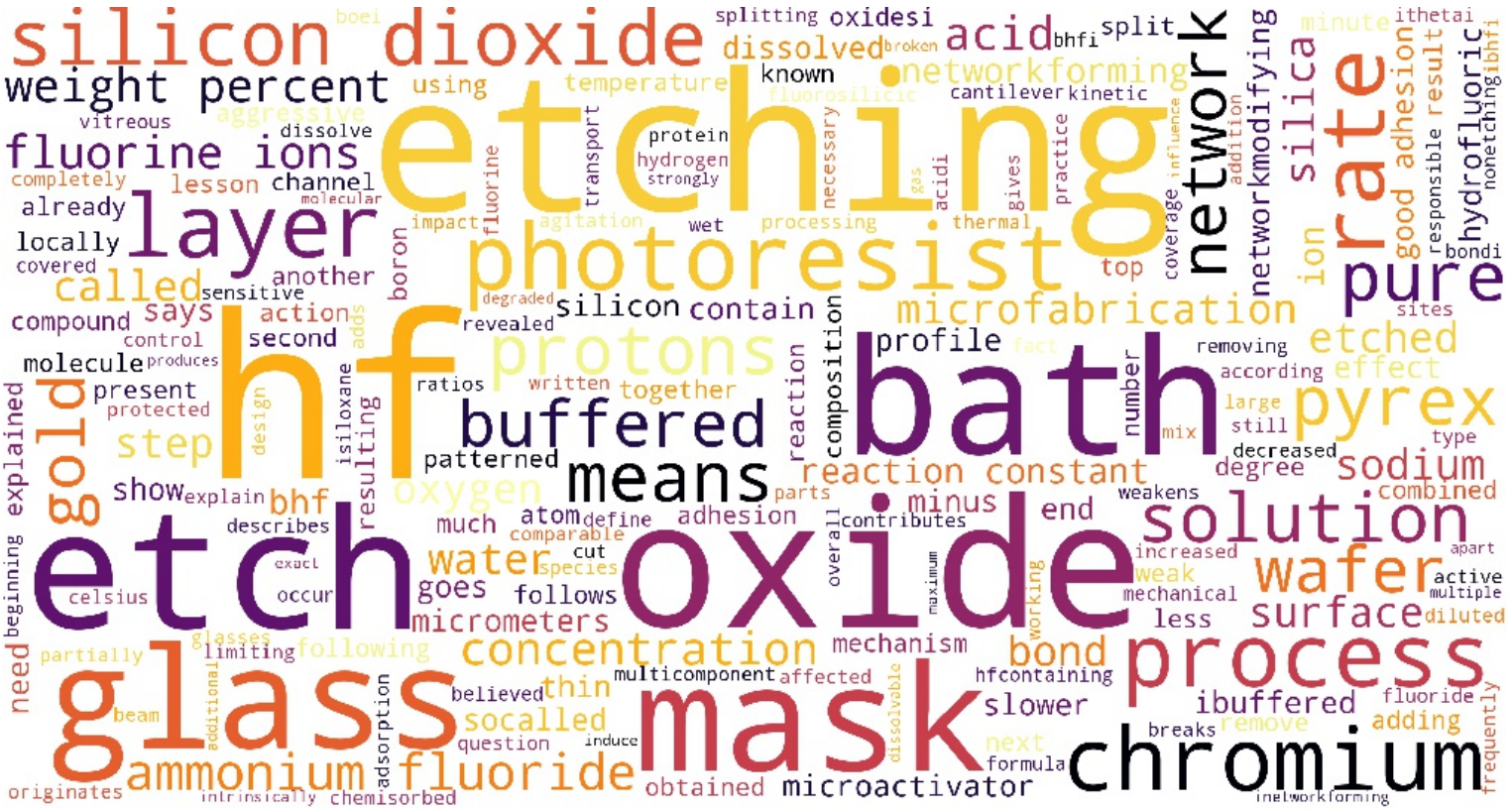

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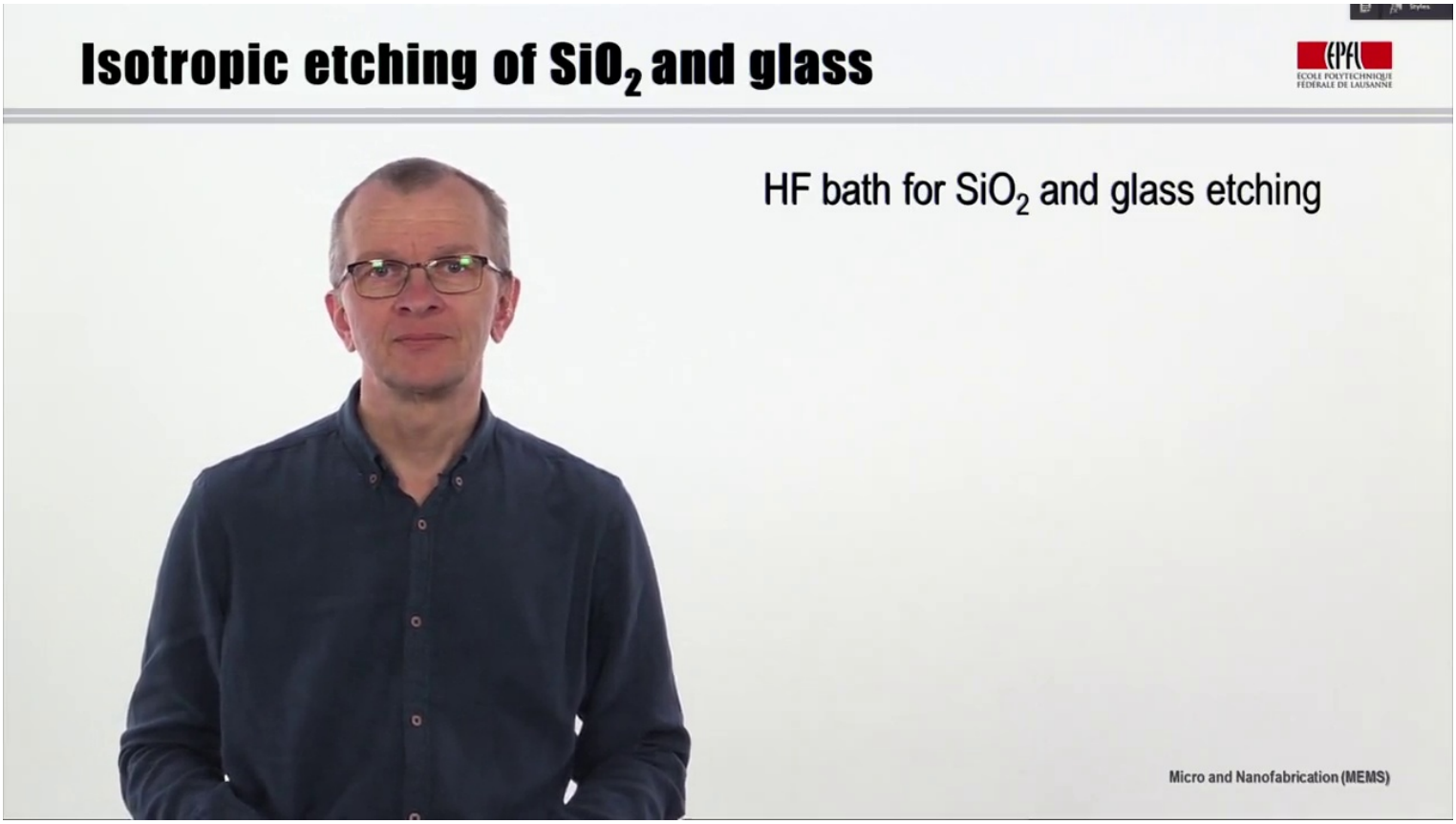
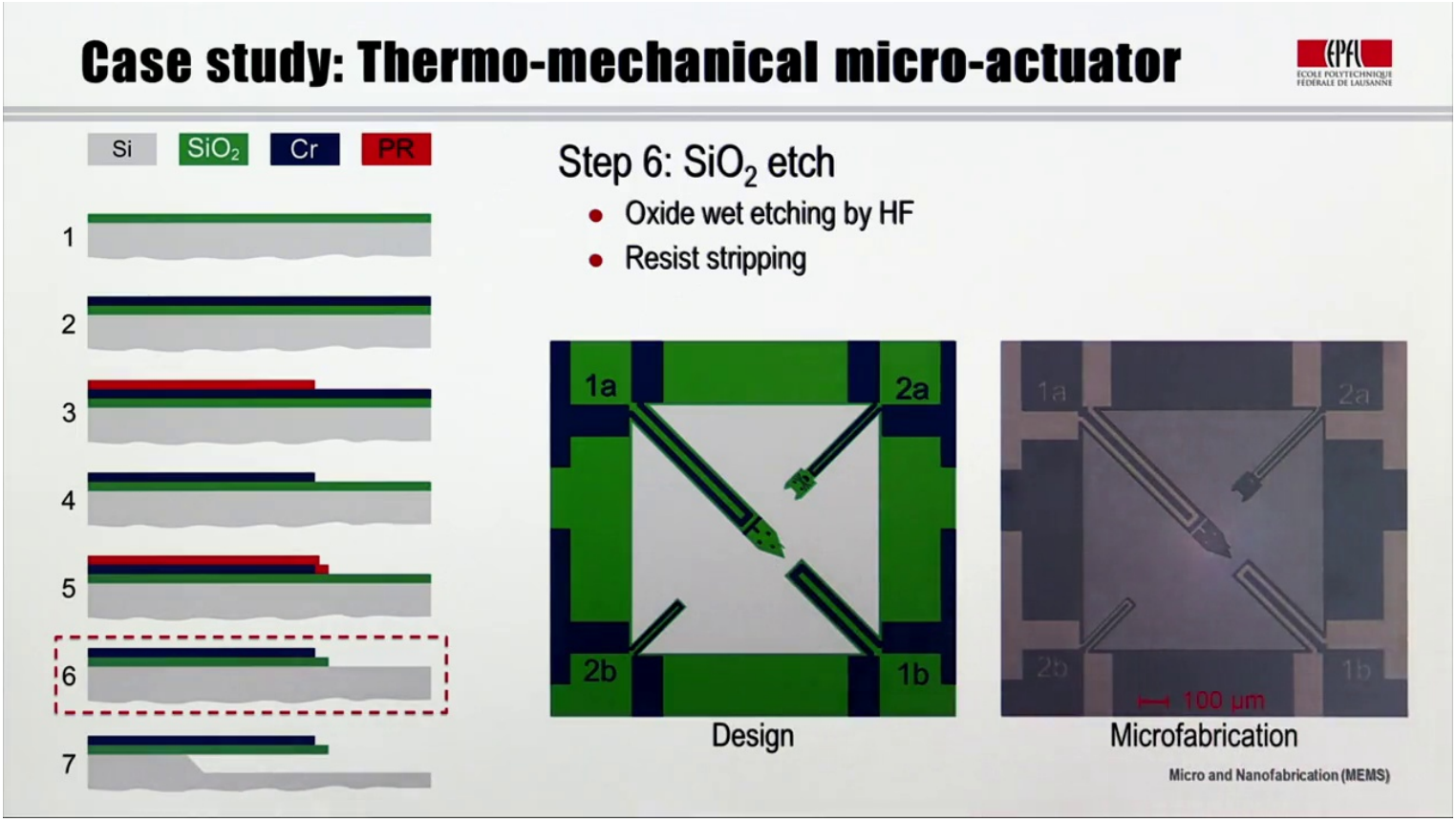


In this lesson, we will explain the hydrofluoric acid or HF bath that is used for silicon dioxide and glass wet etching.



This type of etching was already used in the process for the microfabrication of the thermal mechanical micro-activator for locally removing the silicon dioxide layer to define the oxide cantilever beam. We used a diluted HF solution, known also as buffered hydrofluoric acid, or BHF, and locally protected the chromium and silicon dioxide layer by a photoresist. During the buffered hydrofluoric acid etch, the chromium layer was then completely covered with the photoresist, so that it is not affected by the HF solution. Here, I show again the mask design of the micro-activator, and this is the result after this processing step.

HF etching of glass

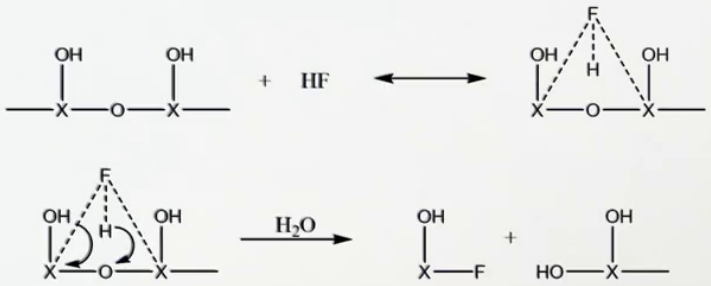
- Glass is dissolved by HF or HF-containing solutions
- HF in water is a weak acid; the solution contains H^+, F^- and HF_2^- ions
- Vitreous SiO_2 and multicomponent silica glasses are etched
  Overall reaction : $SiO_2 + 6\,HF \rightarrow H_2SiF_6 + 2\,H_2O$
- Reaction constants at 25 °C : $K_1 = [H^+][F^-]/[HF] = 6.7 \times 10^{-4}$ mol/l
  $K_2 = [HF][F^-]/[HF_2^-] = 0.26$ mol/l
- NaF or NH_4F do not etch SiO_2 → reactivity of F^- ions is negligible
- Insensitivity of etch rate to agitation → etching is kinetically controlled

Micro and Nanofabrication (MEMS)

Glass is dissolved by HF or HF-containing solutions. When HF is dissolved in water, it is a weak acid. That means it is partially split in protons, fluorine ions, and HF2 minus ions. Vitreous silicon dioxide and multicomponent silica glasses are etched according to this overall reaction, where this compound is called fluorosilicic acid, so this is the molecule that goes into solution, and that originates from the silicon dioxide. These are the two reaction constants at 25 degrees Celsius. K1 describes the splitting of HF into protons and fluorine ions, and the fact that this number is not large means that it's a weak acid. A second reaction constant says that also HF2 minus ions are present in the bath, and in comparable concentration to the fluorine ions. It's revealed by this number. Sodium fluoride or ammonium fluoride are known to not etch silicon dioxide, so that means that it is not the fluorine ions that are responsible for the etching. Also, the etching is not sensitive to agitation of the bath and that means it's not a question of transport, but it's kinetic control of the reaction at the surface which is the limiting step.

HF etching mechanism

- Nucleophilic chemisorption of HF to a X-O (X=Si) network
- Opening of silica surfaces from dissociated water species
- H^+, HF_2^- and HF adsorb on lattice bonds



- Rate-determining step : breakage of siloxane bond by combined action of the adsorbed species
- Etching rate $= k_1 \cdot \theta(H^+) \cdot \{k_2 \cdot \theta(HF_2^-) + k_3 \cdot \theta(HF)\} + k_4 \cdot \theta(H^+)$

θ : degree of coverage of active adsorption sites

in practice a few µm/min for 50 wt % HF at 25 °C

Micro and Nanofabrication (MEMS)

The following etching mechanism is believed to occur. HF is chemisorbed on the silicon oxide network, and there is a combined action of the hydrogen on the oxygen atom, and of the fluorine to the silicon atom, which weakens the bond between the silicon and oxygen. This is a so-called siloxane bond. At the end, this bond breaks, and the network is cut in two parts. The etching rate can be written by the following formula: theta is the degree of coverage of active adsorption sites on the glass, so this means that there are protons on the surface. This says that the etching rate is there if there are protons on the surface, and there is a second species, which is necessary: these are HF2 minus ions. So, this says that there is a combined action of the two to etch. And also this protein concentration is working together with HF, together, to remove the silicon dioxide. There is another process where there are only protons, so only protons can already dissolve the silicon dioxide. In practice, the etching rate in the HF bath, at this temperature, is a few micrometers per minute for 50 weight percent of HF in water.

Addition of NH_4F

- Addition of NH_4F shifts reaction equilibria

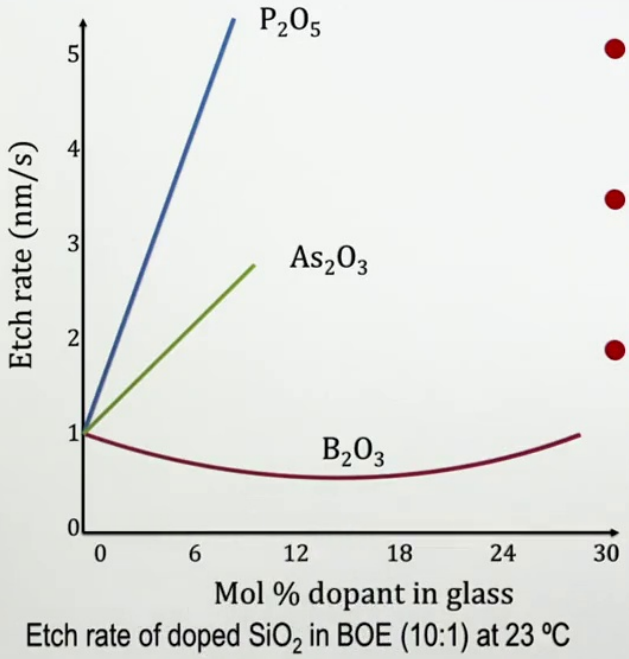
$$K_1 = [H^+][F^-]/[HF] = 6.7 \times 10^{-4} \text{ mol/l}$$
$$K_2 = [HF][F^-]/[HF_2^-] = 0.26 \text{ mol/l}$$

  results in increase in HF_2^- concentration and pH
- Mix of 40 wt% NH_4F with 49 wt% HF (in ratios from 6:1 to 10:1) is called buffered oxide etch (BOE) or buffered HF (BHF)
- Less agressive etch, so photoresist masks can be used

Micro and Nanofabrication (MEMS)

An etching bath that is frequently used is the one in which one adds the non-etching ammonium fluoride to the HF baths. The ammonium fluoride contributes with fluorine ions, which has an impact on this reaction constant, but, as this reaction constant still has to be the same, this means that this increased concentration here gives a decreased concentration of protons so, hence, less etching. So, the etching rate goes down by addition of the ammonium fluoride. A mix of 40 weight percent ammonium fluoride, with 49 weight percent HF, in these ratios, is called buffered oxide etch, BOE, or what we have called, in the beginning, buffered HF, BHF. 49 weight percent of HF is also called pure HF, as HF is, intrinsically, a gas which is dissolved in water, and this is the maximum dissolvable weight percent concentration. The use of buffered HF produces a slower and less aggressive etch so that photoresist masks can be used, as we have seen for the micro-activator. Photoresist would be very strongly degraded in pure HF baths.

Effect of glass composition



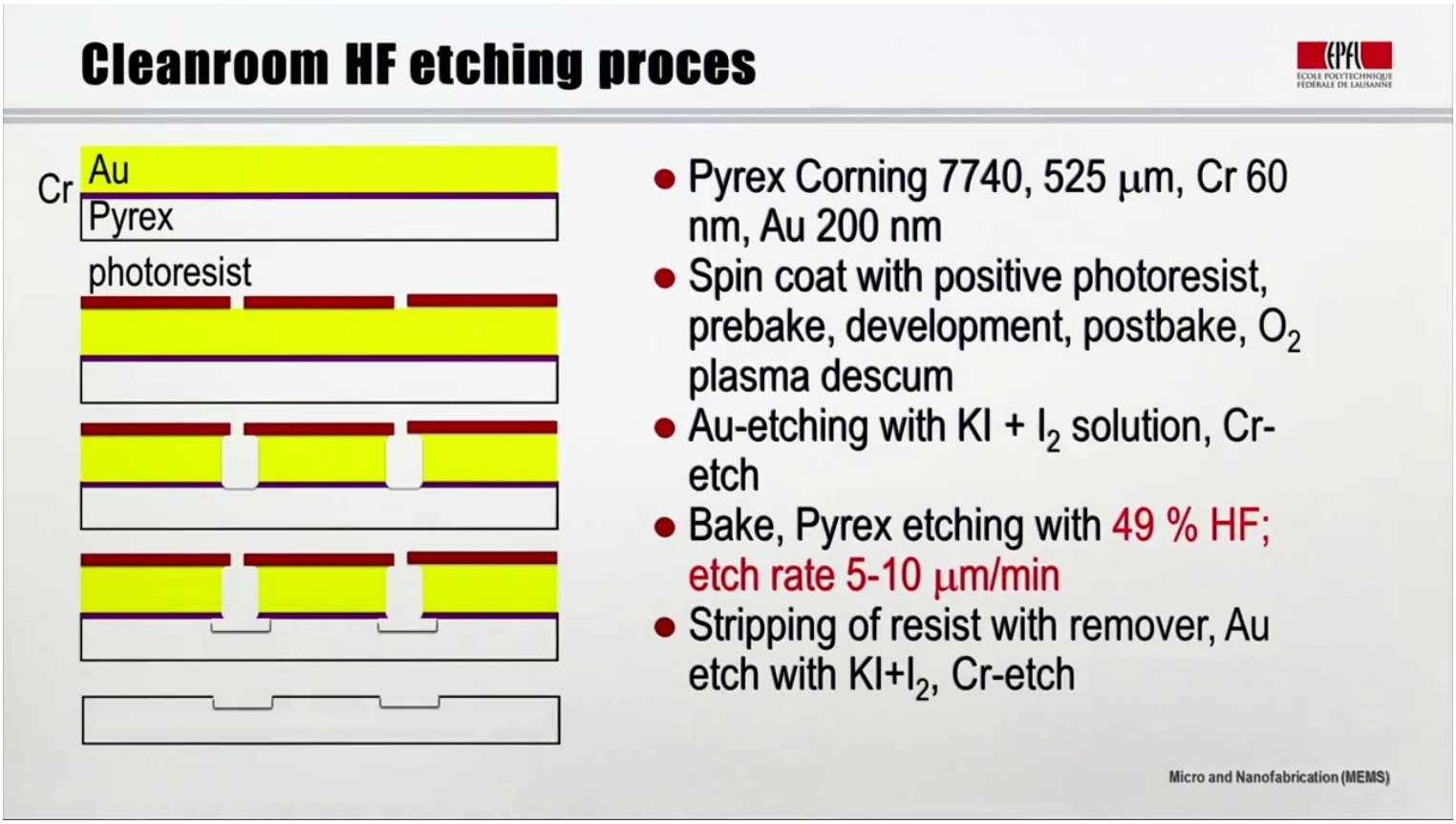
Etch rate of doped SiO_2 in BOE (10:1) at 23 °C

- SiO_2 interconnect structure is changed by 'network modifiers' and 'network-forming oxides'
- Network-forming oxide A_xO_y creates ≡Si-O-A- and -A-O-A- bonds, which need to be broken, resulting in slower etching
- Network-modifying oxides such as Na_2O, K_2O, CaO and BaO are incorporated by breaking a siloxane bond, forming non-bridging oxygen, resulting in faster etching

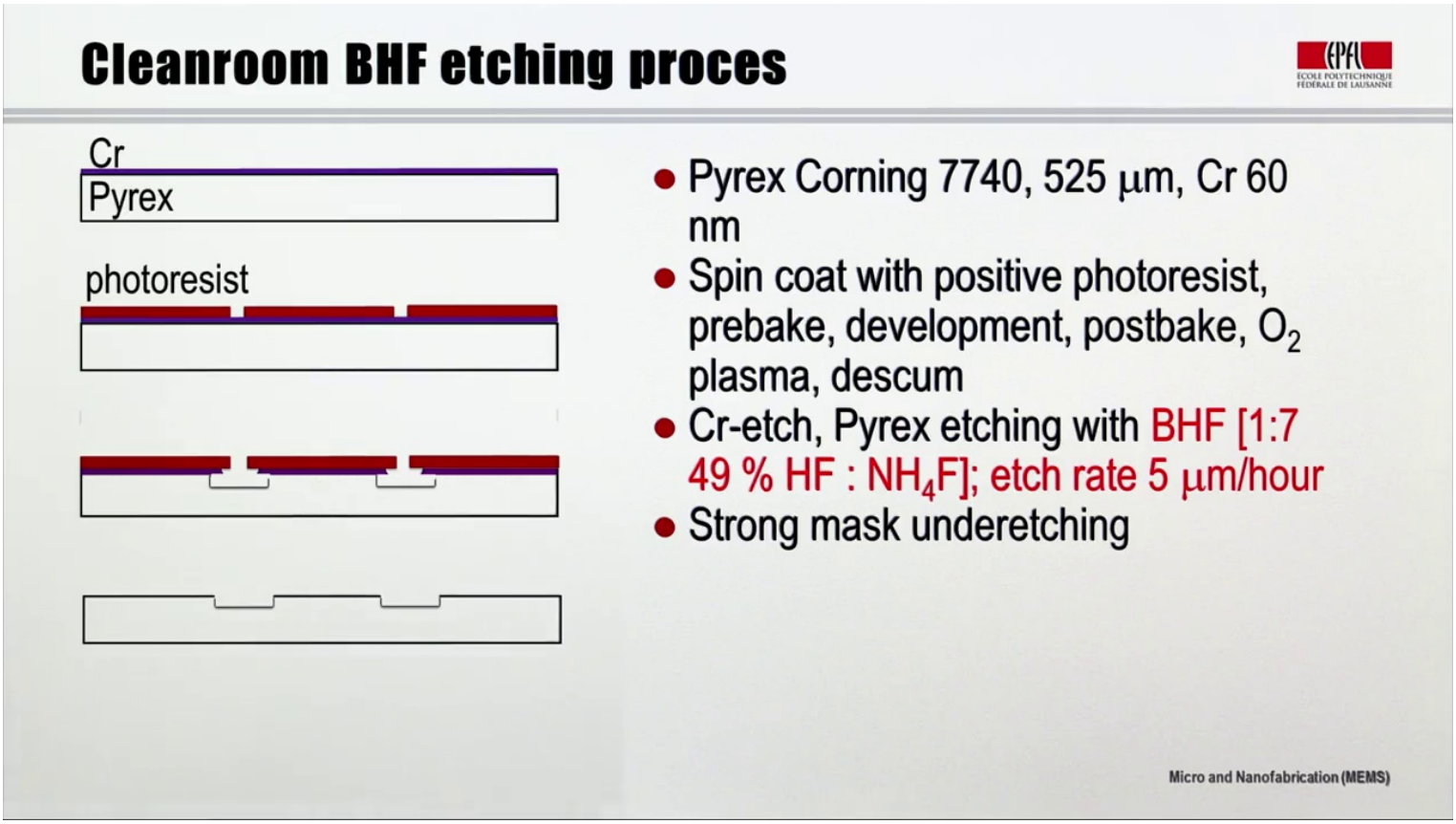
e.g. $Na_2O + \equiv Si - O - Si \equiv \rightarrow 2 \equiv SiO^- \cdot Na^+$

Micro and Nanofabrication (MEMS)

The exact glass composition also has an influence on the etch rate. A glass can contain multiple other oxides apart from silicon dioxide. It can contain so-called network-forming oxides, which are compounds that induce additional molecular bonds which need to be broken, resulting in slower etching. Boron oxide is an example of such network-forming oxides. A glass can also contain network-modifying oxides, such as sodium oxide, and when these are introduced in the silica network, they generate so-called non-bridging oxygen sites, resulting in faster etching. So, here, we see, by adding the sodium oxide to the network, splits somewhere the network, as the bond is fulfilled by the sodium ion. The effect of network-forming oxides and network-modifying oxides is illustrated in the curves obtained in buffered oxide etch for silica doped with the network-forming boron oxide, and these two network-modifying oxides. So, here, when there is more dopant, these etch rates go up, and this goes down, at least initially.

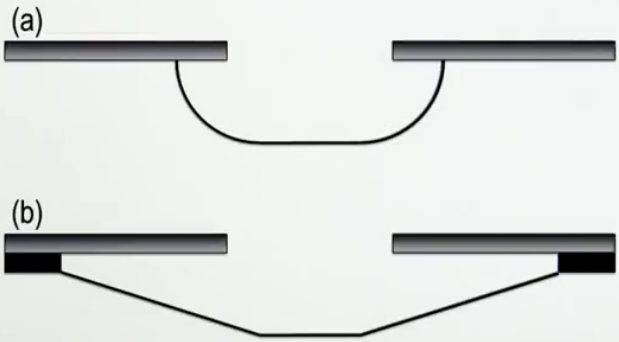


Here, we introduce a pure HF-based microfabrication process for Pyrex wafer. A mask that resists to this aggressive bath is gold, which, for good adhesion, needs to be deposited on a very thin chromium layer. On top of this gold layer, one deposits a photoresist, which is prebaked, developed, postbaked, after which an oxygen plasma descum step is performed to clear the liberated gold surfaces from organic molecules. Now follows a gold-etching step in a potassium iodide-iodine solution, followed by a chromium etch to remove the very thin chromium adhesion layer. Next follows the etching in pure HF. That means the 49% HF in water solution. Etching rates of five to ten micrometers per minute are obtained. At the end, the photoresist is removed, and the gold is etched away, as well as the chromium, leaving behind the microstructure etched in the Pyrex wafer.

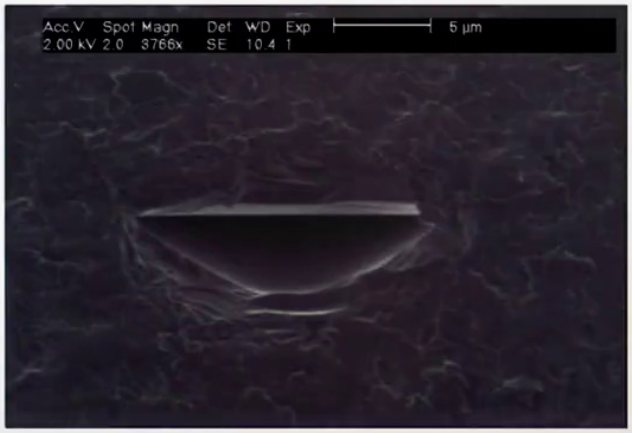


Now we present a Pyrex-etching process, in buffered HF, that does not require the microfabrication of the expensive gold mask, as photoresist can be maintained in the buffered HF bath. The process starts by sputtering a very thin chromium layer onto the Pyrex to which there is a good adhesion by the photoresist. Then we spin coat the photoresist layer in which the mask structure is patterned via the usual procedure. Next, we have to do the chromium etch, and then the Pyrex etch using the BHF solution. The etch rate is now five micrometers per hour, much slower than with a pure HF bath. However, we do not need to use a gold mask now. Note that, like in the pure HF case, there is mask underetching in this process, because it's a pure chemical process. The process ends by removal of the photoresist and chromium adhesion layers.

HF etching profiles



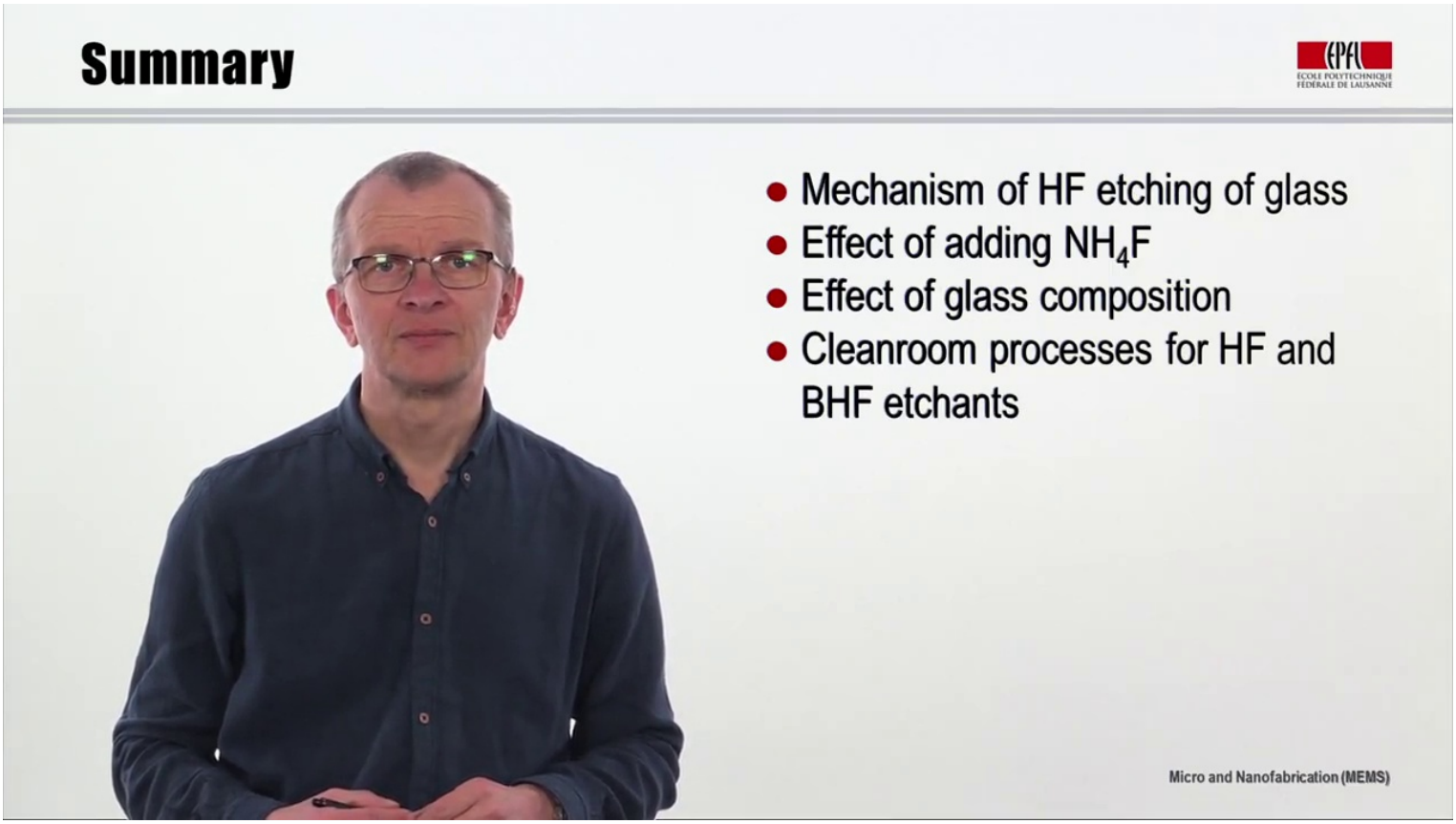
(a) Good adhesion of masking material
(b) Etchant penetration between mask and Pyrex



Pyrex-etched profile with second bonded Pyrex wafer to form microchannel

Micro and Nanofabrication (MEMS)

Here, we show typical profiles that result from an HF or BHF etching process. The profile in a) is the normal one, but, sometimes, one obtains a profile like shown here; much more widened with respect to the original hole dimension in the mask. This is an indication that there was not a good adhesion of this mask to the glass, and that the etching liquid could infiltrate in between the glass wafer and the mask, so that there is continuous etching underneath the mask. The picture on the right shows an etched channel in Pyrex, and, here, this was patterned on top of the wafer, which was then bonded, at high temperature, with another Pyrex wafer to make a closed channel.



In this lesson, we have explained the mechanism of HF etching of glass wafers. We demonstrated the effect of adding ammonium fluoride to the bath, which produced a buffered oxide etch, or BHF bath. Then we explained the effect of glass composition on the etch rate by incorporating either network-forming oxides or network-modifying oxides in the silica network. Finally, we showed cleanroom processes for Pyrex microfabrication using both HF and BHF baths.