

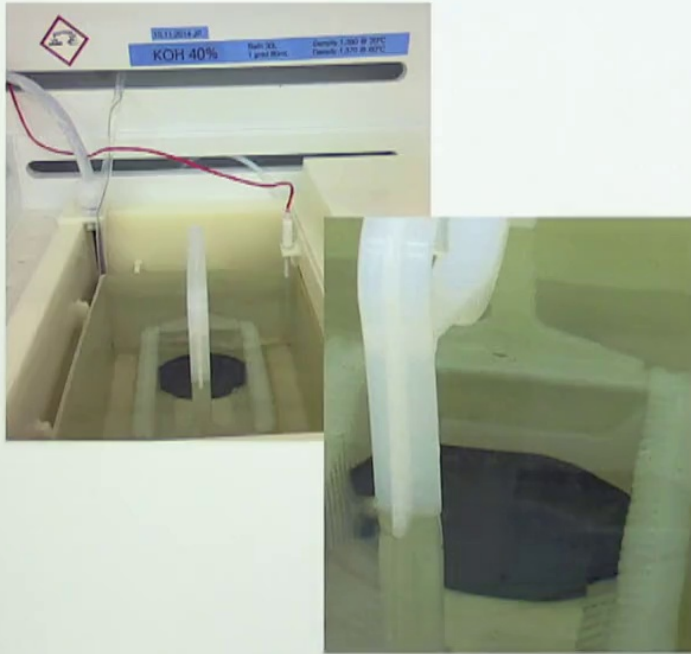


- Thin films
- Thick Si substrates
 - Anisotropic etching
 - Isotropic etching
 - Thin membrane microfabrication
- Applications
 - Wafer cleaning
 - Removing sacrificial layers to realize free-standing structures
 - Electrochemical etching for porous Si

Micro and Nanofabrication (MEMS)

This is our introductory lesson on wet etching where one uses liquid chemical baths to etch away materials. Wet etching can be used to etch away thin films that are locally not protected by a mask, but one can also etch through thick substrates. In the present lesson we will introduce several topics which will be more completely discussed in upcoming lessons. We will introduce anisotropic etching of silicon substrates where certain lattice planes are etched and others not. We will discuss isotropic etching baths of silicon and finally how we can make thin membranes using wet etching. We will then discuss applications of wet etching, such as wafer cleaning and removal of sacrificial layers underneath a functional layer to realize free-standing structures as has already been presented in a previous lesson on dry etching. Finally we will discuss electrochemical etching of silicon substrates for making porous silicon.

Wet etching

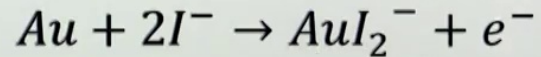
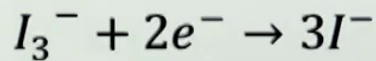
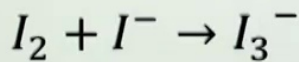
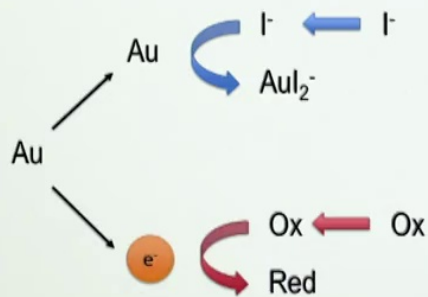


- Use of a liquid bath for removing material
- Baths exist for all type of materials (metals, oxides, polymers,...)
- Based on a chemical reaction
 - Transport of etching solution to the material (by diffusion or agitation)
 - Occurrence of chemical surface reaction generating soluble reaction product
 - Transport of reaction product away from the surface
 - The slowest step of these determines the reaction rate

Micro and Nanofabrication (MEMS)

As the name *wet etching* says, we will use a liquid bath for removing material. Chemical baths exist for all types of materials, like metals, oxides, polymers and so on. As there is a chemical reaction involved, the different stages of an etching process involve, first, the transport of the etching solution to the material to be etched. And this can be done by diffusion or by agitation in the bath which is faster than a purely diffusion-like transport. Then one should have a chemical surface reaction that generates a soluble reaction product. And finally, one has to transport the reaction product away from the surface, and this is mostly by diffusion or by agitation. The slower step of these three determines the actual reaction rate. The two pictures illustrate the etching of a silicon wafer which was immersed in a KOH bath.

Example : etching of gold

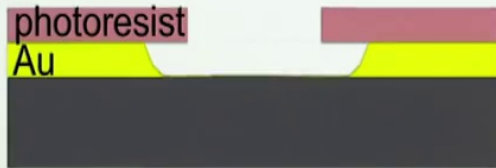


- Important material for interconnections, contacts, etc..
- Example: iodine-iodide system (0.6 M KI and 0.2 M I_2 aqueous solution; etch rate of about 1 $\mu\text{m}/\text{min}$ at room temperature)
- Oxidant is needed for electron transfer, in this case the triiodide ion I_3^-
- Complexing ligand is needed for gold dissolution

Micro and Nanofabrication (MEMS)

As an example of thin filler material that can be etched, we present here the etching of gold films. Gold is an important material for interconnections and for making contacts due to its very inert character. For etching gold, one needs a special bath as it is not easily etched by common etching solutions. A popular bath is the iodine-iodide system which is made by adding iodine and potassium iodide to an aqueous solution. One obtains an etching rate of about one micrometer per minute at room temperature. The mechanism of this bath is the following: Iodine and a negative iodide ion recombine into a tri-iodide ion. By reception of two electrons, this is converted in three iodide ions. The gold atom reacts with two iodide ions that forms a complex that goes into the solution under the release of an electron.

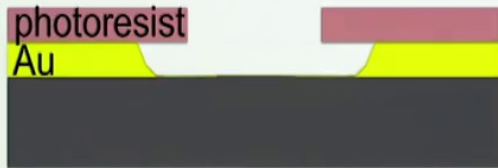
Etching of gold film



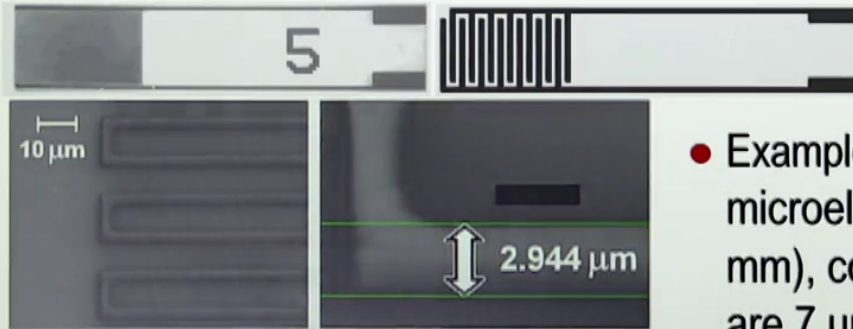
- Isotropic etching process, resulting in widening of etch features over time

This is a purely chemical etching process, so that etching occurs in all directions. If you have a gold film covered by a photo-resist masking layer etching goes both in the vertical and the horizontal direction. The structure gets more and more underetched with time and the underetching only stops when one removes the substrate from the etching solution.

Etching of gold film



- Isotropic etching process, resulting in widening of etch features over time
- For Au, a thin adhesion layer, like Cr, is necessary to apply



- Example of interdigitated microelectrode sensor (3.2 mm x 16.0 mm), consisting of 500 fingers that are 7 μm wide with 3 μm gaps)

Micro and Nanofabrication (MEMS)

In order to avoid a too-important mask underetching, one needs to control the etching time. A problem that can occur when depositing gold directly on a substrate is that it can be easily peeled off due to the weak film-to-substrate interaction. Therefore, often one deposits a very thin metal adhesion layer, like chromium, just before the position of the gold. The pictures below illustrate the gold etching process. Here one has made an interdigitated electrode structure as schematically illustrated here. In reality, there are much more of these fingers, more than 500 in this area, which you cannot see anymore in this picture. This is a detail of these electrodes where you see that we have seven micron-wide electrodes with three micrometer-wide gaps.

Etching of a Si substrate



- A silicon substrate is about 500 μm thick and is single-crystalline material
- Both **isotropic** and **anisotropic** etching baths exist

Next, we introduce etching of a hole in a silicon substrate. The substrate is covered by a masking layer with an opening. Both isotropic and anisotropic etching baths exist.

Etching of a Si substrate



Isotropic etching



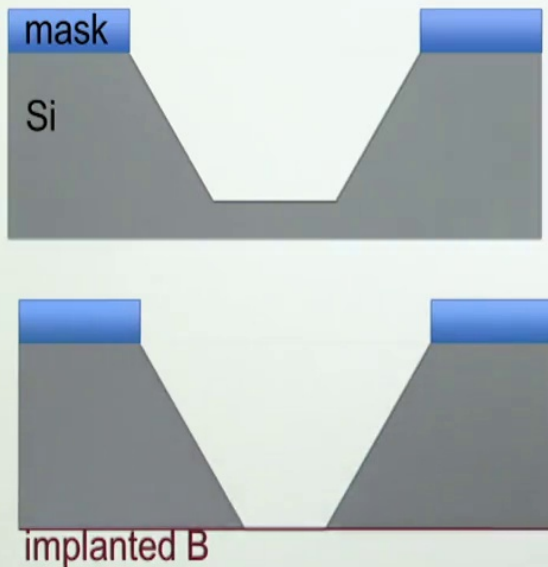
Anisotropic etching

- A silicon substrate is about 500 μm thick and is single-crystalline material
- Both **isotropic** and **anisotropic** etching baths exist
- Anisotropy results from the fact that atoms in certain planes are more bound than in other planes and is hence a direct consequence of the single-crystallinity
- While **acidic baths** etch Si in an **isotropic** way, **alkaline baths** result in **anisotropic** etching

Micro and Nanofabrication (MEMS)

If one has an isotropic etching bath, etching proceeds both in a vertical and in a horizontal direction, so mask underetching occurs. If one has an anisotropic etching bath, etching does not occur for certain directions or certain planes of the silicon crystal structure. For example, here etching stops when the etchant comes into contact with this plane. Such anisotropic etching results from the fact that atoms in certain planes are more bound than in other planes and that we have a single-crystalline substrate and that the etching bath is only strong enough to remove the weaker bound atoms here and leave the stronger bound atoms on these planes. While acidic baths etch silicon in an isotropic way, alkaline baths usually result in anisotropic etching.

Etching of a thin Si membrane



- A silicon substrate is about 500 μm thick and is single-crystalline material
- Anisotropic etching in a KOH bath can be designed into a 'self-stopping' process resulting in very thin membranes (of order 1 μm) by implanting B in the membrane layer; no need to control the etching time
- A thin membrane can be used, for example, in pressure sensors, thermal sensors, etc..
- This is an example of 'bulk micromachining'

Micro and Nanofabrication (MEMS)

Anisotropic etching baths can also be used for making very thin membranes of the order of one micrometer thickness. The single crystalline silicon substrate normally is around 500 micrometers in thickness. If we have, again, our mask opening structure and we put the silicon wafer in an alkaline potassium hydroxide or KOH bath, the etching stops at a certain plane of the crystal, we will see later in more detail. So there is no etching for these planes here. If we proceed in time, the thickness of the silicon layer in the middle becomes always smaller but it is impossible to stop this process exactly when there is only one micrometer left by just looking at the time of the etching process. Instead, as we will see later, one can implant boron in a very thin layer and when the KOH etchant reaches this boron-implanted layer, the etching stops. This technique of microstructuring a whole substrate wafer for making a thin membrane or device, is also called *bulk micromachining*, as one etches away part of the bulk of the substrate.

'Piranha' wafer cleaning

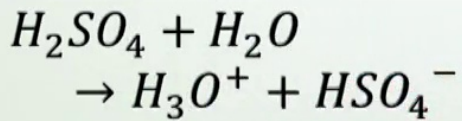
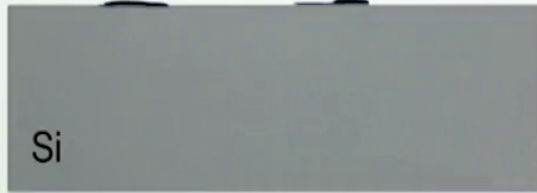


- Piranha solution is a mixture of concentrated sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2)
- It is used for cleaning of organic residues (e.g. from photoresists) on wafers

Micro and Nanofabrication (MEMS)

As an example of a wet etching application, we discuss here the so-called *piranha* wafer-cleaning procedure. A piranha solution consists of a mixture of concentrated sulphuric acid and hydrogen peroxide. It is used for removal of organic residues like photoresists from wafer surfaces. The schematic diagram illustrates some organic residues that have been left on a silicon wafer.

'Piranha' wafer cleaning

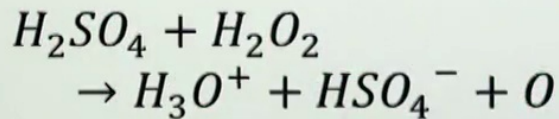
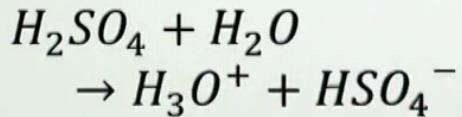


- Piranha solution is a mixture of concentrated sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2)
- It is used for cleaning of organic residues (e.g. from photoresists) on wafers
- 1st process: rapid (violent) dehydration by H_2SO_4

These organic residues are first attacked by the sulphuric acid, which violently dehydrates the organic molecules. These get a black appearance as water molecules have been extracted and a carbon-based structure remains.

'Piranha' wafer cleaning

Si



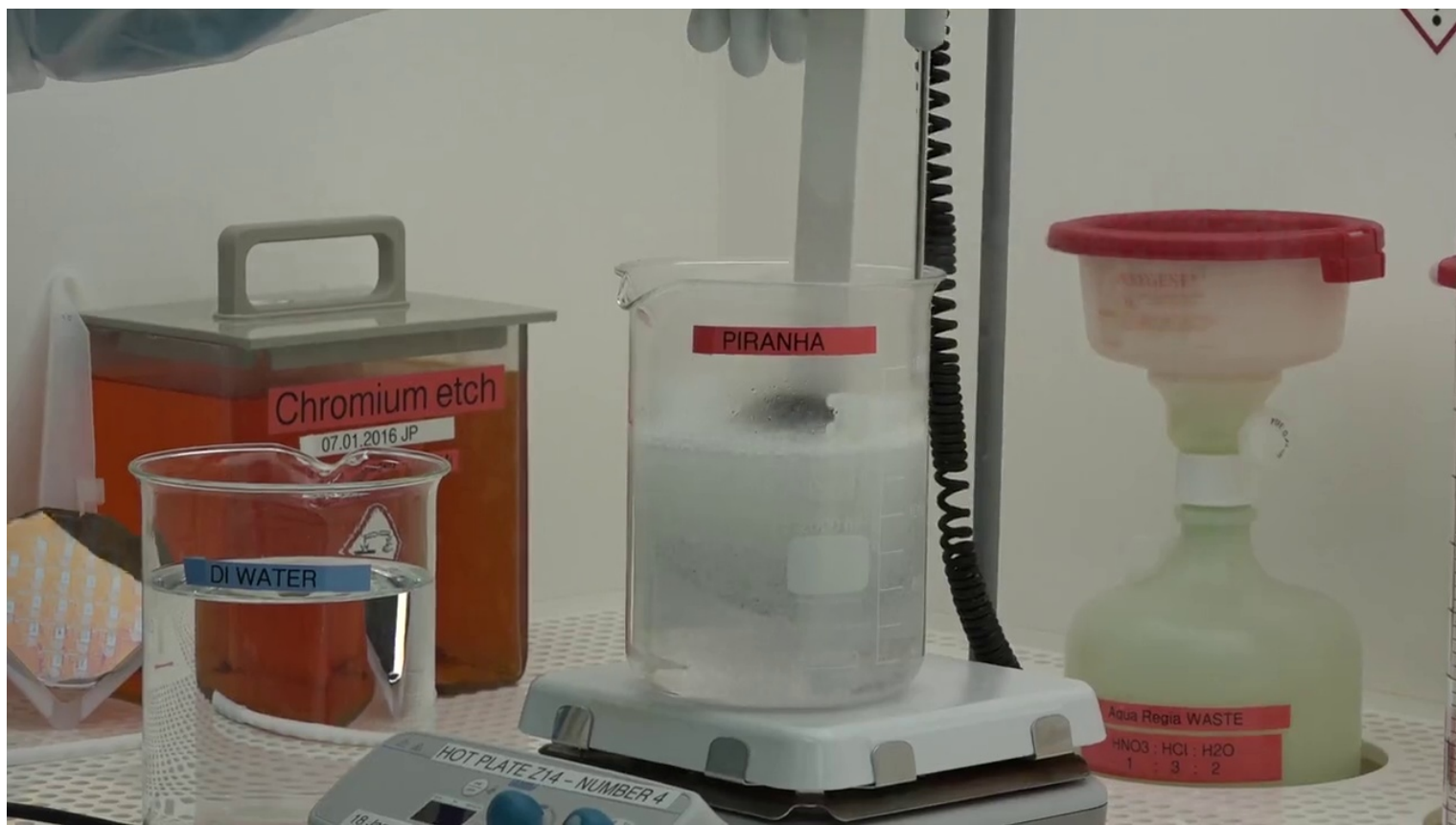
- Piranha solution is a mixture of concentrated sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2)
- It is used for cleaning of organic residues (e.g. from photoresists) on wafers
- 1st process: rapid (violent) dehydration by H_2SO_4
- 2nd process: generation of reactive oxygen species that can dissolve elemental carbon

Micro and Nanofabrication (MEMS)

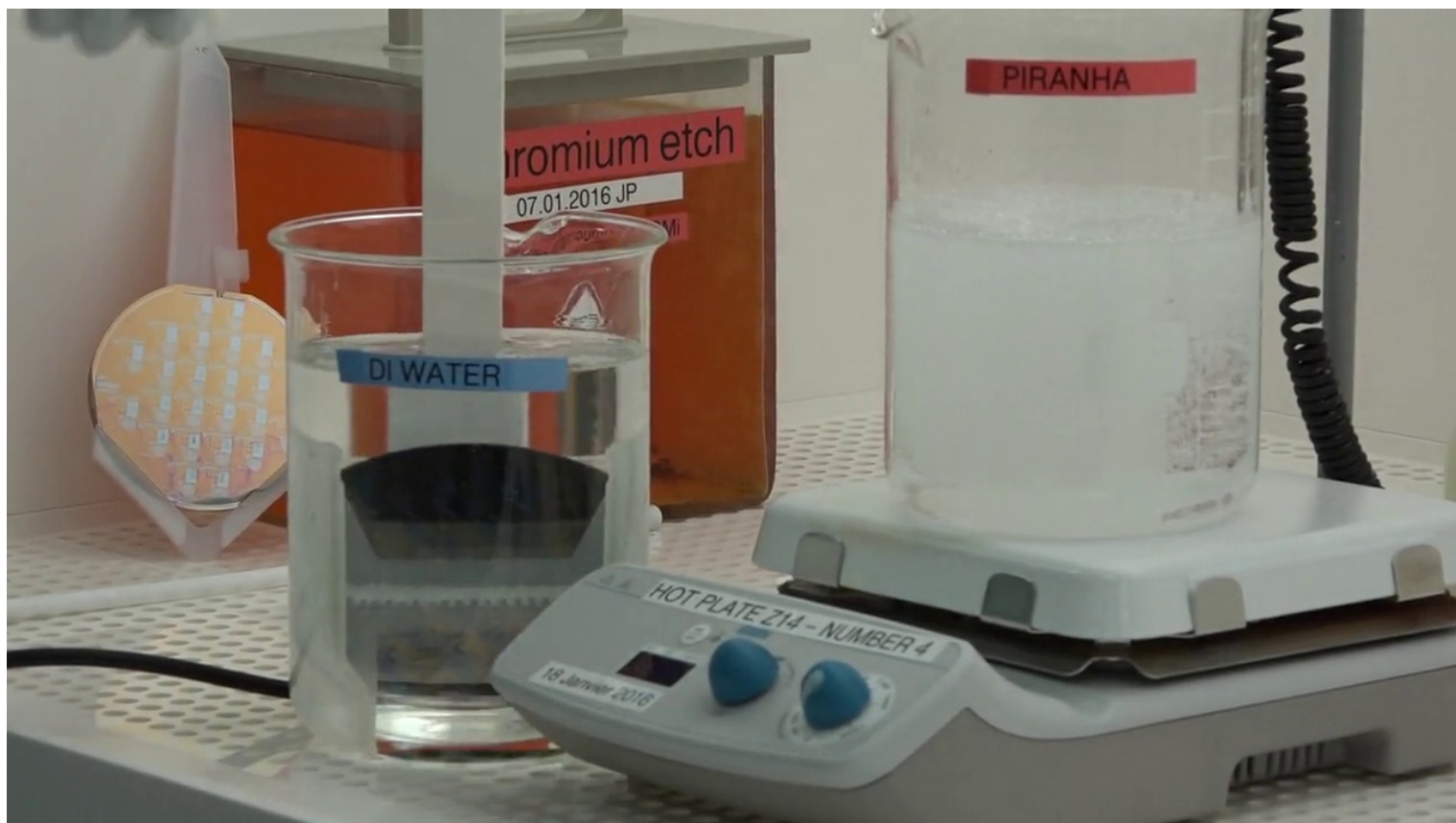
Subsequently, a second reaction starts: the sulphuric acid reacts with the hydrogen peroxide to produce atomic oxygen, which can dissolve elemental carbon. After these two reactions in the process, all organic residues are removed from the surface.



This movie illustrates the violent cleaning of a substrate in a piranha bath. One first prepares the sulphuric acid at the right temperature and then adds the hydrogen peroxide, which results in the development of fumes.

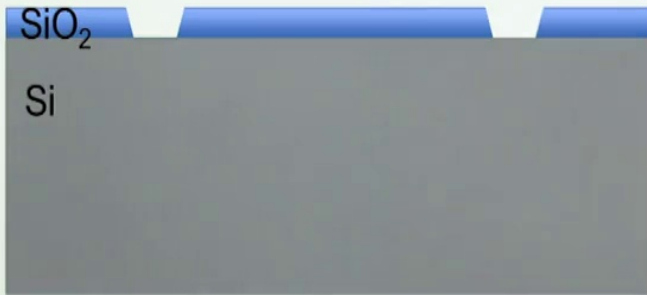


In this bath, a silicon wafer is immersed and cleaning proceeds here at a temperature above 130 degrees celsius.



The violent action of the bath on the substrate is like the attack of piranha fish on their prey and this fact gave the bath its name.

Etching of sacrificial layers



- A thin membrane can also be made by removing a sacrificial layer beneath a functional layer
- Step 1: patterning of SiO₂ sacrificial layer

Before we have seen that one can use bulk micromachining to realize a thin membrane on a wafer. Now we will see that wet etching permits to make thin membranes by another way. This technique uses the removal of a so-called *sacrificial* layer by the wet etching bath from beneath a functional layer. The first step in this process is the deposition and patterning of a sacrificial layer, in this case, a silicon dioxide layer. This patterning can be by dry or wet etching of this oxide layer.

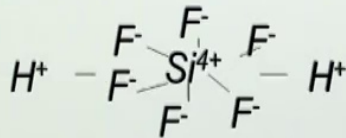
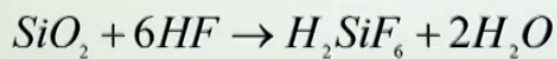
Etching of sacrificial layers



- A thin membrane can also be made by removing a sacrificial layer beneath a functional layer
- Step 1: patterning of SiO₂ sacrificial layer
- Step 2: deposition of polySi layer (for example by LPCVD)

The next step in the process is deposition of a functional layer, and this can be polysilicon in our example. It can be deposited by a low-pressure chemical vapor deposition technique.

Etching of sacrificial layers

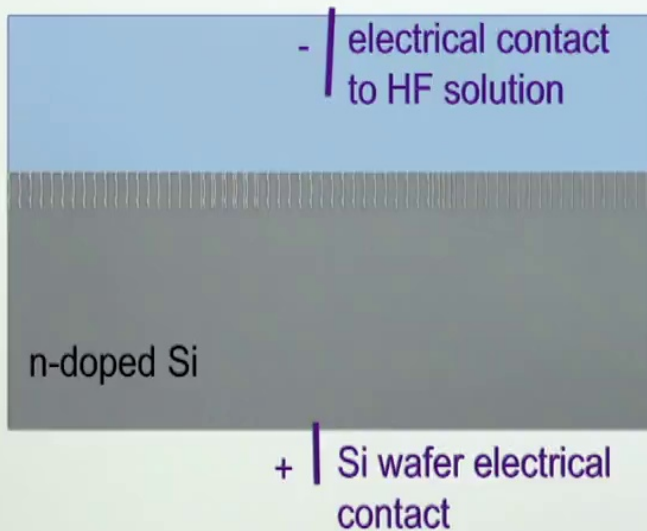


- A thin membrane can also be made by removing a sacrificial layer beneath a functional layer
- Step 1: patterning of SiO₂ sacrificial layer
- Step 2: deposition of polySi layer (for example by LPCVD)
- Step 3: wet etching of SiO₂ in a HF bath forming fluorosilicic acid (H₂SiF₆) and water
- This is an example of 'surface micromachining'

Micro and Nanofabrication (MEMS)

The final step in the process is the wet etching of the silicon dioxide using an HF bath, forming fluorosilicic acid as a reaction product. This is a fluorosilicic acid molecule. To remove the silicon dioxide from underneath the polysilicon layer, evidently one needs locally some access holes through the polysilicon layer so that there is access to the HF bath. Such a process where one makes a very thin membrane on top of a wafer is an example of a so-called *surface micromachining* process.

Realisation of porous Si



- Si can be made micro- or nano-porous by etching in a HF bath under certain conditions
- The unidirectional pores provide a large effective surface area and create a mechanically more fragile material

Micro and Nanofabrication (MEMS)

As a final application example of wet etching micromachining, we mention here the realization of so-called *porous silicon*. We will see later that silicon can be made micro- or nano-porous, as illustrated by these pores in the drawing, by etching the wafer in an HF bath while connecting the wafer to a positive voltage and the counter-electrode is in the HF solution. Doing so, one can create unidirectional pores that go into the silicon and that have a large effective surface area per wafer surface. Also, we can create locally at the top of the wafer a mechanically more fragile material due to the presence of so many pores.

Summary



- Thin Au films
- Thick Si substrates
 - Anisotropic etching
 - Isotropic etching
 - Thin membrane microfabrication; bulk micromachining
- Applications
 - Piranha wafer cleaning
 - Removing sacrificial layers; surface micromachining
 - Porous Si

Micro and Nanofabrication (MEMS)

This ends our introduction of wet etching. We have seen the isotropic etching of a thin gold film and subsequently, we have shown the phenomena of anisotropic and isotropic etching of a bulk silicon substrate. As well as the realization of a thin membrane in a silicon substrate, a technique we called *bulk micromachining*. Then we introduced wet etching applications such as piranha wafer cleaning, the removal of a sacrificial layer underneath a functional layer, a technique we called *surface micromachining*. Finally, we discussed the realization of porous silicon in an HF bath, under application of a voltage bias on the silicon wafer.
