1 Deposition

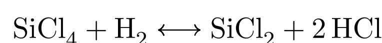
1.1 Chemical vapor deposition

1.1.1 Silicon vapor phase epitaxy

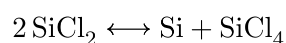
Epitaxy means "on top" or "assigned to", and represents a process in which a layer is created on top of another layer and inherits its crystal structure. If the deposited layer is of the same material as the substrate one speaks of homoepitaxy, if it's another material it's so-called heteroepitaxy. The most significant process in the homoepitaxy is the deposition of silicon on silicon, in heteroepitaxy usually a silicon layer is deposited on an insulator such as oxide (Silicon On Insulator: SOI).

Homoepitaxy:
Depending on the process, the wafers can be delivered from the wafer manufacturer with an epitaxial layer (e.g. for CMOS technology), or the chip manufacturer has to make it himself (for example in the bipolar technology).

As a gas for generating the epitactical layer, pure hydrogen is used in conjunction with silane (SiH_4), dichlorosilane (SiH_2Cl_2) or silicon tetrachloride ($SiCl_4$). At about 1000 °C, the gases cleave off the silicon, which is deposited on the wafer surface. The silicon inherits the structure of the substrate and is growing, for energy reasons, layer by layer successively on. To not grow up a polycrystalline silicon, one must always prevail a shortage of silicon atoms, e.g. it is always slightly less silicon available as material could actually grow up. When silicon tetrachloride is used, the reaction proceeds in two steps:



$$\mathrm{SiCl_4 + H_2 \longleftrightarrow SiCl_2 + 2\,HCl}$$



$$\mathrm{2\,SiCl_2 \longleftrightarrow Si + SiCl_4}$$

In order to inherit the substrate's orientation the surface must be absolutely clear. So one can utilize the equilibrium reaction. Both reactions can occur in the other direction, depending on the ratio of the gases. If there is only few hydrogen in the atmosphere, as in the trichlorosilane process for the purification of raw silicon, material is removed from the silicon wafer surface due to the high chlorine concentration. Only with increasing concentration of hydrogen growth is achieved.

With $SiCl_4$ the deposition rate is approximately 1 to 2 microns per minute. Since the monocrystalline silicon grows only on the bare surface, certain areas can be masked with oxide where the silicon grows as polycrystalline silicon. This polysilicon, however, is etched very easily compared to single-crystalline silicon through the backward-running reaction. Diborane (B_2H_6) or phosphine (PH_3) are added to the process gases, to create doped layers, since the doping gases decompose at high temperatures and the dopants are incorporated in the crystal lattice.

The process to create home-epitactical layers is realized under vacuum atmosphere. Therefor the process chamber is heated to 1200 °C to remove the native oxide, which is always present on the silicon surface. As mentioned above, due to a low hydrogen concentration there occurs a back etch on the silicon surface. This can be used to clean the surface before the actual process starts. If the gas concentration is varied post this cleaning the deposition begins.

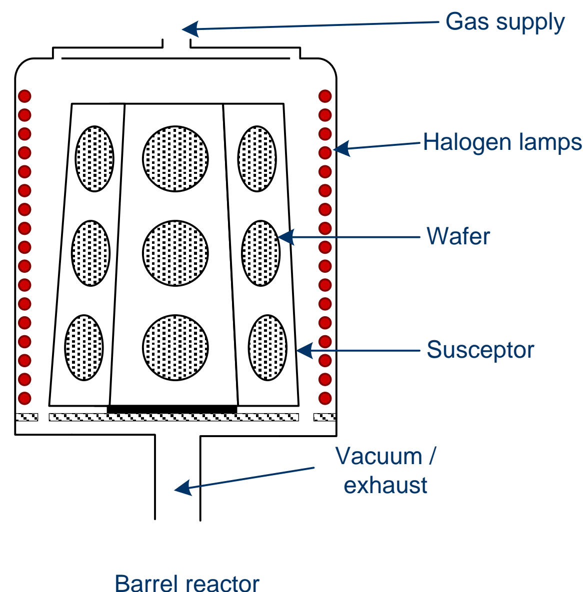


Fig. 1.1: Illustration of a barrel reactor for epitactical processes

Due to the high process temperatures there's a diffusion of dopants in the substrate or impurities, which have been used in earlier processes, can move to the substrate. If SiH_2Cl_2 or SiH_4 are used there's no need for such high temperatures, so these gases are used primarily. To achieve the etch back process to clean the surface, HCl has to be added separately. The disadvantage of this silanes is that they form germs in the atmosphere right before deposition, and thus the quality of the layer is not as good as with $SiCl_4$.

1.1.2 CVD process: Chemical Vapor Deposition

There is often a need of layers which can't be created right from the substrate. To deposit layers of silicon nitride or silicon oxynitride one has to use gases which contain all necessary components. The gases are decomposed via thermal energy. That's the principle of the chemical vapor phase deposition: CVD. The wafer surface doesn't react with the gases but serves as bottom layer. Depending on the process parameters - pressure, temperature - the CVD method can be devided in different methods whose layers differ in density and coverage. If the growth on horizontal surfaces is as high as on vertical surfaces the deposition is conform.

The conformity K is the ratio of vertical and horizontal growth, $K = R_v/R_h$. If the deposition is not ideal, the conformity is less than 1 (eg $R_v/R_h = 1/2 \Rightarrow K = 0.5$). A high conformity can only be achieved by high process temperatures.

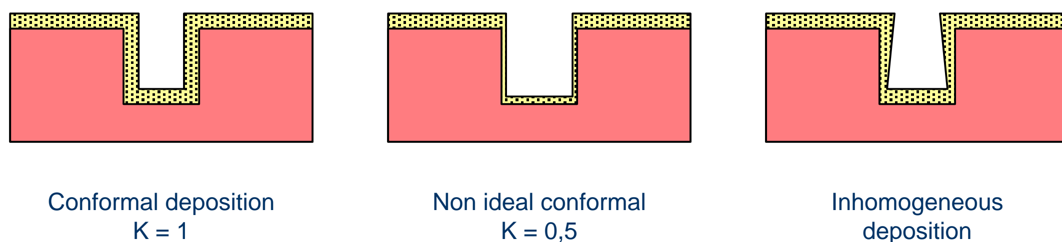


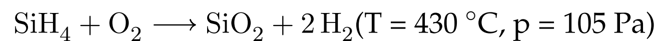
Fig. 1.2: Deposition profiles with different conformity

1.1.3 APCVD: Atmospheric Pressure CVD

APCVD is a CVD method at normal pressure (atmospheric pressure) which is used for deposition of doped and undoped oxides. The deposited oxide has a low density and

the coverage is moderate due to a relatively low temperature. Because of improved tools, the APCVD undergoes a renaissance. The high wafer throughput is a big advantage of this process.

As process gases silane SiH_4 (highly deluted with nitrogen N_2) and oxygen O_2 are used. The gases are decomposed thermal at about 400 °C and react with each other to form the desired film.



$$SiH_4 + O_2 \longrightarrow SiO_2 + 2\,H_2 (T = 430\ °C, p = 105\ Pa)$$

Added ozone O_3 can cause a better conformity because it improves the movability of the accumulated particles. The oxide is porous and electrical instable and can be densified by a high temperature process.

To avoid edges which can result in difficulties at the deposition of additional layers, phosphorus silicate glass (PSG) is used for interlayers. Therefor phosphine is added to SiH_4 and O_2, so that the deposited oxide contains 4 to 8 % phosphorus. A high amount of phosphorus leads to a high increase of the flow properties, however, phosphoric acid can be formed which corrodes aluminum (conductor paths).

Because annealing affects earlier processes (e.g. doping) only short tempering is done with powerful argon lamps (several hundrets kW, less than 10 s, T = 1100 °C) instead of annealing in longsome furnace processes. Analog to PSG boron can be added simultaneously (boron phosphorus silicate glass, BPSG, 4 % B and 4 % P).

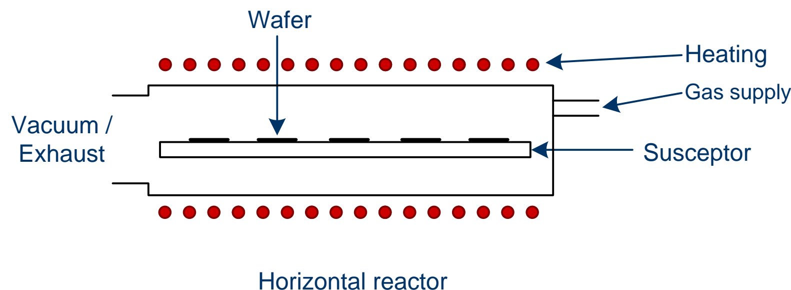


Fig. 1.3: Illustration of a horizontal APCVD reactor

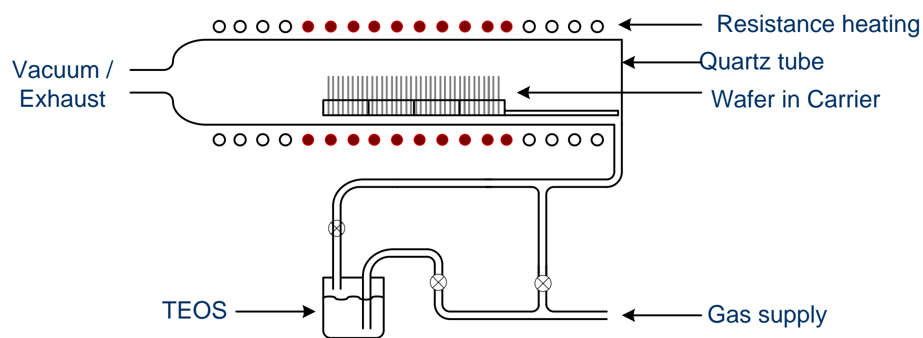


Fig. 1.4: Illustration of a LPCVD reactor for TEOS films

1.1.4 LPCVD: Low Pressure CVD

In LPCVD a vacuum is used. Thin films of silicon nitride (Si_3N_4), silicon oxynitride (SiON), SiO_2 und tungsten (W) can be created. LPCVD processes enable a high conformity of almost 1. This is because of the low pressure of 10 to 100 Pa (atmospheric pressure = 100.000 Pa) which leads to a non-uniform movement of the particles. The particles dispread due to collisions and cover vertical surfaces as well as horizontal ones. The conformity is supported by a high temperature of up to 900 °C. Compared to APCVD the density and stability is very high.

The reactions for Si_3N_4, SiON, SiO_2 and tungsten are as follows:

- **Si_3N_4 (850 °C):** $4\,NH_3 + 3\,SiH_2Cl_2 \longrightarrow Si_3N_4 + 6\,HCl + 6\,H_2$
- **SiON (900 °C):** $NH_3 + SiH_2Cl_2 + N_2O \longrightarrow Si_3N_4 + \text{byproducts}$
- **SiO_2 (700 °C):** $SiO_4C_8H_{20} \longrightarrow SiO_2 + \text{byproducts}$
- **Tungsten (400 °C):** $WF_6 + 3\,H \longrightarrow 2\,W + 6\,HF$

In contrast to gaseous precursors which are used for Si_3N_4, SiON and tungsten, liquid tetraethyl orthosilicate is used for SiO_2. Besides there are other liquid sources like DTBS ($SiH_2C_8H_{20}$) or tetramethylcyclotetrasiloxane (TMTCS, $Si_4O_4C_4H_{16}$).

A tungsten film can only be fabricated on bare silicon. Therefore silane has to be added if there is no silicon substrate.

1.1.5 PECVD: Plasma Enhanced CVD

The PECVD takes place at 250 to 350 °C. Due to low temperatures the process gases can not be decomposited thermal. With a high frequency voltage, the gas is transformed into a plasma state. The plasma is energetic and disposes on the surface. Because metallization, such as aluminum, can not be exposed to high temperatures, the PECVD is used for SiO_2 and Si_3N_4 deposition on top of metal layers. Instead of SiH_2Cl_2 silane is used because it decomposes at lower temperature. The conformity is not as good as in LPCVD (0.6 to 0.8), however, the deposition rate is much higher (0.5 microns per minute).

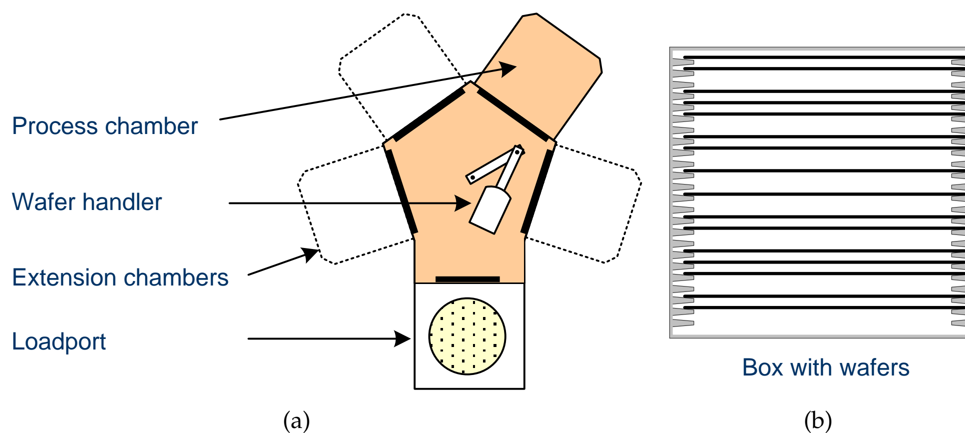


Fig. 1.5: Illustration of a PECVD reactor.

1.1.6 ALD: Atomic Layer Deposition

Atomic Layer Deposition (ALD) is a modified CVD process to manufacture thin films. The process uses several gases which are led into the process chamber alternating. Each gas reacts in such a way that the current surface is saturated, and therefore the reaction comes to a standstill. The alternative gas is able to react with this surface in the same way. Between the reactions of these gases the chamber is purged with an inert gas, like nitrogen or argon. A simple ALD process could look like this:

1. self-limiting reaction at the surface with first gas
2. purging with an inert gas
3. self-limiting reaction at the surface with second gas

4. purging with an inert gas

A specific example for an ALD process is the deposition of aluminum oxide, this can be realized with trimethylaluminum (TMA, C_3H_9Al) and water (H_2O).

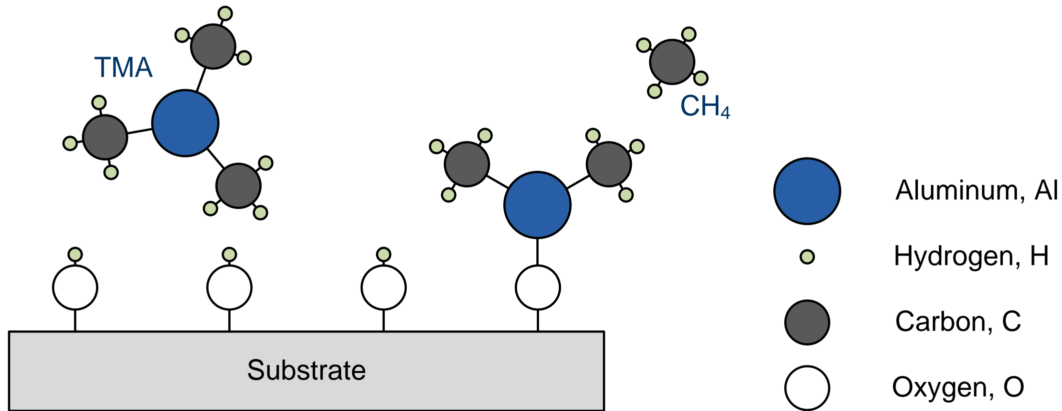


Fig. 1.6: Introduction of TMA into the process chamber

First step is the elimination of hydrogen atoms which are bound to oxygen at the wafer surface. The methyl groups (CH_3) of TMA can react with the hydrogen to form methane (CH_4). The remaining molecules bond with the unsaturated oxygen.

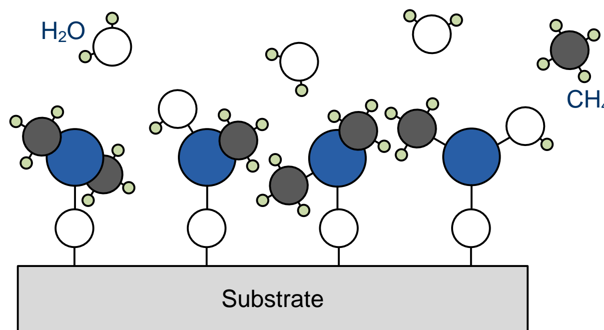


Fig. 1.7: Adhesion of TMA at the surface atoms

If these atoms are saturated, no more TMA molecules can react at the surface.

The chamber is purged and subsequent water steam is led into the chamber. Ever one hydrogen atom of the H_2O molecules now can react with the former deposited surface atoms to form methane, while the hydroxyl anion is bond to the aluminum atoms.

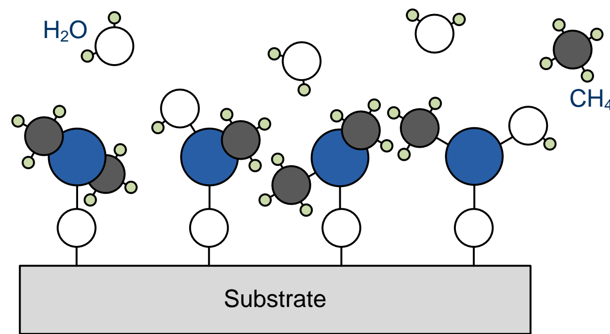


Fig. 1.8: Introduction of water into the process chamber

Hence, there are new hydrogen atoms at the surface which can react in a afterwards step with TMA like in the beginning.

The atomic layer deposition provides significant advantages over other deposition techniques, and therefore it's a very important process to manufacture thin films. With ALD even 3-dimensional structures can be deposited very uniform. Insulating films are possible as well as conductive ones, which can be created on differet substrates (semiconductors, polymers, ...). The film thickness can be controlled very precise by the number of cycles. Since the reactive gases are not led into the chamber simultaneously, they can not form germs right before the actual deposition. Thus the quality of the films is very high.

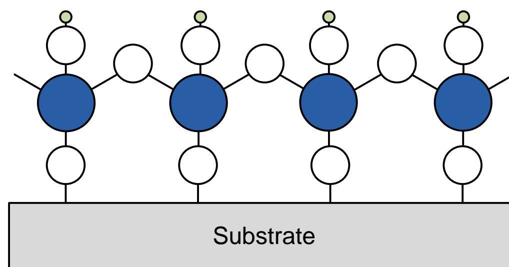


Fig. 1.9: Saturated surface at the end of one cycle