

Types of CVD processes



- CVD at different operating pressures (APCVD; SACVD; LPCVD; UHV/CVD)
- Plasma-enhanced CVD (PECVD)
- Metal-organic CVD (MOCVD)

Micro and Nanofabrication (MEMS)

In this second lesson on Chemical Vapor Deposition we will discuss in somewhat more detail, common types of CVD processes. First, we will discuss the CVD as operated at different operating pressures. First technique is called *Atmospheric Pressure CVD*, or *APCVD*. Then, *Sub-atmospheric Pressure CVD*, or *SACVD*, followed by *Low Pressure CVD*, or *LPCVD*, and finally, *Ultra High Vacuum CVD*, for the lowest pressure used. Next, we will discuss a technique called *Plasma-enhanced CVD*, or *PECVD*. And finally, the technique *Metal organic CVD*, or *MOCVD*.

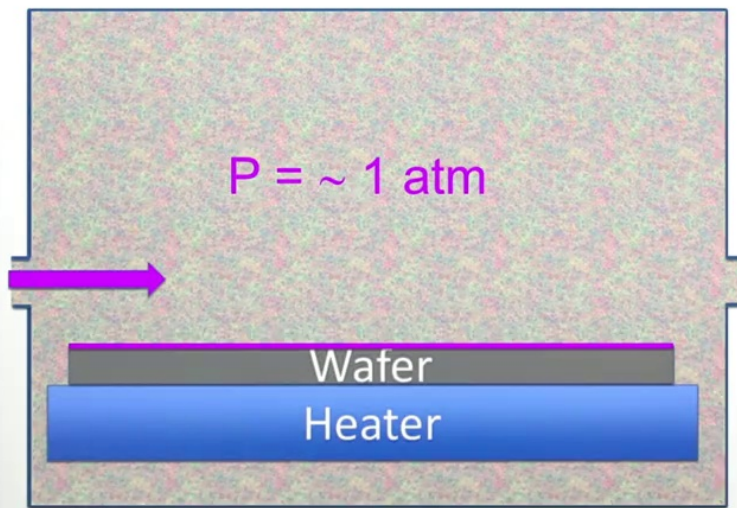
Classification of CVD by pressure

- Atmospheric pressure CVD (APCVD)
- Sub-atmospheric pressure CVD (SACVD)
 - $1000 \text{ mbar} > P > 10 \text{ mbar}$
 - Reduction of unwanted gas phase reactions
 - Improvement of film uniformity across the wafer
- Low-pressure CVD (LPCVD)
 - $1 \text{ mbar} > P > 0.1 \text{ mbar}$
- Ultrahigh vacuum CVD (UHV/CVD)
 - Initial vacuum of $10^{-7} - 10^{-8} \text{ mbar}$; growth at $P \sim 10^{-3} \text{ mbar}$
 - No gas phase reactions
 - No gas boundary layer near wafer surface, but molecular flow transport

Micro and Nanofabrication (MEMS)

This slide is taken from the first lesson and lists again the different CVD techniques according to the pressure of the gas used for deposition. The first technique is practiced at atmospheric pressure. SACVD is at lower pressure, down to 10 millibar. And low pressure CVD is in between 1 millibar and 0.1 millibar. While ultrahigh vacuum CVD is using very high initial vacuum but standard growth is typically performed at 10 minus 3 millibar of gas pressure.

Atmospheric pressure CVD (APCVD)

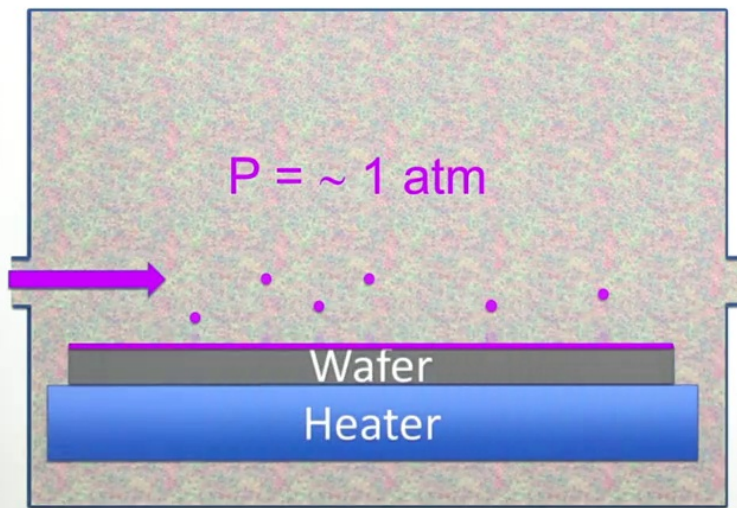


- High pressure results in fast film growth rates (micron/minute)
- High gas consumption
- Also carrier or diluent gas can be used (e.g. N_2 or H_2)
- $350^\circ\text{C} < T < 1200^\circ\text{C}$
- Growth of oxides at low temperatures
- Epitaxial Si growth at high temperatures

Micro and Nanofabrication (MEMS)

In atmospheric pressure CVD, the high pressure of the gas that is used leads to fast film growth rates. Typically microns per minute. This leads to a high consumption of gas and often a carrier or diluent gas is used like nitrogen or hydrogen. Typical deposition temperatures are between 350 degrees Celsius and 1200 degrees Celsius. The technique is used for growing oxides at lower temperatures and also for the growth of epitaxial silicon films on silicon substrates at higher temperatures.

Atmospheric pressure CVD (APCVD)

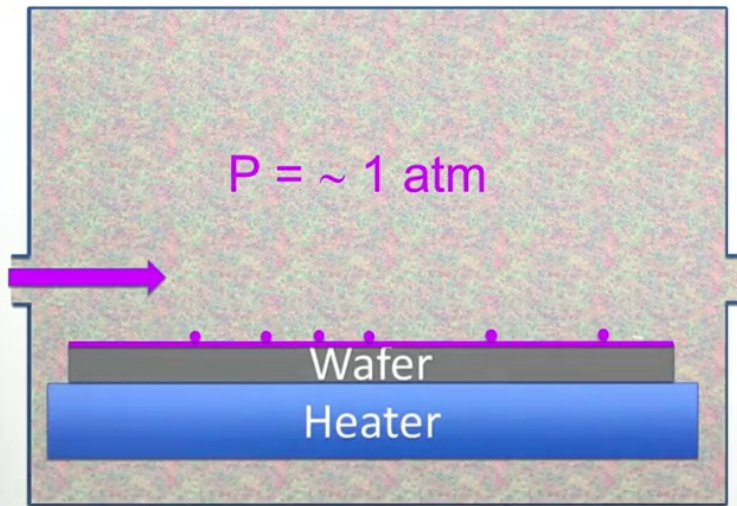


- At high temperature, growth is in the mass transport-limited regime $\rightarrow$ gas flow control is very important
- Wafer is placed horizontally in the gas flow $\rightarrow$ limits throughput
- Reaction may already start in the gas phase, resulting in unwanted precipitates on the wafer $\rightarrow$ non-uniformities or pinholes in deposited film

Micro and Nanofabrication (MEMS)

At the high temperatures that are used, film growth is in the mass transport-limited regime. Therefore gas flow control and local concentration of the gas is very important. To enable a good control of the gas flow, the wafer is placed horizontally so that the flow smoothly passes over it in a very controlled way. However, not so many wafers can be used at the same time as the exploitable surface in the reactor is basically limited by the area of the heater. As a consequence, the throughput of this technique is limited. A possible disadvantage of this technique is that the reaction may already start in the gas phase itself, rather than on the substrate. So there is formation of particles in the gas.

Atmospheric pressure CVD (APCVD)

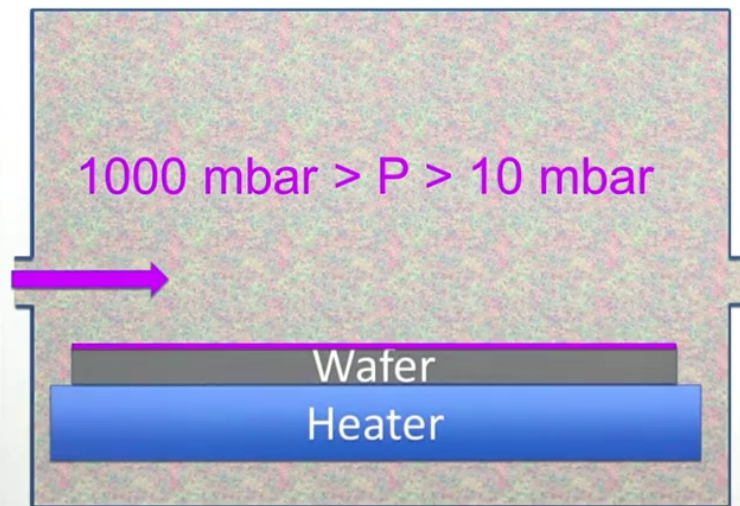


- At high temperature, growth is in the mass transport-limited regime $\rightarrow$ gas flow control is very important
- Wafer is placed horizontally in the gas flow $\rightarrow$ limits throughput
- Reaction may already start in the gas phase, resulting in unwanted precipitates on the wafer $\rightarrow$ non-uniformities or pinholes in deposited film

Micro and Nanofabrication (MEMS)

This results in deposition of unwanted precipitates on the wafer. And when continuing the deposition, this results in non-uniformities, or pinholes in the deposited film.

Sub-atmospheric pressure CVD (SACVD)

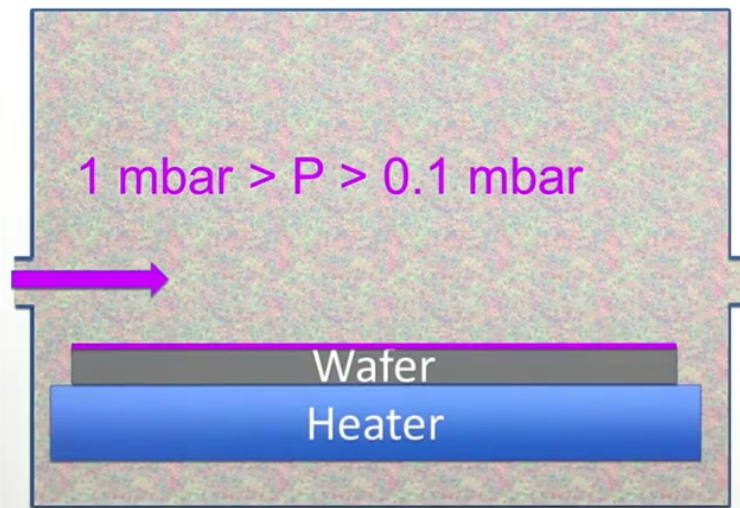


- Reduced gas consumption
- More uniform films grown
- No particle formation
- Wafers still horizontally placed → low throughput

Micro and Nanofabrication (MEMS)

In sub-atmospheric pressure CVD, the gas concentration is reduced. And also the deposition rate decreases but due to the larger mean free path of the gas inhomogeneities in the concentration are less important and more uniform films are grown. Also as the gas molecules have less probability for interaction, no or very little particles are formed. Still wafers need to be placed horizontally occupying a lot of surface and resulting in a relatively low throughput of the deposition process.

Low-pressure CVD (LPCVD)

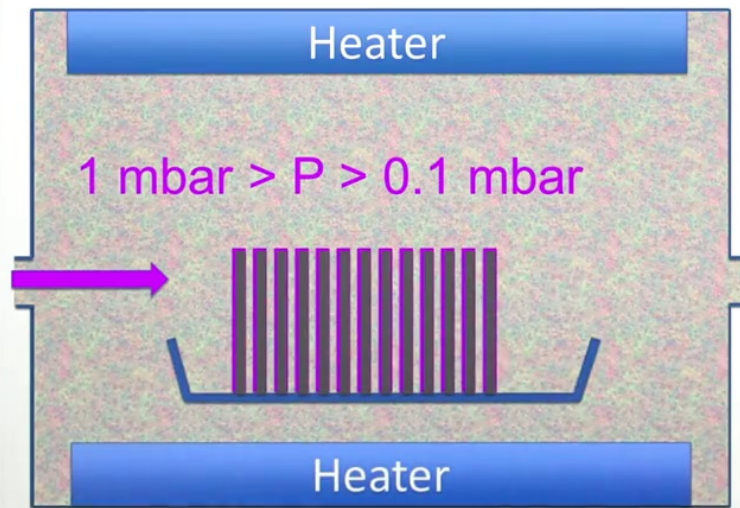


- Low pressure results in increased gas diffusion
- No gas concentration gradient perpendicular to flow direction
- More uniform films
- $400\text{ }^{\circ}\text{C} < T < 900\text{ }^{\circ}\text{C}$
- Growth in reaction-limited regime
- Precise temperature control is important
- Usually 10-100 $\times$ lower deposition rates compared to APCVD

Micro and Nanofabrication (MEMS)

In low-pressure CVD, the pressure of the gas is further reduced, leading to still longer mean free paths, and has an increased diffusion. Also, no gas concentration gradient is present perpendicular to the flow direction, except of course the gradient that will develop very close to the wafer where deposition occurs. More uniform films can be deposited and typical growth temperatures are in between 400 degrees Celsius and 900 degrees Celsius. Growth of the film is in the reaction-limited regime, hence a precise temperature control is very important because the temperature variation immediately results in a changing reaction rate. Usually the LPCVD technique has 10 to 100 times lower deposition rates compared to APCVD.

Low-pressure CVD (LPCVD)

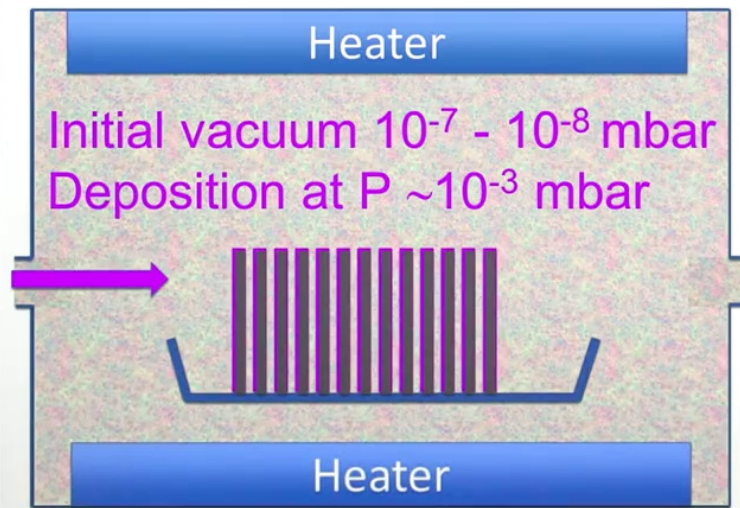


- Wafers can be stacked vertically in batches due to homogeneous gas conditions → wafer throughput can be enhanced
- Downstream depletion of gases can be compensated by establishing a temperature gradient in the heater system

Micro and Nanofabrication (MEMS)

Due to the low pressure and the resulting homogenous gas conditions, wafers can be stacked vertically in batches, occupying less horizontal space. Therefore, in LPCVD, the wafer throughput can be enhanced. Wafers that are situated more upstream of the gas flow may be exposed to a higher concentration of gas than wafers that are placed further downstream. This would result in a different film thickness, but this gas depletion effect can be compensated by establishing with a heater system, a slightly higher temperature further downstream of the flow, so that the film thickness becomes uniform.

Ultrahigh vacuum CVD (UHV/CVD)

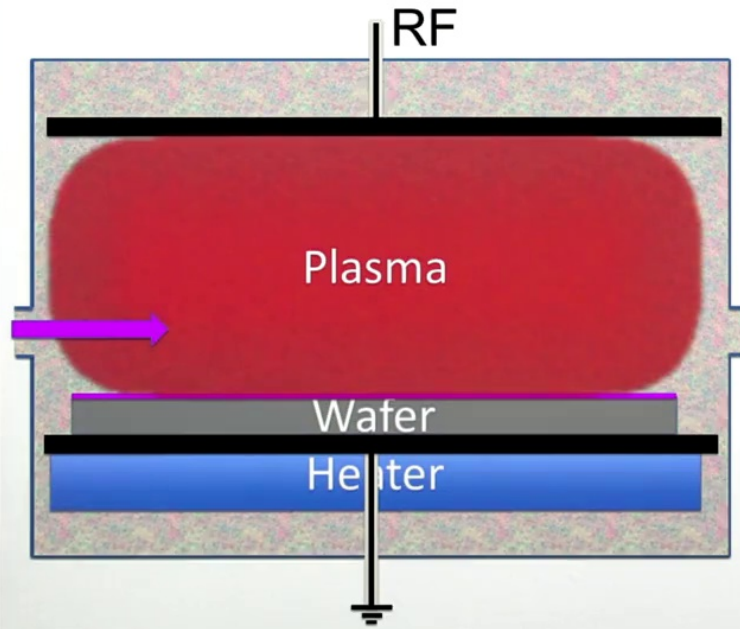


- Molecular mean free path is of the order of the chamber dimension
- No gas boundary layer effects near wafer surface, only molecular flow
- No gas-phase chemical reactions
- $500\text{ }^{\circ}\text{C} < T < 600\text{ }^{\circ}\text{C}$
- Low partial pressure of contaminant gases
→ enables low-temperature growth with minimum thermal budget-related dopant diffusion in semiconductors

Micro and Nanofabrication (MEMS)

In ultrahigh vacuum CVD, the molecular mean free path is as big as the reactor dimension itself. The gas behaves not so much as a viscous liquid but as a collection of individual molecules. There are no gas-phase chemical reactions and a typical temperature for operation is between 500 and 600 degrees Celsius. Due to the high initial vacuum, the partial pressure of contaminant gasses is reduced so that one can deposit during longer times at lower temperature without incorporating too much impurity molecules in the grown film. Keeping a low temperature during growth can be important for sensitive semiconductor micro-fabrication processes, where a too high temperature may result in too high diffusion of active dopants.

Plasma-enhanced CVD (PECVD)

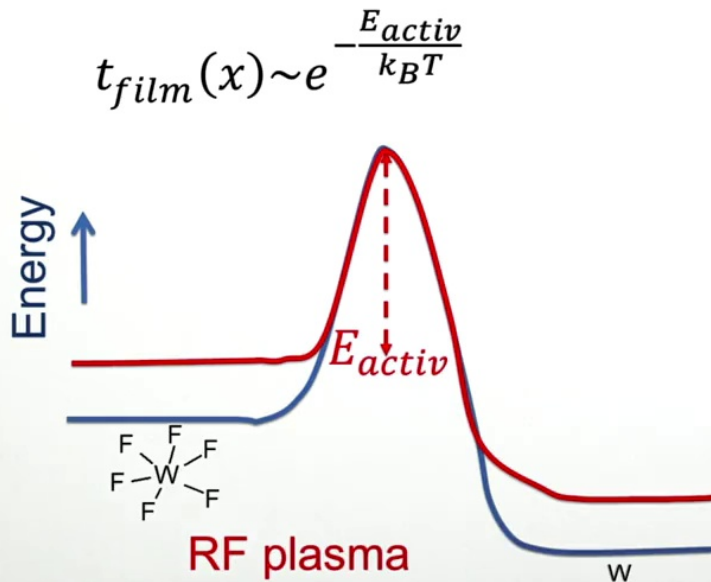


- Based on LPCVD-like configuration
- Radio Frequency (RF) power coupled into the gas, typically at 400 kHz or 13.56 MHz
- RF power induces plasma, i.e. a partially ionized gas, containing ions, electrons and excited gas molecules

Micro and Nanofabrication (MEMS)

Plasma-enhanced CVD is based on the LPCVD configuration we discussed before. The difference is that now a radio frequency power can be coupled via two electrodes into the gas. And typically this is done at a frequency of 400 kilohertz or 13.5 megahertz. The RF power induces a plasma, which is a partially ionized gas, containing ions, electrons, and neutral excited gas molecules. It can be perceived in the reactor by the gas that is lighting up. The light is caused mostly by accelerating free electrons, but all molecules in the plasma become agitated as a result of the applied RF power.

Plasma-enhanced CVD (PECVD)

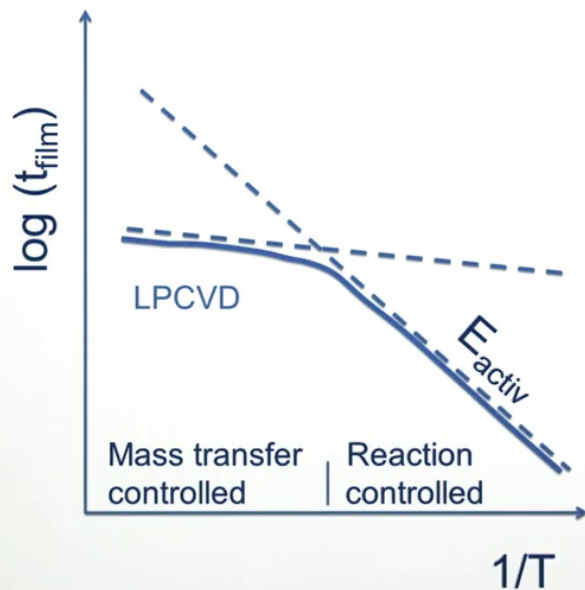


- Film growth is in the reaction-limited regime
- Plasma raises all molecular energies
- Effective activation energy is reduced
- Increased growth rate possible
- Growth becomes possible **at lower temperature** → less restrictions to the used substrate

Micro and Nanofabrication (MEMS)

As the film growth is in the reaction-limited regime, the exponential factor that contains the reaction activation energy and the temperature plays an important role. Schematically, one can imagine that without plasma there is initially a gas molecule that then, by a temperature fluctuation, has to acquire sufficient energy to be converted to a metal atom in this example. If now the RF plasma is switched on, all molecules gain in energy as indicated on the red curve, so energy goes up everywhere. As a result, the effective activation energy for the reaction to occur is lower- the barrier height is lower. This immediately leads to a thin film growth that becomes possible at lower temperatures than before without the plasma. So in PECVD, deposition is done typically at lower temperature. Therefore with this technique substrates do not need to be heated as much as an LPCVD for the reaction to occur. So one has a wider choice of substrate materials.

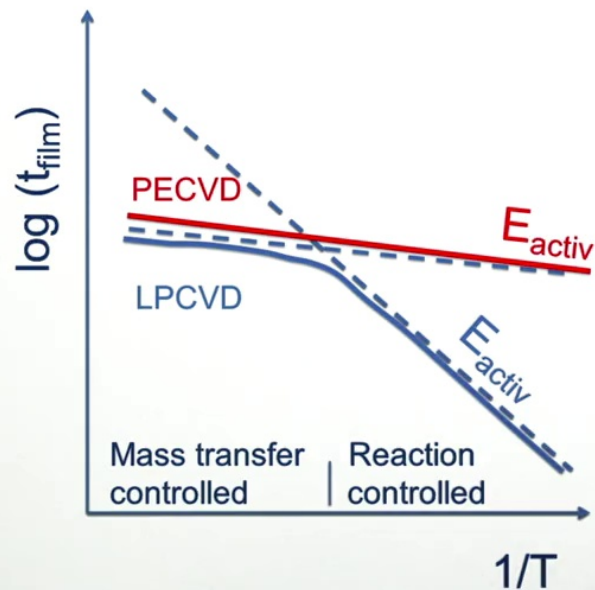
Arrhenius plot of film growth rate



ication (MEMS)

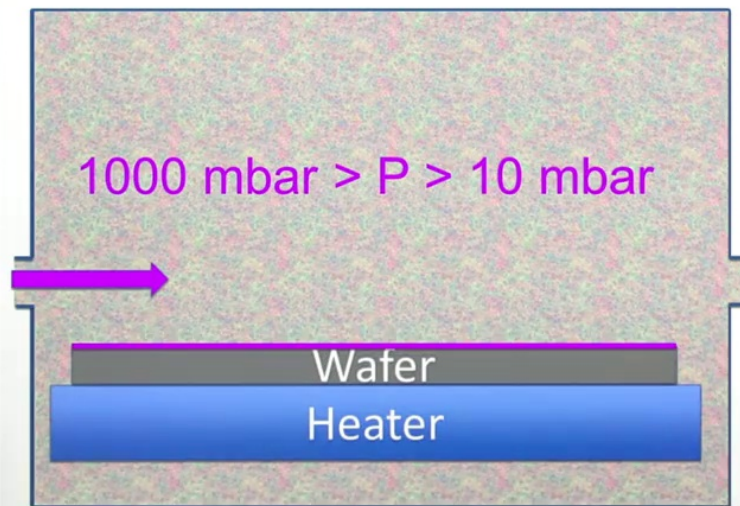
In this graph we show again the Arrhenius plot of the film growth rate, indicating the mass transfer controlled and the reaction controlled regimes. This was the case without using RF power.

Arrhenius plot of film growth rate

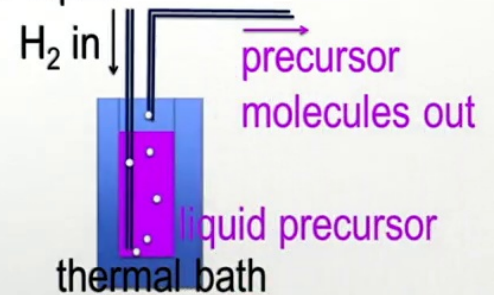


We have now switched on the RF power in the PECVD system and obtained the red curve for the thin film thickness. The slope of the red curve is not as steep because the slope gives the effective activation energy of the chemical reaction which is lower for the PECVD deposition. Also one observes that there is a more appreciable growth rate or film thickness at lower temperatures- that means at higher $1/T$ values.

Metal-organic CVD (MOCVD)



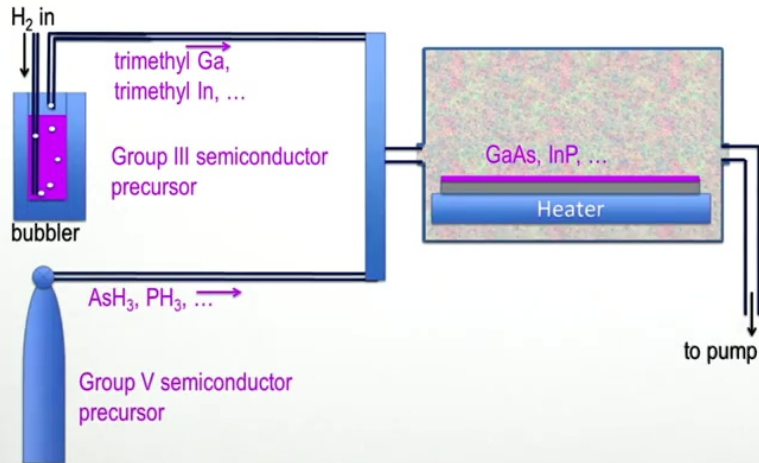
- Also called “metal-organic vapour phase epitaxy (MOVPE)”
- Transport of volatile metal-organic precursor molecules by a carrier gas (H_2 or N_2) that bubbles through the precursor liquid



Micro and Nanofabrication (MEMS)

The last technique that we will discuss in this lesson is metal organic CVD, or MOCVD. This technique is also called, *metal-organic vapour phase epitaxy*. Here one wants to deposit certain metals from liquid precursor molecules that normally are not in the gaseous phase. To lead these molecules to the substrate, one uses a carrier gas, like hydrogen, that bubbles through the precursor liquid and in that way one transfers the precursor molecules towards the substrate.

Metal-organic CVD (MOCVD)



- Surface reaction of metal-organic compounds (liquid precursors) and hydrides (gaseous precursors) allows deposition of compound semiconductors, e.g. GaAs or InP
- $300\text{ }^{\circ}\text{C} < T < 500\text{ }^{\circ}\text{C}$
- Vapour pressure control of metal-organic source critical
- Safety aspects important

Micro and Nanofabrication (MEMS)

Here we give an example in which trimethylgallium or trimethylindium is transported to the reactor. In parallel there is a line where the gaseous products arsine or phosphine can be led to the reactor chamber. Doing so one can deposit compound semi-conductors, like gallium arsenide or indium phosphide. Typical growth temperatures are between 300 and 500 degrees Celsius. The vapor pressure of the metal-organic source is a critical parameter and also due to the use of the very toxic precursor compounds, safety aspects generally are very important in MOCVD deposition.



This video shows a typical MOCVD equipment. The MOCVD reactor itself, reagent sources, and supply lines are all inside of a cabinet that is isolated from the outside to avoid release of toxic products into the environment.



One can manipulate items inside the cabinet via the use of gloves that are attached to the cabinet. We see here an operator who accesses the inside and in particular he opens the MOCVD reactor itself to take out a wafer after a deposition run.



- Overview of CVD processes classified by operation pressure
- Plasma-enhanced CVD: enhanced deposition due to activation of precursor molecules in the plasma
- Metal-organic CVD based on liquid precursor materials

Micro and Nanofabrication (MEMS)

In this lesson we have given an overview of most common CVD processes as classified by the reactor operation pressure. These were atmospheric pressure CVD, sub-atmospheric pressure CVD, low pressure CVD, and ultrahigh vacuum CVD. We also introduced plasma-enhanced CVD, where the use of RF power results in a smaller effective activation energy for the chemical reaction so that deposition of the thin film can take place at lower temperature than in the LPCVD reactor. Finally, we introduced metal-organic CVD.
