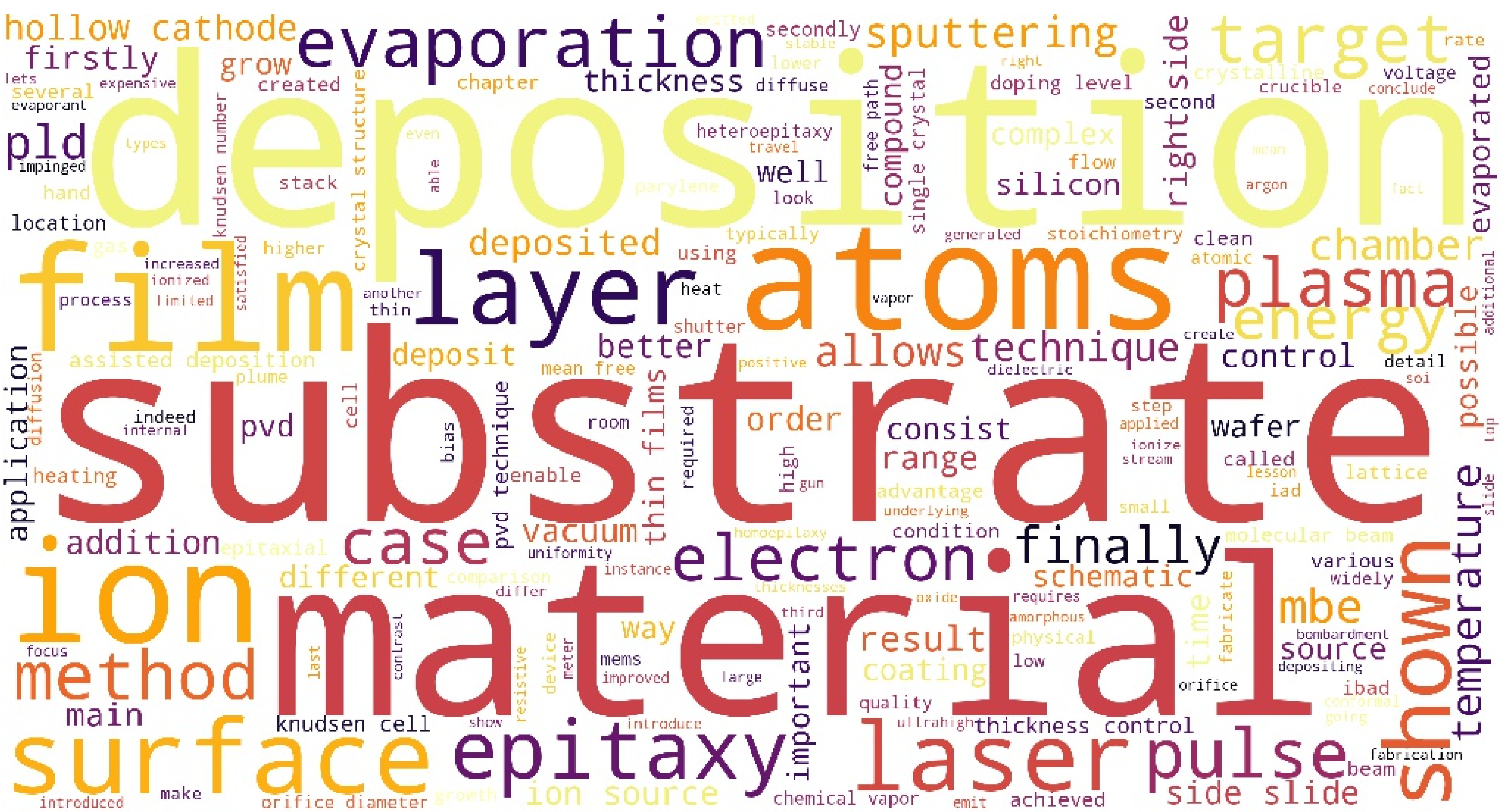

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PVD 7: Other Techniques

- Physical principle
  - Plasma, spatial zones, Paschen law
- Sputter variations
  - DC sputtering
  - RF sputtering
  - Magnetron sputtering
- Ions-target interactions
- Sputter examples
- Other PVD methods
- Film growth and control parameters

Micro and Nanofabrication (MEMS)

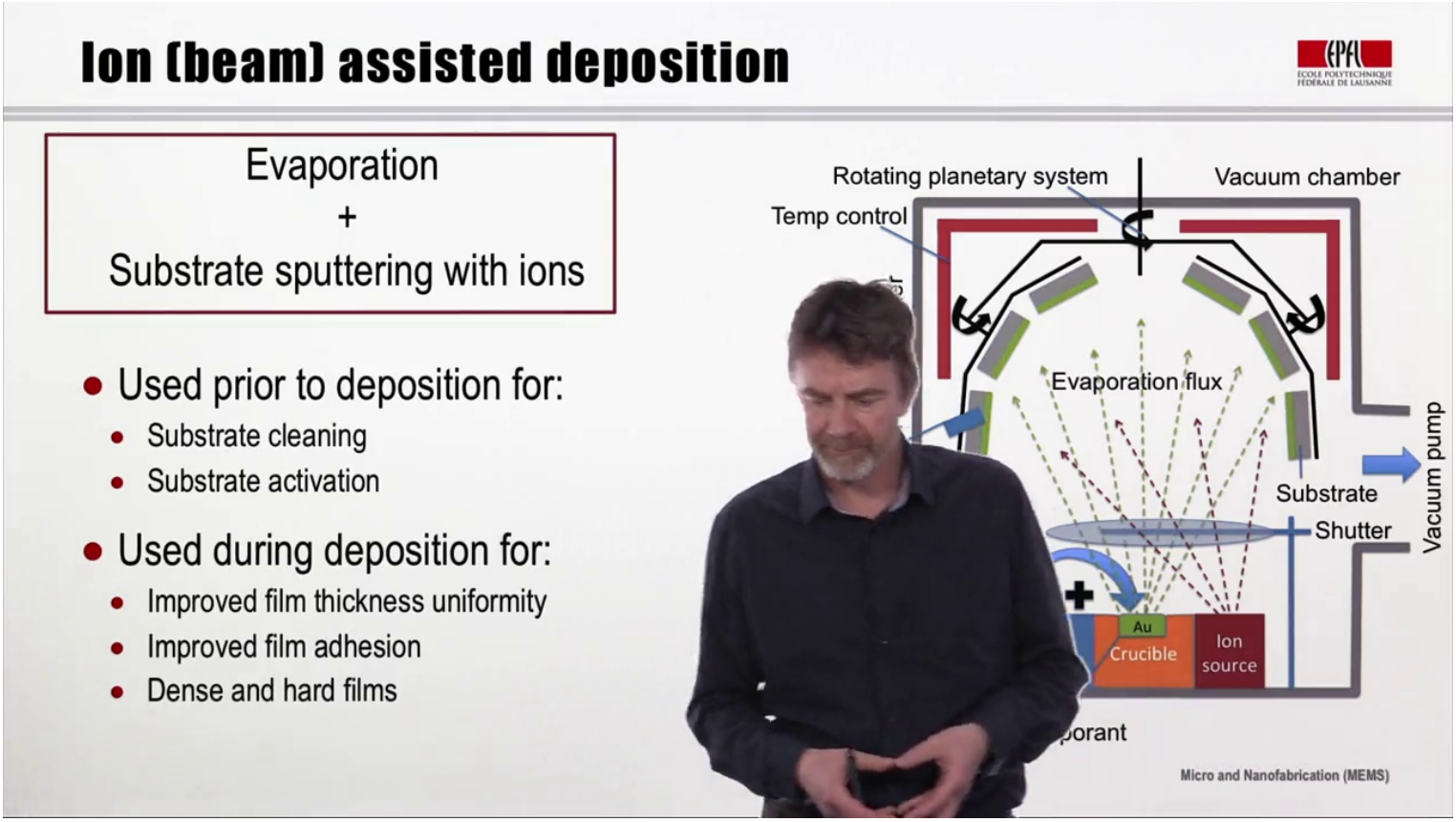
Welcome to this lesson on other PVD techniques that are of interest for micro/nanofabrication.

PVD 7: Other Techniques

- Ion plating
- Molecular beam epitaxy
- Pulsed laser deposition
- Supplementary methods
- PVD methods comparison

Micro and Nanofabrication (MEMS)

I will first show the so-called ion assisted methods, which are combination of evaporation and ion induced surface preparation. Second, I will introduce MBE which is an important technique to create crystalline thin films. Third, I will present PLD, which is a further method to deposit composite material with complex stoichiometry at high quality. These methods are more complex and expensive than the previously shown evaporation and sputtering but they are very important for advanced film control and formation. This lesson will conclude with some supplementary methods and the comparison of the various PVD methods shown.

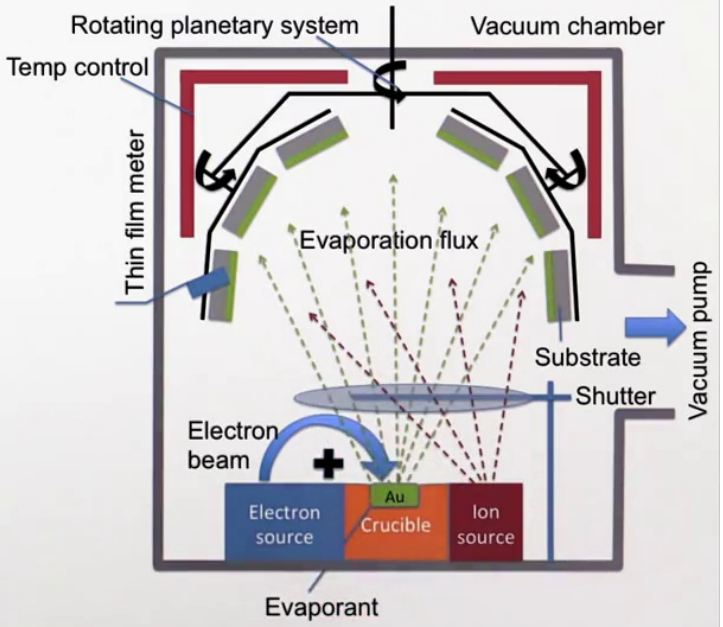


Ion assisted deposition (IAD), and ion beam assisted deposition (IBAD), are 2 techniques combining material evaporation and substrate sputtering with ions. They differ in how the ions are created. In the case of IBAD, ions are generated using an ion source or ion gun as shown in the schematics on the right side of the slide

Ion (beam) assisted deposition

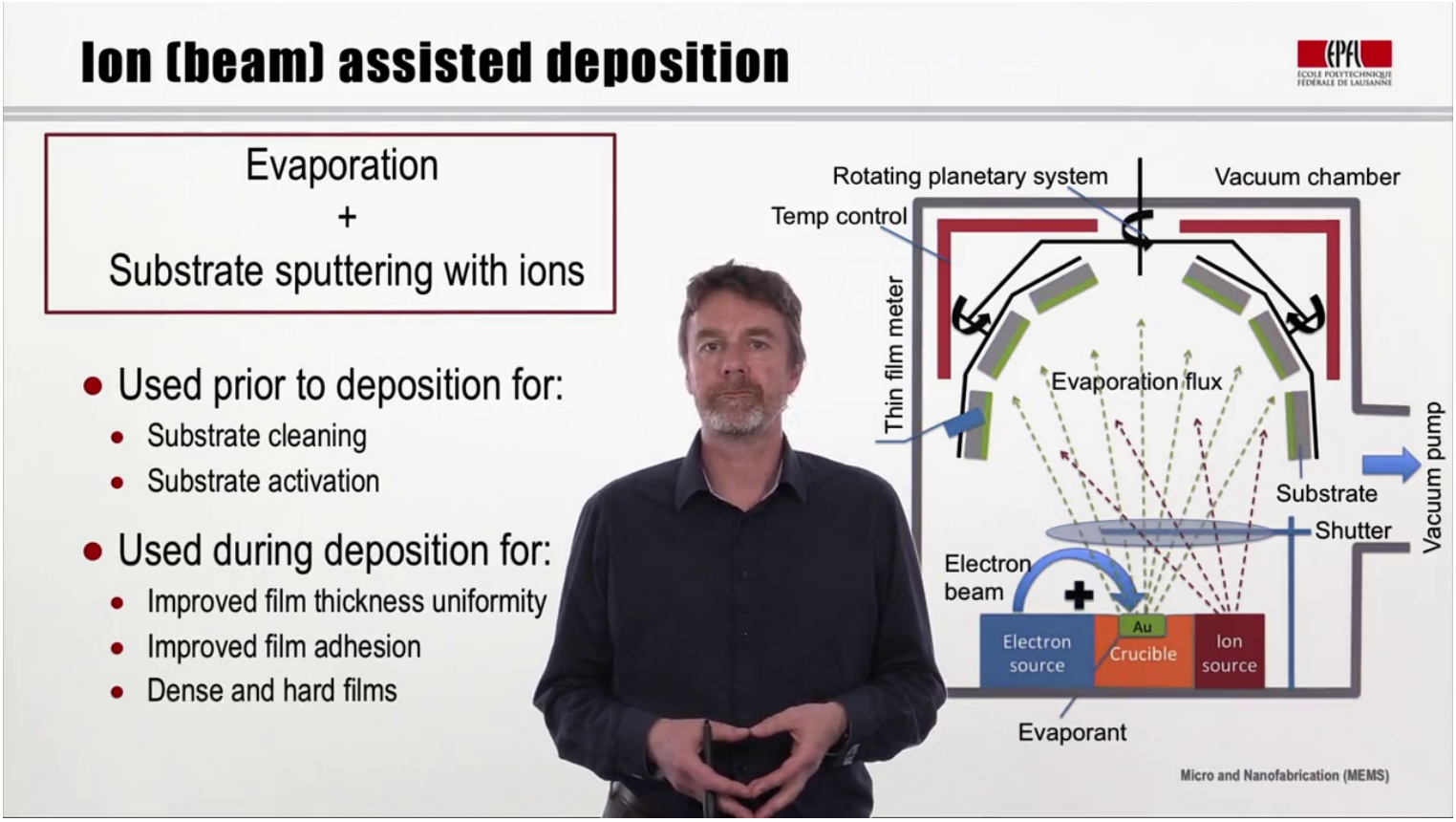
Evaporation
+
Substrate sputtering with ions

- Used prior to deposition for:
  - Substrate cleaning
  - Substrate activation
- Used during deposition for:
  - Improved film thickness uniformity
  - Improved film adhesion
  - Dense and hard films



Micro and Nanofabrication (MEMS)

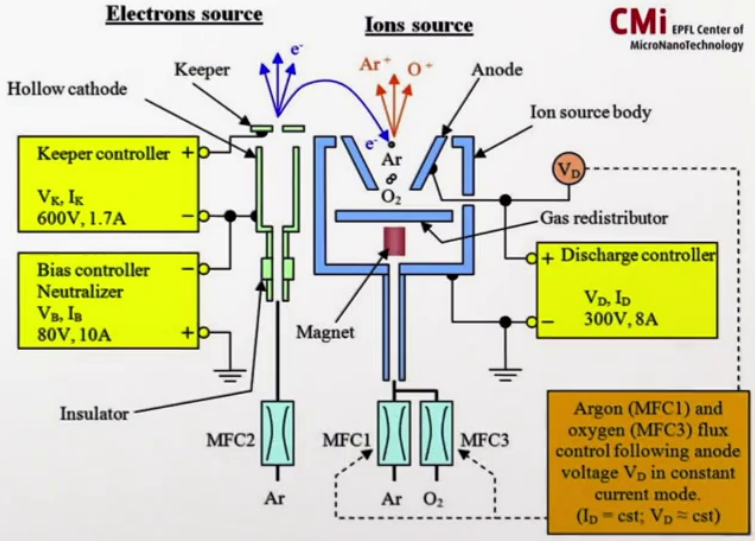
So here you can see the setup that we already introduced in the evaporation. Now, in addition to the crucible and the electron source that evaporates the material that is going to be deposited on the substrate in the chamber. We have, in addition, an ion source or ion gun, which emits ions into the vacuum chamber that heats the substrate before or during the deposition. In such we can clean the surface, and add additional energy, to enhance the control of the film growth on the wafer during the deposition.



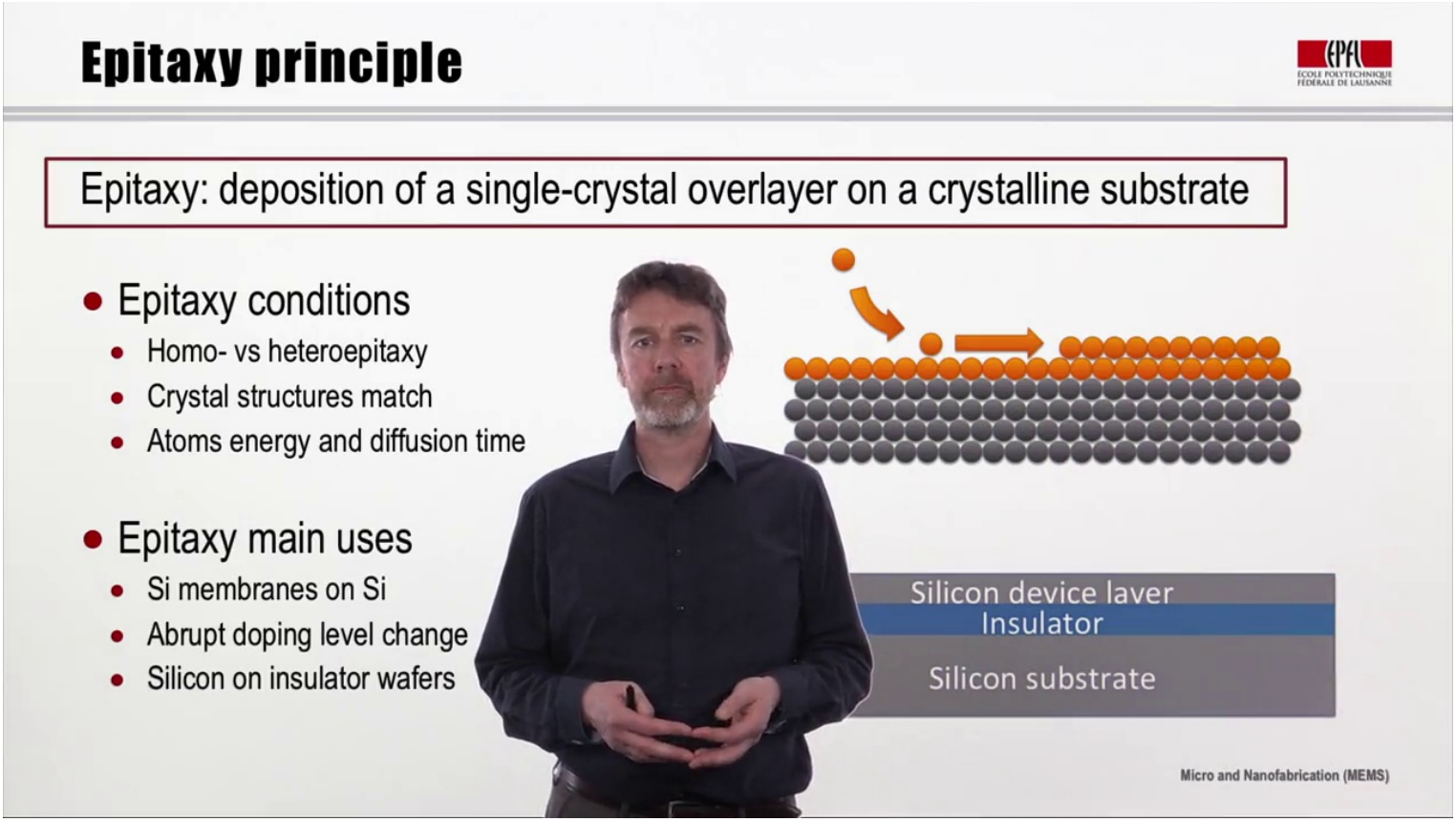
In the case of IAD, a plasma is created in the evaporation chamber and ions are accelerated by applying a negative bias voltage on the substrate. In both cases, the high energy ion bombardment of the substrate is used to clean and activate the surface prior to the deposition and to improve the film quality during the deposition. By doing so, thickness uniformity, as well as film adhesion can be improved. In fact, energetic ions enable atoms to diffuse on the surface and also enable atoms to penetrate into the surface. By this mechanism, film density and hardness can be increased, which is particularly useful when depositing dielectric films. As we know, denser films have lower etch-rates and higher dielectric constant.

Ion (beam) assisted deposition

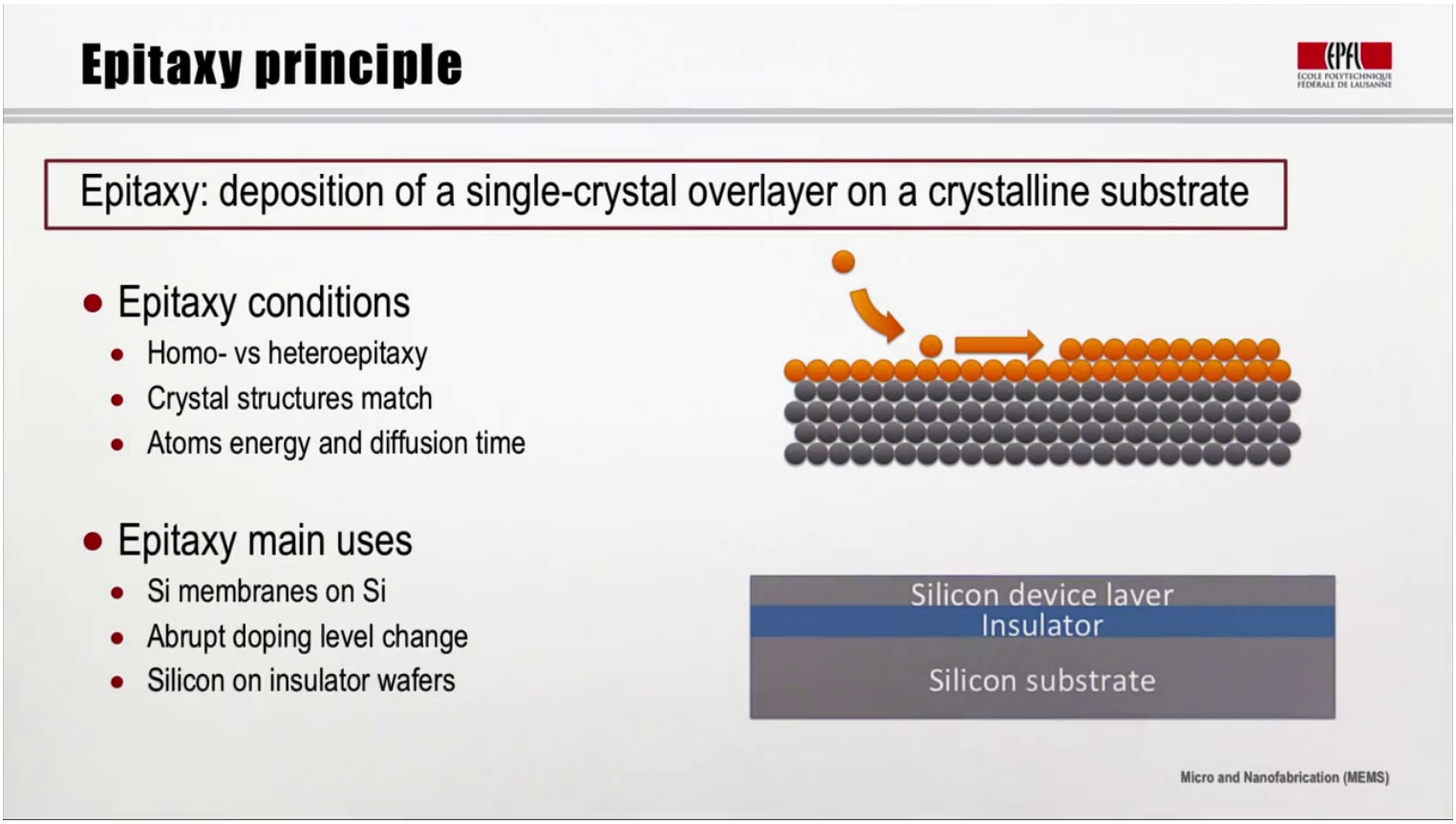
- Ion source
  - Hollow cathode to create electrons
  - Magnetic field to deflect electrons
  - Positive anode to accelerate ions
- Advantages of IBAD
  - Films with higher purity
  - Good internal stress and microstructure control
- Advantages of IAD
  - Compounds deposition
  - Conformal coatings
- IAD and IBAD are also possible with sputtering deposition and CVD



Let's now have a look at how a typical ion source for IBAD works. You can see on the right side of the slide a schematic of a source used in one of the evaporator in the EBF clean room. The substrate is not shown, it will be somewhere on the top of the slide. The source consists of two parts, the hollow cathode electrode source, and the ion source itself. Firstly, argon gas enters the hollow cathode and a high voltage is applied between the keeper and the hollow cathode, creating a plasma within the hollow cathode. Shown here. Once the plasma is stable in the hollow cathode, a bias voltage is applied with a bias controller to emit electrons out of the hollow cathode. Emitted electrons are deflected towards the ion source using a magnetic field. Shown here. In the ion source electrons collide with gas atoms, here we use argon or oxygen, and ionize them. Resulting ions are then repulsed by the positive anode and bombard the substrate. Upwards. Which is not shown here. Electrons emitted from the hollow cathode are also used to neutralize the substrate, which charges positively with ion bombardment. Ion beam assisted deposition has 2 main advantages over non-beam ion assisted deposition. Both come from the fact that no plasma is used in the actual deposition process in contrast to sputtering. Firstly, better film purity is achieved as a higher vacuum can be used. Thin films, with improved internal stress and microstructure control, can be deposited as substrate temperature can be better controlled. As there is no plasma close to the substrate. On the other hand, non-ion beam deposition also has some advantages over the beam assisted deposition. As evaporated atoms travel through the plasma, they will be scattered and some of them will ionize. As a result, conformal coatings and compound deposition can be achieved. For compound deposition, an additional gas is added to the chamber and it will react with evaporated atoms that will have been ionized in the plasma. For instance, dense and very hard titanium nitrate coatings are thereby possible. Finally, IAD and IBAD can be combined with sputtering deposition as well as chemical vapor deposition.



Let's have now a look at epitaxy which is a method to create crystalline material films that are not possible with evaporation and sputtering processes. Indeed, in evaporation and sputtering PVD the deposited layers are either amorphous or sometimes polycrystalline, but never monocrystalline. The crystal structure of deposited thin films will be studied in more detail in the chapter about film growth. Epitaxial deposition consists in growing a single crystal film on the crystalline substrate, as shown in the top schematic on the right side of the slide. If the film is of the same material as the substrate, the process is called "homoepitaxy". It is called "heteroepitaxy" if the materials differ. In order to have a successful growth of the epitaxial layer, several conditions have to be satisfied. In a general way, the epitaxial layer crystal structure is the same as the substrate crystal structure. In the case of homoepitaxy, this is rather straightforward. On the other hand, in the case of heteroepitaxy, things are more complex. Indeed, if there is a lattice mismatch between the material to grow and the substrate, the single-crystal film thickness will be limited or even zero. In addition to the crystal structure condition, there is also a condition on the energy and diffusion time atoms have when they arrive on the substrate. If they are too low or too short, respectively atoms will not be able to go to the right location in order to grow a single crystal. There are several main applications of epitaxy, such as the fabrication of silicon membranes on silicon substrate with predetermined thicknesses and doping levels. And stacks of silicon layers with sharp and large doping level changes. Such stacks can be used in microprocessors, high-performance logic circuits, and as electrochemical etch stop for MEMs fabrication. More details are given' about this last application in the chapter about wet-etching.



Another widely used application of epitaxy is silicon-on-insulator wafers or SOI. SOI wafers consist of a thin surface or device layer of silicon an underlying layer of insulating material typically SiO2 or aluminum oxide and a support silicon wafer as shown in the bottom schematic on the right side of the slide. Such wafers can be used to fabricate faster and more compact transistor chips in the thin epitaxial device layer. It can also be used to fabricate mechanically and electrically insulated layers in MEMs devices Two main types of epitaxy exists: Chemical vapor deposition and physical vapor deposition In this chapter we will focus on the latter one, also called ”Molecular Beam Epitaxy”, or MBE.

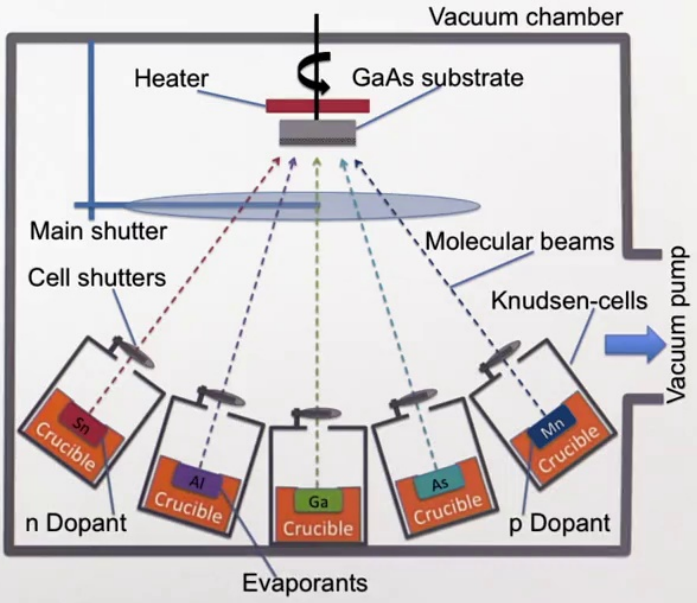
Molecular beam epitaxy (MBE)

- Evaporation from a Knudsen cell

$$Kn = \lambda / D > 1$$

Kn = Knudsen number
λ = mean free path in [m]
D = cell orifice diameter in [m]

  - Molecular flow
- Ultrahigh vacuum: 10^{-11} [Torr]
  - Line-of-sight deposition
- Multiple cells
  - Alloys and compounds deposition

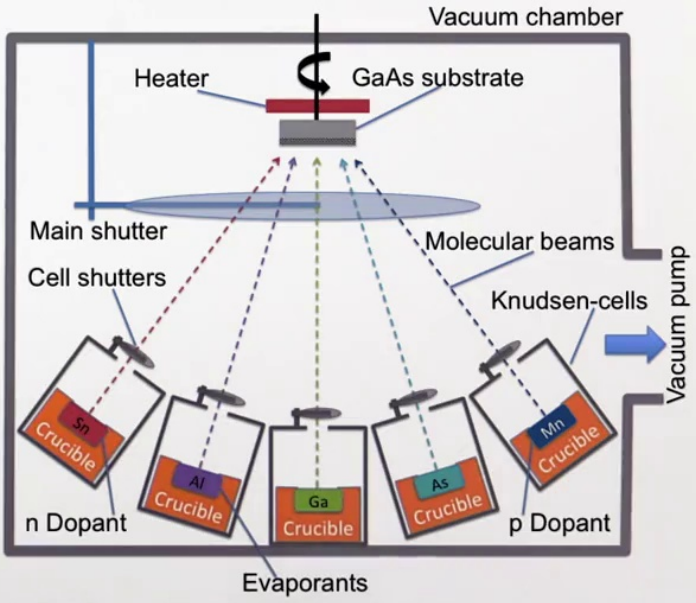


Micro and Nanofabrication (MEMS)

Molecular beam epitaxy, or MBE, is a PVD technique very similar to resistive heating evaporation, but with significant technical differences. Firstly, the crucible containing the evaporant is placed in a cavity with a very small aperture in the millimeter-side range called Knudsen cell as you can see on the figure on the right side of the slide. Typically, graphite crucible with tantalum foil, resistive heatings are used here. The use of a Knudsen cell allows to better control both the temperature of the evaporant and the flow of atoms exiting the cell. The flow of atoms is characterized by the Knudsen number, which is defined as the ratio of the atoms mean free path over the Knudsen cell orifice diameter. Shown here. If the Knudsen number is smaller than 0.01 the mean free path is comparable to the orifice diameter. This means that atoms bounce against the orifice sidewalls. In such a case, atoms exit the cell in a continuous viscous flow. In the case of MBE, the mean free path is in the range of ten-to-the-sixth meters, and the orifice diameter in the range of 10 to the -3 meter. As a result, the Knudsen number is much greater than 1 and atoms are passing through the orifice one by one in a single, straight track. Secondly, MBE requires an ultrahigh vacuum of about 10 to the -11 Torr. in contrast to a vacuum of 10 to the -6, 10 to the -7 used in standard evaporation. As a result, atomic stream evaporated from Knudsen cells in MBE, impinged on the substrate surface in a line-of-sight manner, and then diffuse to their thermodynamically minimal crystallographic location. Finally, as shown in the schematic on the right side of the slide multiple Knudsen cells can be used with the same MBE chamber, which allows depositing compounds, alloys, and even multiple types of dopants. In addition to the main shutter, that covers all the cells, each cell has its own shutter. This way, stacks of different material with various different doping levels can be deposited.

Molecular beam epitaxy (MBE)

- Atoms needs enough energy and time to diffuse to the right location
  - Substrate must be absolutely clean
  - Substrate is heated to 400-800 [°C]
  - Rate is very slow: 0.1-2 [Å/s]
  - Rates depend on crystal orientation
  - Lattice mismatch limits epitaxial layer thickness
- Slow rate and shutters allow precise and accurate thickness control



Micro and Nanofabrication (MEMS)

In order to grow a single crystal film, having molecular flow of atoms impinging the substrate is not sufficient. As mentioned in the introduction slide about epitaxy, once the atoms land on the surface they need to move around until they find an atomic site to chemically bound to it. To do so, atoms on the surface must have enough energy and time to reach the right crystallographic location. Several conditions have then to be satisfied. Firstly, the substrate has to be absolutely clean. Secondly, the substrate is heated from 400° C up to 800° C, to increase the atoms energy. And thirdly, giving atoms enough time to travel to their energy minimum location leads to very low deposition rates in the range of 0.1 to 2 ångström (Å) per second. Which results in very long deposition times. Finally, in the case of heteroepitaxy, if the lattice from the material to grow is different from that of the substrate epitaxy might still be possible, but the thickness of the thin crystal film will be limited. Indeed, the film will strain in order to match the substrate lattice and at some point internal stresses will become too important and dislocations will appear. Such a slow deposition rate and fast acting shutters to control the atomic stream allows very precise and accurate thickness control for each material. Ultra-sharp doping profiles and layers with a thickness precision of +/- 2Å can be achieved routinely

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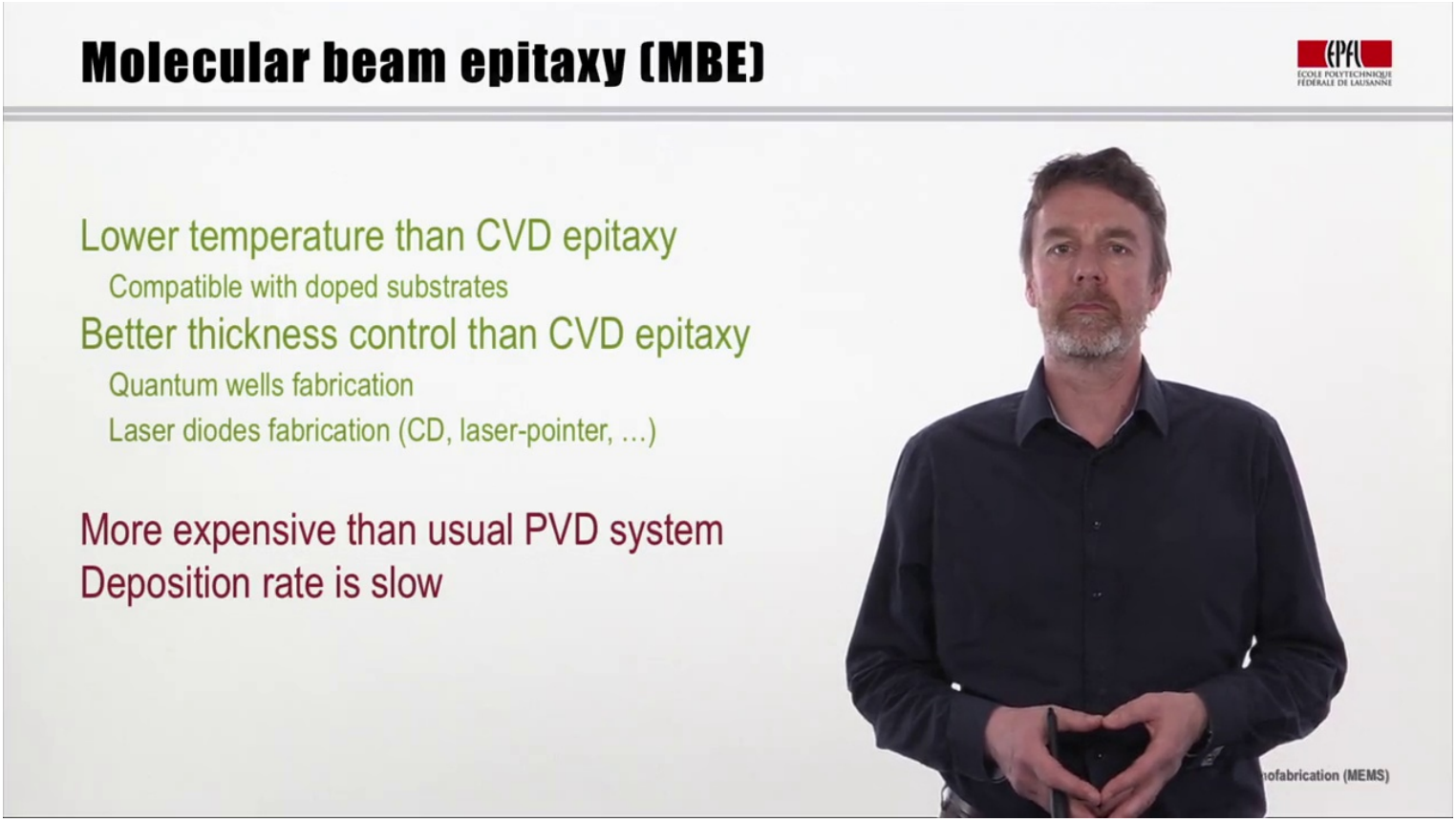
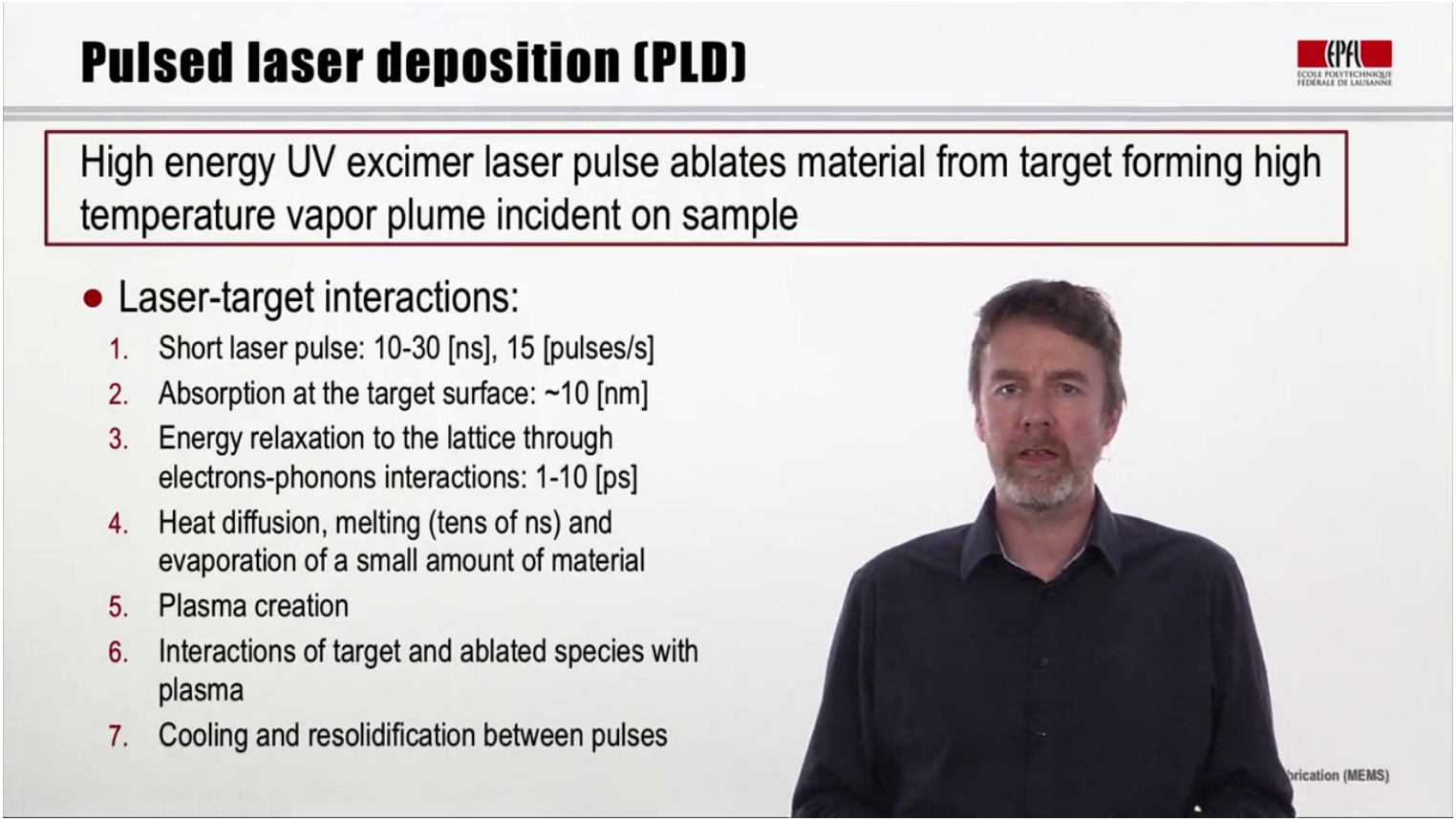


So in comparison to other PVD techniques epitaxy allows for better thickness control and enables the deposition of single crystal layers. And in addition, in comparison to chemical vapor deposition epitaxy molecular beam epitaxy requires lower temperature 400° to 800° C versus 1200° C. And allows better thickness control. Working at lower temperatures enables to work with doped substrates and to deposite doped films without auto-doping and diffusion problems. Better thickness control allows for fabricating quantum wells where layer control of 40 +/- 2 Å is required. Finally, both low temperature and precise thickness control are required to fabricate semi-conductor lasers, such as laser diodes. They are made of a stack of different materials with very specific doping levels and they are widely used for CD, DVD, BluRay Discs, reading and recording, as well as pen-sized laser pointers. On the other hand, MBE is more expensive than other PVD systems because of the required ultrahigh vacuum and because the deposition rate is very slow It is used only for applications where no other technique can be used

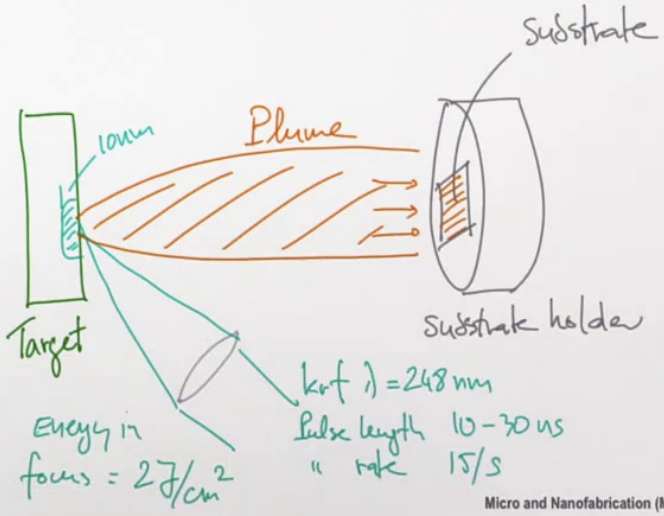


Pulse laser deposition (PLD) consists in using a high-energy UV excimer laser to ablate material from a target. The physical ablation forms a high-temperature vapor plume that reaches the sample surface. We will see that the main advantage of such a system is its ability to deposit compounds with very complex stoichiometry. The working principle of PLD is as follows:

Pulsed laser deposition (PLD)

High energy UV excimer laser pulse ablates material from target forming high temperature vapor plume incident on sample

- Laser-target interactions:
  1. Short laser pulse: 10-30 [ns], 15 [pulses/s]
  2. Absorption at the target surface: ~10 [nm]
  3. Energy relaxation to the lattice through electrons-phonons interactions: 1-10 [ps]
  4. Heat diffusion, melting (tens of ns) and evaporation of a small amount of material
  5. Plasma creation
  6. Interactions of target and ablated species with plasma
  7. Cooling and resolidification between pulses



Micro and Nanofabrication (MEMS)

First, a high-energy UV excimer laser pulse is focused on a target made of the material, to deposit. Shown here. The laser is focusing on the target in green. Typically, a krypton fluoride laser, at 2.48 nanometer is used and pulses of 10 to 30 nanoseconds with an energy in the focus of 2 Joules per centimeter square. Pulse repetition is in the order of 15 per second. The energy of the pulse is absorbed by the target a plasma plume is created at the surface of the target and it interacts with ablated pieces and the target itself. Finally, the vaporized material rapidly expands and condenses on the substrate. In between pulses, the target cools down and solidifies. For metal, the absorption depth is about 10 nanometer. The energy is further relaxed through electron phonon interactions in a phenomena which takes 1 to 10 picoseconds time. Concretly, the electrons are removed from the atoms and oscillate in the strong magnetic field, created by the laser. The generated heat diffuses around due to collisions of these free electrons with other atoms. In the first time, this melts the material. And finally, a small amount of material is evaporated and ionized

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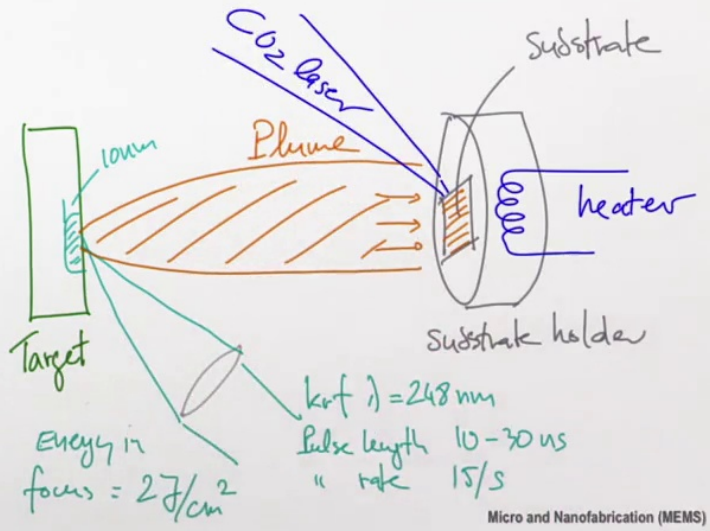
Pulsed laser deposition (PLD)

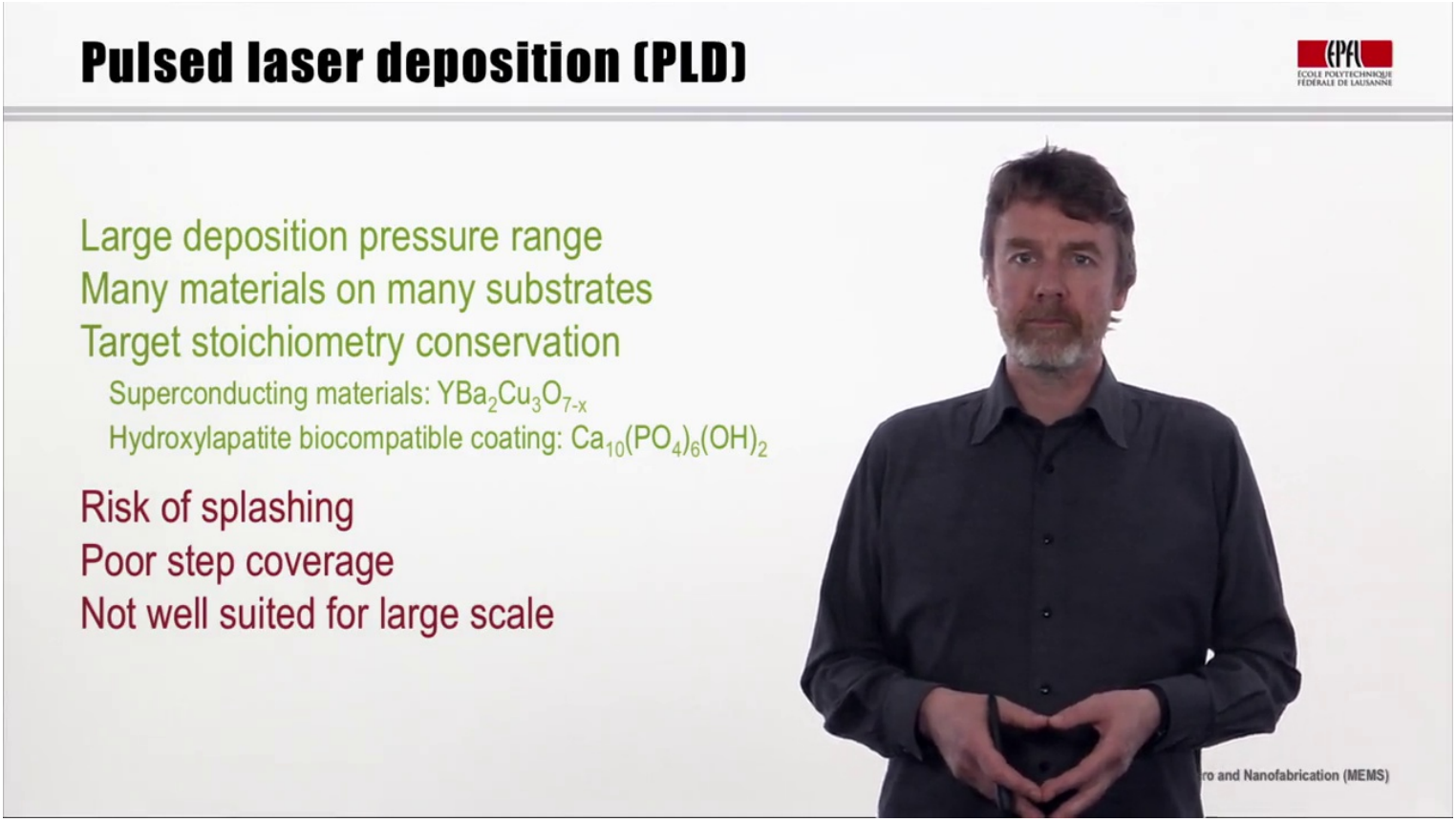
High energy UV excimer laser pulse ablates material from target forming high temperature vapor plume incident on sample

- Deposition at room temperature
  - Deposited film is amorphous
- Substrate heating: 700-900 [°C]
  - Deposited film is crystalline
  - Heater in substrate holder
  - Heating with CO_2 laser



Micro and Nanofabrication (MEMS)

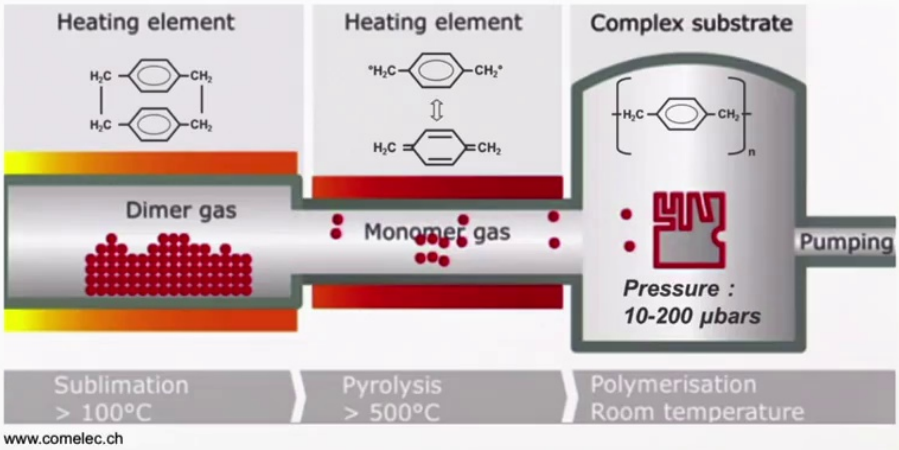
PLD deposition at room temperature usually results in amorphous thin films. However, heating the substrate to 700° to 900° C, allows to get crystalline thin films. Substrate heating can be achieved in two ways. One conventional way is to use a substrate holder with an integrated heater. Another way is to use a CO2 laser which is focused on the substrate.



Pulse laser deposition has several advantages that make it an attractive PVD technique. Firstly, the deposition pressure range varies from atmospheric pressure to high vacuum. Secondly, it is almost possible to deposit any material on any substrate and there is no X-ray generation as it is the case with sputtering. Finally, the most important strength of PLD is that the target material is deposited onto the substrate with almost no decomposition. A stoichiometry is conserved complex compounds and alloys can be deposited. This makes PLD a unique technique to deposit, for instance, functional oxides, such as super conducting materials or bio-compatible based ceramics to protect sensors from body fluid. On the other hand, PLD also has some severe limitations. Firstly, there is a risk of splashing, because of surface boiling or shockwaves due to the plasma plume expansion. Boiling occurs when the layer below the surface of the target reaches its evaporation point before the surface of the target itself. As a result, micrometer particles are injected and impinged to substrate surface. This problem can be partially solved using ultra-short laser pulses of less than 1 picosecond. A such pulse with a shorter than the electron lattice relaxation time, the heat diffusion and melting is reduced and the material is forced directly into plasma state without going into liquid phase first. This leads to cleaner, smoother and higher quality films. Secondly, PLD is a line-of-sight technique, and results in poor step coverage which means on the positive side that it can be used for lift off and shadowmask techniques. Finally, because of the small source size this technique is not suited for large scale deposition Call for new equipment is being developed for this purpose.

PVD: Parylene coating

- Structural material
  - 50 nm to 10 µm thick layers
- Protective coating:
  - chemically resistant, conformal
- Thermal insulator
- Thermally stable
- Biocompatible



To conclude this chapter, I briefly want to introduce one important and recently very prevailing coating material for MEMs, which is parylene. It is widely used in microfabrication as structural material, thick protective coating and thermal insulator. Deposition process consists of 3 subsequent steps. During the first step, a solid parylene diamond is evaporated in a chamber at 150° C. Then, in a second chamber, the temperature is further increased up to 670° C, in order to separate the dimers into monomers. And finally, in the third chamber, the monomer gas is cooled at room temperature so that it condenses on the substrate and polymerizes. Layer thicknesses ranging from 50 [nm] to 10 µm double side coating, as well as conformal and stress-free layer are possible. In addition, parylene shows excellent thickness uniformity below 1%. Is thermally stable. Has a good resistance to solvents, acids, and bases. Last but not least, it is biocompatible, which makes it an ideal candidate for packaging application for bioMEMs.

PVD methods comparison

	Evaporation		Sputtering			IAD / IBAD	MBE	PLD
	Resistive	E-beam	DC	RF	Magnetron			
Rate [Å/s]	0.1 - 20	10 - 100	1 - 100	1 - 100	1 - 200	0.1 - 200	0.1 - 10	1 - 10
Thickness range [nm]	10 - 2000	10 - 2000	10 - 6000	10 - 6000	10 - 6000	10 - 6000	0.4 - 1000	0.1 - 1000
Material	Metals	Metals, oxides	Metals, alloys	Metals, alloys, dielectrics, compounds	Metals, alloys, dielectrics, compounds	Metals, alloys, dielectrics, compounds	Si, Ga, Al, As, In, P, Sb, Mn, …	All materials + complex compounds
Purity	+	+ +	- -	- -	-	- - / -	+ + +	+
Step coverage	-	-	+	+	+	+ + / +	++	- -
Adhesion	-	-	+	+	+	+ +	+ + +	+
Large area uniformity	-	-	+	+	+	+ +	+ + +	- -
Pressure [Torr]	10^{-6} - 10^{-7}	10^{-6} - 10^{-7}	10^{-1} - 10^{-2}	10^{-1} - 10^{-2}	10^{-3}	10^{-1} - 10^{-2}	10^{-11}	750 - 10^{-9}
Substrate temp. [°C]	20 - 400	20 - 400	20 - 400	20 - 400	20 - 400	20 - 400	400 - 800	20 - 900
Other	Lift-off	Lift-off	Substrate cleaning & activation	Substrate cleaning & activation	Substrate cleaning & activation	Cleaning & activation, densification	Single-crystal, expensive	

This table summarizes the key features of the main PVD techniques introduced so far. It allows to compare the various parameters and to select the proper method for one's own use. Please have a look at the variations in parameters and try to get an overview of the pros and cons of each of the methods.

PVD 7: Other Techniques

- Physical principle
  - Plasma, spatial zones, Paschen law
- Sputter variations
  - DC sputtering
  - RF sputtering
  - Magnetron sputtering
- Ions-target interactions
- Sputter examples
- Other PVD methods
- Film growth and control parameters

Micro and Nanofabrication (MEMS)

We have looked at the wide range of different PVD methods, such as thermal evaporation sputtering, ion plating, molecular beam epitaxy and pulse laser deposition. The underlying physical principles have been explained. So you should now be able to distinguish the various methods and to eventually choose the proper one for your purpose. In an upcoming video lecture, we will analyze more in details how PVD films grow onto the substrates.