Fundamentals of Micro and Nanofabrication

Prof. Shankar Kumar Selvaraja
Centre for Nano Science and Engineering
Indian Institute of Science, Bengaluru

Lecture – 50
Dry etch: Etch chemistry

In this lecture on dry etching, we look at etch chemistry; in particular etch chemistry of silicon and silicon dioxide. These two materials are predominantly used in many applications including microelectronics, MEMS, NEMS, photonics and various other sensors as well. So, let us look at the chemistry that is required to etch these two materials: silicon and silicon dioxide and how to achieve selectivity as well.

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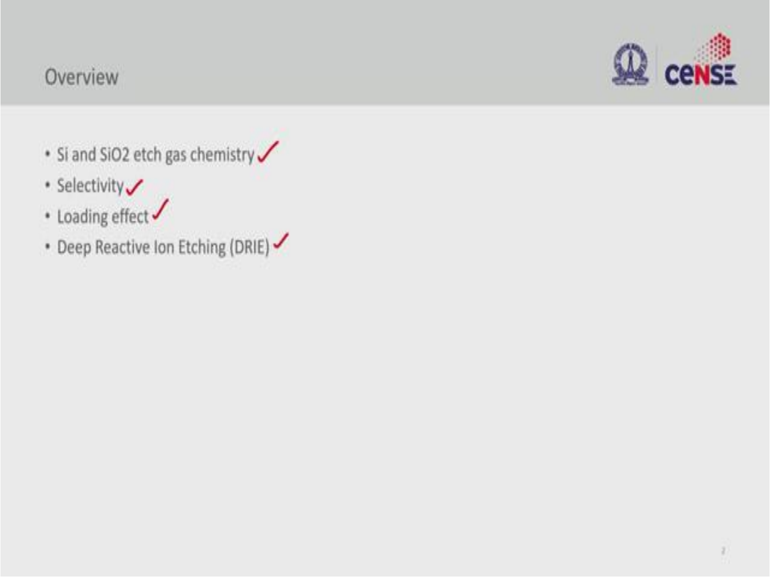

Overview

- Si and SiO2 etch gas chemistry ✓
- Selectivity ✓
- Loading effect ✓
- Deep Reactive Ion Etching (DRIE) ✓

Firstly, we are going to look at etch gas chemistry. So, what kind of precursor gases will we use, and how we tune the chemistry. Secondly, we shall go through selectivity; how to etch one material preferentially while the other material is exposed and differentiate the etch rate between the materials.

Also, we shall understand the loading effect—the loading effect results from various factors in the design and the process. Finally, we will also look at a special type of etching called deep reactive ion etching used in modern-day integration.

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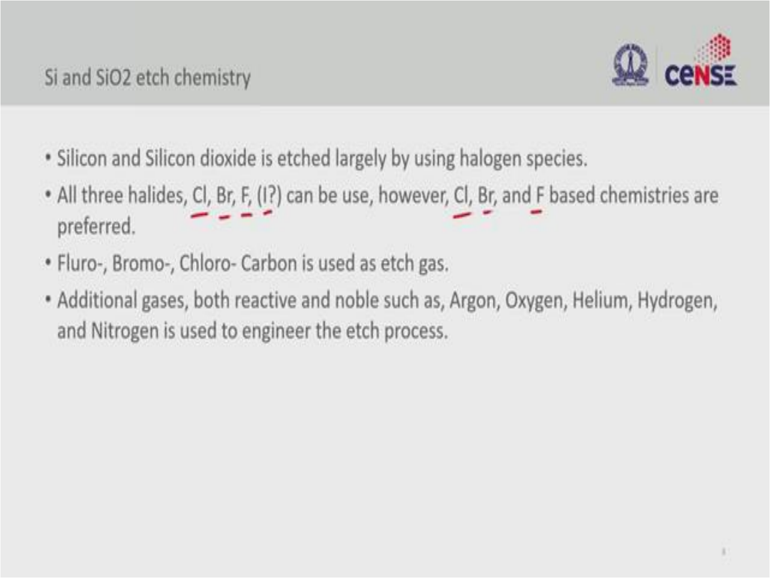

Si and SiO2 etch chemistry

- Silicon and Silicon dioxide is etched largely by using halogen species.
- All three halides, Cl, Br, F, (I?) can be use, however, Cl, Br, and F based chemistries are preferred.
- Fluro-, Bromo-, Chloro- Carbon is used as etch gas.
- Additional gases, both reactive and noble such as, Argon, Oxygen, Helium, Hydrogen, and Nitrogen is used to engineer the etch process.

Silicon and silicon dioxide etch chemistries primarily use halides which could be chlorine, bromine, or fluorine. Iodine also comes under the category of halide, but the pressure is very hard to control in case of iodine. So, iodine is not used for etching. Chlorine, bromine, and fluorine in combination with carbon is used as etch gas. By using CCl_4 instead of chlorine, we can have more number of chlorine radicals. The idea is to have a stable gas carrying the large number of reactive species.

In addition to the reactive gases, we also add some reactive and noble gases for dilution and enabling the reaction. So, a few of them are argon, oxygen, helium, hydrogen, and nitrogen. So, this helps us in engineering the plasma and chemistry. We shall look at shortly how these chemistries work.

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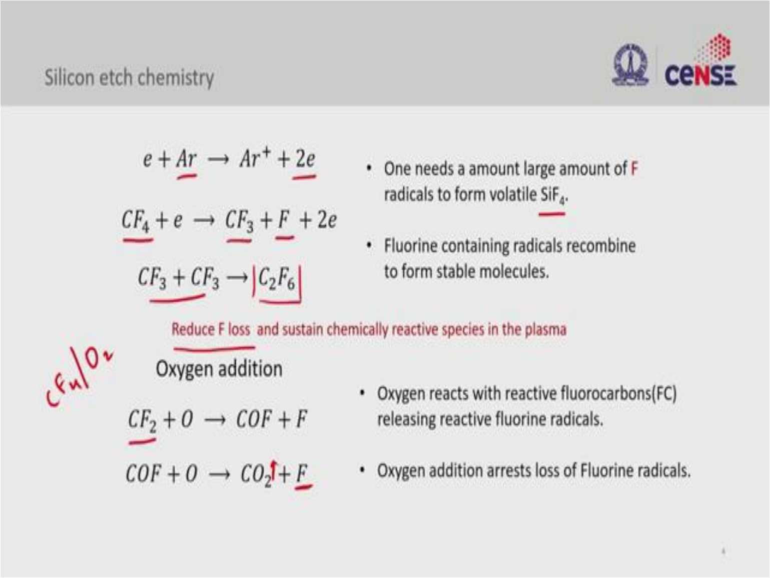

Silicon etch chemistry

$e + Ar \rightarrow Ar^+ + 2e$

$CF_4 + e \rightarrow CF_3 + F + 2e$

$CF_3 + CF_3 \rightarrow \boxed{C_2F_6}$

- One needs a amount large amount of F radicals to form volatile SiF_4.
- Fluorine containing radicals recombine to form stable molecules.

Reduce F loss and sustain chemically reactive species in the plasma

CF_4/O_2

Oxygen addition

$CF_2 + O \rightarrow COF + F$

$COF + O \rightarrow CO_2\uparrow + F$

- Oxygen reacts with reactive fluorocarbons(FC) releasing reactive fluorine radicals.
- Oxygen addition arrests loss of Fluorine radicals.

First of all, let us look at silicon etch chemistry. Silicon etch uses tetrafluoromethane that supplies fluorine. Here, fluorine is the gas that would react with silicon to make a volatile product SiF_4. So, as we already discussed in the previous lectures, argon is the diluting gas that supplies large number of electrons, and thus, helps dissociate the etch gas to create radicals.

Trifluoromethane, CF_3, radical formed during the dissociation can react with itself, giving stable hexafluoroethane. This reaction reduces the number of possible fluorine radicals. To avoid the loss of fluorine and sustain chemically reactive species, oxygen is added to the system. Oxygen reacts with tetrafluoromethane radicals producing carbon dioxide gas and fluorine radicals. Because carbon has an affinity towards oxygen, we always generate volatile carbon dioxide gas. Being a stable gas, we can easily extract carbon dioxide, while fluorine can be used for a reaction.

By introducing these additive gases into the system, reaction chemistries can be made to increase the reactive species. So, the addition of oxygen to CF_4 helps increase fluorine radicals which also helps achieve higher etch rates. In the absence of oxygen, etch rate is going to be low.

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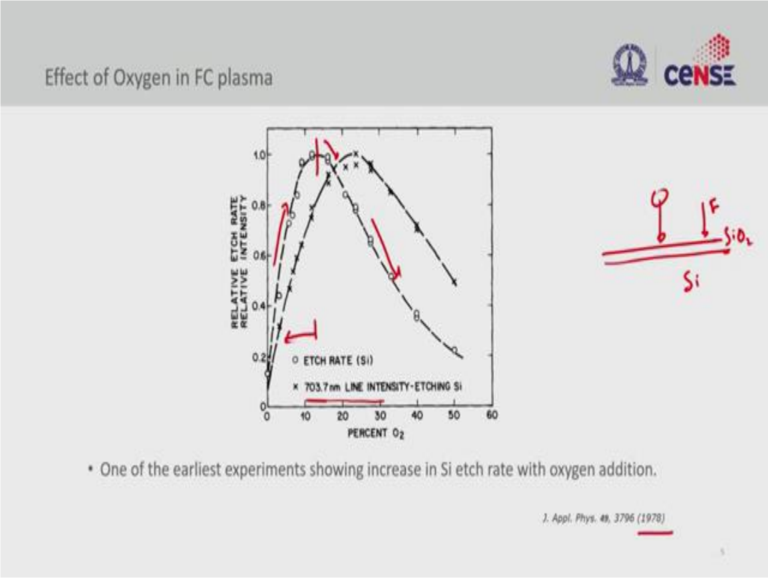

Effect of Oxygen in FC plasma

- One of the earliest experiments showing increase in Si etch rate with oxygen addition.

J. Appl. Phys. 49, 3796 (1978)

Here we look at the experiment done a long time ago to understand the effect of oxygen percentage on etch rate of silicon. The graph contains the etch rate and emission spectrum of silicon. Silicon etching results in emission at around 703.7 nm. So, when we look at this particular emission from the plasma, we know the silicon is being etched.

The etch rate of silicon increases with oxygen content in the plasma up to a certain percentage of oxygen and then decreases. When plasma contains too much oxygen, the oxygen radicals can create oxide surface on silicon and prevent the chemical reaction. Also, the presence of a high concentration of oxygen dilutes CF_4 concentration. In both these cases, the reaction rate of radicals with silicon is less, and hence etch rate reduces.

So it is better to operate below the optimal oxygen percentage, and required etch rates can be achieved.

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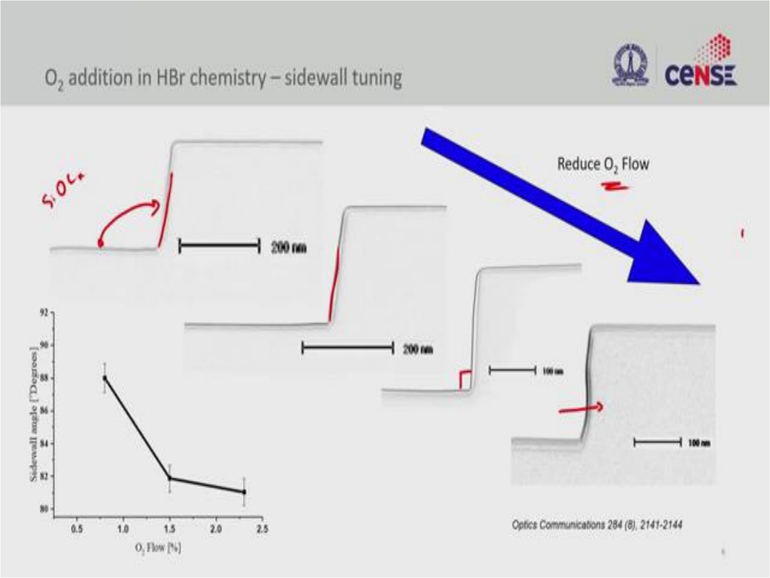

O_2 addition in HBr chemistry – sidewall tuning

Optics Communications 284 (8), 2141-2144

The addition of oxygen can tune the sidewall angle as well. When oxygen is introduced into the system, siliconoxycarbide polymers are generated that settles on the sidewall. It can be seen that when the oxygen flow is reduced, we get an anisotropic etch with almost 90° angle at the sidewall.

The reason why this is 90 degrees is that the sidewall coating slowly reduces with the reduction in oxygen. In the last case, we see the commencement of isotropic etch. So, as there will be no sidewall coating, silicon gets etched.

So, by adjusting oxygen flow, one could tune the sidewall angle. The process discussed here is the chemistry-driven profile improvement.

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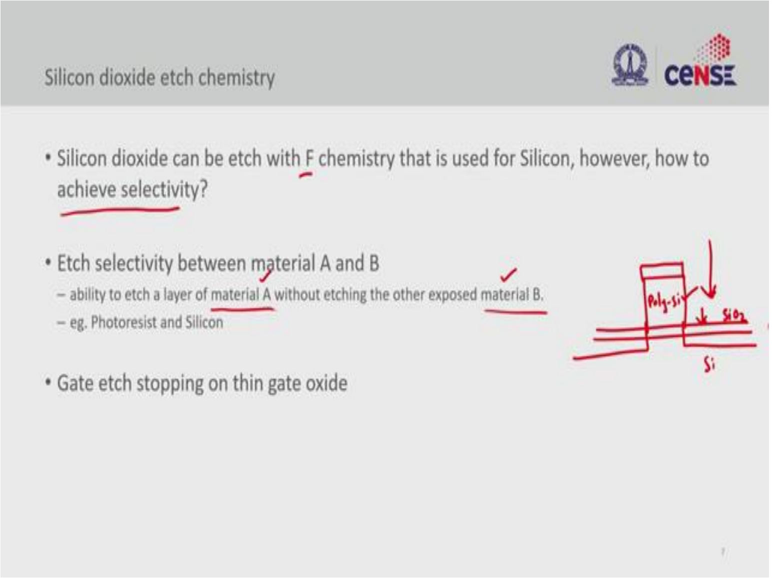

Silicon dioxide etch chemistry

- Silicon dioxide can be etch with F chemistry that is used for Silicon, however, how to achieve selectivity?
- Etch selectivity between material A and B
    - ability to etch a layer of material A without etching the other exposed material B.
    - eg. Photoresist and Silicon
- Gate etch stopping on thin gate oxide

By using fluorine chemistry, it is possible to etch silicon dioxide also. But, of course, the etch rates could be slightly different. The task here is to achieve selectivity because while etching silicon dioxide, we need silicon to be unaffected and vice versa.

So, we have material A and B both exposed to etching, and we want only A to be etched. For instance, let's consider gate dielectric; so, we have silicon dioxide as gate with silicon underneath while polysilicon is covered with photomask on the top of silicon dioxide layer.

We start with polysilicon etching, and when the silicon dioxide layer is reached, the reaction should stop. Otherwise, the device will be damaged. So, the polysilicon etch process should etch polysilicon and stop etching as soon as the silicon dioxide layer is exposed; chemistry should not etch silicon dioxide. So, this is what selectivity is all about.

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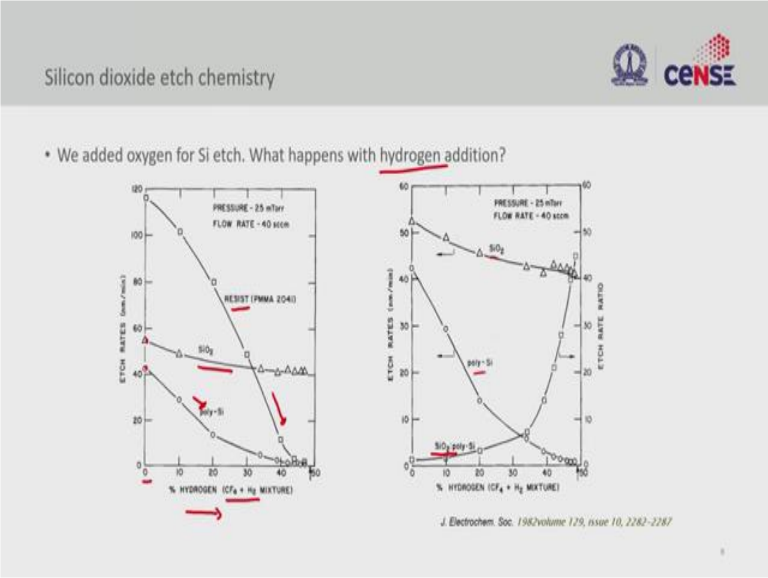

Silicon dioxide etch chemistry

- We added oxygen for Si etch. What happens with hydrogen addition?

J. Electrochem. Soc. 1982volume 129, issue 10, 2282-2287

In the case of silicon, the addition of oxygen increased its etch rate. Now we shall look at the influence of hydrogen on silicon dioxide etching. So the etchant mixture comprises of CF_4 and hydrogen. In the absence of hydrogen, we see that the selectivity between silicon and silicon dioxide is very small. The etch rate difference is within 5-10 nanometer per minute. As the hydrogen content is slowly increased in the plasma, the etch rate of polysilicon reduces tremendously while that of silicon changes marginally.

Another interesting point to notice is that the etch rate of resist decreases dramatically with the increase in hydrogen percentage in the plasma. Thus, the addition of hydrogen not only improves the selectivity between silicon dioxide and polysilicon but also with resist. The graph on the right side displays the same information along with the selectivity of silicon dioxide with respect to polysilicon.

So, adding any kind of additive inert gas can also help in achieving selectivity.

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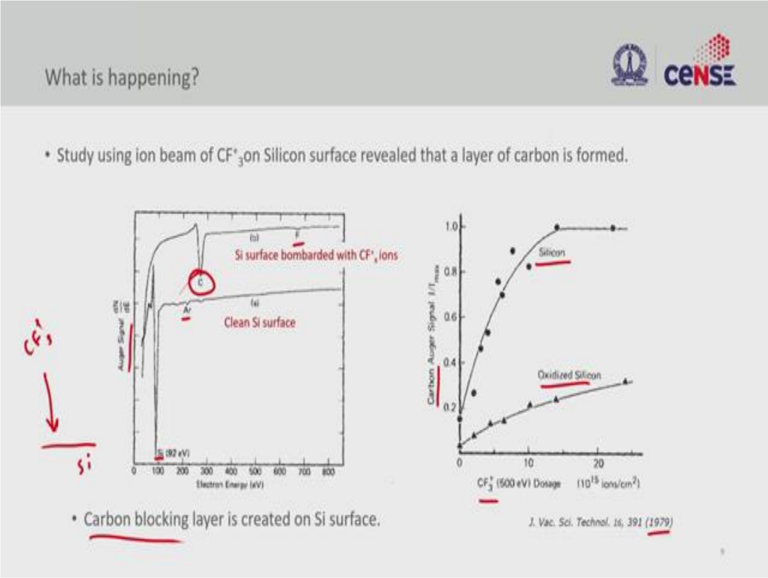

What is happening?

- Study using ion beam of CF^+_3 on Silicon surface revealed that a layer of carbon is formed.
- Carbon blocking layer is created on Si surface.

J. Vac. Sci. Technol. 16, 391 (1979)

Here we look at the experiment which was carried out to understand the driving mechanism behind selectivity. In this experiment, an Auger spectroscopy was conducted on a clean silicon wafer. Signal due to silicon and little amount of argon is observed. When the surface is bombarded with CF_3 for a while, we observe signals due to carbon and a little bit of fluorine indicating the presence of carbon deposits on the surface.

So, these carbon deposits act as a blocking layer and prevent radicals from reaching the silicon surface. On the right-hand side graph, we see carbon content in the auger spectrum of silicon and silicon dioxide when irradiated by CF_3^+ ions various concentrations. So, the carbon signal from pure silicon keeps increasing, while from oxidized silicon, we see a marginal change in the surface property. The main reason for this is the chemistry that happens between oxide and CF_3^+.

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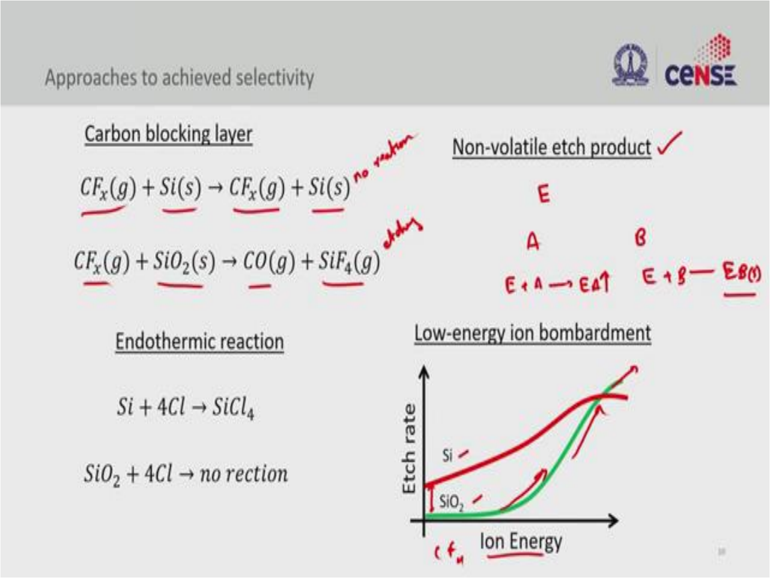

Approaches to achieved selectivity

Carbon blocking layer

$CF_x(g) + Si(s) \rightarrow CF_x(g) + Si(s)$ no reaction

$CF_x(g) + SiO_2(s) \rightarrow CO(g) + SiF_4(g)$ etching

Endothermic reaction

$Si + 4Cl \rightarrow SiCl_4$

$SiO_2 + 4Cl \rightarrow no\ rection$

Non-volatile etch product ✓

E

A B

$E + A \rightarrow EA\uparrow$ $E + B — EB(s)$

Low-energy ion bombardment

When the carbon blocking layer is formed on silicon, CF_x remains as the gas and silicon remains in the solid state. So, basically, there is no reaction with the radical. However, when the same radical is exposed to silicon dioxide, SiF_4 and CO are created, which are gases. So, here we are able to remove silicon dioxide. Thus, by creating a blocking layer, the radicals can be stopped from reaching silicon, and hence, selectivity is achieved.

The other way to create selectivity is by producing a non-volatile product. So, let us say we have material A and material B, an etch gas be E. E reacts with A to produce EA and similarly, E reacts with B to create EB. So, in this case, high selectivity can be created if EA is a volatile product while EB is solid. Then all the reactions leading to EB will not generate any etch product, as EB sits on the surface. This is how we can create non-volatile product-driven selectivity.

One more way of achieving selectivity is through an endothermic reaction. When the reaction pathways are endothermic, then the reaction can be arrested and create selectivity. The other interesting way is by using low-energy ion bombardment. So, for instance, if we take a CF_4 based plasma, which etches both silicon dioxide and silicon, the only difference is a slight lag in the etch rate.

When ion energy is increased, the silicon dioxide etch rate increases. So, we need to find the right ion energy that allows maintaining the etch differential. But, if we keep on increasing the ion energy, the silicon dioxide etch rate can be beyond the silicon etch rate because we start doing physical etch instead of chemical etching. So, by adjusting the ion energy, we can achieve selectivity.

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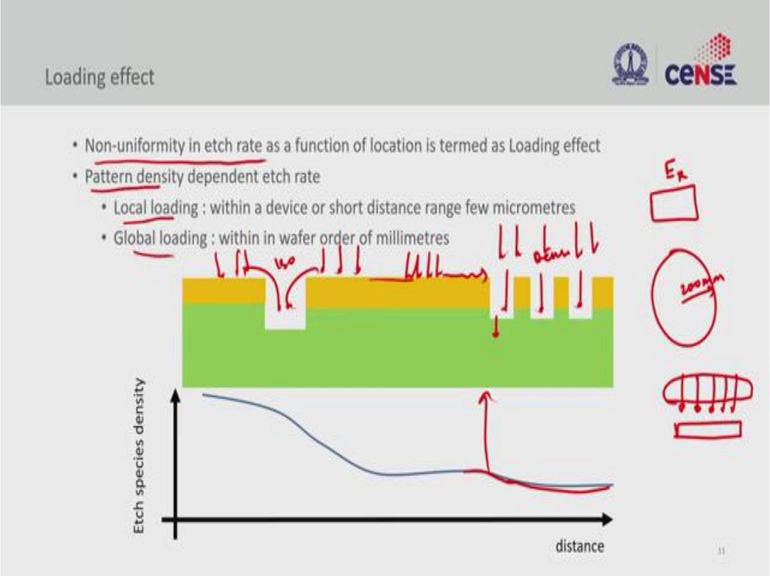

Loading effect

- Non-uniformity in etch rate as a function of location is termed as Loading effect
- Pattern density dependent etch rate
  - Local loading : within a device or short distance range few micrometres
  - Global loading : within in wafer order of millimetres

Another important phenomenon in dry etching is the loading effect. So, loading effect is non-uniformity in etch rate as a function of distance or location within the sample. This effect is observed is primarily due to pattern density coming from the design and the exposure, or the non-uniformity in plasma

When plasma is created over the wafer, the ion energy and the radical concentration need not be uniform across the wafer. So, we need to design the chamber in such a way that we have a very good uniformity of ion energy and flux. Otherwise, we get non-uniform etch rates.

The other reason is pattern-dependent coming from the wafer itself. So, there are two types; local loading and global loading. Global loading is observed throughout the wafer. So, for example, if we have a 200 millimeter wafer, the variation across is global loading. If etch rates change within the device or few tens of micrometer distance, it is called local loading.

So, the schematic in the above slide shows variation in the etch species density when we have densely patterned region and isolated pattern in a sample. So, in the isolated region, the number of etch species is large because all the radicals reaching the surface is available.

They can migrate for the reaction and etch the single pattern. In the densely patterned region, we have multiple open areas where these radicals could be consumed. So, the species density is lower compared to an isolated pattern. In the region where the first trench begins after the isolated pattern, we see a sudden dip in the graph.

This is the region where there is a transition from no patterns at all to multiple patterns. So, all the radicals that are in no patterns region can migrate and then help in the etching of the first tooth. This is a micro loading effect.

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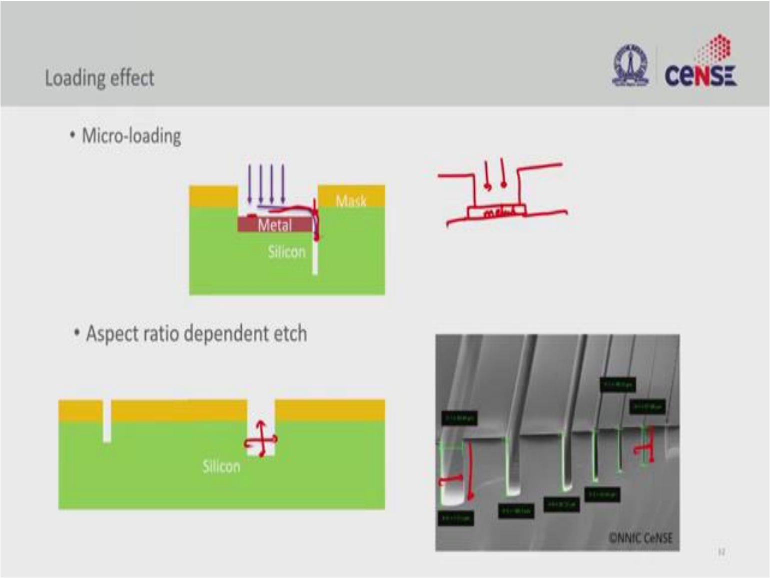

Loading effect

- Micro-loading
- Aspect ratio dependent etch

So, there are two types of local loading. The first type is micro loading. In the schematic, we see an opening close to the metal giving access to underneath silicon. Only the metal portion was supposed to be exposed to radical. Due to misalignment, small opening has been developed.

So, now, once the radicals hit the metal, they all can move into the opening and react with silicon. No reaction happens on metal, and we will see a high etch rate in silicon. Such an accelerated etch is called micro loading.

The second type is aspect ratio dependent etch. Aspect ratio is the ratio between width and height. A smaller opening with a large depth has a higher aspect ratio compared to a large opening. On the right side, we see the cross-section image, which shows the effect of aspect ratio dependent etch. In a large opening trench, the etch is deeper than in a narrow opening trench. So, the etch depth difference is coming from the aspect ratio.

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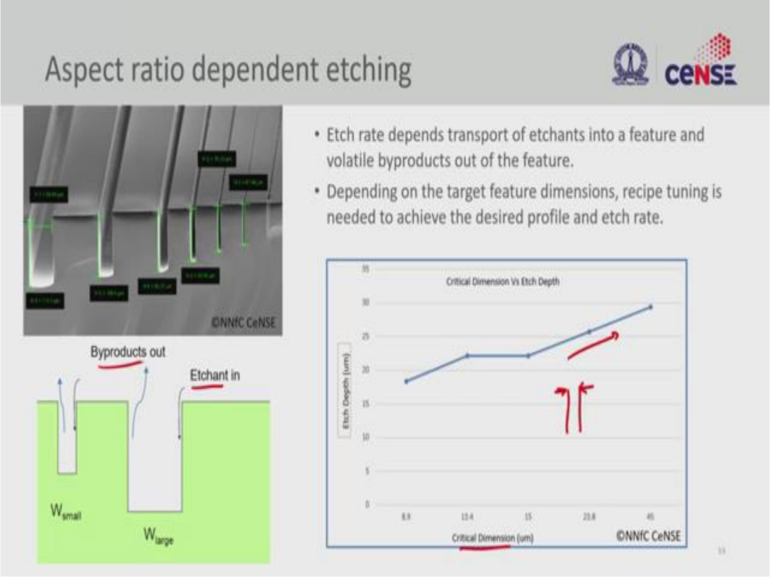

Aspect ratio dependent etching

- Etch rate depends transport of etchants into a feature and volatile byproducts out of the feature.
- Depending on the target feature dimensions, recipe tuning is needed to achieve the desired profile and etch rate.

The reason for the difference in etch rate is the transport of etchants and the products. When the opening is large, the impedance for the etchants to go in and come out is small. So, we have a free flow of etchants and byproducts. However, when the width is reduced, the etchants and byproducts face a large impedance to move in and come out. So, this differential in the movement of etchants and byproducts creates this etch lag.

In the graph of etch depth versus critical dimension, we see as the trench width increased, the etch depth also increases. So, this is indicating that the etch rate is much higher in patterns with lower aspect ratios.

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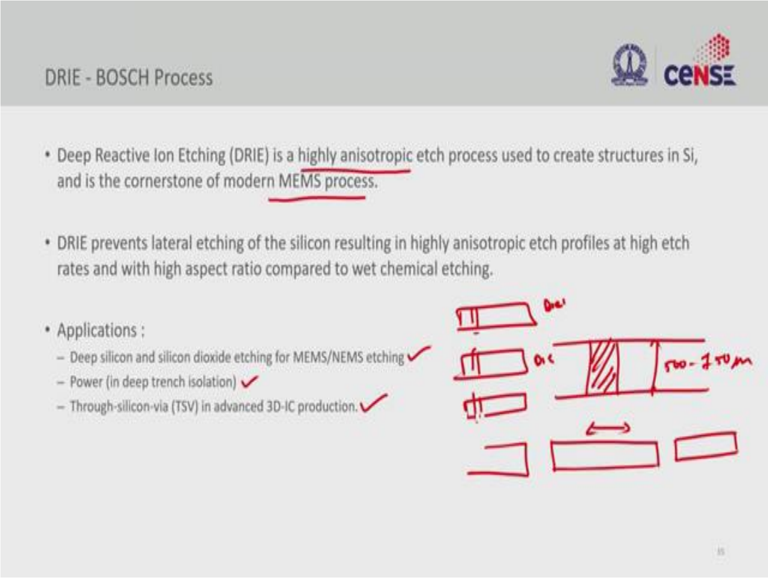

DRIE - BOSCH Process

- Deep Reactive Ion Etching (DRIE) is a highly anisotropic etch process used to create structures in Si, and is the cornerstone of modern MEMS process.
- DRIE prevents lateral etching of the silicon resulting in highly anisotropic etch profiles at high etch rates and with high aspect ratio compared to wet chemical etching.
- Applications :
  - Deep silicon and silicon dioxide etching for MEMS/NEMS etching ✓
  - Power (in deep trench isolation) ✓
  - Through-silicon-via (TSV) in advanced 3D-IC production. ✓

Now we look at deep reactive ion etching. Here, deep refers to tens or hundreds of micron depth. This process was developed by Bosch in which highly anisotropic etch is carried out in silicon. A silicon wafer can be anywhere between 500 to 750 micrometers thick. Let us say, we want to etch through the whole thickness. We have already seen that if the aspect ratios are high, it is very hard to get the etchants in and out. The Bosch process or deep reactive ion etching was really used in etching substrates to enable MEMS processing. MEMS process uses free-hanging features like a thicker layer of silicon which is being released and free to move. So, that is those are all the structures that uses DRIE.

In DRIE, a combination of isotropic and anisotropic processes is used. In an isotropic etch, we have lateral etch, and preventing the lateral etch is the specialty of DRIE.

As mentioned before, we use this process for MEMS applications. Also, for a lot of power devices where the silicon substrates are required to be removed to have good contact with the device. DRIE also finds applications in etching through-silicon vias to connect two different dies. For instance, we have die-1 and die-2 one above the other. We can connect them electrically by making deep trenches. This process is used in present-day memory chips with high-density memory we use through-silicon via right for 3D integration.

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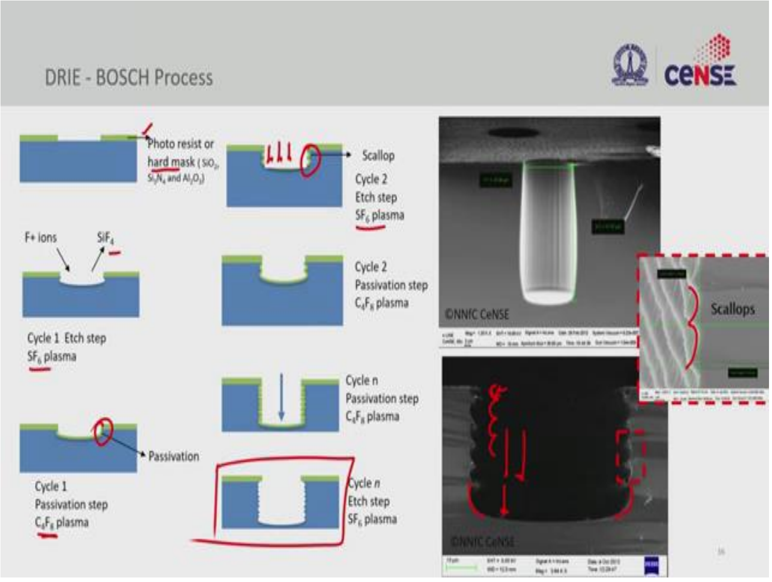

DRIE - BOSCH Process

Photo resist or hard mask (SiO_2, Si_3N_4 and Al_2O_3)

F+ ions

SiF_4

Cycle 1 Etch step
SF_6 plasma

Passivation

Cycle 1
Passivation step
C_4F_8 plasma

Scallop

Cycle 2
Etch step
SF_6 plasma

Cycle 2
Passivation step
C_4F_8 plasma

Cycle n
Passivation step
C_4F_8 plasma

Cycle *n*
Etch step
SF_6 plasma

So, let us look at how this process works. We start with a photoresist or hard mask, which depends on how deep we want to etch. If we want to etch completely through the wafer, we can use a hard mask that can be oxide, nitride, or alumina. Here we use SF_6 plasma, which supplies fluorine in order to generate SiF_4. This is followed by C_4F_8 plasma. So, in the first step, we use SF_6 to etch, and in the next step, we put a passivating layer creating carbon deposits on the surface, including the sidewall.

In the next cycle, the vertical the isotropic etch is carried out again while protecting the sidewalls. So both steps involving SF_6 etching and C_4F_8 passivation are repeated until the required depth is achieved. We get a deep trench, as shown in the SEM image; depth is about 40 microns. The zoomed-in image shows the pattern called scallops which is a result of isotropic etching and sidewall protection. In each cycle, these scallops are created, but sometimes they are undesirable.

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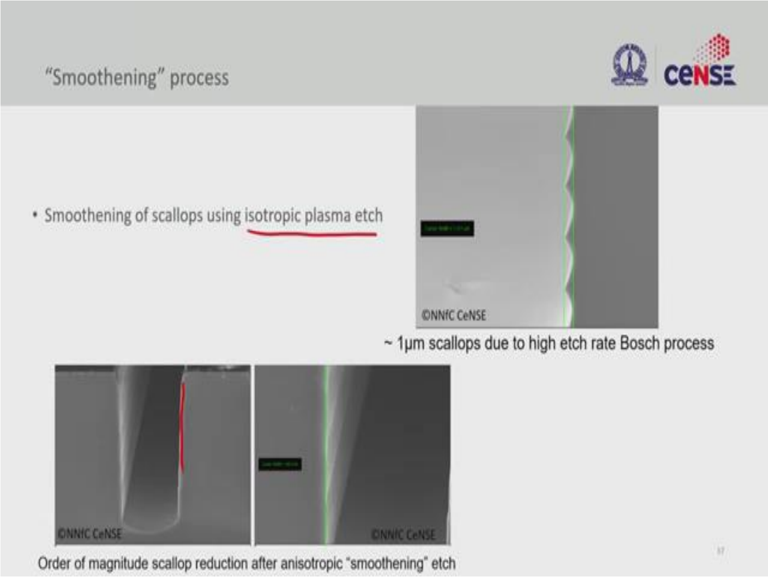

“Smoothening” process

- Smoothening of scallops using isotropic plasma etch

~ 1μm scallops due to high etch rate Bosch process

Order of magnitude scallop reduction after anisotropic “smoothening” etch

We can smoothen it out by using isotropic plasma, and we see about one micron reduction in the scallops. In the more optimized case, we do not see any scallops at all. So, by using a combination of isotropic and anisotropic etching, we could etch very deep trenches without having this isotropic artifact.

So, here we come to the end of the dry etching lecture series. We have discussed the required plasma processes, the etch chemistry, and the tool requirement. We have also looked at using different additive gases for optimizing the etch process, for changing the profile. Also, we have seen some of these undesirable features that we get because of loading. By understanding the pattern density distribution, we should be able to address the non-uniformity in etch due to loading as well.