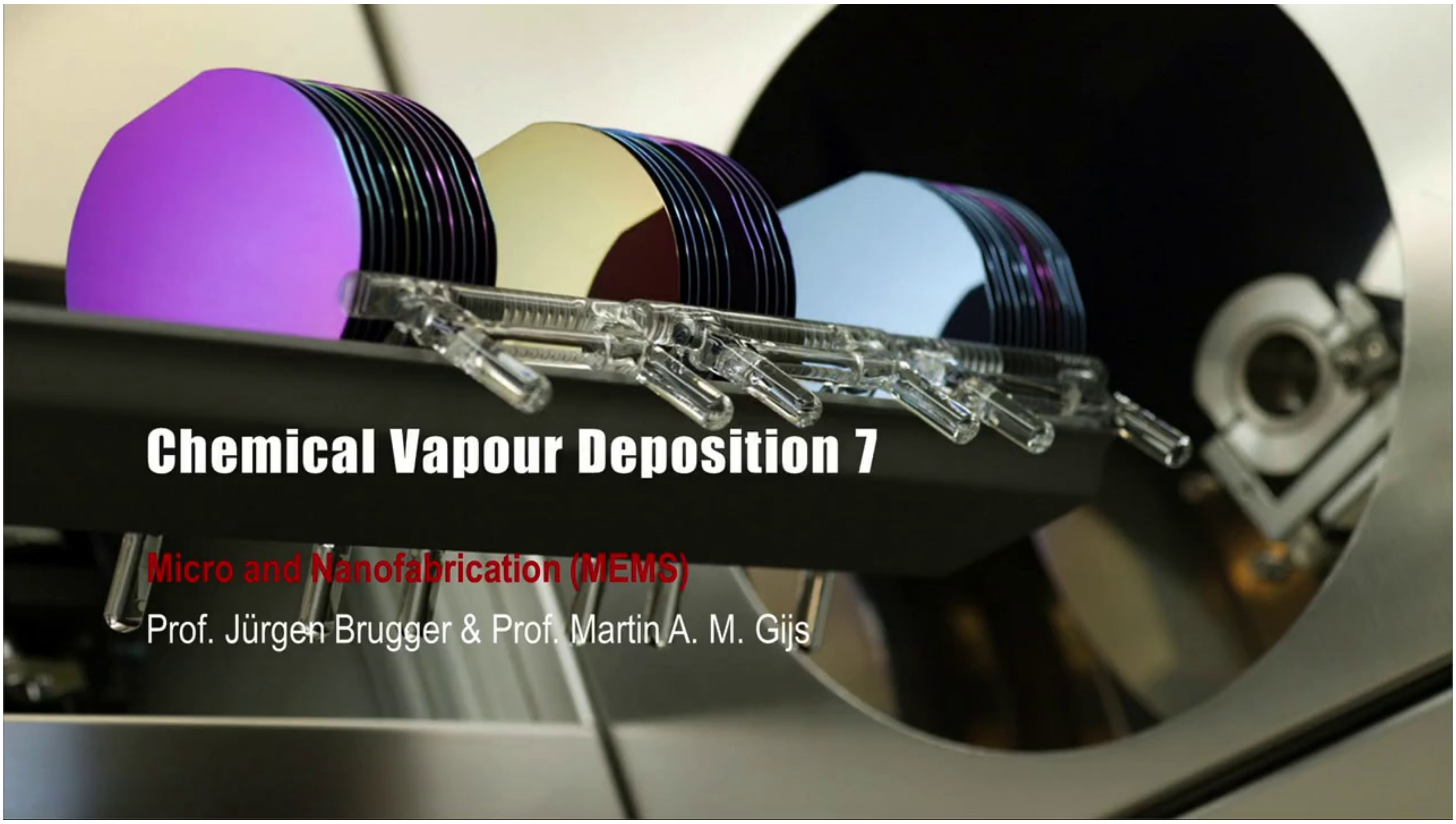

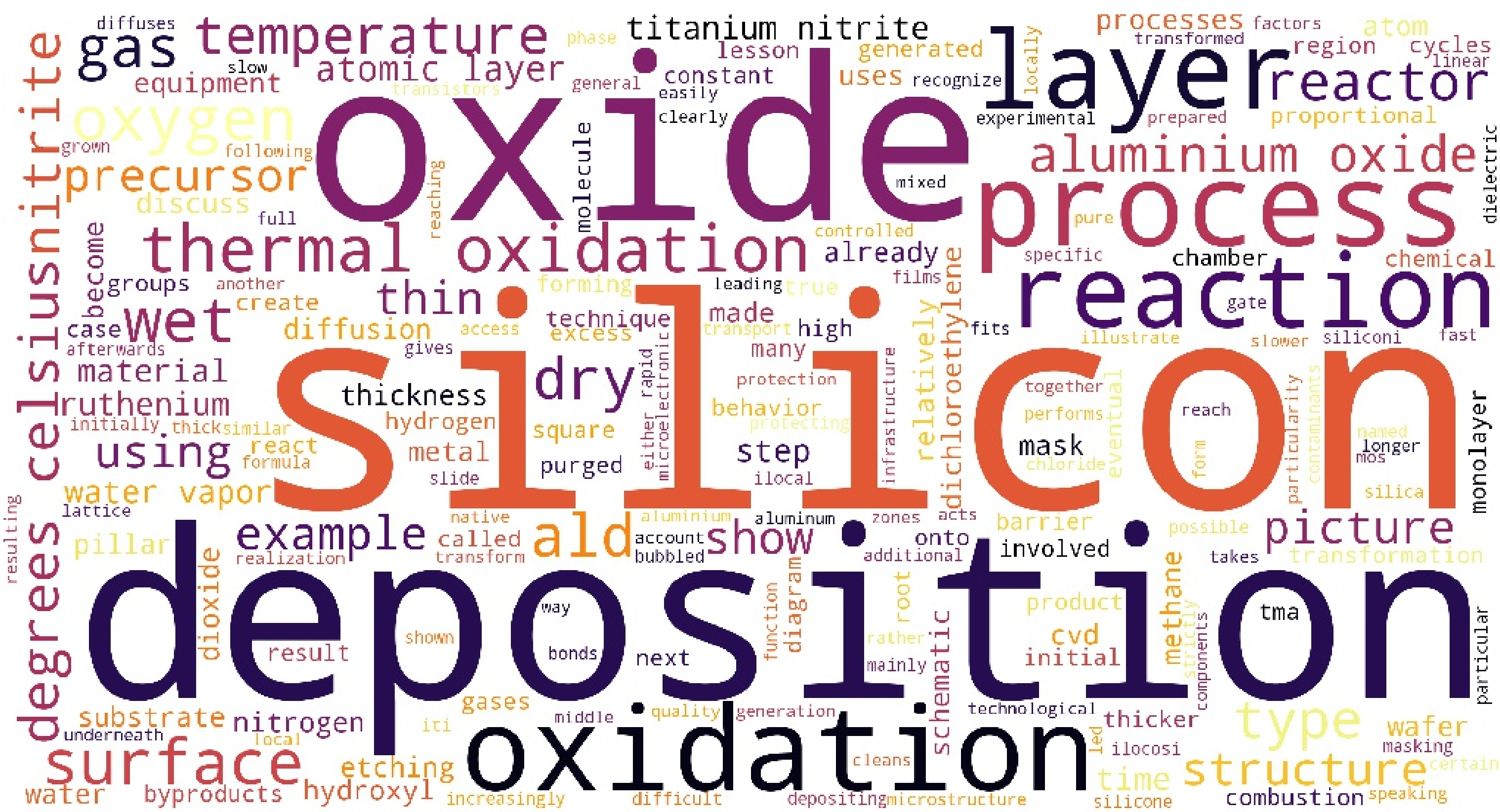

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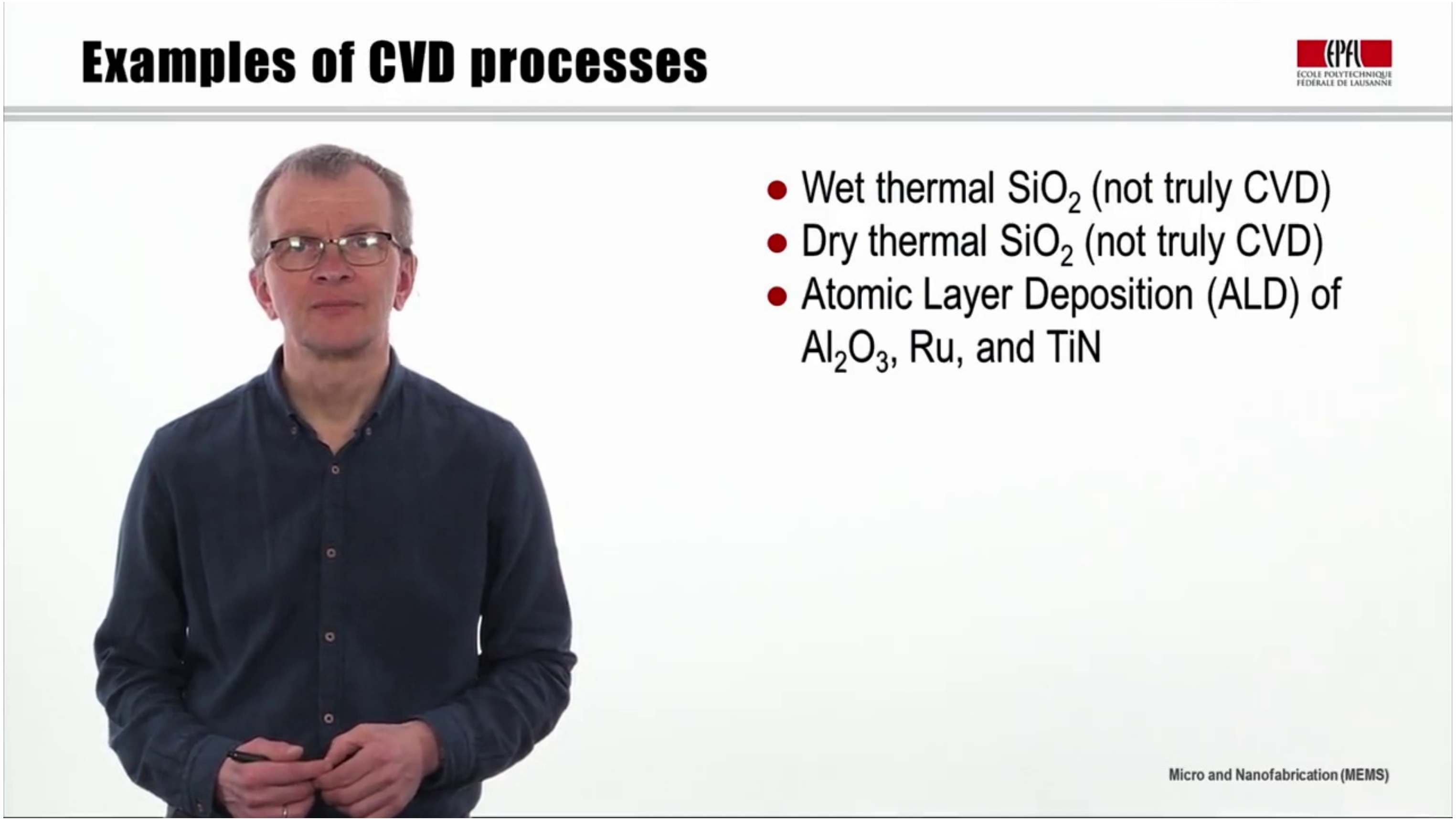
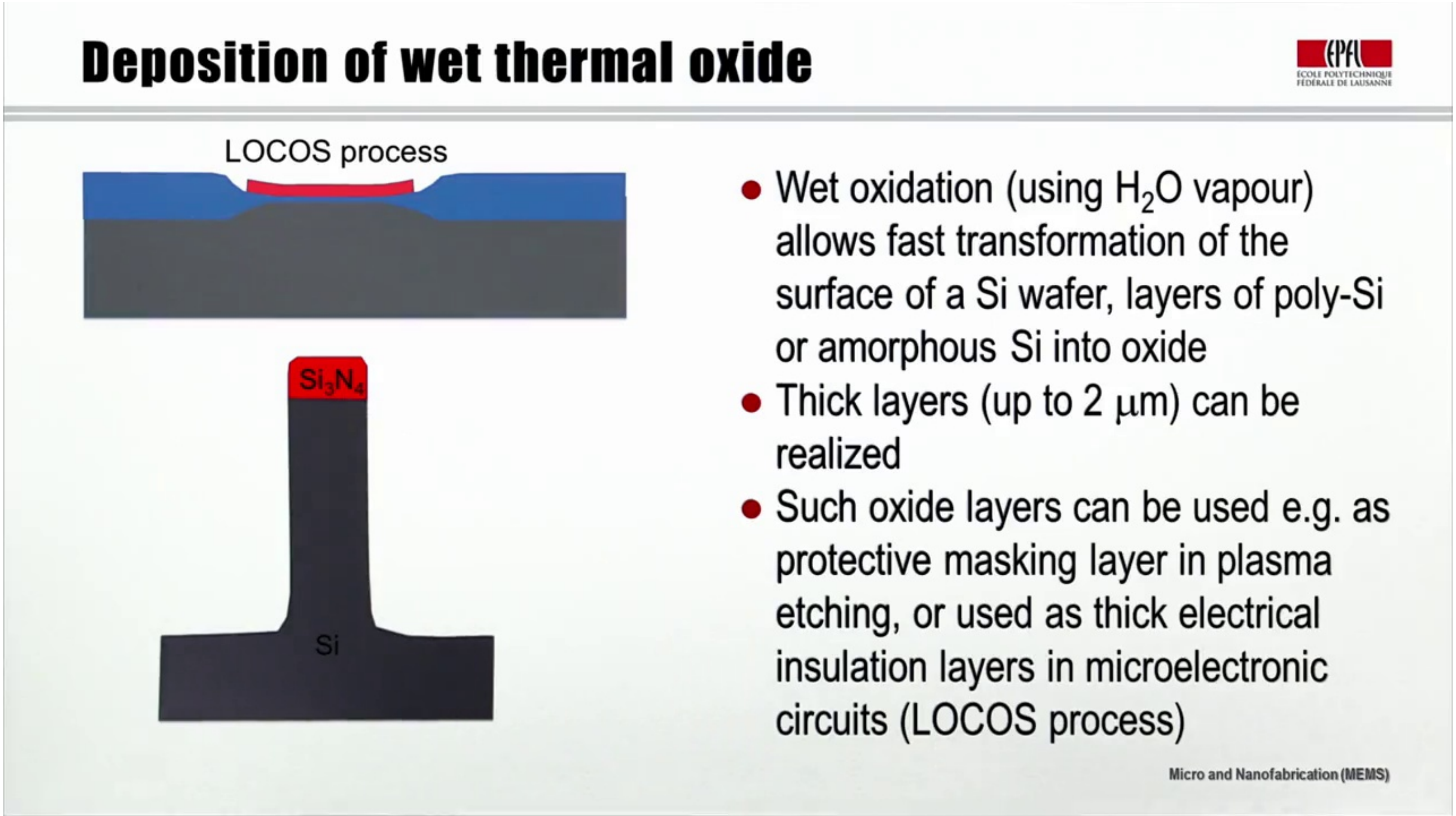
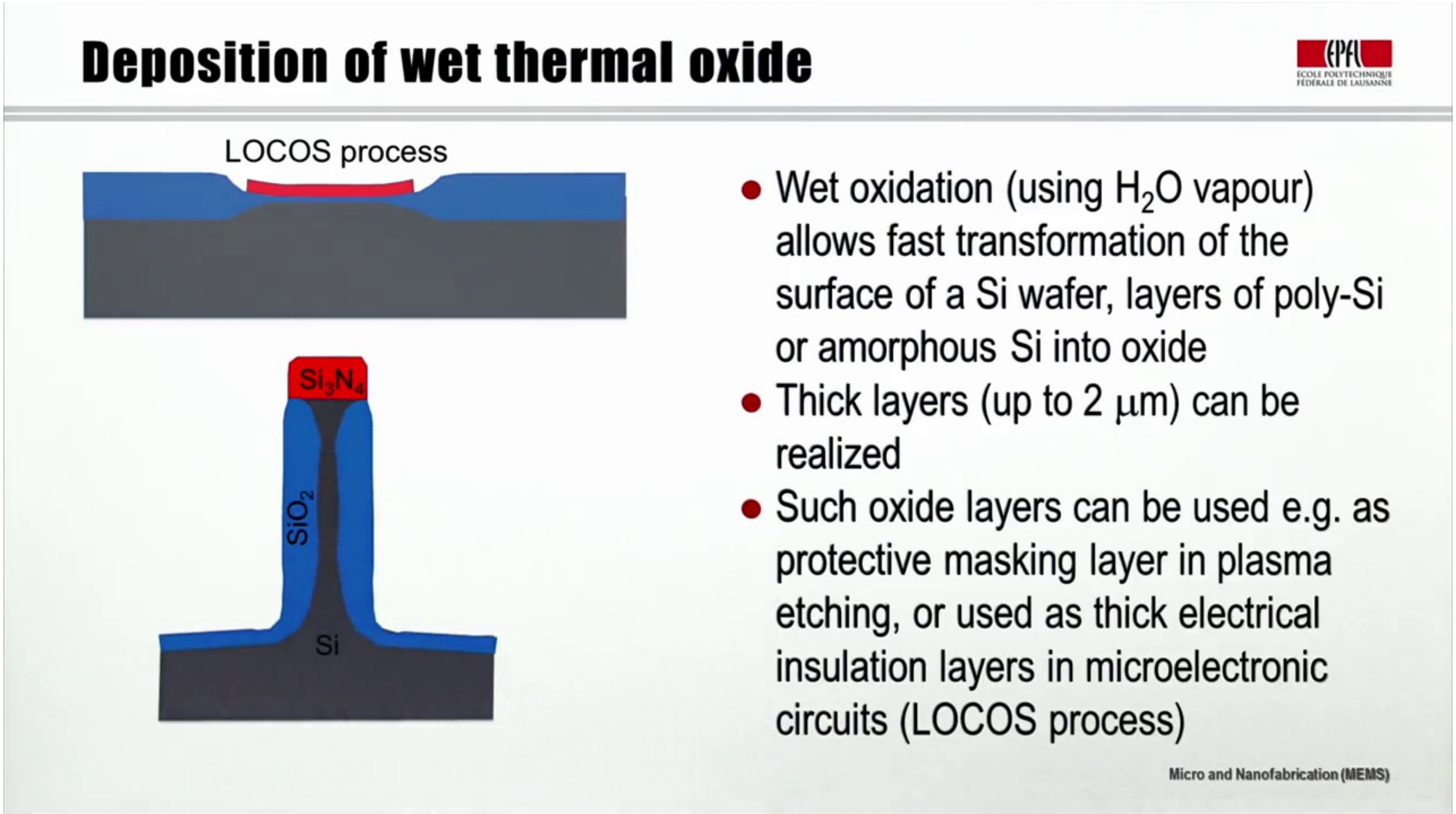


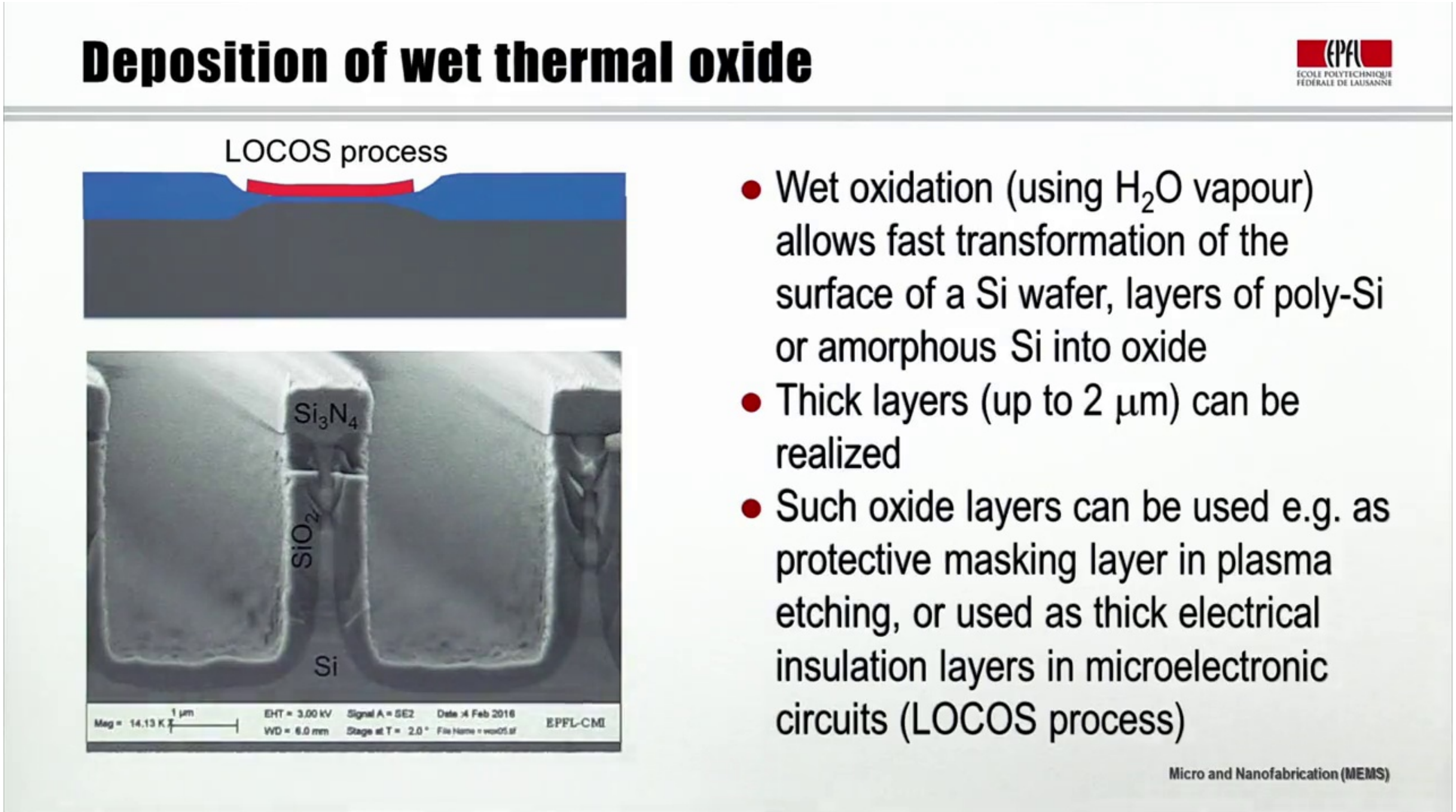
In this lesson we will discuss three additional types of specific CVD and Atomic Layer Deposition processes. We have already seen that wet and dry thermal oxidation, strictly speaking, are no true CVD techniques as they transform the silicone surface into an oxide by diffusion of oxygen atoms into the silicon lattice rather than depositing a layer on the substrate from the gas phase. However, the technique is using the same technological infrastructure as a true CVD process. As examples of atomic layer deposition we will discuss the deposition of aluminum oxide, ruthenium, and titanium nitrite films.



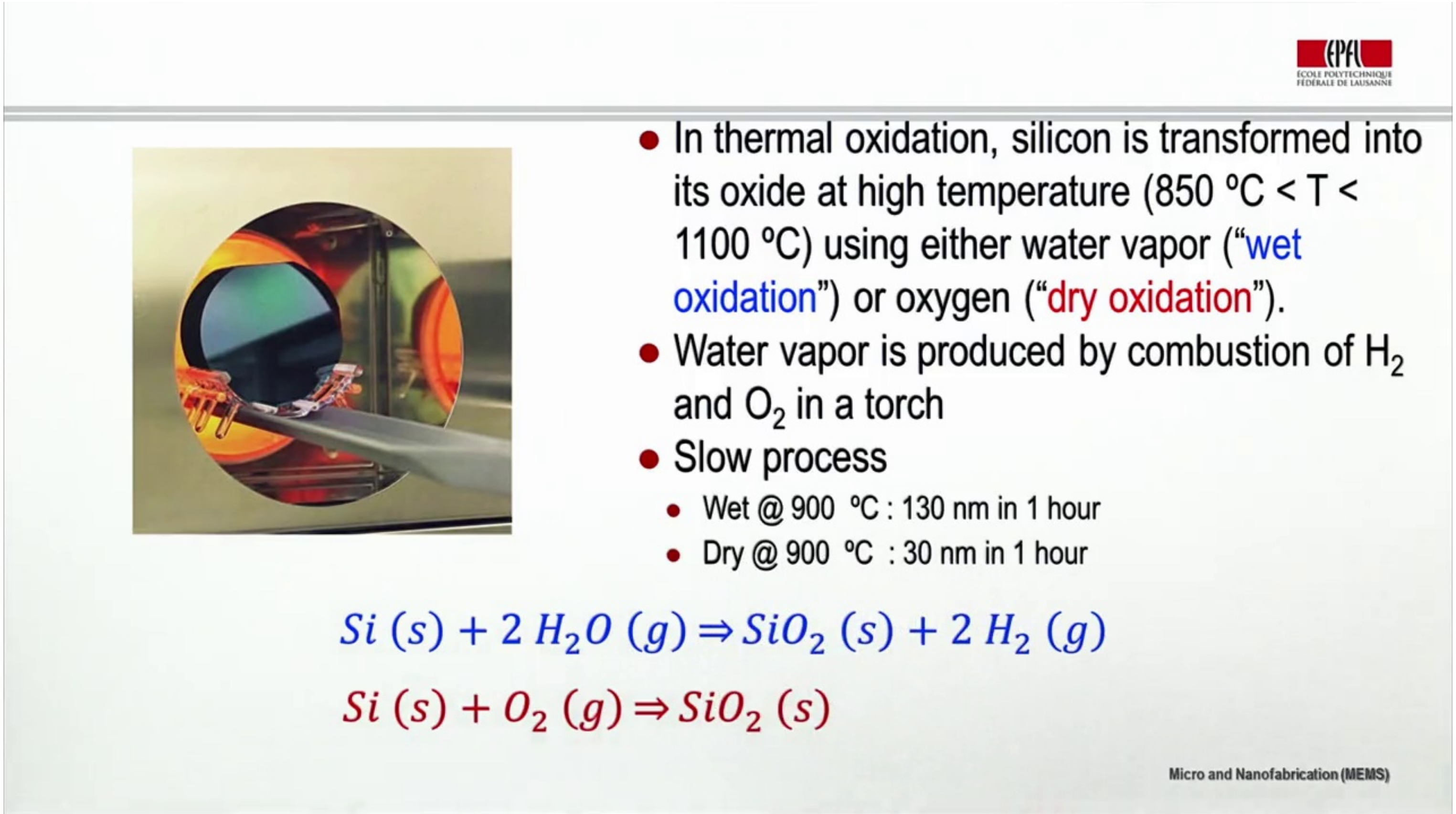
Wet oxidation uses water vapor resulting in a relatively fast transformation of the surface of a silicon wafer into oxide. We have already seen that if one has a local thin silicon nitrite layer as protection it is possible to create locally thick silica layers while protecting the region in the middle against oxidation. And this process was named <i>Local Oxidation of Silicon</i>, or <i>LOCOS</i>. Here we illustrate the wet thermal oxidation process using another type of silicon microstructure. One has prepared here a pillar structure by etching, using silicon nitrite as a masking material in the etching process.



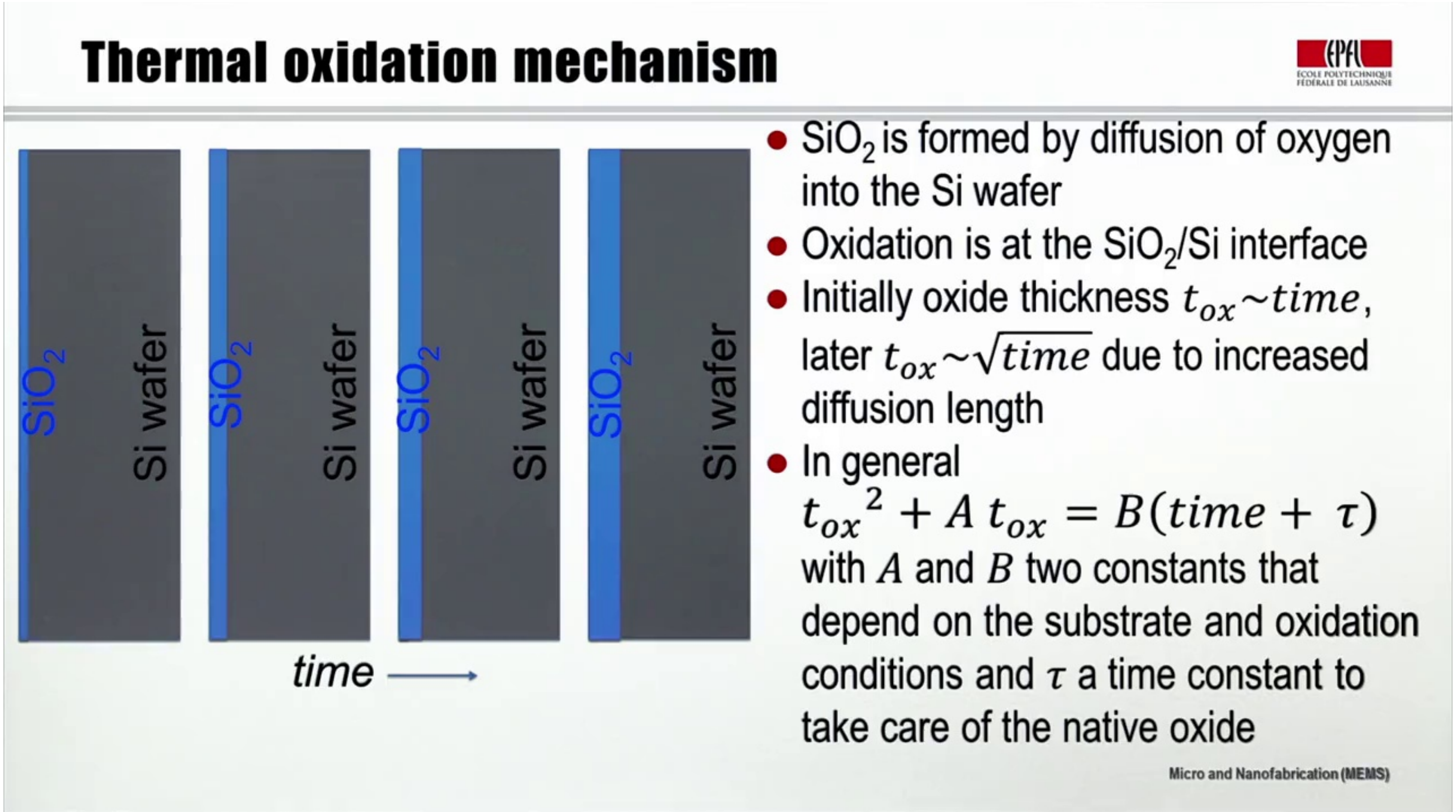
If one now performs the thermal oxidation step, the silicon nitrite again acts as a barrier against the diffusion of oxygen atoms. This gives relatively few oxidation underneath the silicon nitrite and thicker regions here where there is full access for the oxygen.



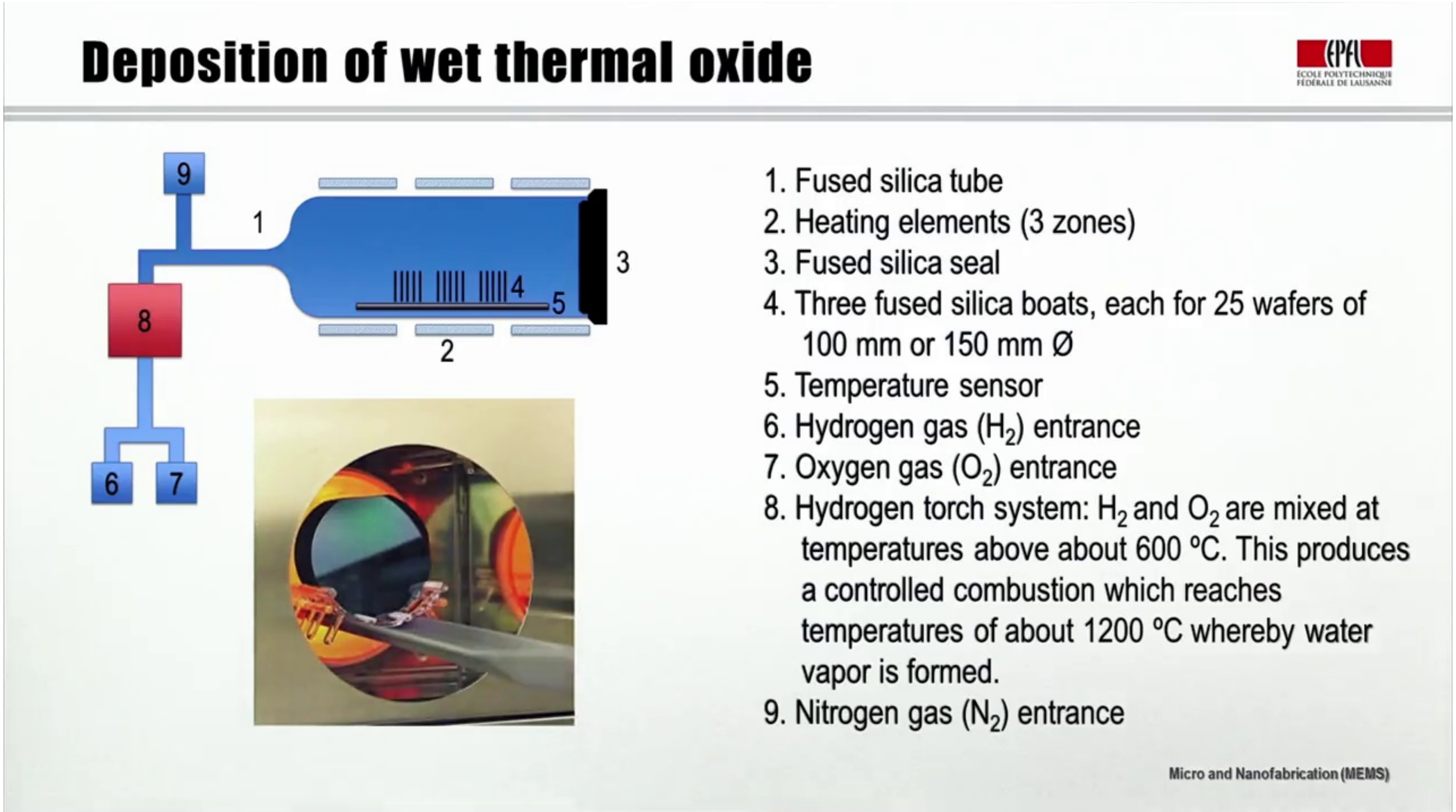
This picture shows the experimental example. And we clearly recognize here the three types of materials. So first we had here the silicon structure made using the silicon nitrite mask, and here we see the zones where the silicon is transformed to silicon dioxide.



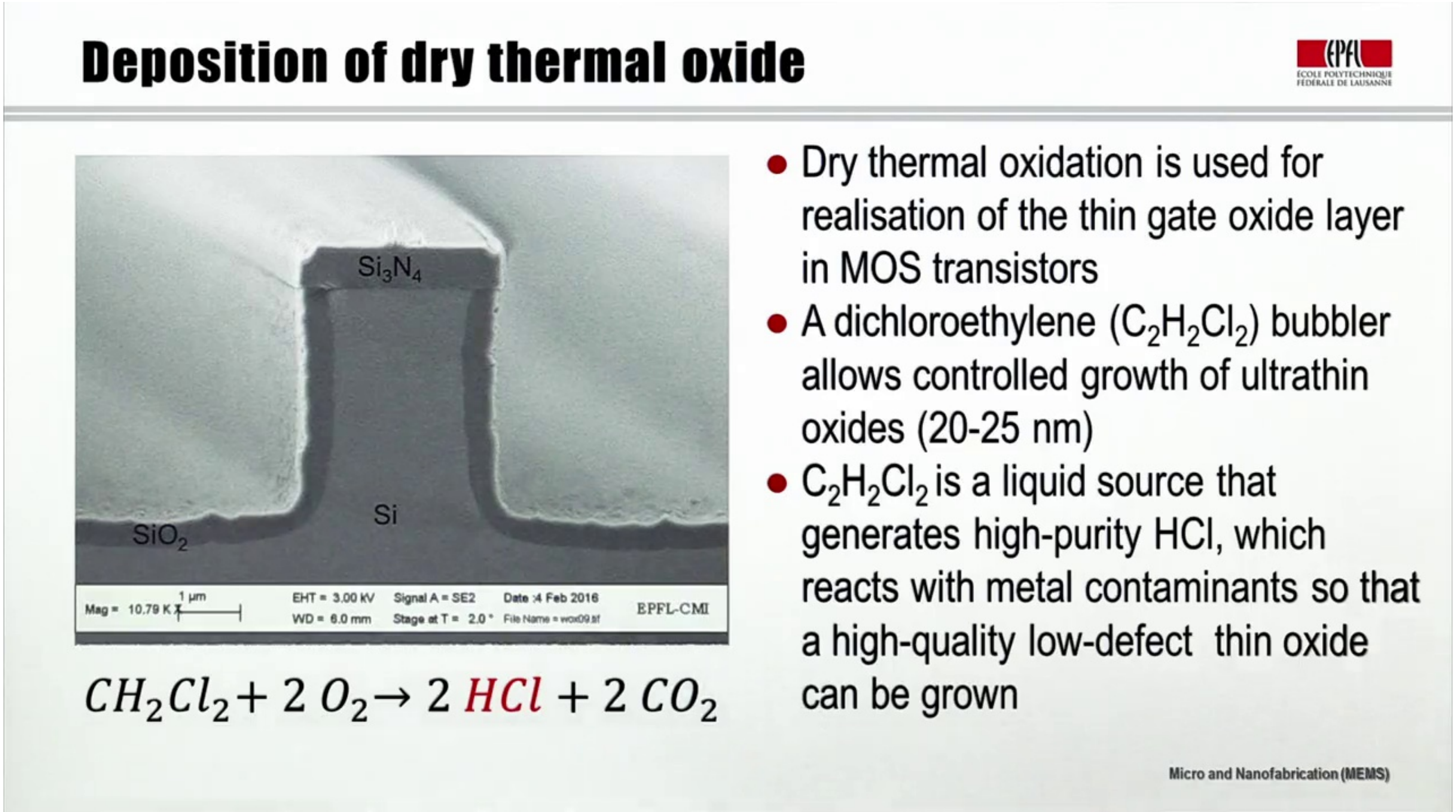
In thermal oxidation one uses temperatures in between 850 degrees Celsius and 1100 degrees Celsius. We have already seen that one can use either water vapor in the reaction, and then the process is called "wet oxidation", or one can use oxygen gas, and then the process is called "dry oxidation". Both processes are relatively slow. Wet oxidation is a few factors more rapid than dry oxidation, however.



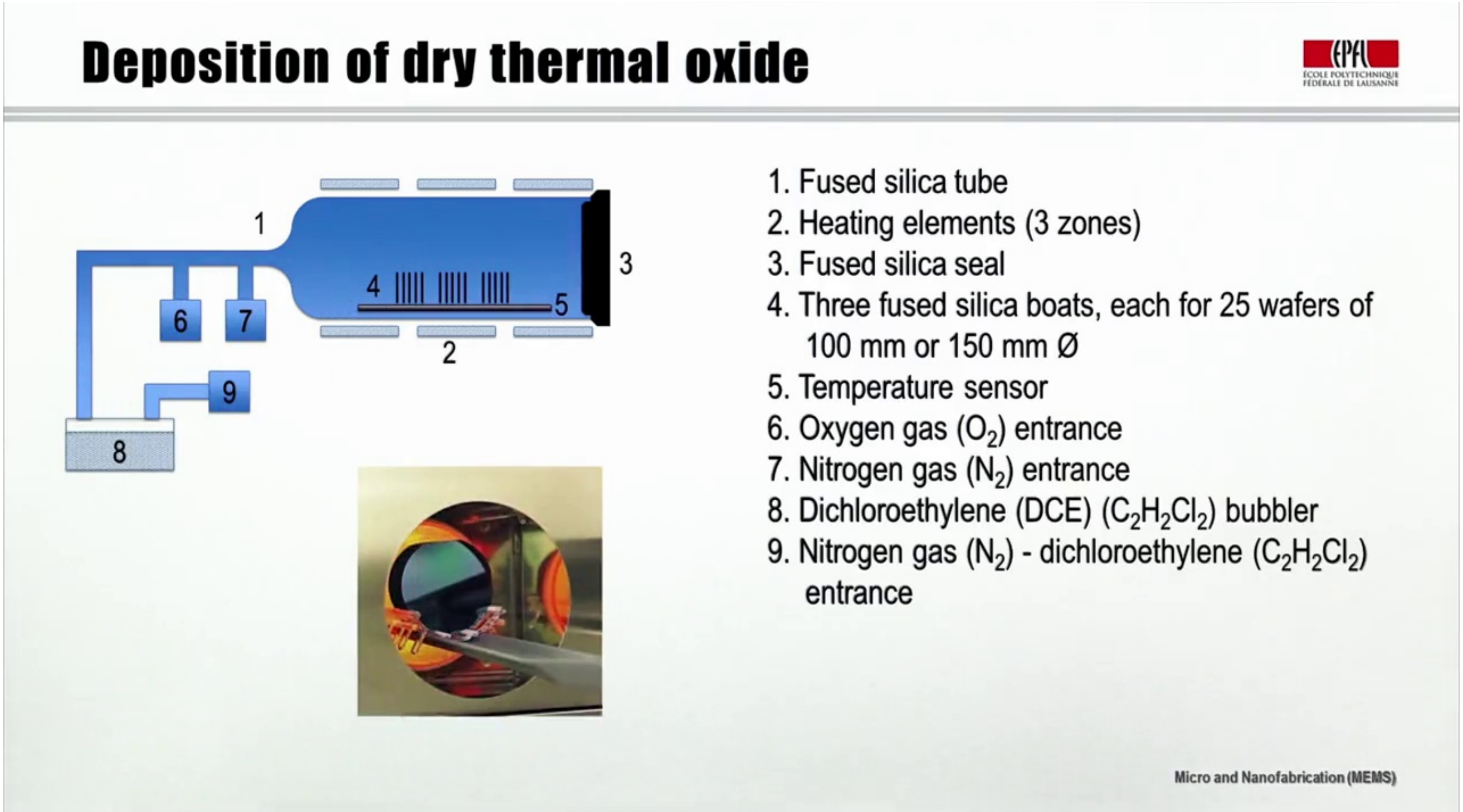
This slide shows the transformation of the silicon into silicon dioxide as a function of time. Initially, the oxygen easily diffuses to the silicon surface so that the oxide thickness is proportional to the time. However, when the oxide becomes thicker it becomes increasingly difficult for the oxygen atom to reach the silicon surface, and the oxidation will become slower. That is why the oxide thickness is proportional to the square root of the oxidation time. In general, we can have the following formula which fits both the initial linear behavior and the square root behavior for longer oxidation times. Here <i>τ</i> is a time constant that takes into account the thickness of an eventual initial native oxide of the silicon wafer.



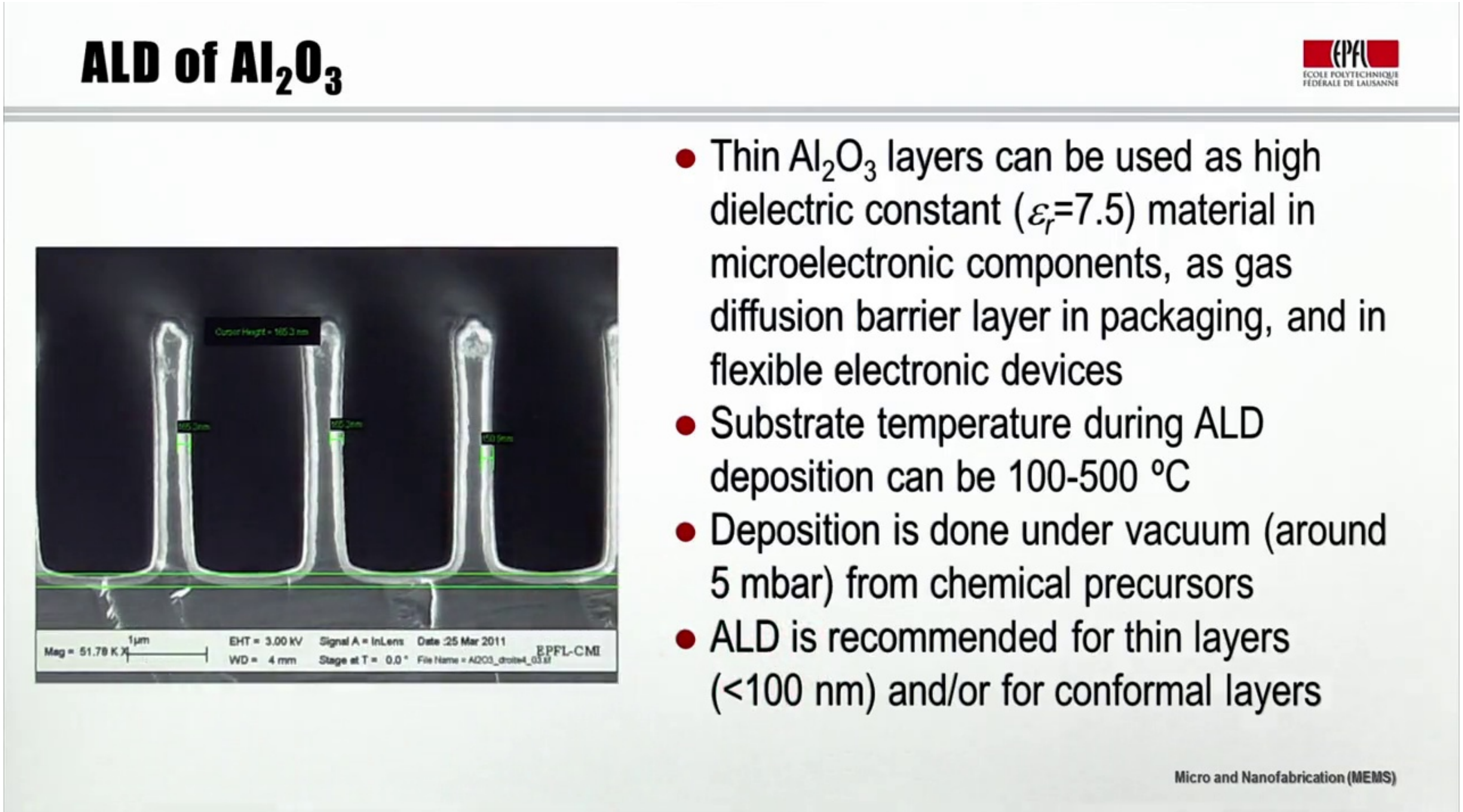
This is a schematic diagram of a wet thermal oxidation equipment. The generation of the water in the wet thermal oxidation process is particular. Hydrogen and oxygen gas are mixed at a temperature of about 600 degrees Celsius and react in a controlled combustion process, reaching temperatures of about 1200 degrees Celsius. And as a result of this combustion water is generated which is then led into the reactor.



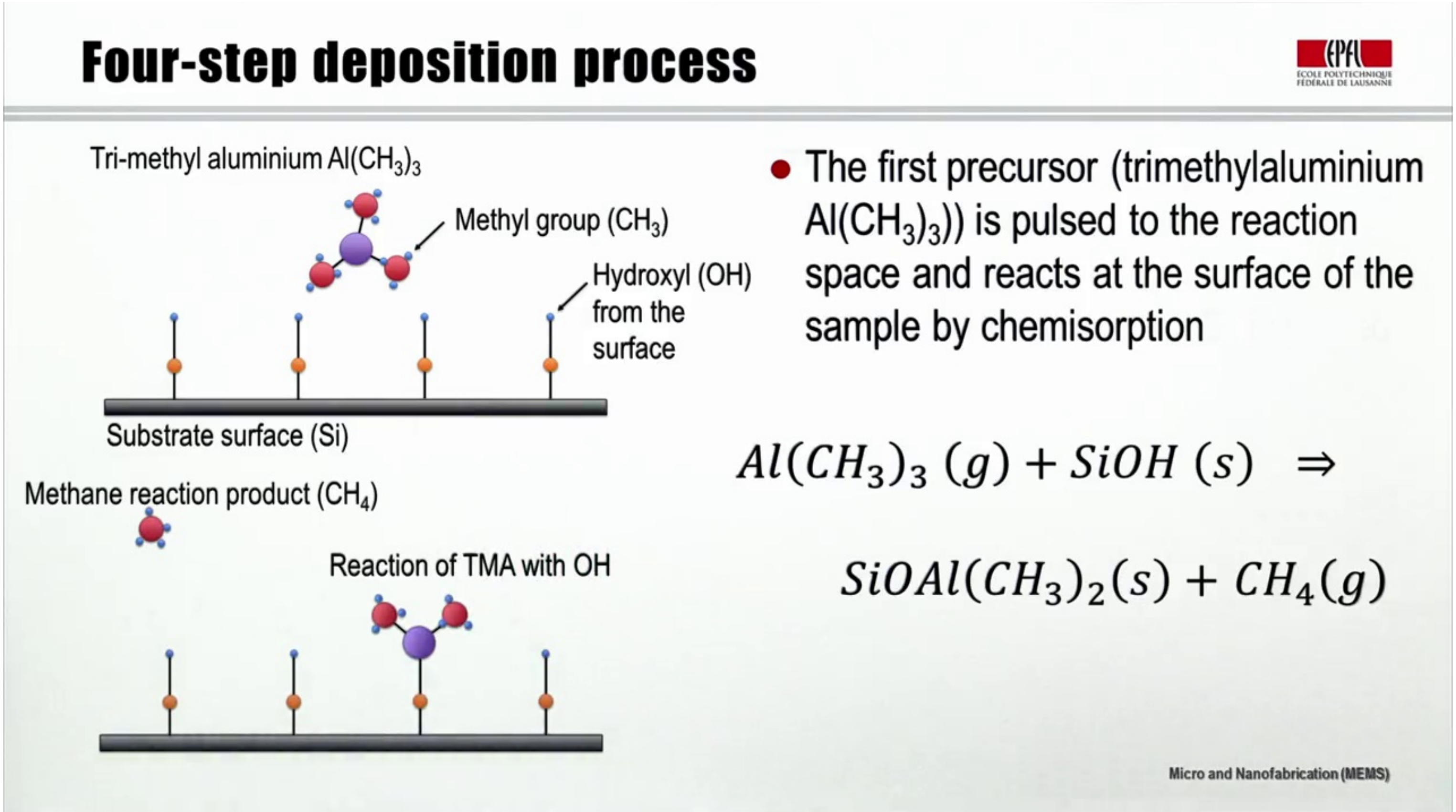
Dry thermal oxidation is mainly used for the realization of thin oxide layers that form the gate oxide in MOS transistors. In this process, one uses dichloroethylene and oxygen to create together hydrogen chloride that cleans the surface from eventual metal contaminants. In this way, a very thin and pure oxide layer of high quality can be grown. The picture shows a similar type of structure like shown before– a silicon pillar, made with a silicon nitrite mask and afterwards there is dry oxidation leading to these oxide layers.



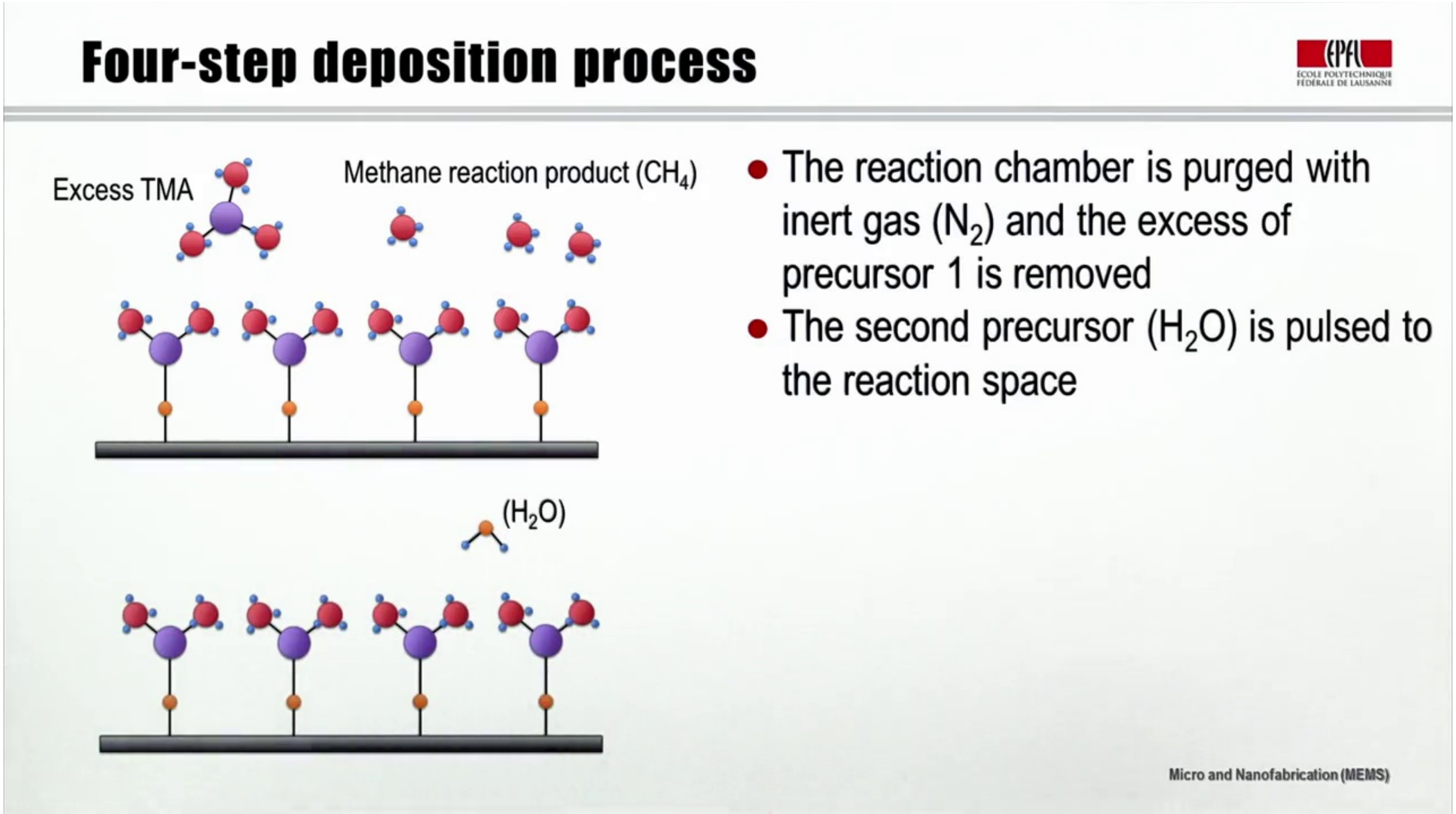
This is a schematic diagram of the dry thermal oxidation equipment. It has the particularity that nitrogen gas is bubbled through the dichloroethylene bonds to transport the dichloroethylene molecules to the reactor.



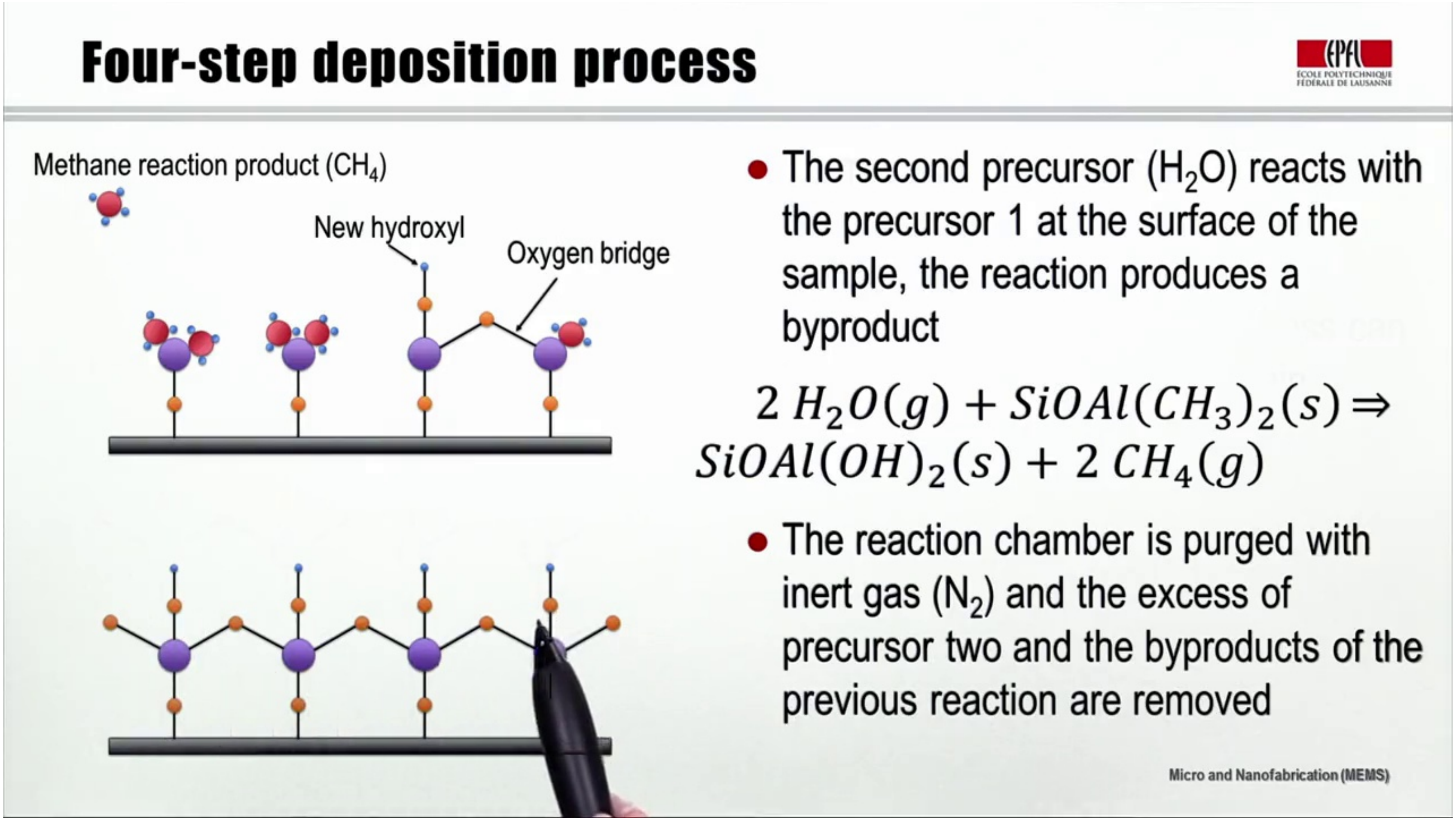
We will now discuss the deposition of thin aluminium oxide layers by atomic layer deposition. This material is used for its high dielectric constant in certain microelectronic components, like capacitors. It can also be used as a gas diffusion barrier in packaging and in flexible electronic devices. The deposition temperature during an ALD process is typically a few hundred degrees Celsius. ALD is very well suited for deposition of very thin layers without pinholes and/or for forming conformal layers onto microstructured substrates. In the picture we see a silicon etched structure which has been coated with an aluminium oxide layer by ALD.



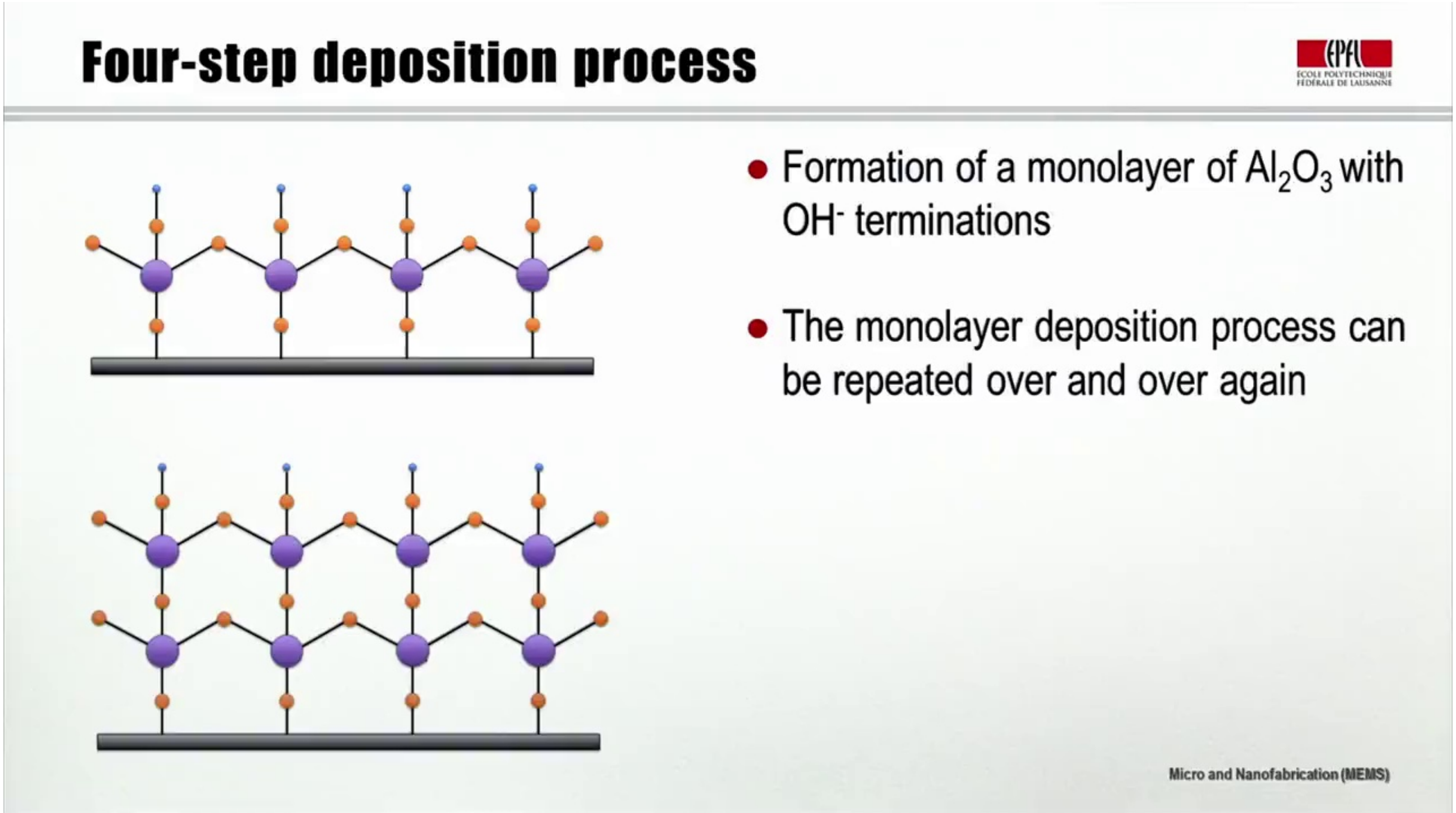
Four steps are involved in the deposition of aluminium oxide by ALD. The first precursor is tri-methyl aluminium; this molecule, which is chemisorpted onto a silicon substrate that has hydroxyl surface groups. Methane is a reaction product that is generated in this step and is pumped away. Here we see the chemical reaction that was depicted in these two schematic illustrations.



The reaction chamber is then purged with inert nitrogen gas, thereby removing all methane reaction products and any excess of the precursor TMA. Next the second precursor water vapor enters the system.



The water precursor reacts with the TMA at the surface forming methane byproducts. The reaction chamber is then, after this reaction, again purged and nitrogen and any excess of the water vapor and the byproducts of the reaction are removed. One is then left with a surface of aluminium oxide with hydroxyl groups.

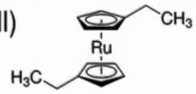


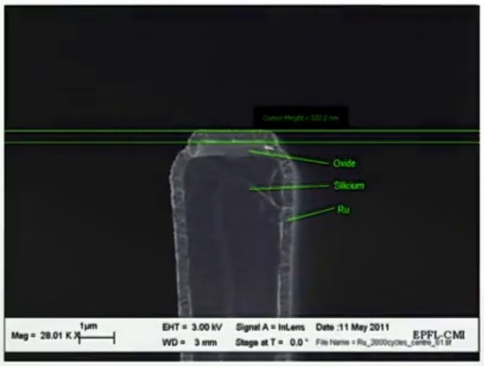
In fact, one has created one monolayer of aluminium oxide with hydroxyl terminations so that the next monolayer deposition process can be executed. And this process can be repeated over and over again many thousand times.

Example of other materials

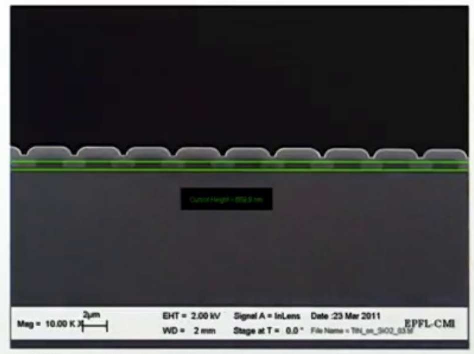
	Precursor 1	Temp. (°C)	Precursor 2	Temp. (°C)
TiN	$TiCl_4$	Room temperature	NH_3	Room temperature
Ru	$(Ru(EtCp)_2)$	110	O_2	Room temperature

$Ru(EtCp)_2$: bis(ethylcyclopentadienyl)ruthenium(II)





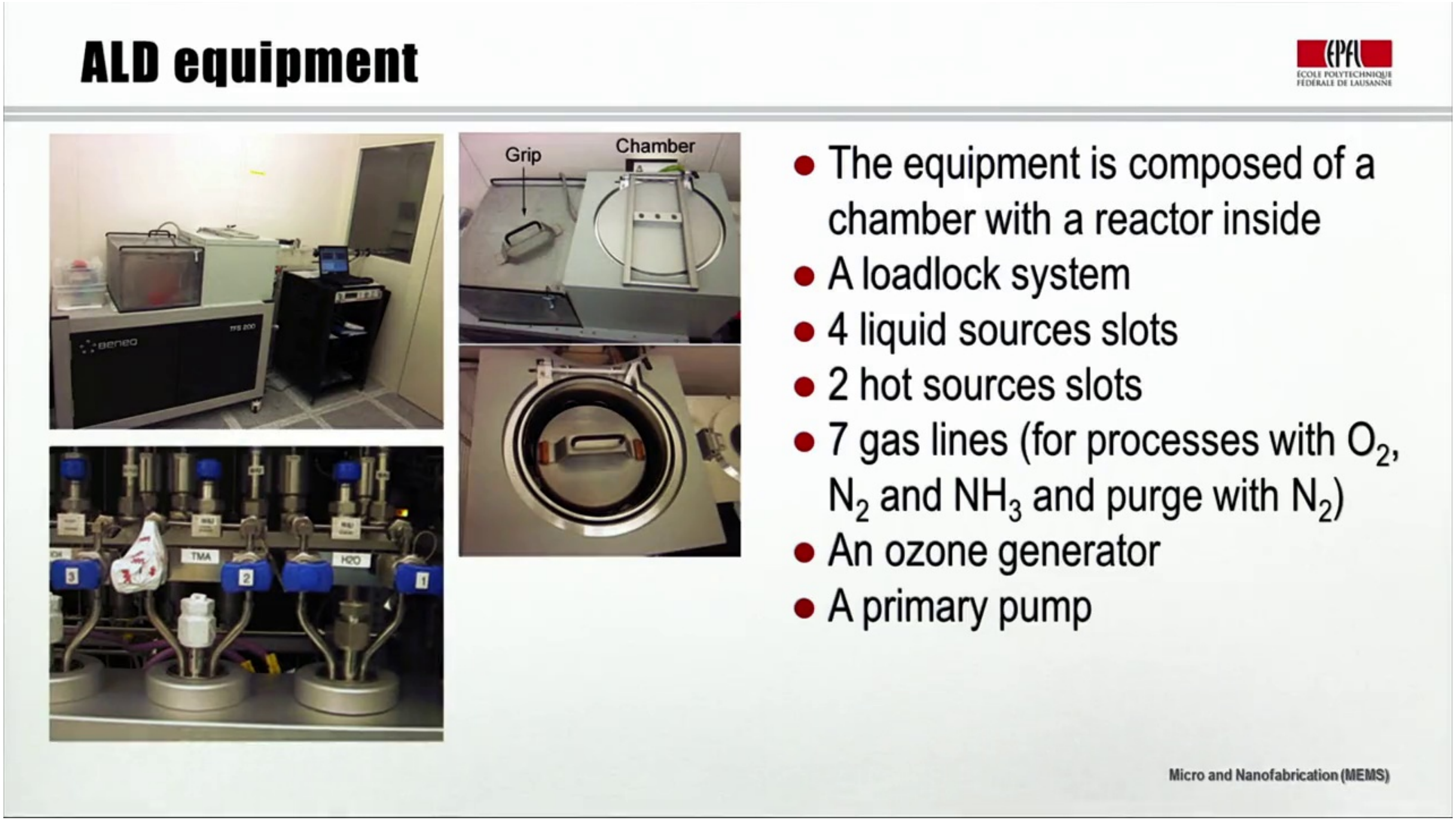
Ru on Si (2000 cycles)



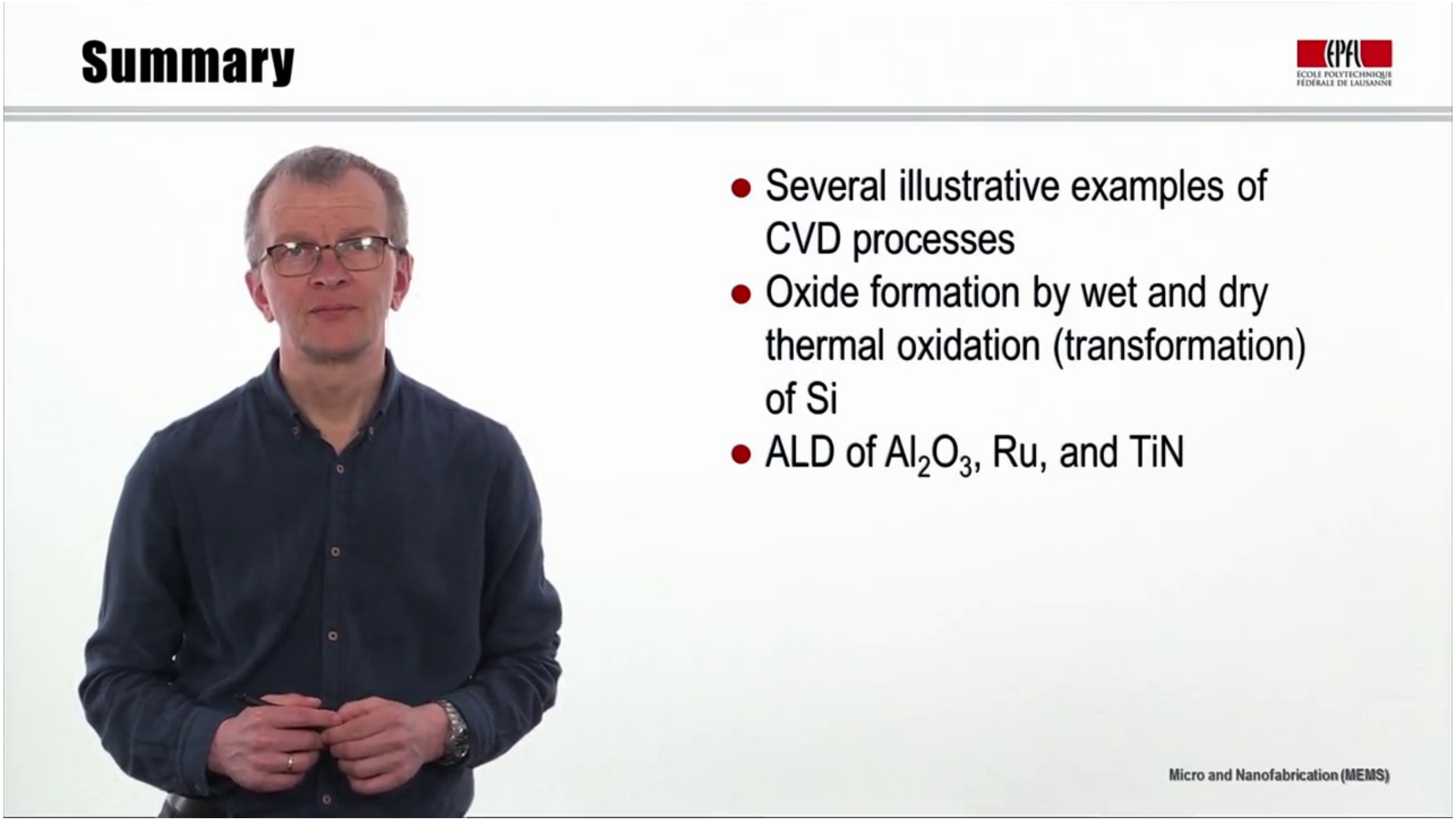
TiN on SiO_2 (2000 cycles)

Micro and Nanofabrication (MEMS)

ALD exists for deposition of many types of materials. Here we show two other examples, namely the deposition of titanium nitrite and the metal ruthenium. The table lists the used precursor gases for each case and the temperature for each step. The two pictures below demonstrate the end result after deposition during 2000 ALD cycles. So here we see the ruthenium which is covering the silicon pillar structure which was made, in this case, using an oxide etching mask. And here we see a picture of a cross-section of the titanium nitrite on silicon dioxide, also after 2000 cycles of ALD.



Here we show an example of atomic layer deposition equipment. It is basically a chemical reactor– if we look inside we see the reaction vessel and one can then lead into this reactor the different gases. For this type of reactor there are seven gas lines and there is an ozone generator, and of course there is also a pump involved to evacuate the reactor when needed.



In this lesson we have given a few illustrative examples of CVD-like processes. We have started with oxide formation on silicon wafers– by wet and dry thermal oxidation– at temperatures of about 1000 to 1100 degrees Celsius. Subsequently we have discussed the atomic layer deposition of aluminium oxide, ruthenium metal and titanium nitrite.