem is that the amount of removed material is minimal; about 200 angstroms of oxide are removed per minute for an energy of 1.5 keV.

So, electrons, without directly involved in etching, participate in neutralizing the charge created by the positive ions in the RIE system.

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Directionality in reactive ion etching

• Positive ions are highly directional
• Neutral species arrive at random angle
• Sheath thickness is greater than the feature size
• Mean free path is larger than the feature size



Positive ion flux

Mask

Ion flux is (most) responsible for directional, anisotropic etching


The diagram shows a cross-section of a substrate with a yellow mask layer. Blue arrows represent the positive ion flux, which is highly directional and perpendicular to the substrate. Red dots represent neutral species, which arrive at random angles. A red box highlights the ion flux hitting the substrate surface. To the right, a red schematic shows a circuit with a voltage source V_{dc} and a capacitor, connected to a substrate, illustrating the self-biasing mechanism.

Now let us look at how do we achieve directionality by using ions. In the previous lectures, we saw that the bottom electrode is supplied with RF through a blocking capacitor with self-bias voltage V_{dc} . This self-bias voltage is negative, and hence, positive ions are attracted towards the substrate. But, the neutral species like fluorine, chlorine which are involve in the reaction, do not respond to the voltage as they are neutral.

If radicals are present in the path of ions, energy is transferred to the radicals, and they react with the substrate. So, the additional energy that is required to enable reactions is given by the positive ions. The directionality is achieved is by creating those access points where we encounter the fluorine atom with positive ions only on the surface not on the side wall because fluorine is also present on the side wall. But we do not want positive ions to go on to the sidewall which will enable this reaction. So, you want all the positive ions to be very directional.

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Deposition chemistry



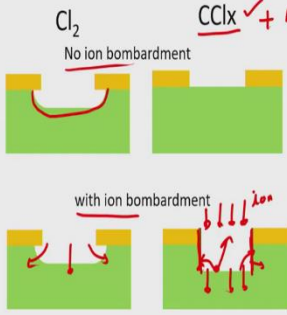
- Al etch using CCl_x as test case
- Cl , CCl_x
- Halogen and halocarbon species create different type of etch products
- Primary etch contributor is Cl
- CCl_x creates thin non-volatile film

Cl_2 $\text{CCl}_x \checkmark + \text{Al}^+$

No ion bombardment

with ion bombardment

*Al as test material



Let us look at the importance of ions in terms of reaction chemistry as well. So, let us consider etching aluminum using CCl_4 as a test case. CCl_4 being a gas, will generate chlorine radical and CCl_x combinations.

In the absence of ions, when the material is exposed to chlorine only, an anisotropic etching is observed. However, no etching is observed when exposed to CCl_x .

When ion bombardment is initiated, let us say argon ion, exposure to chlorine has no change in the profile. Because it is an isotropic etch, the radicals are etching both vertical and horizontal at the same rate. But, in the case of CCl_x , we start etching the material very directionally. The directionality comes from the directionality of ions that we are shooting.


If we shoot the ions at a different angle, we will see an angled etch. This experiment confirms that though the radical alone was unable to etch the material, the addition of ions to the system will enable the directional etching. This showcases the importance of ions.

Another observation of this experiment is the creation of a thin non-volatile film. Normally volatile products are generated when we are etching, but it is also possible to have reaction paths where non-volatile films are formed. In this experiment, the non

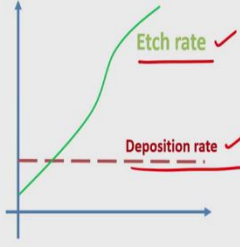
volatile products came and deposited onto this side wall. And this actually protected the side wall and created anisotropy, only the trench base is exposed to ions and radicals.

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Deposition chemistry for directionality



- One has to find the appropriate ratio of etching and condensation species
- By operation just beyond the deposition point one can create anisotropic profile
- Cycling between deposition and etch is another option (used in Deep Si etch)

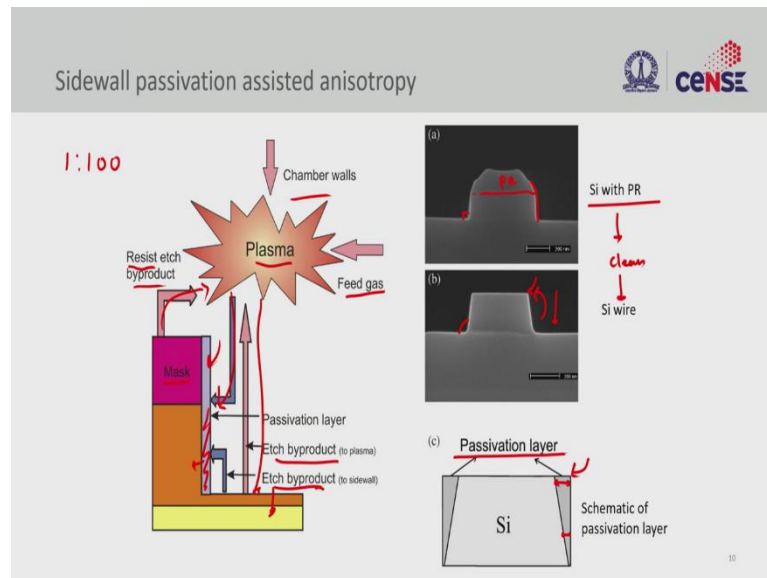


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So, we saw that as the etching progresses we also have deposition of films. In this case, the deposition chemistry depends on the etch rate. So, we should make sure that the etch rates are higher than the deposition rates. Also, it is important to know appropriate ratio of etching to condensation species on wafer.

By operating beyond the deposition point, an anisotropic profile can be created. It is also possible to etching and deposition cycles in a process. By controlling the ratio of etchant to condensation species we can toggle between deposition and etching as used in deep silicon etch called the Bosch process. So, in that process, we use etching and deposition in a sequential fashion.

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Now we look at the characterization of the protective layer formation and the way we use that protective layer to create anisotropy. The slide above shows the comprehensive picture of what goes on between the plasma and the substrate.

So, the feed gas and the chamber wall condition create plasma, and the radicals along with ions react with the substrate. The by-products are either released to the plasma or deposit on the sidewall, protecting the sidewall material. Thus, only the material at the bottom is accessible for etching.

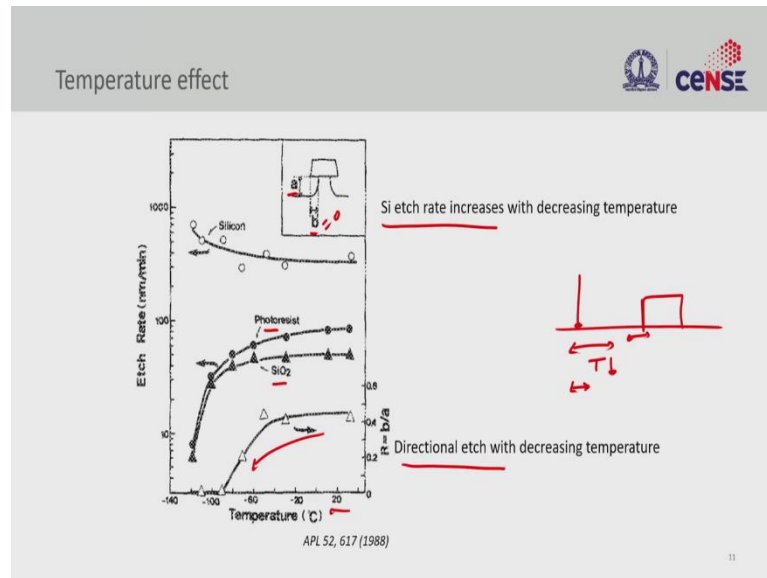
The photomask will also be etched during the process. Ideally, we do not want any reaction between the plasma and the mask, but we never get infinite selectivity. Let us say the selectivity is 1 to 100, meaning 1 nanometer of mask material is removed while 100 nanometer of silicon is removed. The removed photomask material can go into the plasma or deposit on the sidewall.

On the right side, we see SEM images. Image (a) shows silicon with photoresist. On the top, we see photoresist area, and we see strange coatings on the walls. Also, we see perfect sidewalls making 90° with the base. After stripping off the resist and cleaning the sample, the walls are slanted and do not make 90° with the base.

The angle is due to variation in thickness of the passivation layer from top to bottom. The top portion is exposed to etching and deposition for a longer duration. So, the top

portion is the first portion to be etched, and as we go deep, the generated product is deposited on the top. So, that is why we have a sloped sidewall because the thickness of the passivation layer is more at the top.

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The surface temperature of the wafer also determines the etch rate and directionality. In the graph shown above, the silicon etch rate increases with a decrease in temperature, while silicon dioxide and photo resist etch rates decrease when the temperature is reduced. So, this information can be used to improve the selectivity between photoresist and the material or increase the etch rate at lower temperatures.

Directionality is the difference between the vertical and the horizontal etch rate. So, we will call it highly directional or anisotropic when b , horizontal etch, is almost 0. We see from the graph that as the temperature reduces, directionality gets better. The reason is that when the radicals land on the wafer, they will always diffuse. The diffusion length strongly depends on temperature. So, when the temperature is reduced, the energy supplied to the radicals reduces and also their diffusion length. This reduces the reduction in the lateral etch and improves directionality.

So, here we come to the end of the etching mechanism. First, we have seen that in addition to radicals, ions are also necessary to facilitate etching. Secondly, we need directional ions and sidewall coating for anisotropic etching. Finally, we have also seen

that it is not just the chemistry and the ion energies; the temperature also plays a vital role in determining the etch rates and directionality.