

Examples of CVD processes

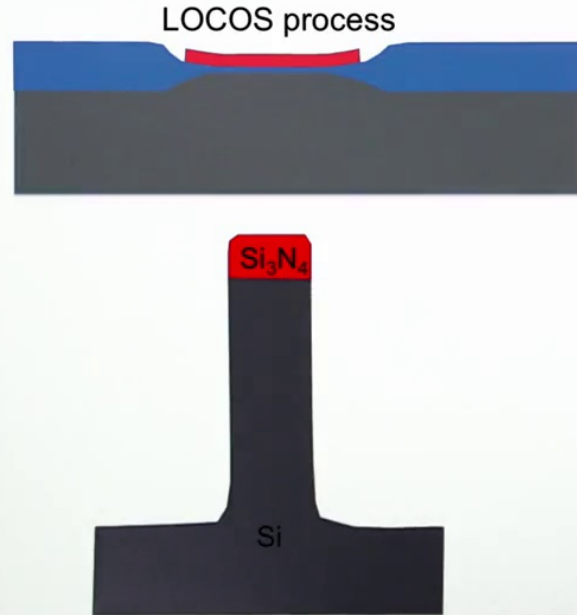


- Wet thermal SiO_2 (not truly CVD)
- Dry thermal SiO_2 (not truly CVD)
- Atomic Layer Deposition (ALD) of Al_2O_3 , Ru, and TiN

Micro and Nanofabrication (MEMS)

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 silicon 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 nitride films.

Deposition of wet thermal oxide

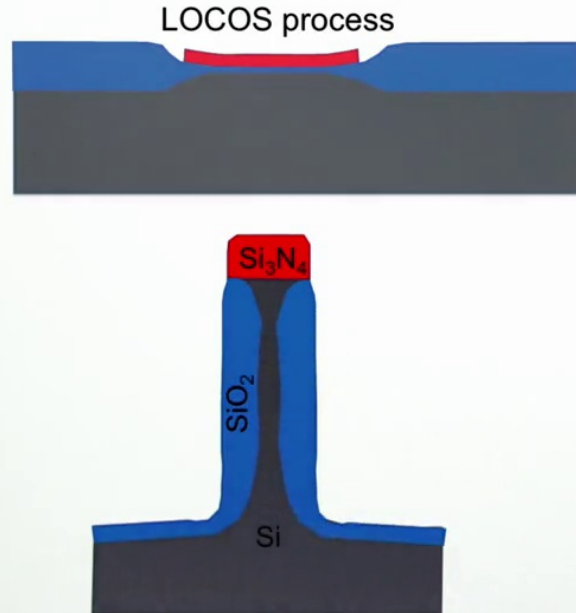


- Wet oxidation (using H_2O vapour) allows fast transformation of the surface of a Si wafer, layers of poly-Si or amorphous Si into oxide
- Thick layers (up to $2\text{ }\mu\text{m}$) can be realized
- Such oxide layers can be used e.g. as protective masking layer in plasma etching, or used as thick electrical insulation layers in microelectronic circuits (LOCOS process)

Micro and Nanofabrication (MEMS)

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 nitride 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 *Local Oxidation of Silicon*, or *LOCOS*. 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 nitride as a masking material in the etching process.

Deposition of wet thermal oxide

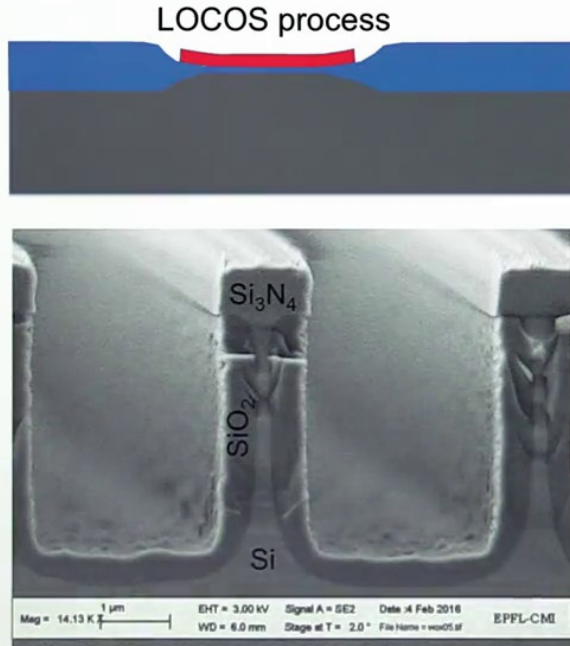


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Micro and Nanofabrication (MEMS)

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

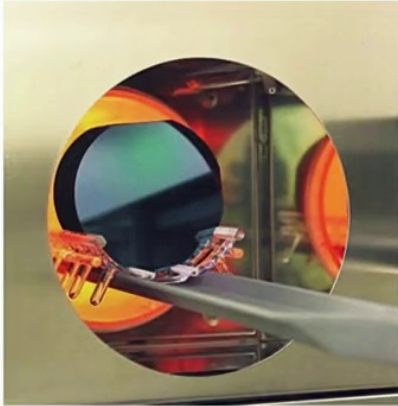
Deposition of wet thermal oxide



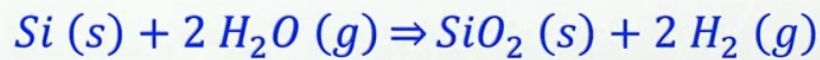
- Wet oxidation (using H₂O vapour) allows fast transformation of the surface of a Si wafer, layers of poly-Si or amorphous Si into oxide
- Thick layers (up to 2 μm) can be realized
- Such oxide layers can be used e.g. as protective masking layer in plasma etching, or used as thick electrical insulation layers in microelectronic circuits (LOCOS process)

Micro and Nanofabrication (MEMS)

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 nitride mask, and here we see the zones where the silicon is transformed to silicon dioxide.

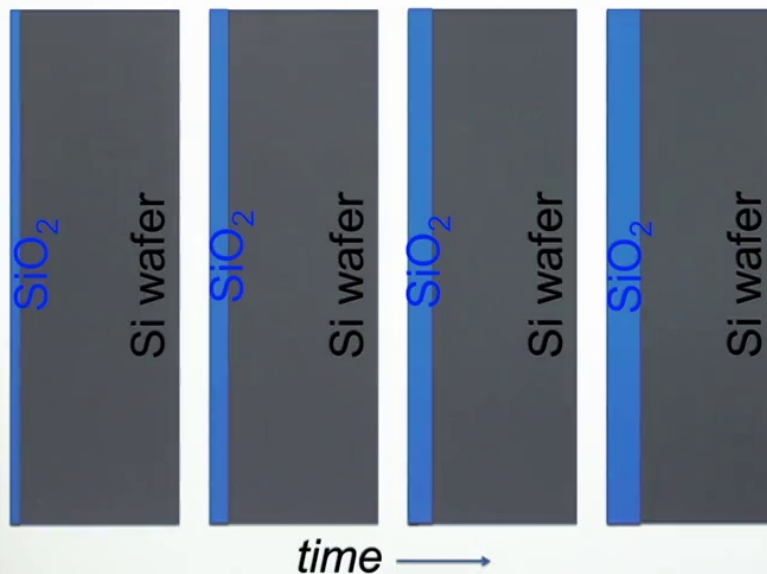


- In thermal oxidation, silicon is transformed into its oxide at high temperature ($850\text{ }^{\circ}\text{C} < T < 1100\text{ }^{\circ}\text{C}$) using either water vapor (“wet oxidation”) or oxygen (“dry oxidation”).
- Water vapor is produced by combustion of H_2 and O_2 in a torch
- Slow process
 - Wet @ $900\text{ }^{\circ}\text{C}$: 130 nm in 1 hour
 - Dry @ $900\text{ }^{\circ}\text{C}$: 30 nm in 1 hour



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.

Thermal oxidation mechanism

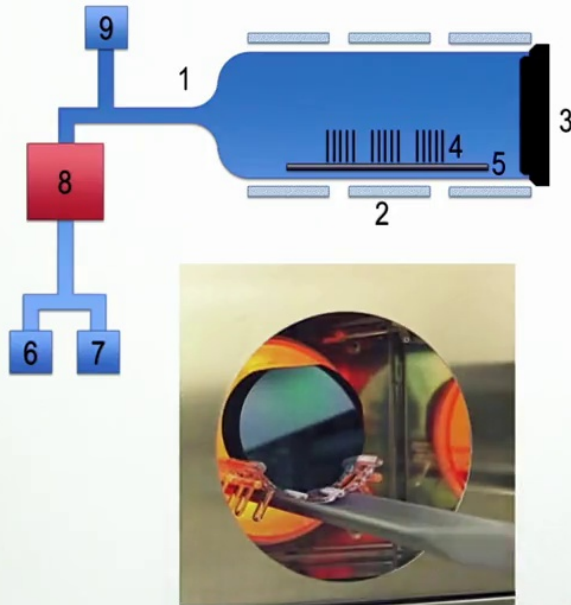


- SiO_2 is formed by diffusion of oxygen into the Si wafer
- Oxidation is at the SiO_2/Si interface
- Initially oxide thickness $t_{ox} \sim \text{time}$, later $t_{ox} \sim \sqrt{\text{time}}$ due to increased diffusion length
- In general
$$t_{ox}^2 + A t_{ox} = B(\text{time} + \tau)$$
with A and B two constants that depend on the substrate and oxidation conditions and τ a time constant to take care of the native oxide

Micro and Nanofabrication (MEMS)

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 τ is a time constant that takes into account the thickness of an eventual initial native oxide of the silicon wafer.

Deposition of wet thermal oxide

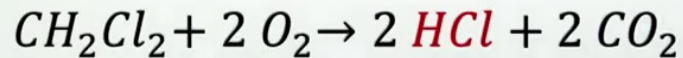
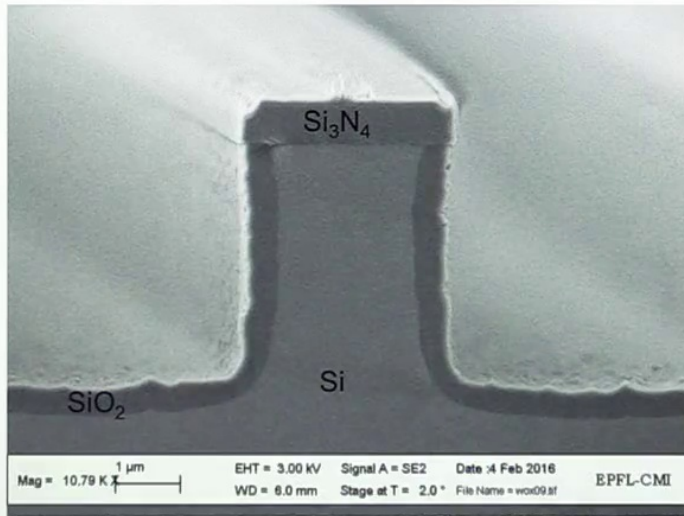


1. Fused silica tube
2. Heating elements (3 zones)
3. Fused silica seal
4. Three fused silica boats, each for 25 wafers of 100 mm or 150 mm Ø
5. Temperature sensor
6. Hydrogen gas (H_2) entrance
7. Oxygen gas (O_2) entrance
8. Hydrogen torch system: H_2 and O_2 are mixed at temperatures above about 600 °C. This produces a controlled combustion which reaches temperatures of about 1200 °C whereby water vapor is formed.
9. Nitrogen gas (N_2) entrance

Micro and Nanofabrication (MEMS)

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.

Deposition of dry thermal oxide

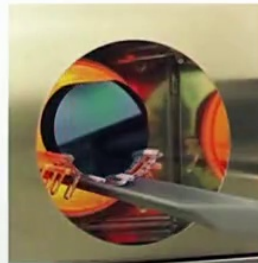
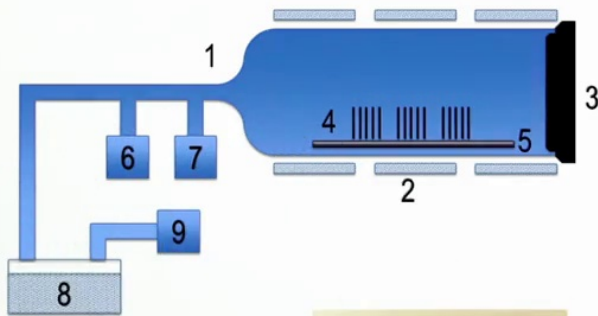


- Dry thermal oxidation is used for realisation of the thin gate oxide layer in MOS transistors
- A dichloroethylene ($\text{C}_2\text{H}_2\text{Cl}_2$) bubbler allows controlled growth of ultrathin oxides (20-25 nm)
- $\text{C}_2\text{H}_2\text{Cl}_2$ is a liquid source that generates high-purity HCl, which reacts with metal contaminants so that a high-quality low-defect thin oxide can be grown

Micro and Nanofabrication (MEMS)

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 nitride mask and afterwards there is dry oxidation leading to these oxide layers.

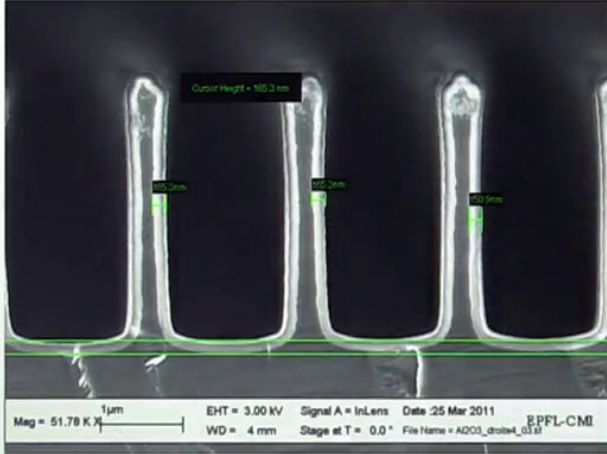
Deposition of dry thermal oxide



1. Fused silica tube
2. Heating elements (3 zones)
3. Fused silica seal
4. Three fused silica boats, each for 25 wafers of 100 mm or 150 mm Ø
5. Temperature sensor
6. Oxygen gas (O_2) entrance
7. Nitrogen gas (N_2) entrance
8. Dichloroethylene (DCE) ($C_2H_2Cl_2$) bubbler
9. Nitrogen gas (N_2) - dichloroethylene ($C_2H_2Cl_2$) entrance

Micro and Nanofabrication (MEMS)

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.

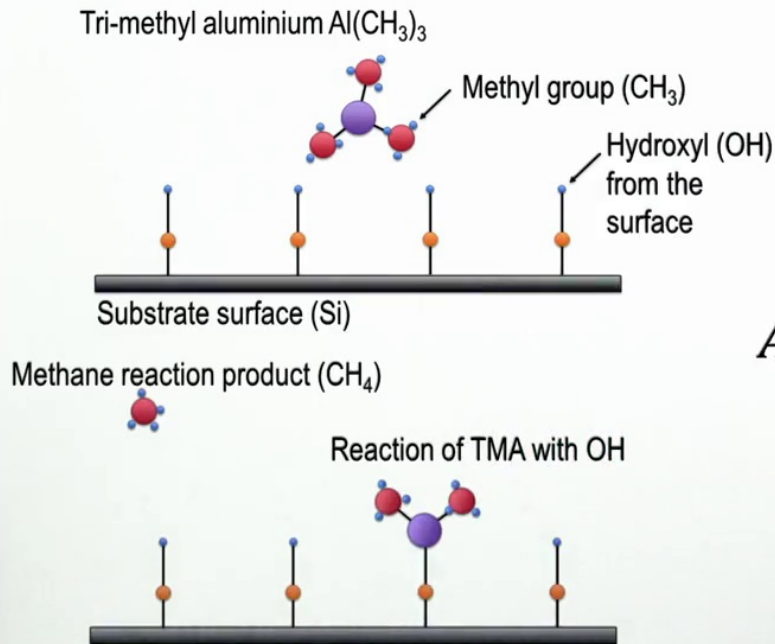


- Thin Al_2O_3 layers can be used as high dielectric constant ($\epsilon_r=7.5$) material in microelectronic components, as gas diffusion barrier layer in packaging, and in flexible electronic devices
- Substrate temperature during ALD deposition can be 100-500 °C
- Deposition is done under vacuum (around 5 mbar) from chemical precursors
- ALD is recommended for thin layers (<100 nm) and/or for conformal layers

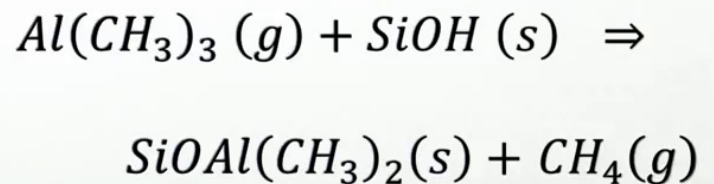
Micro and Nanofabrication (MEMS)

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-step deposition process



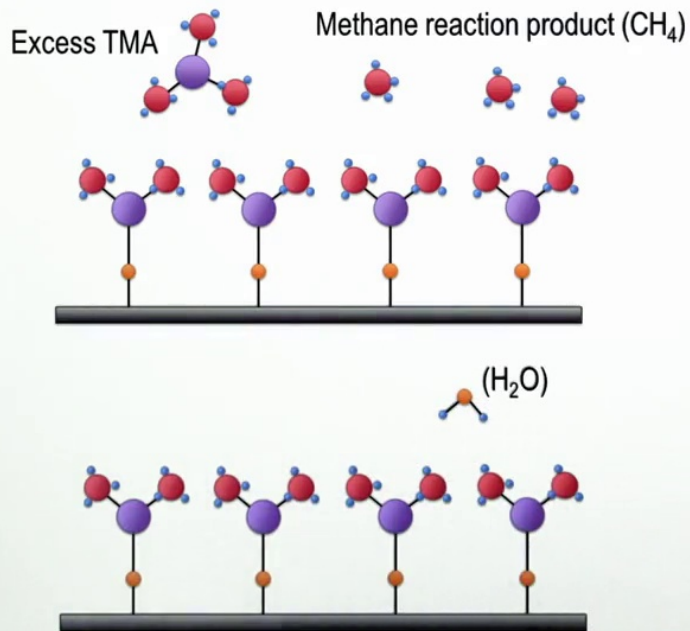
- The first precursor (trimethylaluminium $\text{Al}(\text{CH}_3)_3$) is pulsed to the reaction space and reacts at the surface of the sample by chemisorption



Micro and Nanofabrication (MEMS)

Four steps are involved in the deposition of aluminium oxide by ALD. The first precursor is tri-methyl aluminium; this molecule, which is chemisorbed 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.

Four-step deposition process



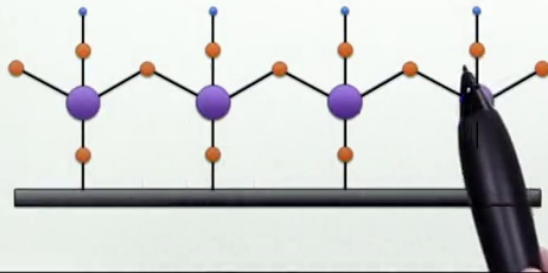
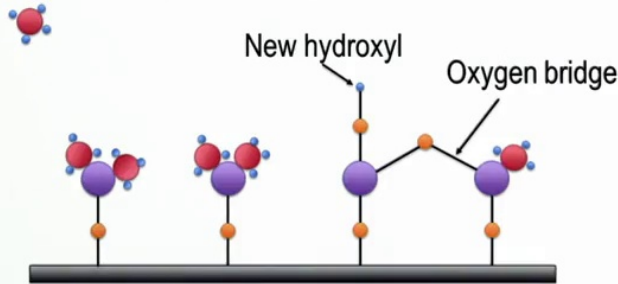
- The reaction chamber is purged with inert gas (N₂) and the excess of precursor 1 is removed
- The second precursor (H₂O) is pulsed to the reaction space

Micro and Nanofabrication (MEMS)

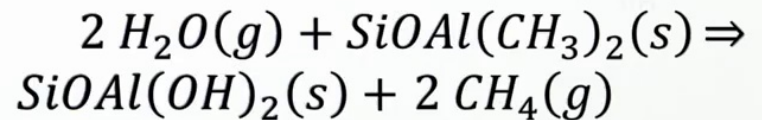
The reaction chamber is then purged with inert nitrogen gas, thereby removing all methane reaction products and any excess of the precursor TMA. Next the second precursor water vapor enters the system.

Four-step deposition process

Methane reaction product (CH_4)



- The second precursor (H_2O) reacts with the precursor 1 at the surface of the sample, the reaction produces a byproduct

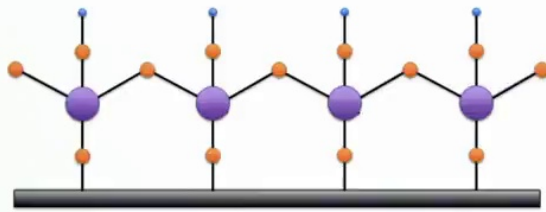


- The reaction chamber is purged with inert gas (N_2) and the excess of precursor two and the byproducts of the previous reaction are removed

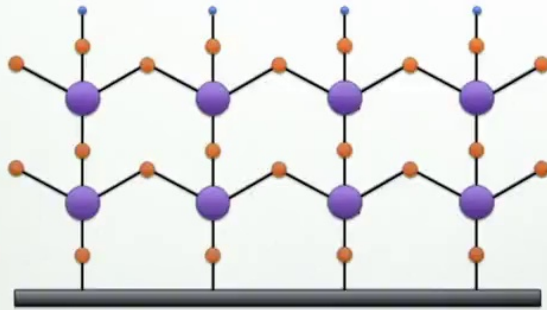
Micro and Nanofabrication (MEMS)

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.

Four-step deposition process



- Formation of a monolayer of Al_2O_3 with OH^- terminations
- The monolayer deposition process can be repeated over and over again



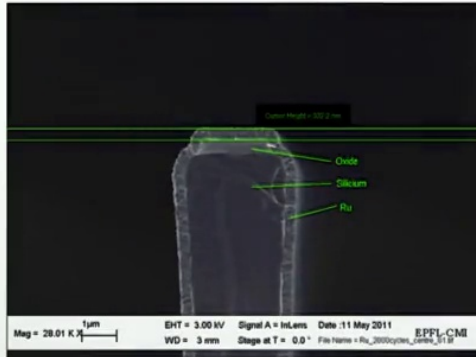
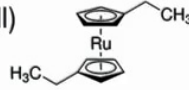
Micro and Nanofabrication (MEMS)

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.

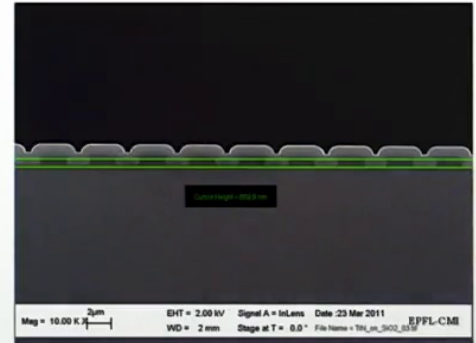
Example of other materials

	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 SiO₂ (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 nitride 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 nitride on silicon dioxide, also after 2000 cycles of ALD.

ALD equipment



- The equipment is composed of a chamber with a reactor inside
- A loadlock system
- 4 liquid sources slots
- 2 hot sources slots
- 7 gas lines (for processes with O_2 , N_2 and NH_3 and purge with N_2)
- An ozone generator
- A primary pump

Micro and Nanofabrication (MEMS)

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.

Summary



- Several illustrative examples of CVD processes
- Oxide formation by wet and dry thermal oxidation (transformation) of Si
- ALD of Al_2O_3 , Ru, and TiN

Micro and Nanofabrication (MEMS)

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 nitride.
