

Dry etching

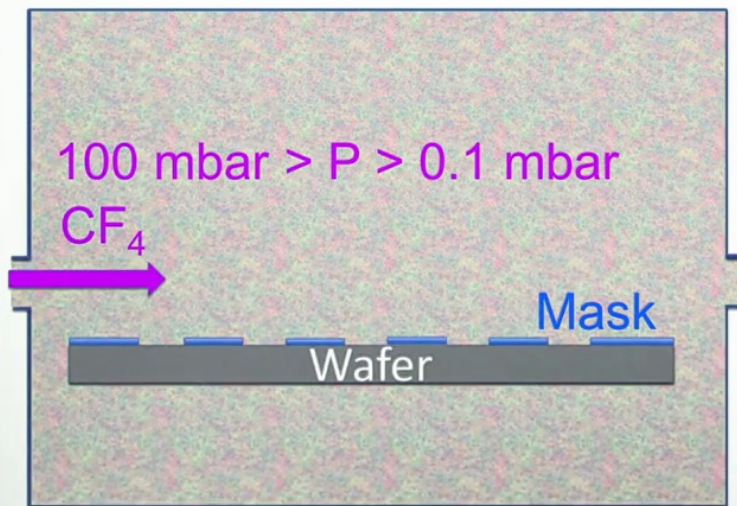


- Dry etching in a gas plasma
- Directionality of etching and etching anisotropy
- Simple rules for choosing dry etching processes

Micro and Nanofabrication (MEMS)

In this lesson, we will introduce dry etching in a gas plasma. A plasma is defined as a collection of excited gas molecules, ions, and electrons. Excitation is obtained by applying a high voltage inside the reactor via electrodes, which leads to ionization events in the gas. We will then introduce the directionality of the dry etching, and the etching anisotropy. That is the ratio of the etching rate in a direction perpendicular to the substrate, and parallel to it. Finally, we will give a few simple rules for choosing dry etching processes to etch specific materials.

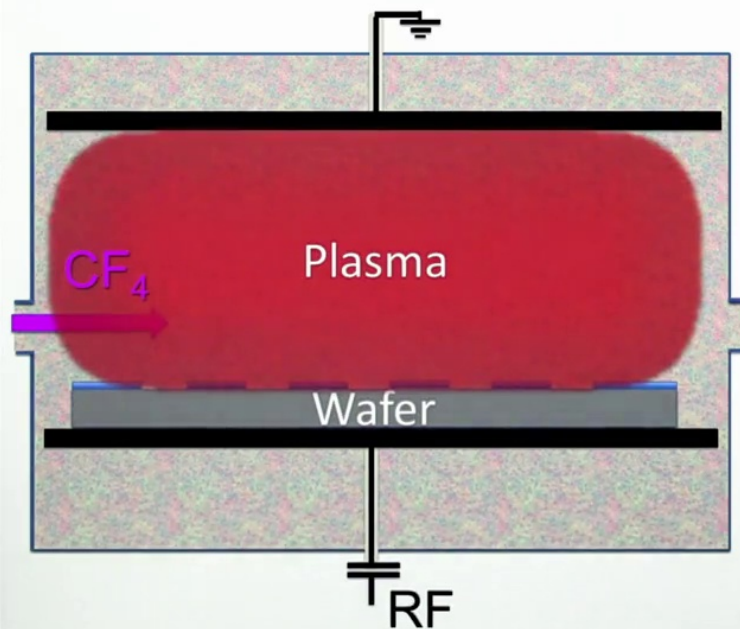
Dry etching



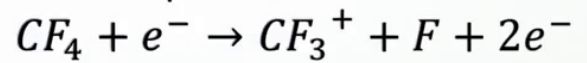
- Etching is done by molecules in the gas (=dry) phase, typically in the 0.1-100 mbar pressure range
- A mask locally protects the wafer from etching
- Example: chemical etching of Si in carbon tetrafluoride (CF₄), an inert fluorocarbon gas
- It becomes a reactive gas when brought in the plasma state

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In a dry etching process, etching is done by molecules in the gas phase, which is the so-called *dry medium*, and one is typically in the 0.1 to 100 millibar pressure range. The wafer is positioned in the reactor, which is subsequently filled with the gas. An etching mask locally protects the wafer against etching. A typical gas that is used in many of the processes is carbon tetrafluoride, or CF₄. This gas normally is an inert fluorocarbon gas, nothing happens. However, this gas becomes reactive when it is brought to the plasma state.

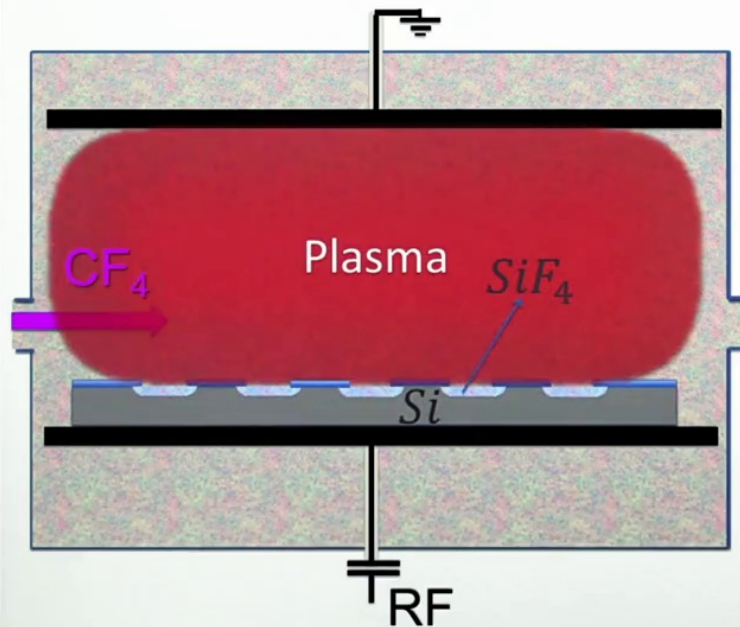


- Chemically reactive fluorine radicals are produced in a plasma upon impact on the CF₄ with an electron e⁻ from the plasma

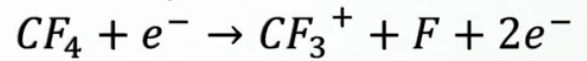


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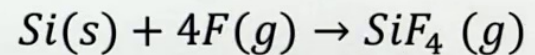
The plasma can be created by applying a high voltage radio frequency field in the reactor. This high voltage ionizes gas molecules, thereby creating ions and electrons. The electrons are accelerated then in the electrical field that is created by the electrodes, and ionize other gas molecules, creating additional ions and electrons. An electron can also dissociate a gas molecule in neutral species, but this can be reactive too. For example, this fluoride atom is, chemically, very reactive.



- Chemically reactive fluorine radicals are produced in a plasma upon impact on the CF_4 with an electron e^- from the plasma

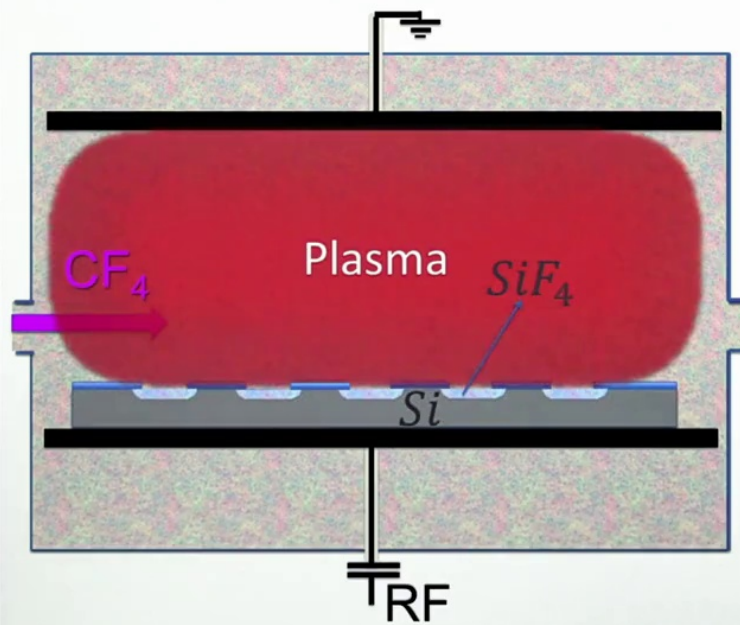


- Fluorine radicals etch the Si in an isotropic way, i.e. mask underetching occurs



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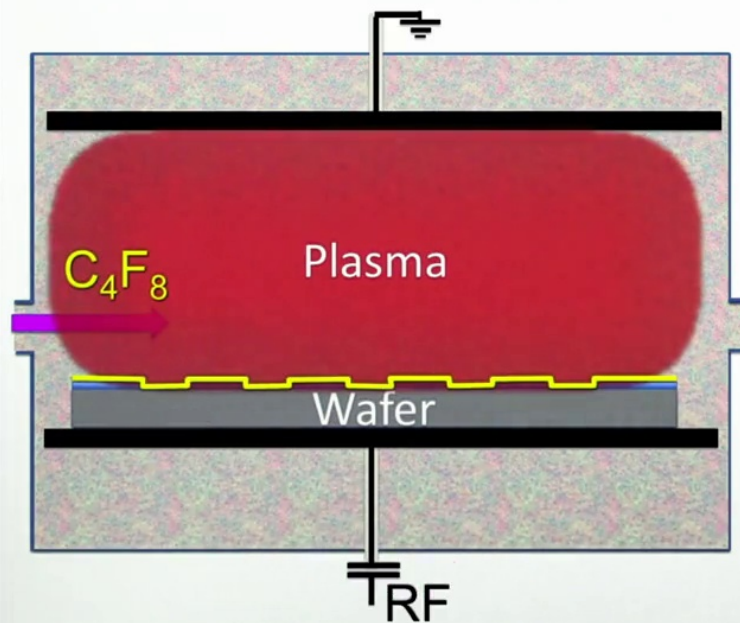
From the gas, CF_4 , fluorine radicals can be created that etch the silicon in an isotropic way. That means that the etching speed in the vertical direction is the same as the etching speed in the horizontal direction, so mask underetching occurs, so one broadens the details of the mask in such a process. In this process, the silicon is recombining with the reactive fluorine radicals to form this gas, which is evacuated.



- Also CF_3 radicals can get adsorbed on the Si but can recombine with F after which CF_4 is desorbed

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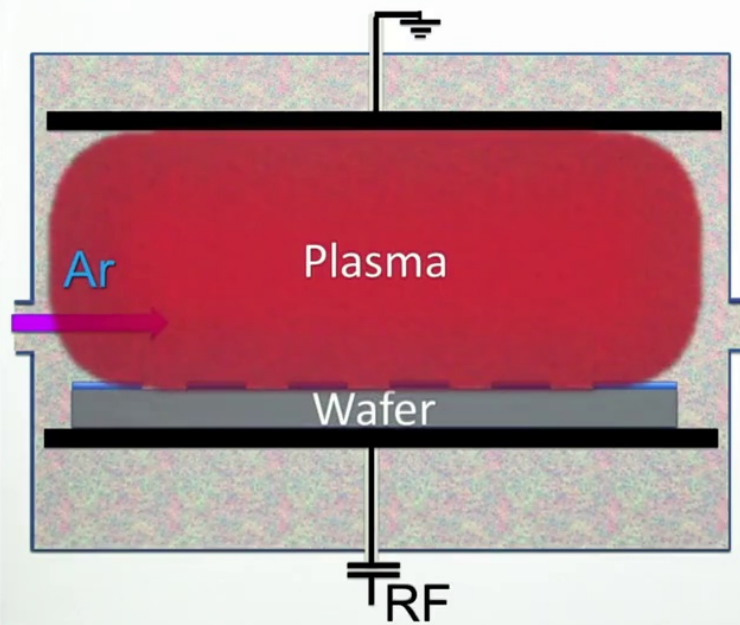
A lot of different interactions and processes can occur in a plasma. For example, CF_3 radicals can get adsorbed on the wafer where they can recombine with the fluorine radical, after which the resulting regenerated CF_4 molecule is desorbed and pumped away.



- Also CF_3 radicals can get adsorbed on the Si but can recombine with F after which CF_4 is desorbed
- However, if a carbon-rich gas like octafluorocyclobutane (C_4F_8) is used, this can lead to deposition of $(CF_2)_n$ -type polymer chains
- The result is deposition of a smooth fluorocarbon polymer passivating film, rather than etching

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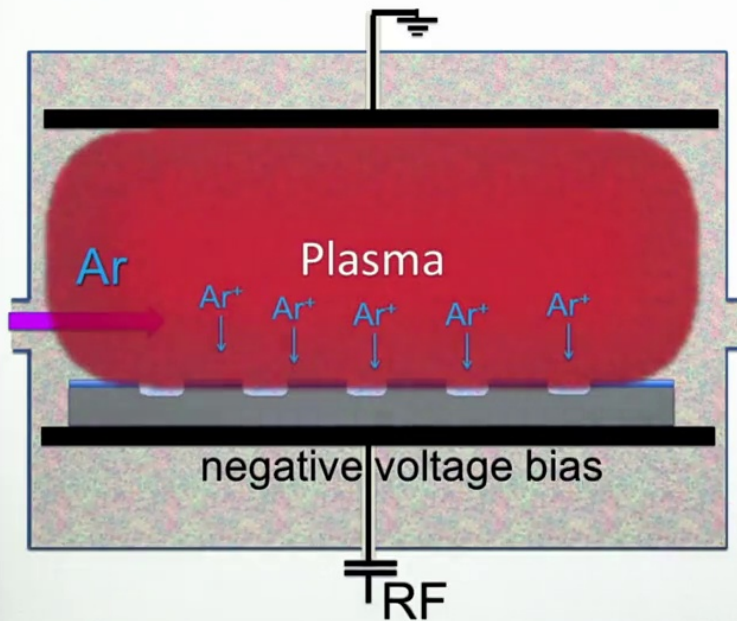
If, instead of the gas CF_4 , one uses a gas that is much richer in carbon, like the gas, octafluorocyclobutane, or C_4F_8 , these radical adsorption processes become relatively more important, and can lead to degeneration of fluorocarbon-type polymer chains that get deposited on the substrate. The result is a thin fluorocarbon layer, as depicted here by this yellow material. So, instead of etching, when one uses this gas, one has deposition.



- If an inert gas like **Ar** is used, there is no reaction with the silicon

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If an inert gas, like argon, is used, ions can be created too, but these are not chemically reactive species that can react with the silicon, so, in principle, no etching occurs.

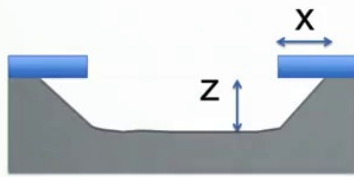


- If an inert gas like Ar is used, there is no reaction with the silicon
- However, if a negative voltage bias is applied to the wafer, Ar^+ ions are accelerated towards the wafer and remove Si by physical impact
- This leads to anisotropic etching, i.e. there is no mask underetching
- Also the mask will be exposed to the physical impact and will be consumed

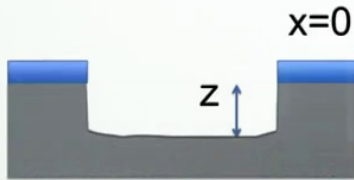
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However, suppose that on top of the radio frequency voltage that one applies, one can apply a negative voltage bias on this electrode. This will provide an attractive force to the positive argon ions. They can then be accelerated towards the wafer. If the kinetic energy of the argon ions is high enough, it is possible for them to remove silicon atoms from the wafer by physical impact. Such process leads then to anisotropic etching, only etching in the vertical direction, because there is the DC voltage bias, and there is no such bias in the horizontal direction. As a result of this physical impact, also the mask material will be slowly deteriorated and gradually consumed during the etching process. The mask lifetime, that is the time during which the mask resists to the physical impact, evidently will provide a limit to the etching depth that one can obtain in such a process.

Directionality of etching



$$A = 0$$



$$A = 1$$

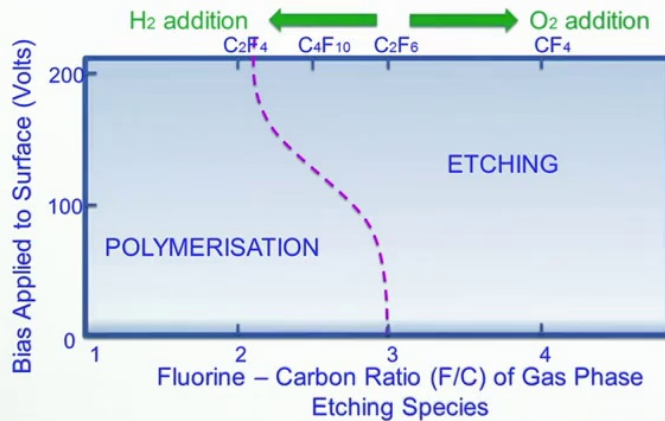
- Anisotropy ratio A

$$A \equiv \frac{(z - x)}{z}$$

- For isotropic (purely chemical) etching $A = 0$
- For perfectly anisotropic etching $A = 1$
- In general $0 < A < 1$

Here, we illustrate the directionality of the etching process, as defined by the factor, A . It's also called the anisotropy ratio A . It is defined in function of the vertical etching distance, z , and the mask underetching distance, x . This is the formula. For isotropic etching, that means a purely chemical process, $x = z$, and A is zero. For perfectly anisotropic etching, x is zero, so that A becomes one, and in general, the A value is in between zero and one.

Increasing the anisotropy by sidewall protection



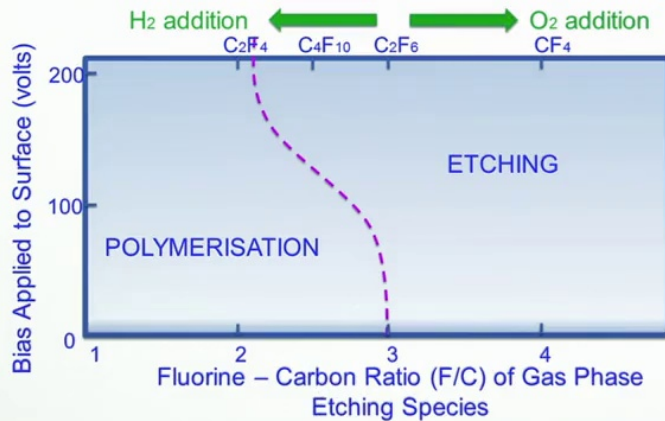
Boundary between etching and polymerization in fluorocarbon plasma as a function of F/C ratio (feed gas) and of the ion bombardment of the surface

- Halocarbon-based plasmas contain etchant species (F, Cl, Br) and carbon halogen radicals (CF_x , CCl_x , CBr_x , $0 < x < 3$) and have very low spontaneous etch rate without negative voltage substrate bias
- Polymeric thin film formation decreases for increasing F/C ratio, ion energy and flux towards the substrate (related to the substrate bias), and the substrate temperature

Micro and Nanofabrication (MEMS)

The use of halocarbon-based plasmas, that is plasmas that contain fluorine, chlorine, or bromine etching species, and carbon halogen radicals, like these ones, offers interesting possibilities in dry etching. These gases have a very low spontaneous etching rate when no negative voltage substrate bias is used. This figure illustrates the case for fluorine-based plasmas. It shows the conditions under which etching occurs, and one finds, on the x-axis, the fluorine-to-carbon ratio of the gas. One can vary this by changing the gas in the reactor. Here, one has CF_4 , which is richest in fluorine, and, here, one has a gas, C_2F_4 , which is richest in carbon. So, when one moves from right to left, one will move from an etching regime towards a polymerization, a deposition regime, due to the increased carbon in the reactor. If one moves along the y-axis, one goes from zero voltage bias, where there will be polymerization, to a regime where there will be etching, as here, these gases have sufficient kinetic energy for etching the silicon by physical impact. This explains the boundary layer between etching and polymerization as given by the dashed curve here.

Increasing the anisotropy by sidewall protection



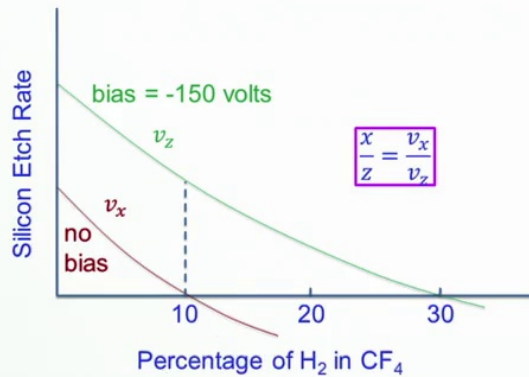
Boundary between etching and polymerization in fluorocarbon plasma as a function of F/C ratio (feed gas) and of the ion bombardment of the surface

- Example: for a ratio of $F/C=2.5$ with 200 eV ions, the horizontal bottom surface of the feature will be etched, but deposition will be dominant on the sidewall, where ion bombardment is lacking
- This results in the absence of underetching and an anisotropic etching profile
- Adding O₂ increases the F/C ratio
- Adding H₂ decreases the F/C ratio

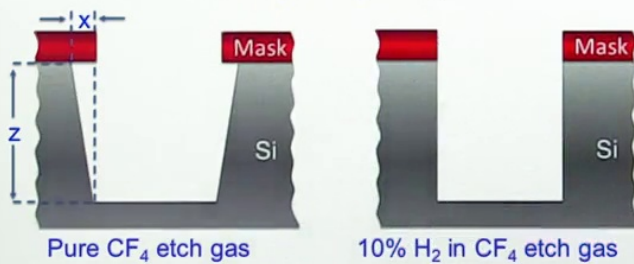
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We give here, as an example, the etching in a halocarbon gas, with the fluorine-to-carbon ratio of 2.5, and using 200 eV ion energy. Under these conditions, one is clearly in the etching regime in this region. However, in a direction that is parallel to the substrate, there is no electrical field, and hence, it is equivalent to having here zero voltage, so in that case, there will be polymerization. So in the vertical direction, there is etching, in the horizontal direction there is polymerization on the substrate. The result is the absence of underetching of the mask, and one obtains a purely anisotropic etching profile. Also, it is possible to add to the halocarbon gas, oxygen gas. In this case, the oxygen will react with the carbon forming CO₂, leaving relatively more fluorine so that etching is favored. Also, an option is to add hydrogen gas and the hydrogen will combine with fluorine radicals, forming HF which is pumped away. So, one is left, in that case, with much more carbon, and hence, addition of hydrogen will lead to polymerization.

Effect of adding H₂ to CF₄ gas



- Adding H₂ to the CF₄ gas decreases etching rate, because fluorine reacts with H so that carbon compounds polymerise
- For 10% of H₂, this results in the absence of underetching and an anisotropic etching profile



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This slide shows specifically what happens when one adds hydrogen to the CF₄ gas under a negative substrate voltage bias of 150 volts. The vertical etching rate is v_z , and when one adds more hydrogen, the etching rate is reduced because fluorine radicals are removed by the hydrogen and one is left with more carbon. v_x is the horizontal etching rate, so it also the mask underetching rate. There is some etching rate without hydrogen, however, it is lower than the vertical etching rate. But, if one now adds hydrogen, also this etching rate diminishes until, here, it passes the curve, and here, one has zero etching rate in x direction, because the polymerization events, in a way, compensate for the etching in that direction. So, the result of this process is shown in these diagrams. If one has pure CF₄ etching gas, one has such a profile, where there is here, underetching and vertical etching, and adding 10% of hydrogen, one has zero etching in the horizontal direction, and only vertical etching. So, it is possible to obtain an anisotropic etching profile by adding 10% of hydrogen to the CF₄ gas.

Simple rules for choosing dry etchants

1. Fluorine-to-carbon (F/C) ratio

- Etching stems from fluorine, polymerisation from hydrocarbons
- Adding H_2 causes HF to form and the F/C ratio drops, leading to more polymerisation and less etching
- Adding O_2 leads to CO and CO_2 reaction product formation, increasing F/C ratio, leading to more aggressive etching

2. Selective versus unselective dry etching

- Polymerisation point of gas determines selectivity
- Decreased temperature, high H_2 concentration, low power, high pressure, and high monomer concentration increase polymerisation, hence selectivity

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Based on what we have learned, we will give now a few simple rules that can help in choosing a dry etching gas. In a halocarbon plasma, the first important parameter is the fluorine-to-carbon ratio, and we have seen, just before, what we can do to change this ratio. A dry etching process can also be selective. That means it only etches the material to be etched and not the mask material. Selectivity can be enhanced by tuning the polymerization point of the gas. More polymerization will lead to extra masking material that gets deposited, so the mask can withstand longer the etching.

Simple rules for choosing dry etchants

3. *Substrate bias*

- A negative voltage bias increases, at constant F/C ratio, the etching behaviour over polymerisation tendency

4. *Metal etching*

- Chlorocarbons and fluorocarbons are used to etch metal films, since they can reduce native metal oxides chemically. O₂ and H₂O vapour must be excluded because of the high stability of the metal-oxide bond. Ion bombardment is essential for etching

Micro and Nanofabrication (MEMS)

We also learned before that the more negative voltage bias is in favor of etching. It favors physical impact and higher anisotropy. For etching metals, one can use chlorocarbon and fluorocarbon gases. They can reduce the native metal oxides chemically. When etching metals, oxygen gas and water vapor must be excluded because they are in favor of oxidation, and metal oxides are normally difficult to remove. For metal etching, ion bombardment is also essential for successful etching.

Simple rules for choosing dry etchants

5. Organic films

- To retain an organic mask, while etching SiO_2 or Si_3N_4 , one should work close to the polymerisation point so that reaction products are formed, e.g. $\text{CF}_4\text{-C}_2\text{H}_4$ and $\text{CF}_4\text{-H}_2$, to compensate for loss of resist
- $\text{CF}_4\text{-O}_2$ plasmas severely etch resists

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Dry etching of organic films, like photoresist, is relatively easy. A CF_4 oxygen plasma severely etches resists. If one wants to retain an organic masking material, like photoresist, one can work close to the polymerization point to regenerate the mask during the etching.



- Introduction to plasma-based dry etching
- Parameters controlling etching anisotropy in a halocarbon plasma : F/C ratio and substrate voltage bias
- Effect of adding oxygen and hydrogen gas
- Simple rules for design of dry etching processes for silicon, metals and polymers

Micro and Nanofabrication (MEMS)

We have introduced plasma-based dry etching, and exposed the parameters that control the etching and isotropy in the halocarbon plasma, like the fluorine-to-carbon ratio and the negative substrate bias. We have pointed out the possibility to vary the conditions of the plasma to result in etching or in polymerization, for example, by adding oxygen or hydrogen gas. Also, we have provided simple rules for designing dry etching processes for silicon, metals, and polymeric materials.
