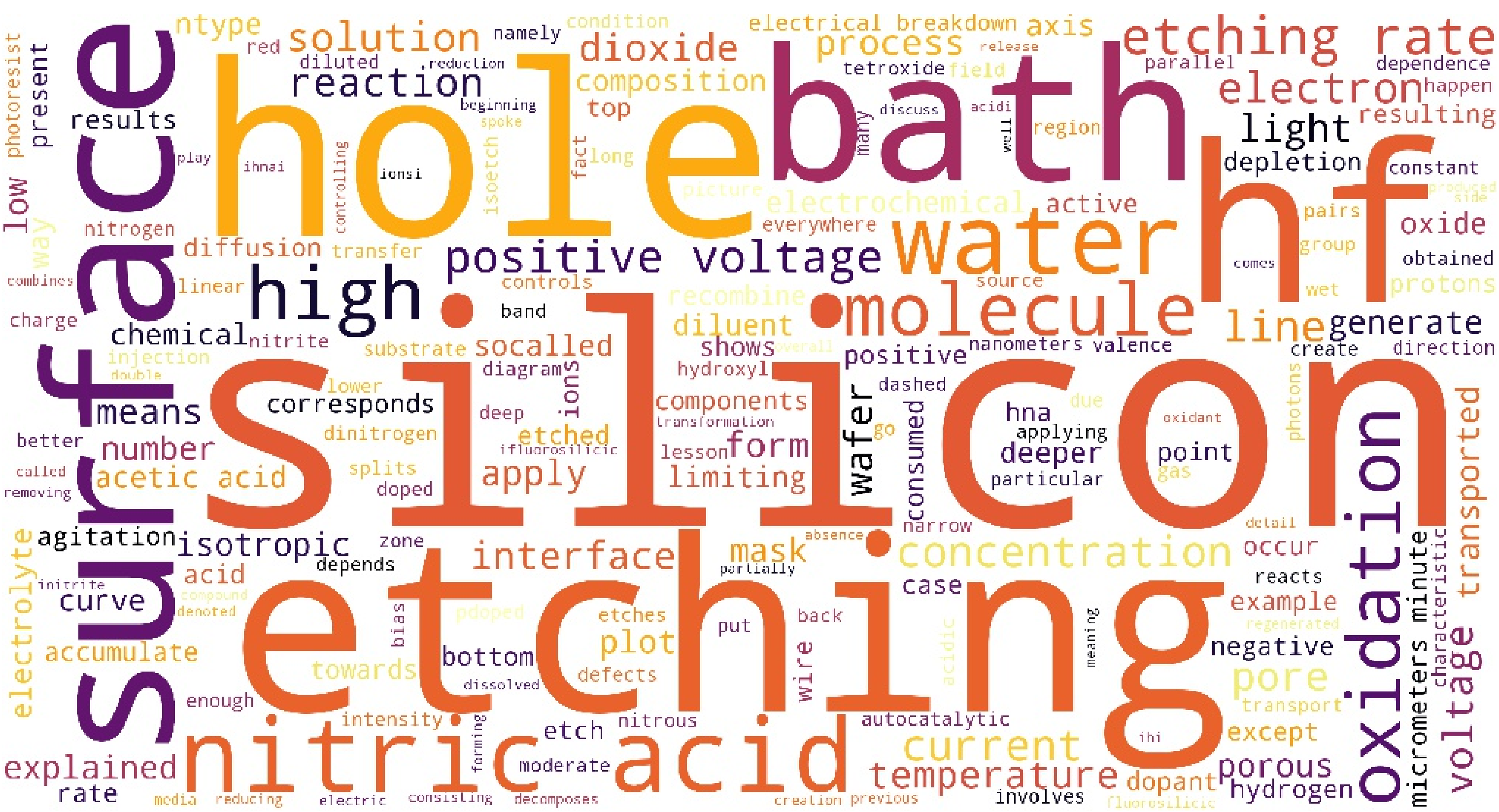

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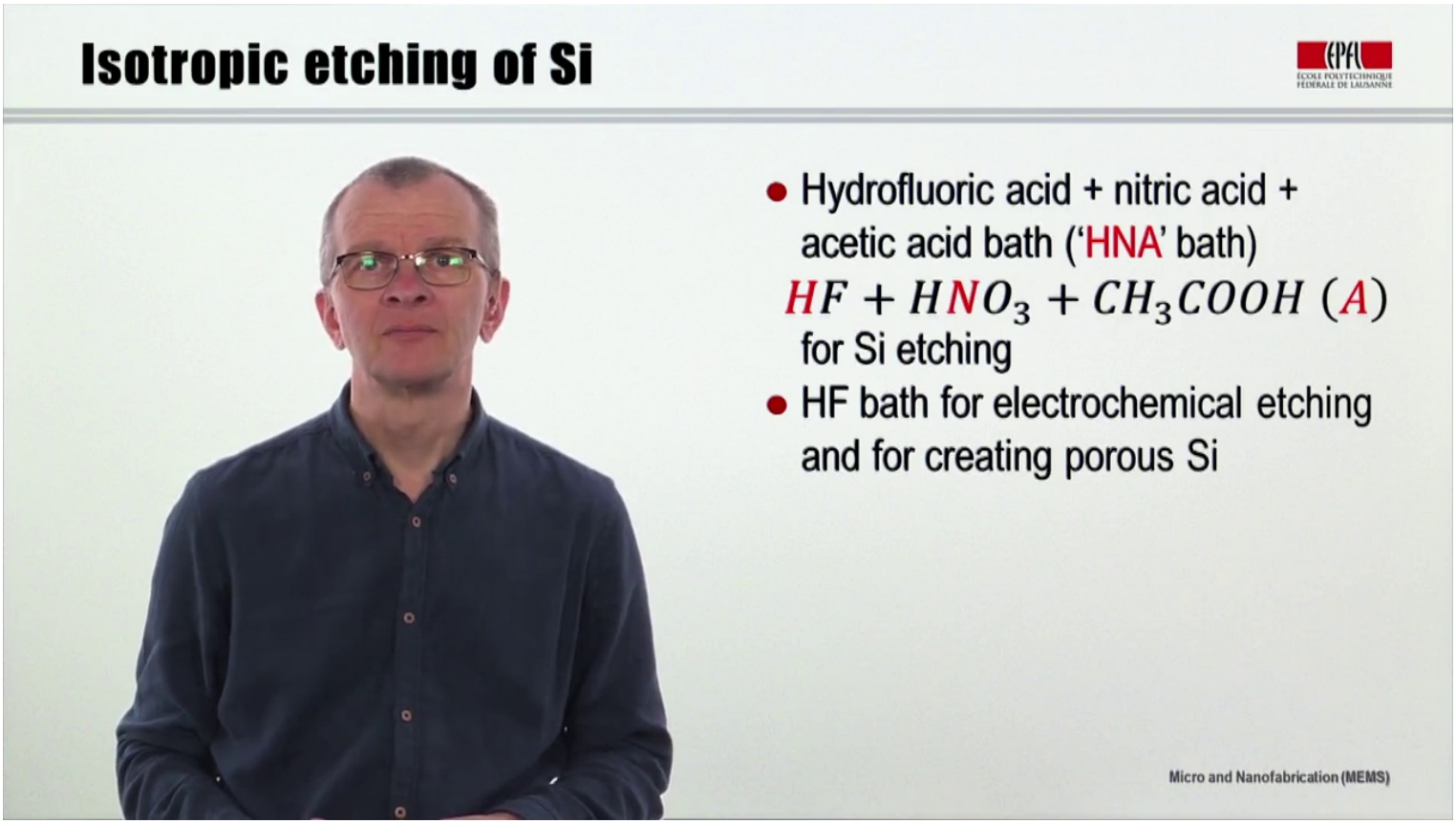
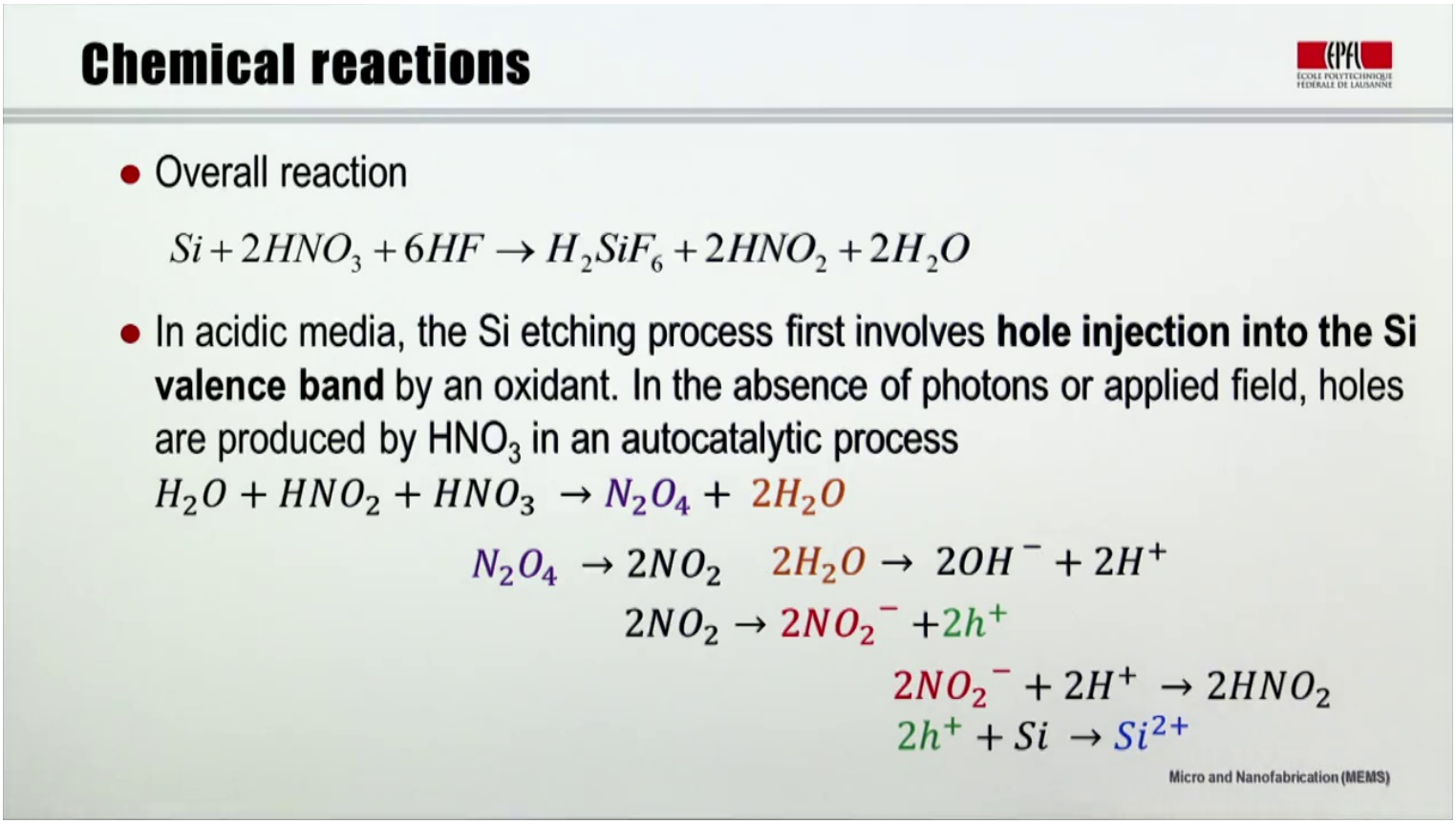


Now we will discuss a chemical etching bath for the isotropic etching of silicon, which is a so-called HNA bath consisting of nitric acid, HF, and acetic acid. Then we present the HF bath for electrochemical etching of silicon, and for creation of porous silicon.



The HNA bath has three components, two of which are active in the etching, namely, the nitric acid and the HF. The acetic acid is a diluent for reducing and for better controlling the etching rate. That is why we only see these two components in the reaction. The silicon is etched from the substrate, and transported into the solution in the form of this molecule, which is called fluorosilicic acid, while the HNO3 and HF are consumed. Now we will detail what happens during etching. In acidic media, like nitric acid, the silicon etching process first involves hole injection into the silicon valence band by the oxidant, in this case, the HNO3, which is meaning the same as removing an electron out of the valence band of silicon. In the absence of light, or an electric field, holes are produced by nitric acid in an autocatalytic process. HNO3, when it is dissolved in water, partially splits up in HNO2, and it is this HNO2 that reacts with HNO3 to form this compound, N204, or dinitrogen tetroxide, and water. The dinitrogen tetroxide decomposes in 2NO2, or nitrogen dioxide molecules, while the water splits up in two hydroxyl ions and two protons. The nitrogen dioxide is the active molecule that generates the holes, denoted as h+, as well as N02-, or so-called nitrite ions. The nitrite ions recombine with protons to form HNO2 molecules, while the holes charge the silicon. We see here that a nitrous acid, the HNO2, is regenerated because, in the beginning, we spoke of an autocatalytic process. HNO2 is not consumed, but the HNO3, in a way, is consumed, as, on the other side, we have 2HNO2 molecules.

Chemical reactions

- Si^{2+} combines with OH^-

  $$Si^{2+} + 2OH^- \rightarrow Si(OH)_2$$

- Generation of SiO_2 with release of H_2O

  Overall oxidation reaction

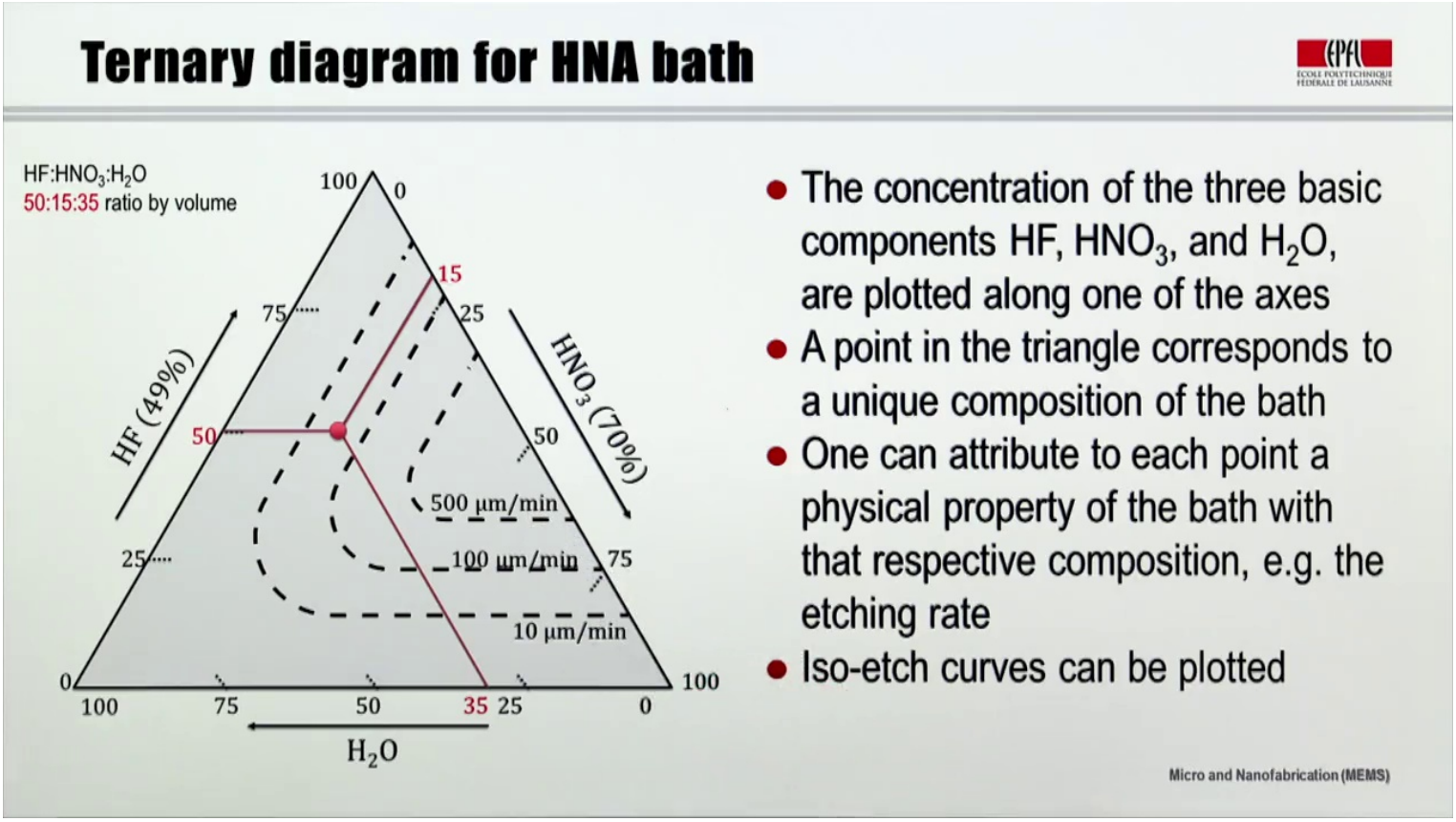
  $$Si + 2HNO_3 \rightarrow 2HNO_2 + SiO_2$$

- Next follows the dissolution of the oxide by HF

  $$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

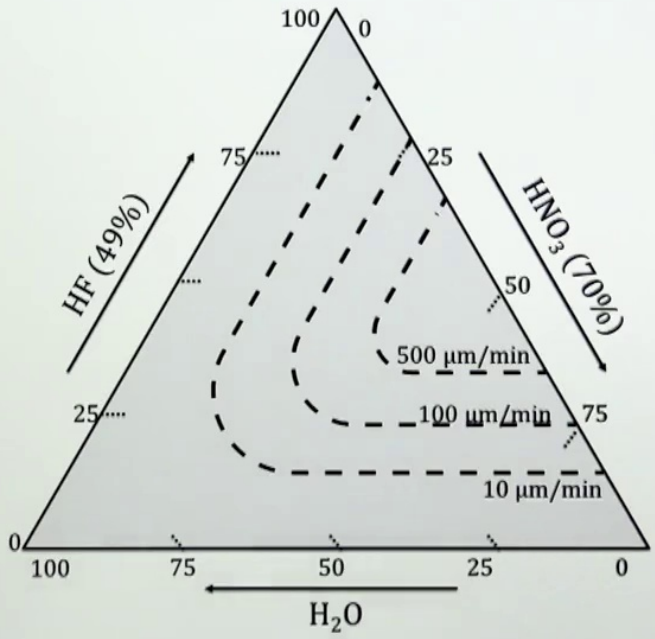
- Acetic acid (CH_3COOH) is a diluting agent (also water can be used)

Now we have a double positive charge on the silicon, and this combines with two hydroxyl ions to form this Si(OH)2 group, and these groups on the surface, they recombine to generate silicon dioxide and the release of water. The overall reaction until now is the transformation of silicon in silicon dioxide, under the reduction of nitric acid into nitrous acid. Now the HF comes into play. We have seen, in the previous lesson, how HF reacts with the silicon dioxide, forming the molecule, fluorosilicic acid, and water. As said before, the acetic acid is not entering in these chemical reactions because it's a diluent. Also, water can be used in the bath as a diluent, by the way.



A ternary diagram like this allows to plot the three chemical components of the bath on a two-dimensional sheet of paper. So, this is an axis where we plot the HF concentration from 0 to 100%. This is an axis where we plot the nitric acid concentration from 0 to 100%, and on this axis, we plot the diluent, in this case water, from 0 to 100%. Each point of the triangle corresponds to a unique composition of the bath. For example, this red point corresponds to a mixture with 50% pure HF, 15% of HNO3, and 35% of water, and you see, together, this forms 100. This red line says that, all along this line, if I continue just like that, there is, everywhere, 50% of HF, and, when moving on the line, one interchanges HNO3 with water. So, the more we go in this direction, more will there be HNO3 and less water. Now we can measure the etching rate for each bath composition, and then plot the ensemble of points where the etching rate is the same. This is a so-called iso-etch curve. For example, this dashed line corresponds to all compositions of the bath, where the etch rate is 500 micrometers per minute. On this line, it is 100 micrometers per minute. We see that the highest etching rates are obtained in a zone of the diagram where one has about the same quantities of HNO3 and HF, because both are needed, and where there's only a small concentration of water, which is logical.

Iso-etch curves

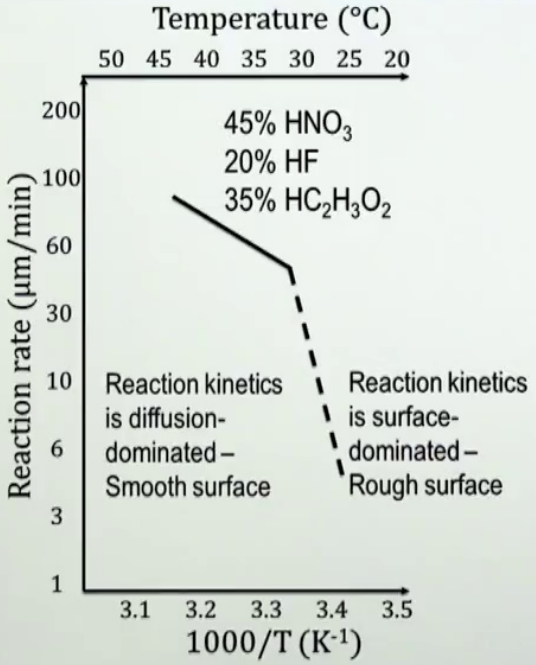


- For high HF concentration, the iso-etch curves are parallel to the lines of constant HNO_3 and HNO_3 controls the etching rate (oxidation process is limiting)
- For high HNO_3 concentration, the iso-etch curves are parallel to the lines of constant HF and HF controls the etching rate (removal of the oxide is limiting)
- Maximum etch rate when HNO_3 and HF are equilibrated and when H_2O concentration is low

Micro and Nanofabrication (MEMS)

For high HF concentration, that's in this region, the iso-etch curves are parallel to the lines of constant HNO3, and this means that it's the HNO3 concentration that controls the etching rate. In fact, there is enough HF, and the little number of HNO3 molecules limit the etching rate. And, in the same way, for high HNO3 concentration, the iso-etch curves are parallel to the lines of constant HF concentration, and this means that HF controls the etching rate, as there are relatively few HF molecules, and the removal of the oxide represents the limiting step.

Arrhenius plot of the etching rate

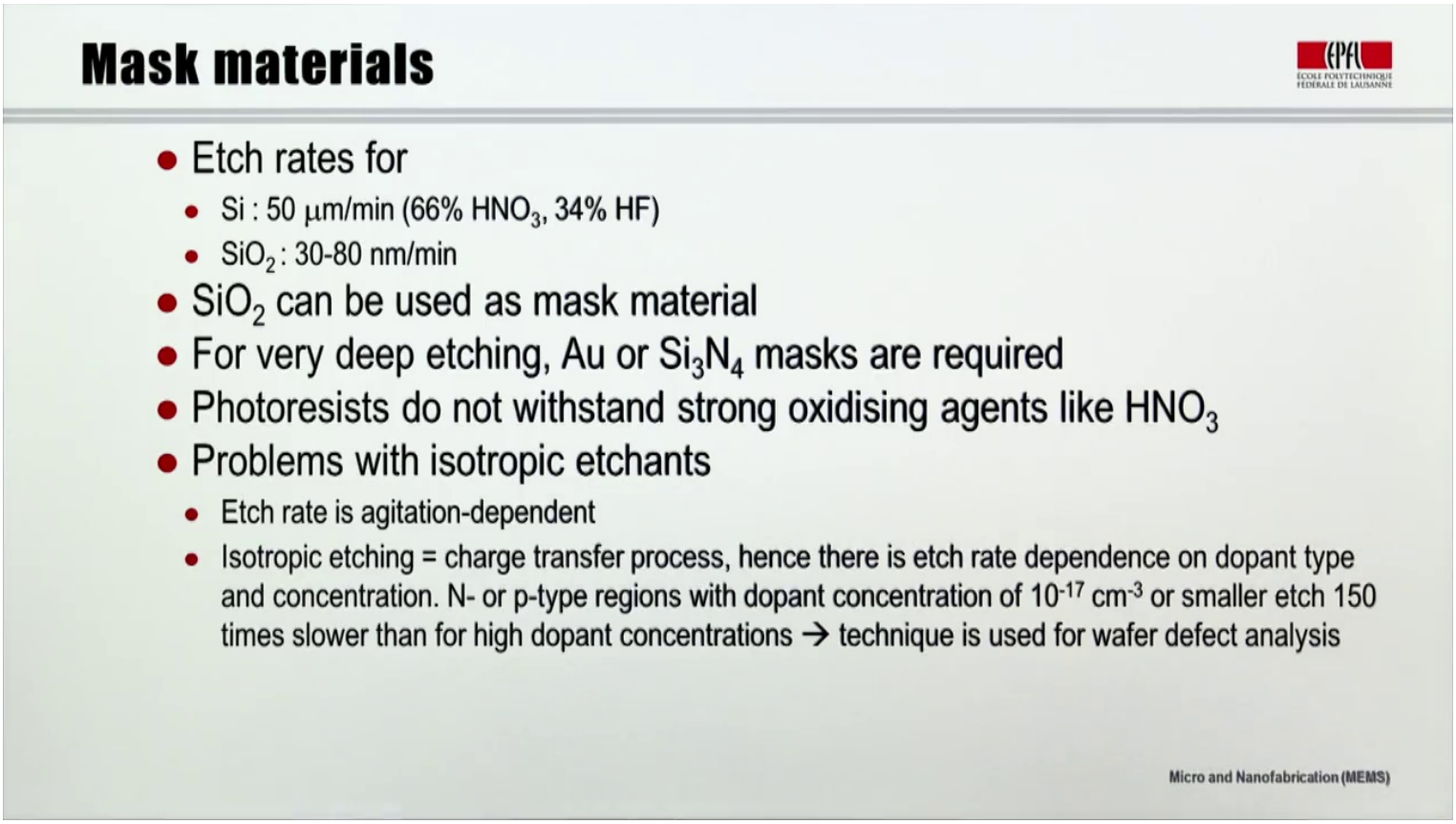


- At low T, the etching reaction is limiting the process and the activation energy is associated with the oxidation reaction
- At high T, diffusion of active species in the bath is limiting and etching leads to smooth surfaces
- Etching rate depends on agitation of the bath at high T

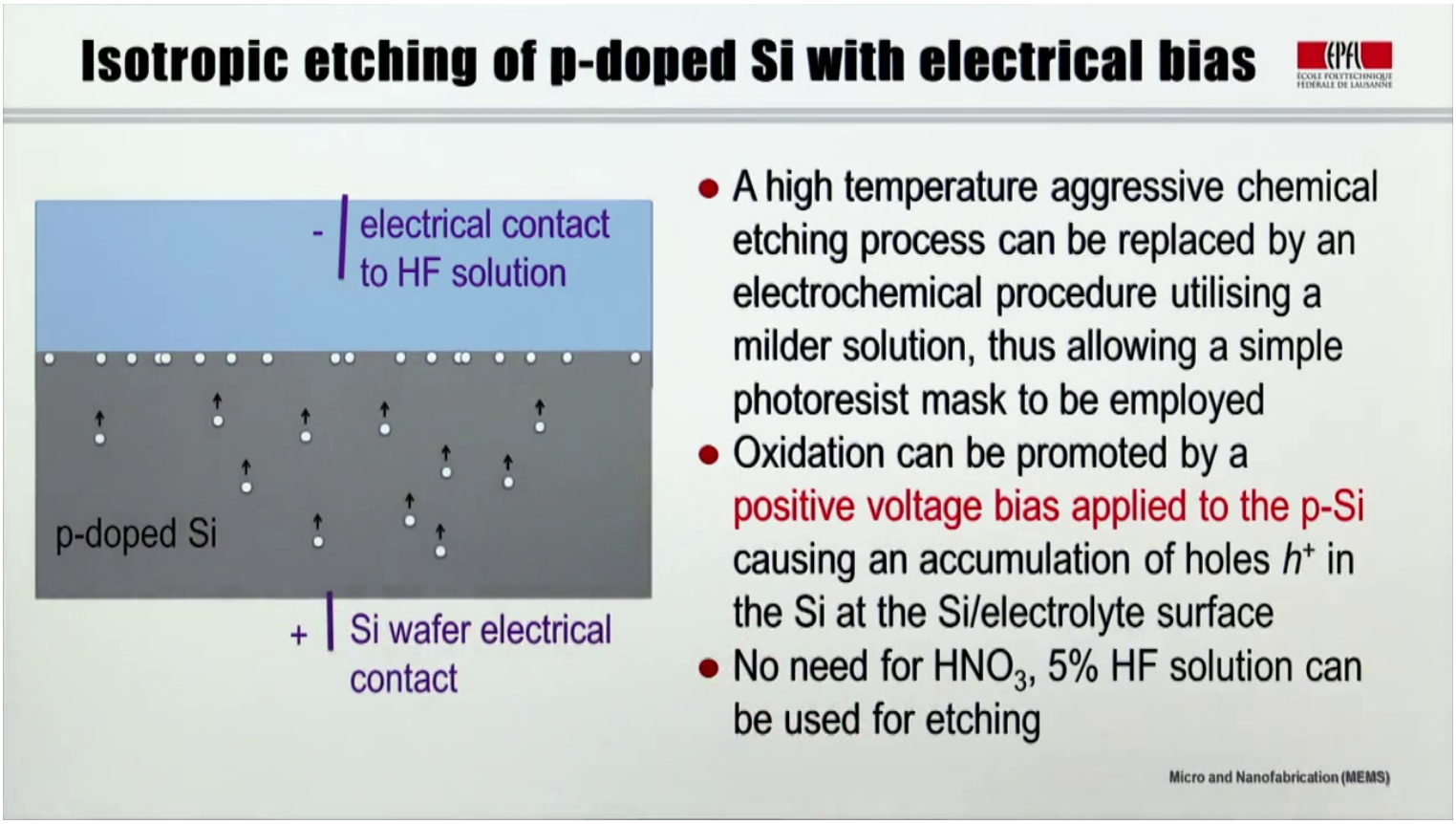
(after Schwartz and Robbins, J. Electrochem. Soc. 108, 365 (1961))

Micro and Nanofabrication (MEMS)

Here, we present the temperature dependence of the etching rate for a bath of particular composition, namely that having 45% of nitric acid, 20% of HF, and 35% of acetic acid. The x-axis is linear in one over the temperature, while, on the top, we have plotted the temperature corresponding to this linear axis. At low temperature, that means at a high one over T value, the etching reaction is limiting the process, and the activation energy, that is the slope of this curve, is associated with the oxidation reaction which is the slowest. After etching, the surface shows some roughness. At high temperature, that means at low one over T, diffusion of the active species in the bath is limiting the etching reaction, and the etching results in smooth surfaces. At high temperature, this etching rate depends now on the agitation of the bath, as, by agitation, transport of molecules is better than by diffusion only. Also, when diffusion is limiting the reaction, when one has a wider opening in the mask, this results in deeper etching, as the access for the reactive molecules is facilitated.

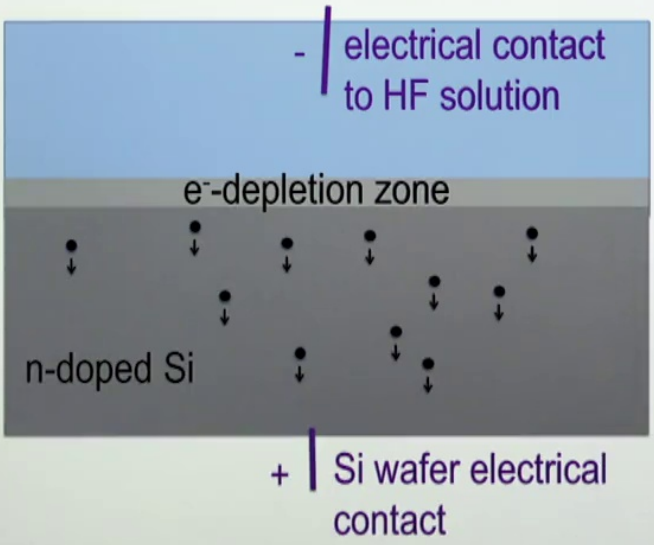


What are the mask materials that one can use in an HNA etching process? If one is at a temperature where the silicon etching rate is 50 micrometers per minute, the silicon dioxide etching time is in between 30 and 80 nanometers per minute, much slower, so that silicon dioxide can be used as a mask when etching silicon. For very deep etching, one needs gold or silicon nitrite masks. One cannot use photoresists as they do not withstand long to a strong oxidizing agent like nitric acid. There are some issues with isotropic etchants, like the etch rate that is agitation dependent and depends on the local condition of the bath. We explained, during the discussion of the isotropic etching mechanism, that there is a hole transfer process to the silicon, hence, there is an etch rate dependence on the dopant type and concentration of the dopant in the silicon, so it makes a difference whether one has n- or p-type regions doped in the silicon, or if they have different dopant concentrations. However, this characteristic can be used to reveal the number of defects on the surface of a silicon wafer, for example. One etches the surface, and defects can be etched faster, and can then be directly seen on the surface.



We explained that etching of silicon in an acidic solution involves the transfer of a hole from the nitric acid to the silicon. It is possible to replace this chemical injection of a hole by an electrochemical procedure, utilizing a milder solution, so that a photoresist mask can be used. Suppose one has a p-doped silicon wafer, and that one attaches a conducting wire where one puts a positive voltage bias. By this, holes will be transported in the silicon, and accumulate at the silicon electrolyte interface. We have seen that these holes are essential for oxidation, so the oxide forms, and this can now be removed by just having an HF solution, so there is no longer nitric acid, but there will be etching because there was oxidation at the surface.

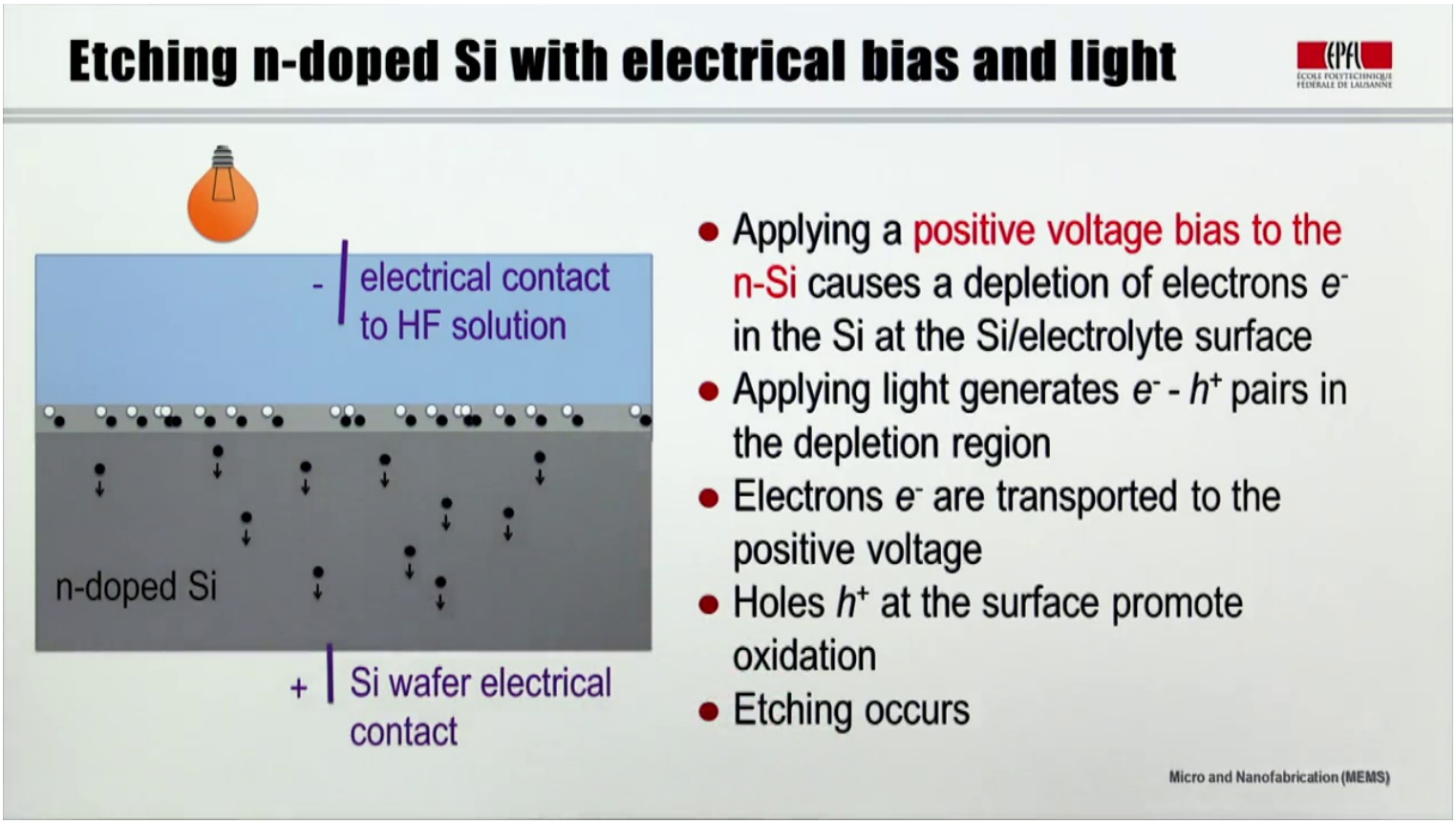
Situation of n-doped Si with electrical bias



- Applying a positive voltage bias to an n-Si wafer causes a depletion of electrons e^- in the Si at the Si/electrolyte interface
- No etching occurs, except when the voltage is so high that electrical breakdown occurs, transporting h^+ to the interface

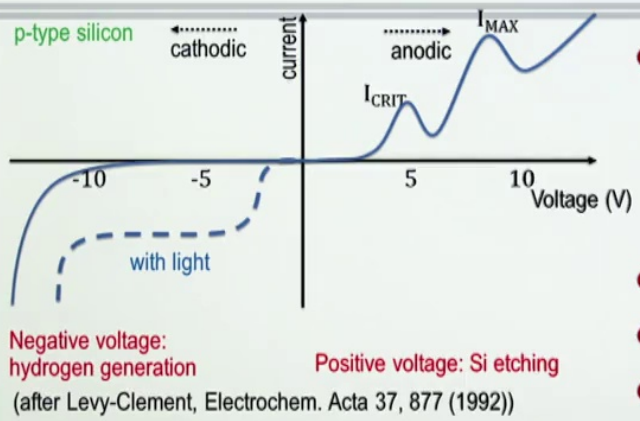
Micro and Nanofabrication (MEMS)

Now we change to silicon with n-doping, and we attach, again, a wire to the back of the substrate, and apply the positive voltage. What will happen now is that the electrons, that are the mobile carriers, will be attracted towards the positive voltage and we will get, here, an electron depletion zone at the contact with the solution. No etching will occur in a diluted HF solution as no holes are present at the surface, except if this positive voltage would be so high that there is an electrical breakdown by which holes can be transported to the surface.



We are now again in the case with n-type doping, and we have applied here a moderate positive voltage. If we now add to the setup a light source, we create photons that generate electron hole pairs, and the electrons go towards the positive voltage, while the holes remain here. Now there can be oxidation, and, subsequently, the HF etches away the oxide.

Current-voltage characteristics

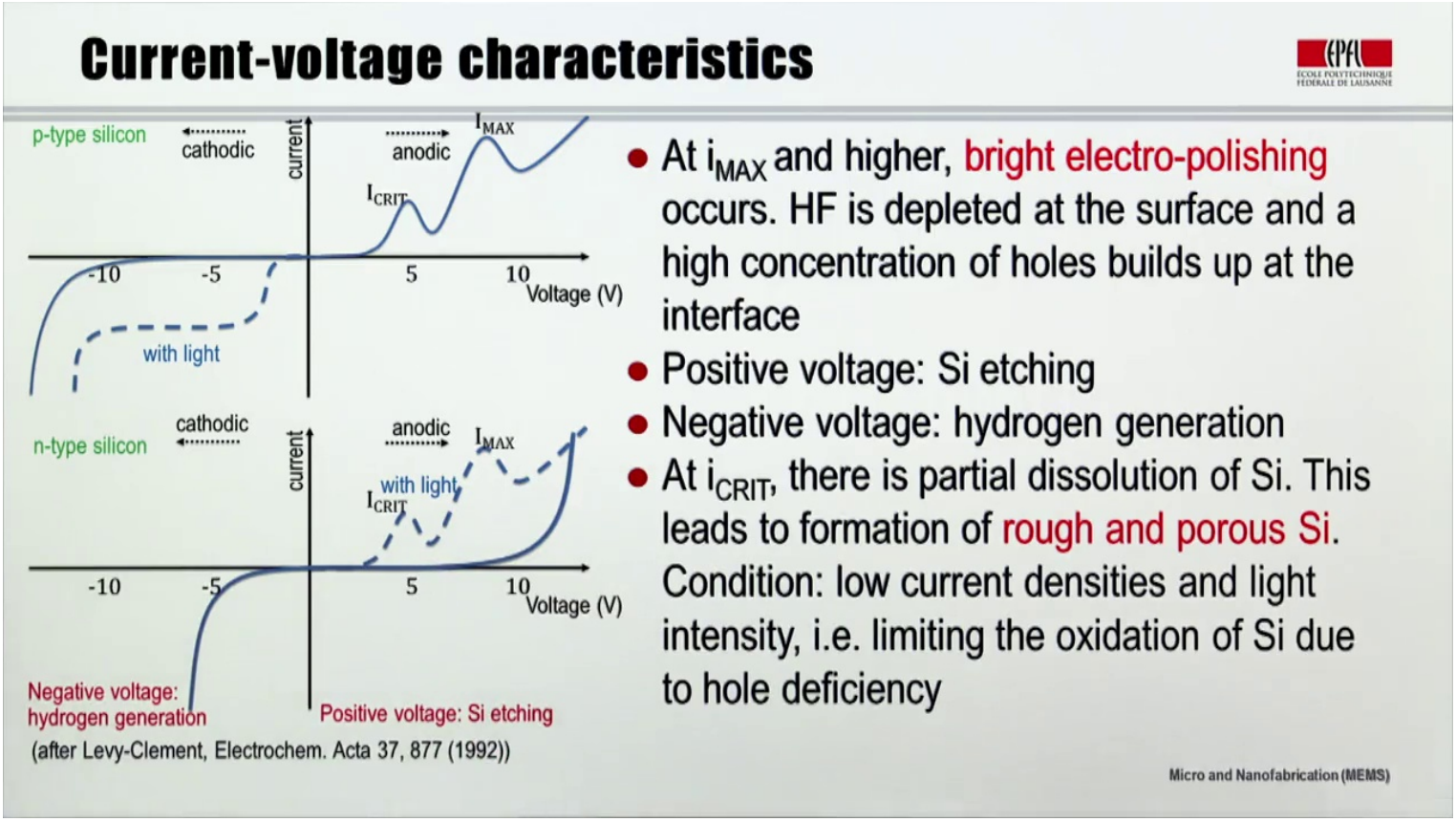


(after Levy-Clement, Electrochem. Acta 37, 877 (1992))

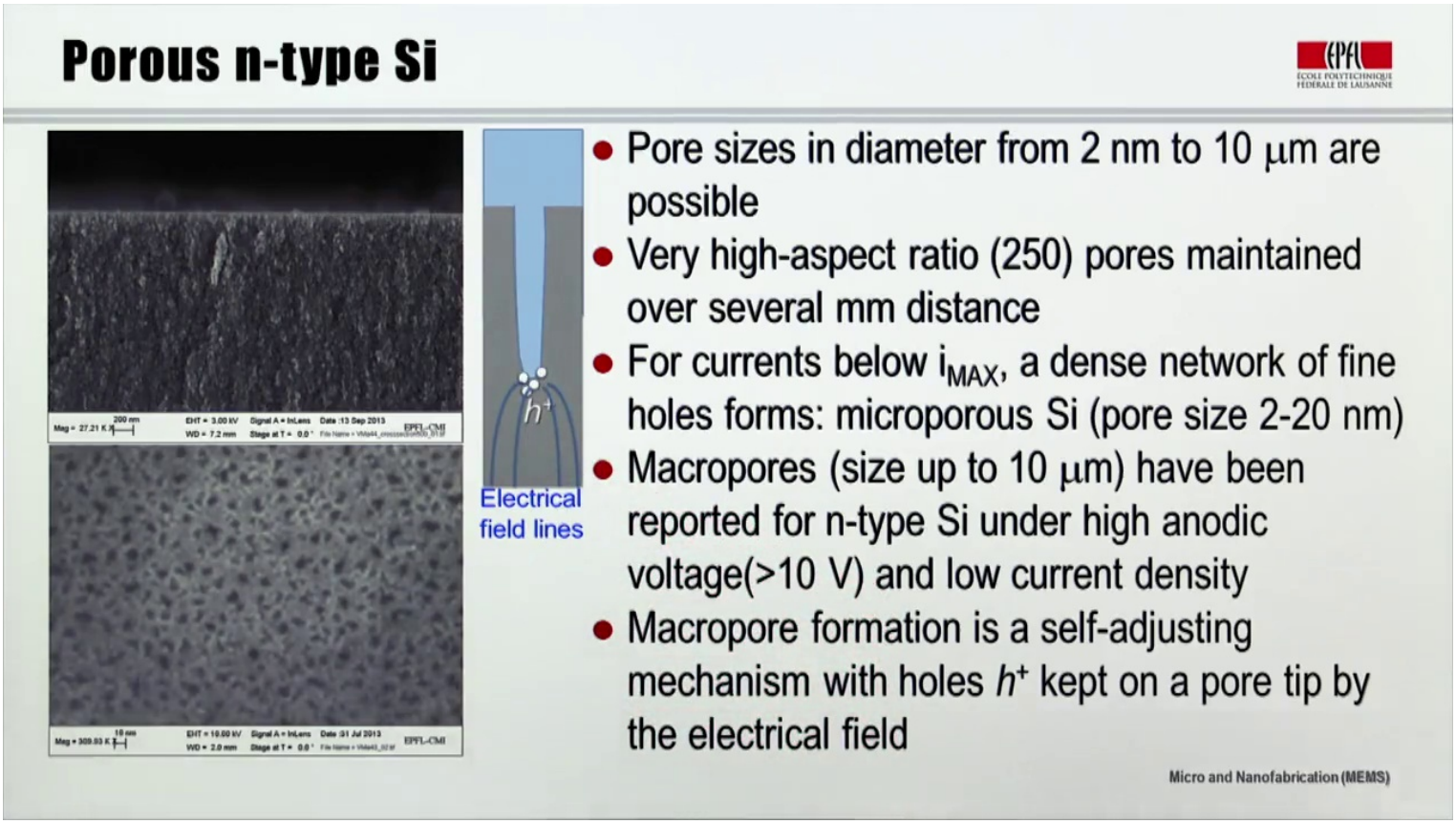
- At i_{MAX} and higher, bright electro-polishing occurs. HF is depleted at the surface and a high concentration of holes builds up at the interface
- Positive voltage: Si etching
- Negative voltage: hydrogen generation
- At i_{CRIT}, there is partial dissolution of Si. This leads to formation of rough and porous Si. Condition: low current densities, i.e. limiting the oxidation of Si due to hole deficiency

Micro and Nanofabrication (MEMS)

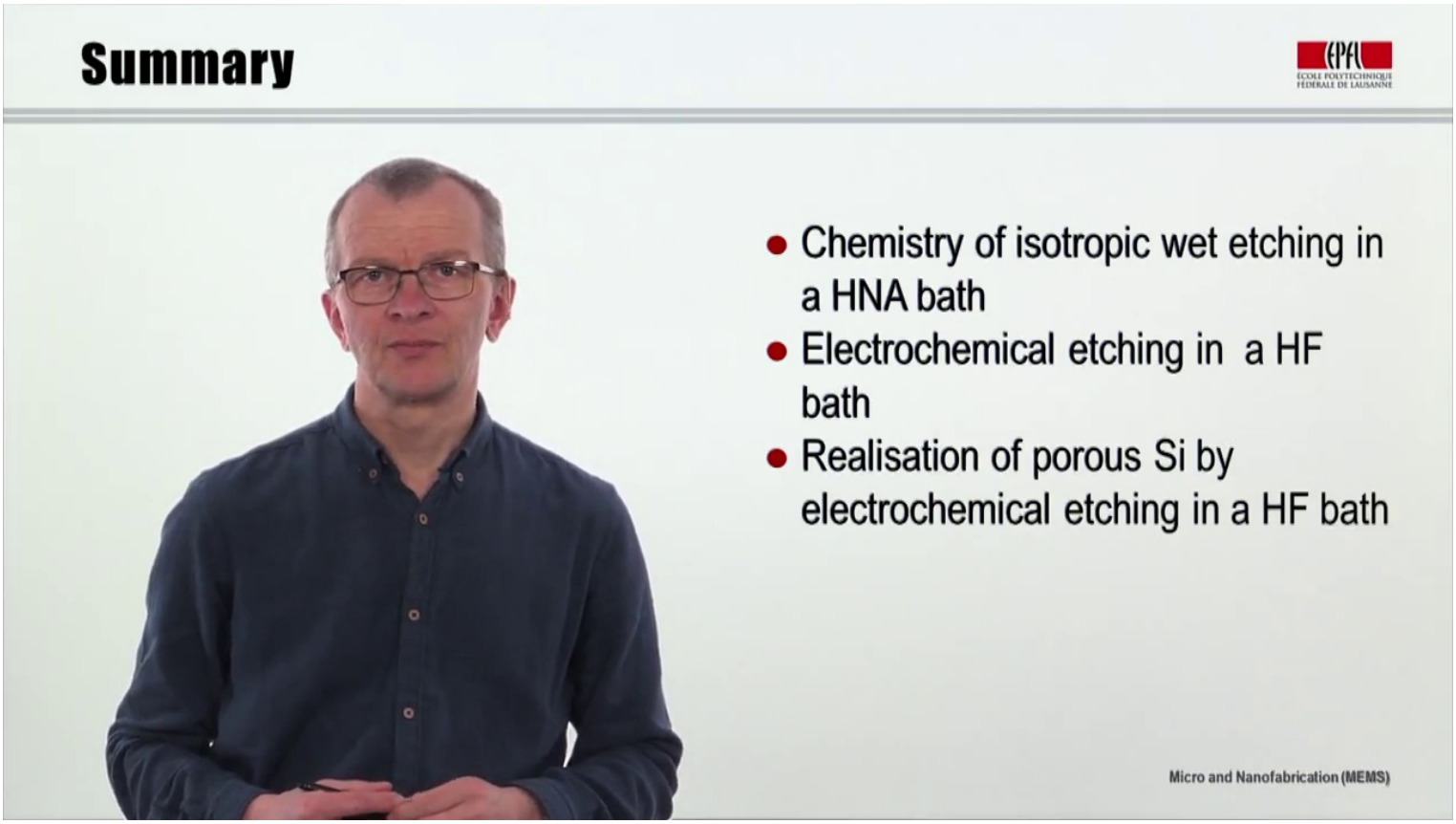
We are now looking at the current voltage characteristics of p-doped silicon, which is put into the dilute HF solution. When we apply a positive voltage, we transport holes to the interface, due to which there is oxidation, and etching occurs. More voltage means more holes, means more etching, and it follows this particular behavior. If we apply a negative voltage, this attracts the holes to the wire, leaving a depletion of holes at the interface. No reaction is occurring, hence, no current is flowing, except if the voltage is so high that one has electrical breakdown. If one now shines light, the photons generate electron hole pairs, the electrons of which stay at the interface, and these electrons recombine with protons from the electrolyte, thereby generating hydrogen gas. So, under negative voltage bias, there is a current that is generated by the generation of hydrogen and not by etching. If you look back again at the positive part of the curve, we know that, for high currents, the surface that was etched appeared bright. Due to the high number of holes, electro-polishing results. If one is at lower current, the number of oxidation events is reduced and one gets only locally oxidation and etching, resulting in a rougher surface.



If we now take an n-type doped silicon wafer, and bring it in the diluted HF solution, and we apply a negative voltage, electrons will be transported to the silicon electrolyte interface, in a straightforward way, to generate hydrogen gas. If we apply a positive voltage we will have the depletion layer effect, which we have introduced before, so there will be no current except if there is voltage breakdown. Shining a light to the wafer creates holes at the interface leading to oxidation and this positive current, represented by the dashed line. A condition for realization of porous silicon is to have a low current and low light intensity in order not to have too many holes at the electrolyte silicon interface.



The top picture shows a cross-section of an n-type wafer, the surface of which was transformed into porous silicon. The lower picture shows a view from the top of the wafer. Pores can be created with diameters ranging from a few nanometers to 10 micrometers. The bigger pores are obtained by applying a high positive voltage, resulting in electrical breakdown of the n-doped silicon. The smallest pores are realized at low voltages and by tuning the intensity of the light source. Pores can be very narrow and very deep, with an aspect ratio of up to 250: they can be 250 times deeper than wide. These very long and narrow pores originate from the fact that the electrical field lines are focused towards the bottom of a pore, where the holes accumulate, resulting in oxidation only there, and continuing etching in the vertical direction. If one has too many holes, the holes will be everywhere, and one will not have porous silicon. If there are just enough holes, only etching will occur at the bottom of the hole, and the pore becomes deeper and deeper.



This ends our lesson on the isotropic wet etching of silicon. We have first explained the chemistry involved in isotropic wet etching in a so-called HNA bath, pointing out the importance of having holes originating from the nitric acid at the silicon surface to induce oxidation, after which the HF removes the oxide. Then we have explained the electrochemical etching in an HF bath. If you apply a positive voltage to the wafer, holes can be transported to the surface, and the nitric acid can be avoided. We then explained how porous n-type silicon can be made by electrochemical etching in an HF bath by applying moderate current and light intensities so that the number of holes at the surface is limited, and they accumulate only at the bottom of the pores.