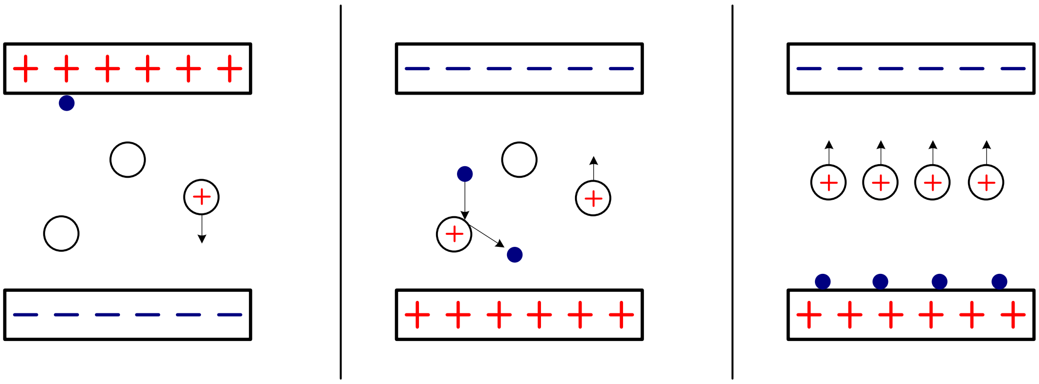
Semiconductor Technology

from A to Z



Deposition

www.halbleiter.org

Contents

List of Figures II

1 Deposition 1

1.1 Plasma, the fourth aggregation state of a material 1
    1.1.1 Plasma state 1
    1.1.2 Plasma generation 2
1.2 Chemical vapor deposition 3
    1.2.1 Silicon vapor phase epitaxy 3
    1.2.2 CVD process: Chemical Vapor Deposition 5
    1.2.3 APCVD: Atmospheric Pressure CVD 6
    1.2.4 LPCVD: Low Pressure CVD 7
    1.2.5 PECVD: Plasma Enhanced CVD 8
    1.2.6 ALD: Atomic Layer Deposition 9
1.3 Physical deposition methods 11
    1.3.1 Molecular beam epitaxy 11
    1.3.2 Evaporating 11
    1.3.3 Sputtering 12

List of Figures

1.1 Illustration of plasma generation 3
1.2 Illustration of a barrel reactor for epitactical processes 5
1.3 Deposition profiles with different conformity 6
1.4 Illustration of a horizontal APCVD reactor 7
1.5 Illustration of a LPCVD reactor for TEOS films 8
1.6 Illustration of a PECVD reactor. 8
1.7 Introduction of TMA into the process chamber 9
1.8 Adhesion of TMA at the surface atoms 10
1.9 Introduction of water into the process chamber 10
1.10 Saturated surface at the end of one cycle 11
1.11 Illustration of a MBE chamber 12
1.12 Illustration of an evaporating chamber 12
1.13 Illustration of the sputter process 13
1.14 Illustration of a sputter chamber 14

1 Deposition

1.1 Plasma, the fourth aggregation state of a material

1.1.1 Plasma state

In many semiconductor manufacturing processes, a plasma is used, e.g. in sputtering, deposition or in dry etch prcesses. An important point here is that the plasma is not heated. Therefore wafers, which were already metallized, can be processed in plasma processes.

Plasma is also called the fourth state of matter or fourth aggregate state. An aggregate state is a qualitative condition of materials, which depends on the temperature and pressure. The three states solid, liquid and gaseous one encounters in everyday's life. If temperature is low, every atom in a solid is fixed at one point. Attractive forces prevent them from moving. At absolute zero (-273.15 °C) substances enter into no reaction. With increasing temperature, the particles start to oscillate, and the bonds of the atoms are unstable. If the melting point is reached, a substance transforms from the first to the second aggregate state: ice (solid) is transformed into water (liquid).

The gravitational forces in liquids are still present, but the particles are able to move and have no fixed places like in solid state, the particles are adapted for example to a predetermined shape. If the temperature increases further, the bonds are completely broken, the particles move independently of one another. At the boiling point of a substance it transforms from second to third state: water (liquid) turns into water vapor (gaseous).

While the volume of solids and liquids is constant, gaseous substances take the existing space completely, the particles are distributed evenly throughout the room.

Each substance has a specific melting and boiling point. Silicon melts at 1414 °C and passes into gaseous state at about 2900 °C. If one introduces even more energy to a substance, the collisions between the particles will strike out electrons from the outermost electron shells. Now there are free electrons and positively charged ions: the plasma state is reached.

1.1.2 Plasma generation

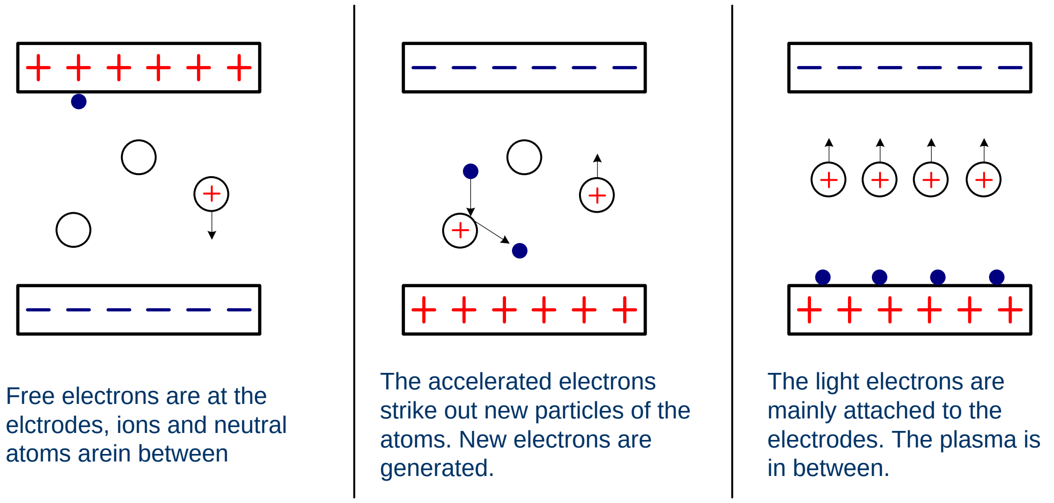
A plasma in semiconductor technology is usually generated by high frequency voltage, for example, argon serves as a gas. The gas is located in a high-frequency field between two charged plates (electrodes) and here it is ionized. Electrons are necessary to strike out electrons from the argon atom's outer shells. These initial electrons can be generated in different ways:

- Electrons are emitted from a thermionic cathode
- By a very high voltage electrons can be pulled out from the negative electrode
- In each gas there always are temporarily free electrons by collisions of the particles

Since the electrons are much lighter than the ions, they are immediately attracted to the positively charged electrode, and the heavy ions moving slowly to the negative electrode. Before they will achieve it, however, the polarity of the electrodes is reversed, the electrons are drawn to the other electrode and on their trajectory they will strike out more electrons from the atoms due to collisions. Typical frequencies for the plasma generation process is 13.56 megahertz and 2.45 gigahertz, so the voltage across the electrodes will be reversed 13.56 million or 2.45 billion times per second.

The electrons are located mainly on the electrodes, while in between the positively charged ions, the plasma, oscillate back and forth, because they can not follow the rapid voltage changes.

The plasma production takes place under vacuum, the produced plasma is not heated, which is important for many processes. The plasma can be used in deposition, sputtering, etching or ion implantation. Due to the rapid oscillations of the positive ions in the high-frequency field they are very energetic. There are not only positive ions and free electrons in the plasma, as other particles are created by collisions: the condition of the plasma changes constantly. Electrons are captured by the ions partially and ejected again, these additional particles, however, do not play a matter in the further use of the plasma. The degree of ionization is 0.001-10 %, depending on the particle density



Free electrons are at the elctrodes, ions and neutral atoms arein between

The accelerated electrons strike out new particles of the atoms. New electrons are generated.

The light electrons are mainly attached to the electrodes. The plasma is in between.

Fig. 1.1: Illustration of plasma generation

in the process chamber ($10^8 - 10^{12}$ particles per cm^3); so the majority of the particles is unloaded.

1.2 Chemical vapor deposition

1.2.1 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:

$$\begin{gathered} \mathrm{SiCl_4} + \mathrm{H_2} \longleftrightarrow \mathrm{SiCl_2} + 2\,\mathrm{HCl} \\ 2\,\mathrm{SiCl_2} \longleftrightarrow \mathrm{Si} + \mathrm{SiCl_4} \end{gathered}$$

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.

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

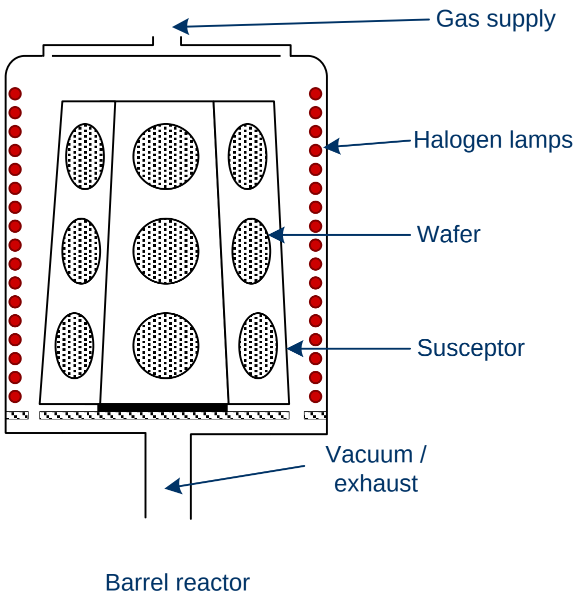


Fig. 1.2: Illustration of a barrel reactor for epitactical processes

atmosphere right before deposition, and thus the quality of the layer is not as good as with $SiCl_4$.

1.2.2 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.

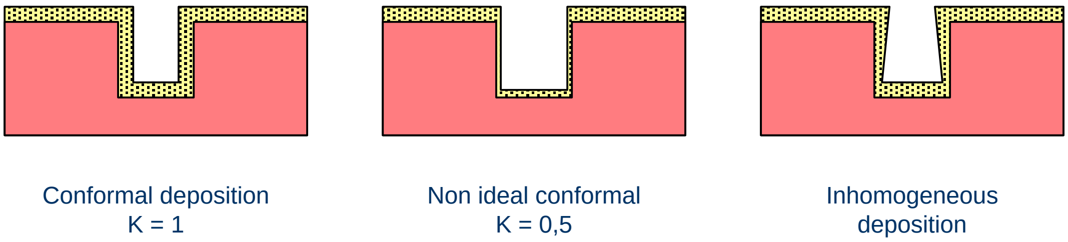


Fig. 1.3: Deposition profiles with different conformity

1.2.3 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.

$$\mathrm{SiH_4 + O_2 \longrightarrow SiO_2 + 2\,H_2 (T = 430\ ^\circ C,\ p = 105\ Pa)}$$

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).

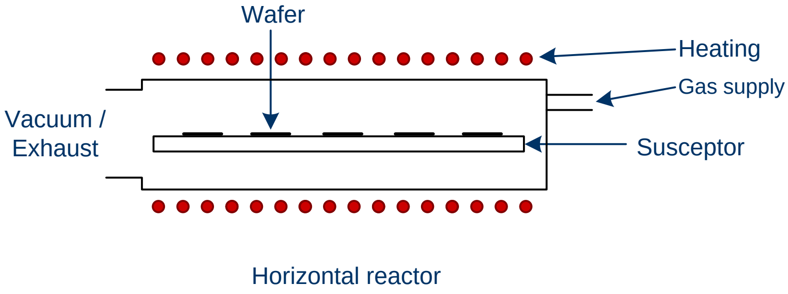


Fig. 1.4: Illustration of a horizontal APCVD reactor

1.2.4 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.

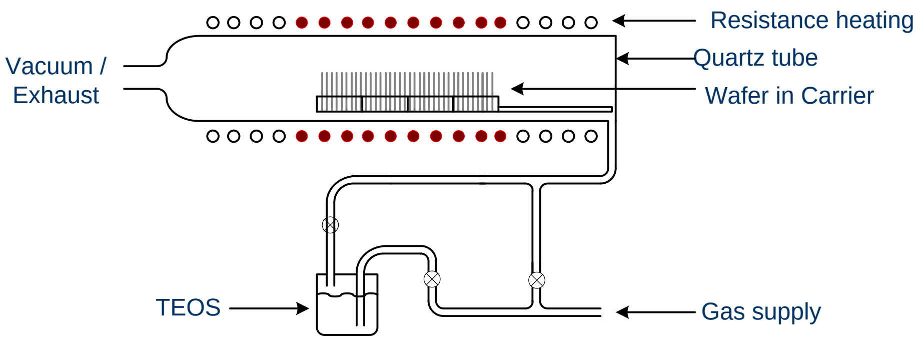
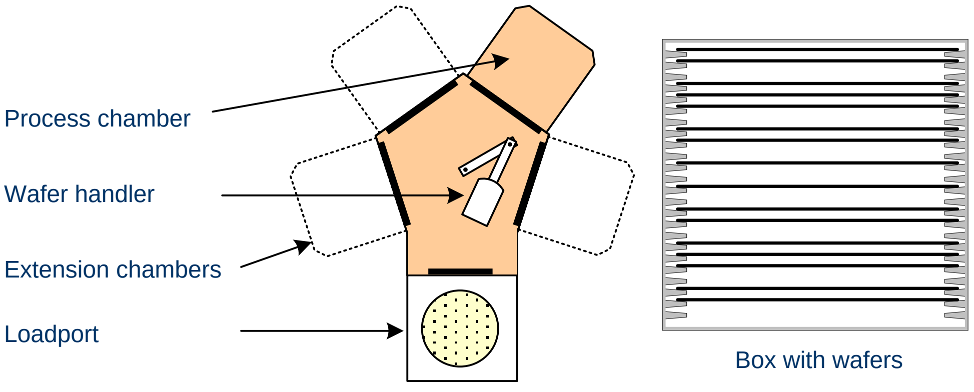

Resistance heating
Quartz tube
Wafer in Carrier
Vacuum / Exhaust
TEOS
Gas supply

Fig. 1.5: Illustration of a LPCVD reactor for TEOS films

1.2.5 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).


Process chamber
Wafer handler
Extension chambers
Loadport
Box with wafers

(a) (b)

Fig. 1.6: Illustration of a PECVD reactor.

1.2.6 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).

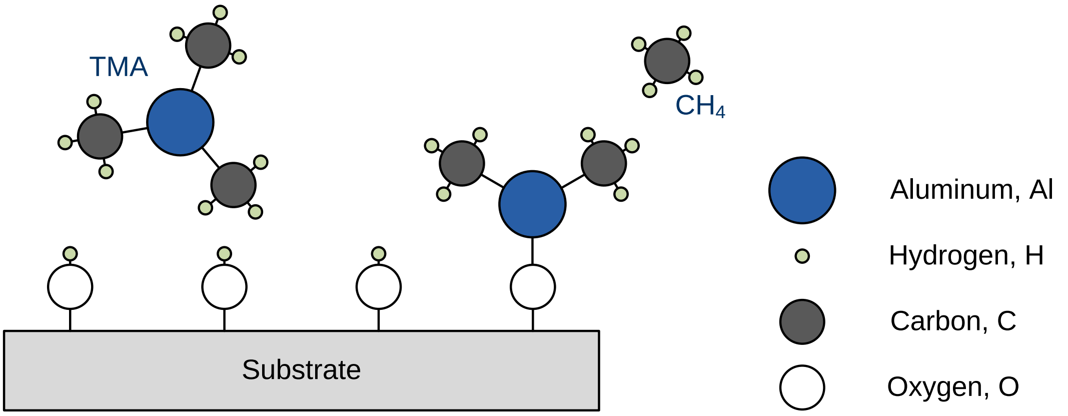


Fig. 1.7: Introduction of TMA into the process chamber

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.

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

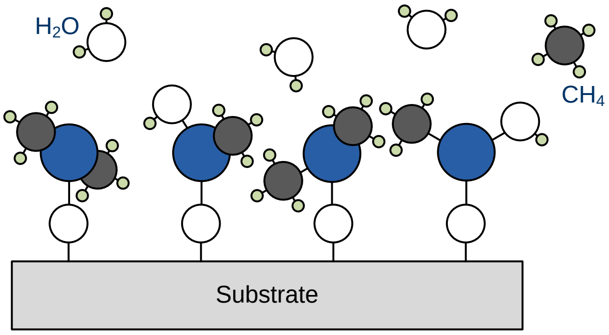


Fig. 1.8: Adhesion of TMA at the surface atoms

atoms to form methane, while the hydroxyl anion is bond to the aluminum atoms.

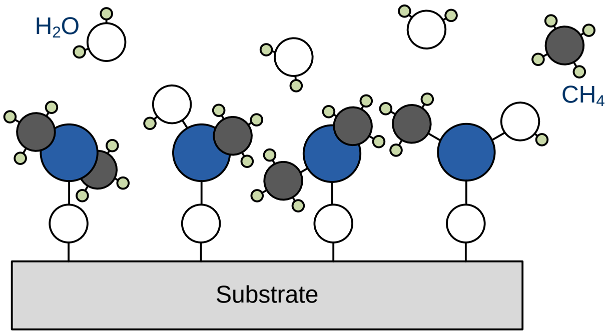


Fig. 1.9: Introduction of water into the process chamber

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.

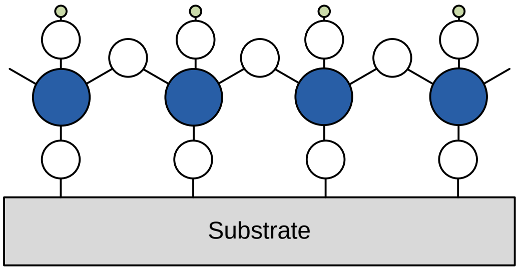


Fig. 1.10: Saturated surface at the end of one cycle

1.3 Physical deposition methods

1.3.1 Molecular beam epitaxy

The deposition characteristics are similar to the silicon vapor phase epitaxy (see CVD), but the deposition technique differs.

The process takes place under ultra-high vacuum (UHV, 10^{-8} Pa), the wafer is held upside down at the top of the chamber, the native oxide is removed at 600 to 800 °C.

With an electron beam highly purified silicon is evaporated and deposes on the wafer. Dopants can be evaporated as well and reach the surface together with the silicon. By selective temperature control and with covers the particle beam can be controlled precisely. This process allows layers of different materials whose dimensions are different and thus can't be deposited with other methods. E.g. a layer of silicon and germanium can be created which is necessary for high frequency devices or in bipolar techniques.

However, the effort to create the ultra-high vacuum is very high. To achieve this pressure, which is less than 10^{-12} of atmospheric pressure, one needs several vacuum pumps and a long time to pump down. Only one wafer can be processed simultaneously, the growth is only about 1 micron per hour.

1.3.2 Evaporating

Also metallic layers, such as aluminum, can be deposed on the wafer. The material is placed in a crucible, made of a hardly meltable metal like tantalum, and heated till evaporation. The vapor reaches the wafer in perpendicular orientation, therefore edges are not covered well, the film is polycrystalline. Alternatively the metal can be evaporated using an electron beam instead of a crucible. Compared with the thermal

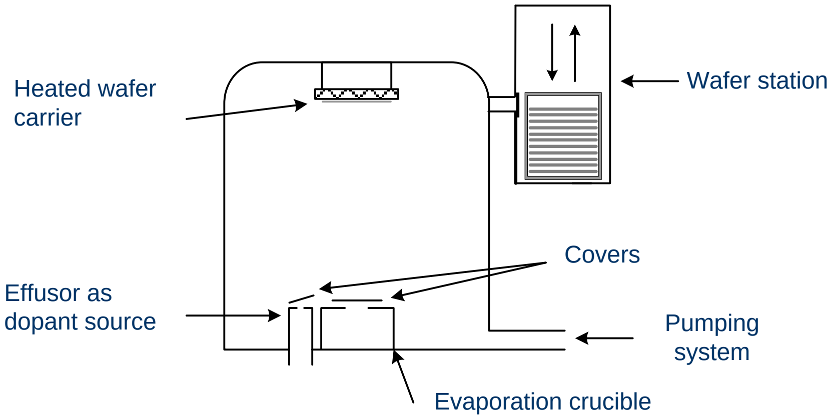

Heated wafer carrier
Wafer station
Covers
Effusor as dopant source
Pumping system
Evaporation crucible

Fig. 1.11: Illustration of a MBE chamber

process, the electron beam allows a precise growth. Because of the bad edge coverage both methods are mostly used for backside deposition for final contacting.

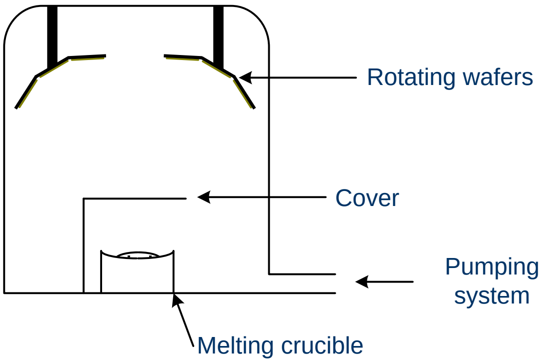

Rotating wafers
Cover
Pumping system
Melting crucible

Fig. 1.12: Illustration of an evaporating chamber

1.3.3 Sputtering

In sputtering ions are accelerated onto a target to strike out atoms or molecules. The target consists of the material which shall be deposited. The mean free path is a few millimeters which means that the particles often collide with each other and therefore also vertical surfaces are covered well. Primarily the noble gas argon is ionized by gas discharge. The disposed particles form a porous film which can be densified by annealing. Sputtering can be devided into passive (inert) and reactive sputtering.

By passive sputtering only the material of the target is disposed on the wafers, accord-

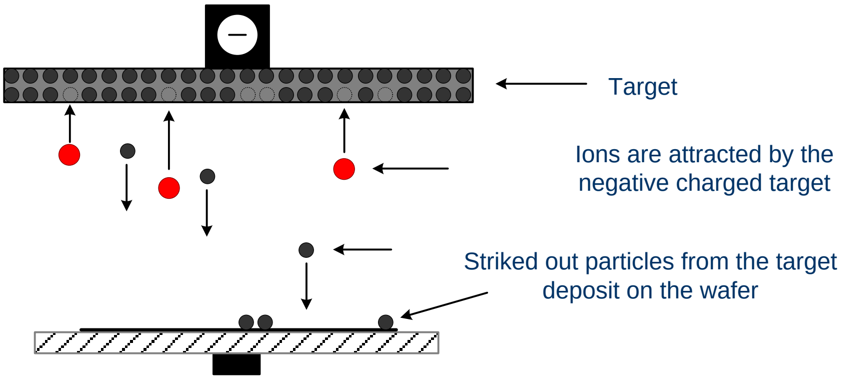

Target
Ions are attracted by the negative charged target
Striked out particles from the target deposit on the wafer

Fig. 1.13: Illustration of the sputter process

ing to the material of the target high-purity films can be created as the mix ratio of the substances in the target can be chosen precisely. In the reactive sputtering an additional reactive gas (e.g. oxygen O2) is added, which reacts with the particles of the target and deposits on the wafer. If one uses a metallic target (e.g. aluminum Al), non-metallic layers like the insulator aluminium oxide are possible:

$$4\,\mathrm{Al} + 3\,\mathrm{O_2} \longrightarrow 2\,\mathrm{Al_2O_3}$$

To create metallic layers, the DC sputtering is used. Thereby the ions are accelerated with up to 3 kV onto the target where they are discharged. To dissipate the charges, only a conductive target can be used. For non-metallic layers the reactive sputtering has to be used. If one wants to create an insulating layer right out of the target the RF sputtering is used.

In RF sputtering a voltage is applied to both electrodes behind both the target (cathode) and the wafer (anode). During the positive half-wave on the target, the electrons were attracted to it, thus the target gets negatively charged. The negatively charged target attracts ions which strike out particles from it. To increase the deposition rate one can attach magnets behind the target to deflect the electrons into a circular path. Thus more ions will be ionized and strike out additional particles from the target. Because the anode is connected to the process chamber its potential difference compared to the plasma is much less than the potential difference of the cathode to the plasma. Thats why the ions are accelerated to the target only and not onto the wafer.

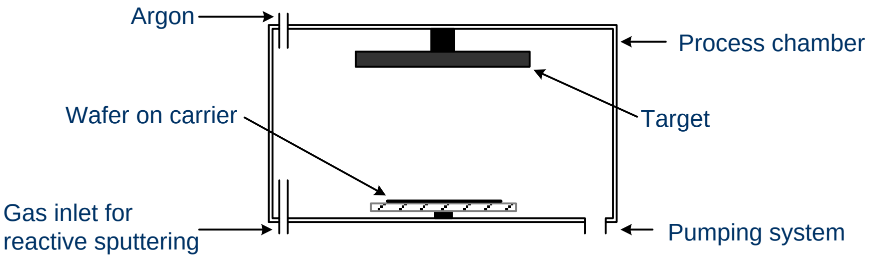

Argon
Process chamber
Wafer on carrier
Target
Gas inlet for
reactive sputtering
Pumping system

Fig. 1.14: Illustration of a sputter chamber

To increase edge coverage the BIAS sputtering is used. A negative voltage is applied to the substrate, so that here particles are striked out at well, which planishes the surface. However, one has to take care that there is no abrasion of the substrate. This so called back-etch process is the principle of most dry etch processes.

Sputtering is suitable to create metallic films with high conformity and very good reproducibility. The effort is little, the low pressure (5 Pa) can be achieved easily.