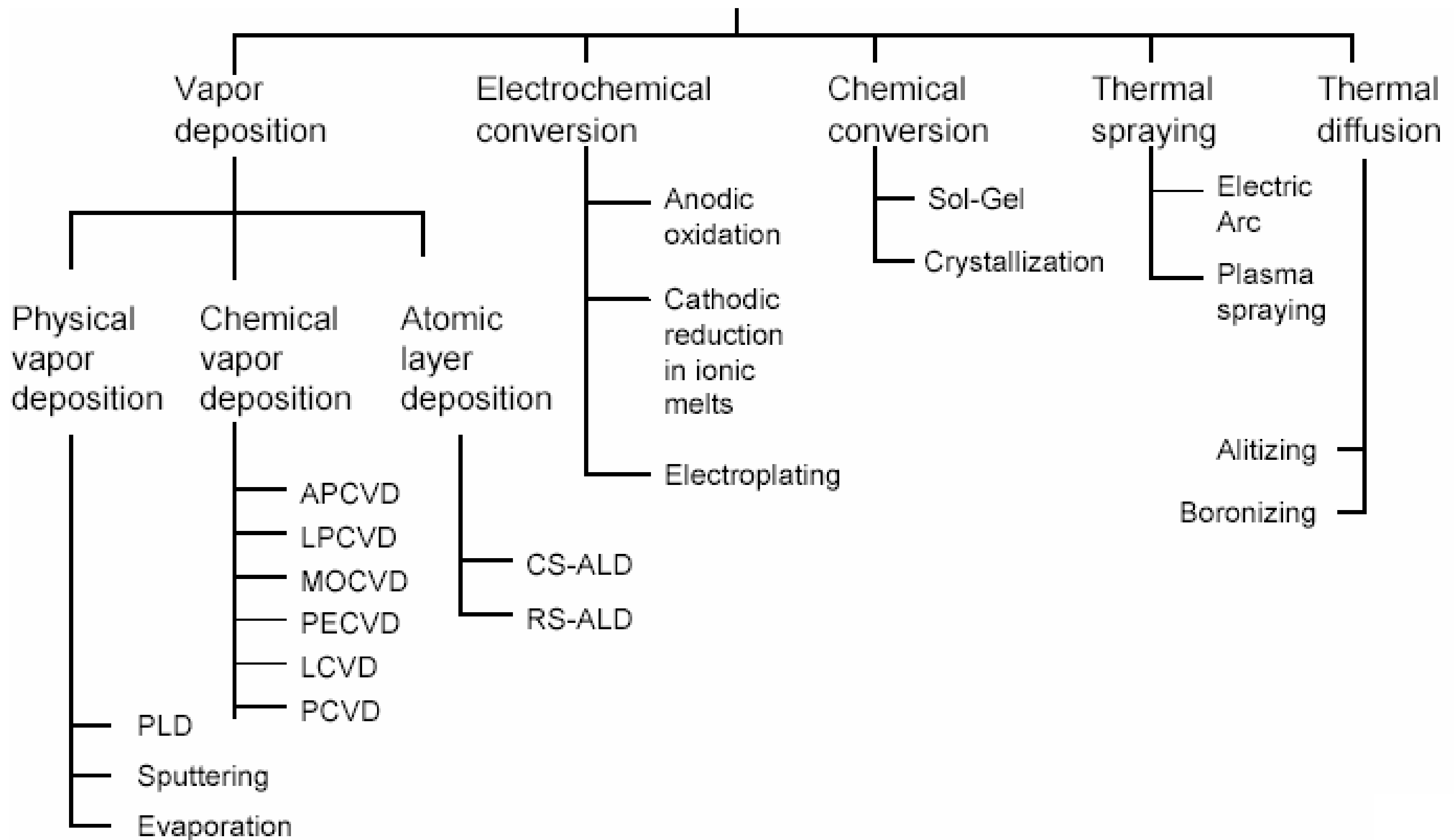
# Preparation of Model Systems by Physical Methods

Ordered thin oxide films grown on metal substrates and exhibiting a LEED pattern (MBE growth techniques not included, $D$: thickness)

| System | Preparation | $D$ (Å) | Possible problems | Refs. |
|---|---|---|---|---|
| *MgO* | | | | |
| MgO(100)/Mo(100) | $Mg + O_2$ at 200–600 K | | [a] | [24,25,195,196] |
| MgO(100)/Mo(100) | $Mg + O_2$ at 300 K | 25 | film grows in domains[a] | [26] |
| MgO(100)/Ag(100) | $Mg + O_2$ | | mosaic structure | [27] |
| MgO(111)/Mo(110) | $Mg + O_2$ at 300 K, ↑ 800 K | ~50 | | [28] |
| *$Al_2O_3$* | | | | |
| $Al_2O_3$/NiAl(110) | $O_2$ at 550 K, ↑ 1100 K | 5 | | [16,17] |
| $Al_2O_3$/NiAl(100) | $O_2$ at 300 K, ↑ 1200 K | ~10 | amorphous $Al_2O_3$ areas | [18,29,194] |
| $Al_2O_3$/NiAl(111) | $O_2$ at 300 K, ↑ 900–1100 K | ~15 | | [19] |
| $Al_2O_3$/$Ni_3Al$ | $O_2$ at 900 K | ~5 | | [20,21] |
| $Al_2O_3$/FeAl | $O_2$ at elevated T | 5–8 | some lateral disorder | [22] |
| $Al_2O_3$/Re(0001) | $Al + O_2$ at 970–1170 K | > 16 | | [30] |
| $Al_2O_3$/Re(0001) | Al, $O_2$ at 970 K | 5–20 | thick films: some disorder | [31] |
| $Al_2O_3$/Ta(110) | $Al + O_2$ at 900 K | 5–40 | | [32] |
| $Al_2O_3$/Mo(110) | $Al + O_2$, ↑ 1200 K in $O_2$ | 4–20 | some degree of disorder | [33] |
| $Al_2O_3$/Ru(0001) | $Al + O_2$ at 1170 K | 25 | some degree of disorder | [30] |
| *NiO* | | | | |
| NiO(100)/Ni(100) | $O_2$ at elevated T, annealing | ~50 | high degree of disorder | [13] |
| NiO(111)/Ni(111) | $O_2$ at elevated T, annealing | ~50 | | [34,197] |
| NiO(111)/Au(111) | $Ni + O_2$ at 573 K | ~5 | | [35] |
| NiO(100)/Mo(100) | $Ni + O_2$, annealing in $O_2$ | | | [36] |
| *$Fe_xO_y$* | | | | |
| FeO/Pt(111) | Fe, $O_2$ at 900 K | ~5 | | [37,38,198] |
| $Fe_2O_3$/Pt(111) | $Fe_3O_4$, $O_2$ (1 Torr) at 1100 K | ~100 | | [37,39,199] |
| $Fe_3O_4$/Pt(111) | Fe, $O_2$ at 900 K | ~100 | | [37,40,200] |
| *CoO* | | | | |
| CoO(100)/Co(100) | $O_2$, annealing | ~20 | some degree of disorder | [41] |
| *$TiO_2$* | | | | |
| $TiO_2$/Pt(111) | Ti, $O_2$ at 573 K, annealing | | holes | [42] |
| *$ZrO_2$* | | | | |
| $ZrO_2$/Pt(111) | $Zr + O_2$, annealing in $O_2$ | | high degree of disorder | [43] |
| *$Cr_2O_3$* | | | | |
| $Cr_2O_3$/Cr(110) | $O_2$ at elevated T, annealing | ~50 | | [14,193,256] |

[a] The MgO films may contain a higher defect density as compared to MgO single crystals. This suspicion has been put forward by CO TDS experiments on vacuum cleaved MgO crystals. These show no CO adsorption above 90 K. The films, however, give rise to a desorption peak at about 120 K [44].

# Methods for catalyst preparation



# Methods discussed in this lecture

## Physical vapour deposition

- PLD (pulsed laser deposition)
- Sputtering
- Evapouration
- MBE (molecular beam epitaxy)

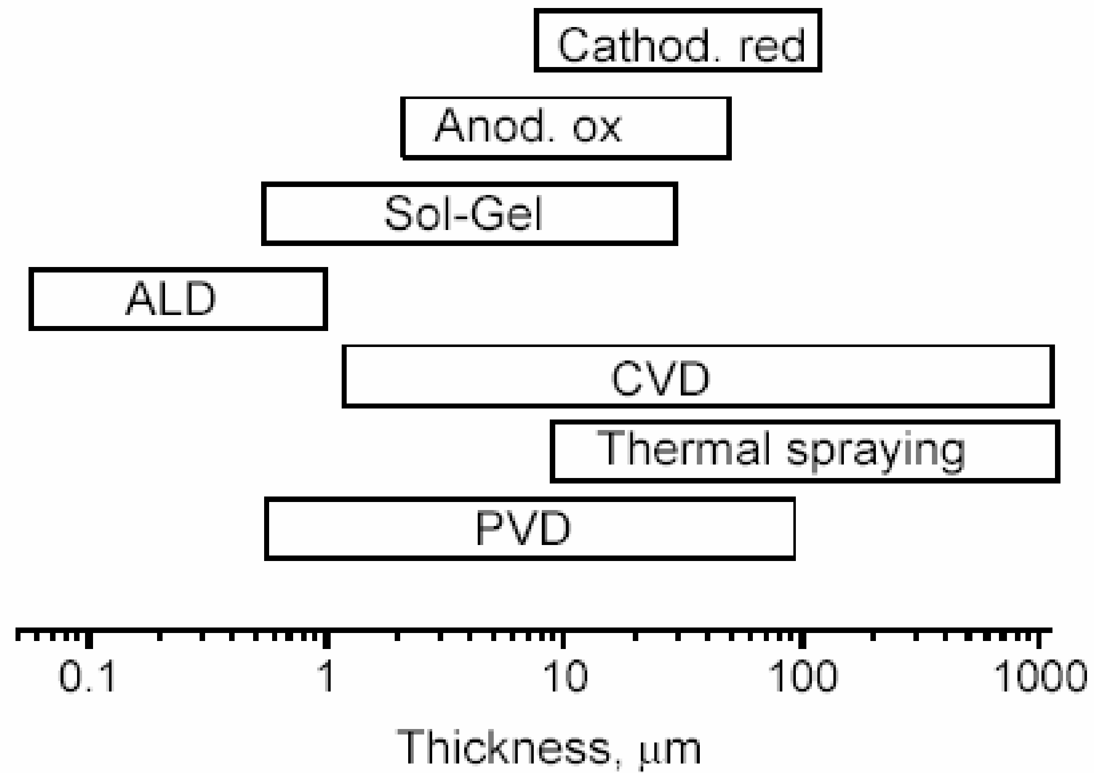
## Chemical vapour deposition

- APCVD (atmospheric pressure CVD)
- LPCVD (low pressure CVD)
- MOCVD (metal organic CVD)
- PECVD (plasma assited CVD)
- LCVD (laser (assisted) CVD)
- PCVD (Photo CVD)

## Atomic layer deposition

- CS-ALD (chemisorption saturation process ALD)
- RS-ALD (sequential surface chemical reaction process ALD)

# Coating thickness



# Epitaxy

Epitaxy: regular growth of a crystalline layer on a crystal surface of the same material (homoepitaxy) or on a different material (heteroepitaxy)

Epitaxy occurs when the free enthalpy of the system is smaller for growing a crystalline layer compared to a amorphous layer. The interface energy must have a minimum as a function of relative orientation.

The morphplogy of the growing solid is determined by the surface energy.

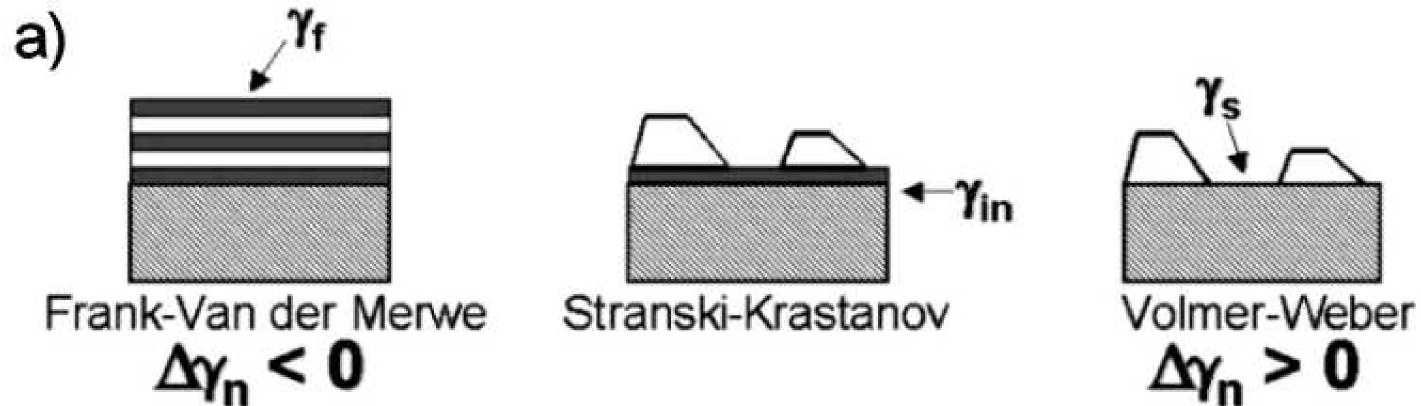
$$\Delta g = g_{f,n} + g_{in} - g_{s}$$

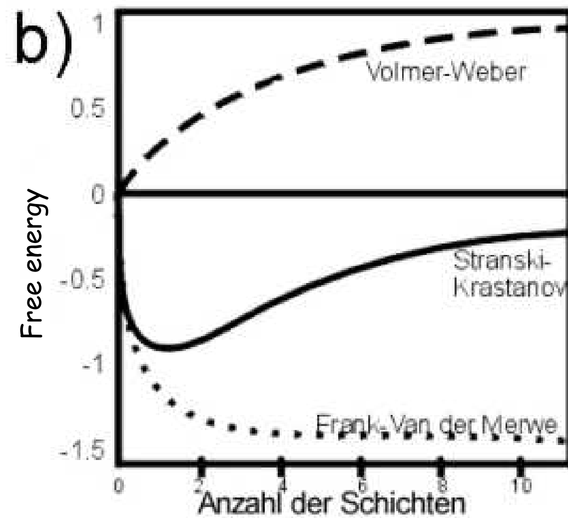
$g_{s}$ : *surface energy of the substrate*

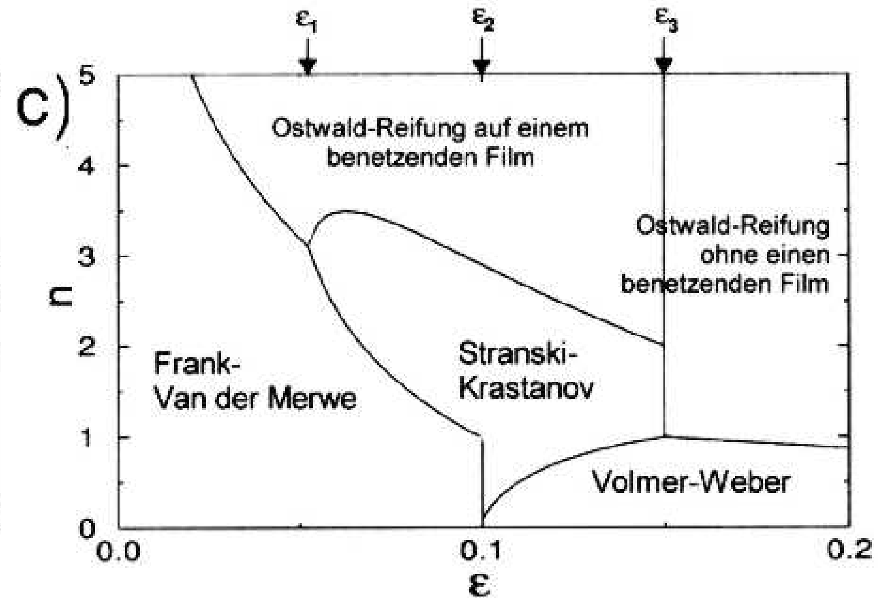
$g_{f,n}$ : *surface energy of the growing solid*

$g_{in}$ : *energy of the interface*

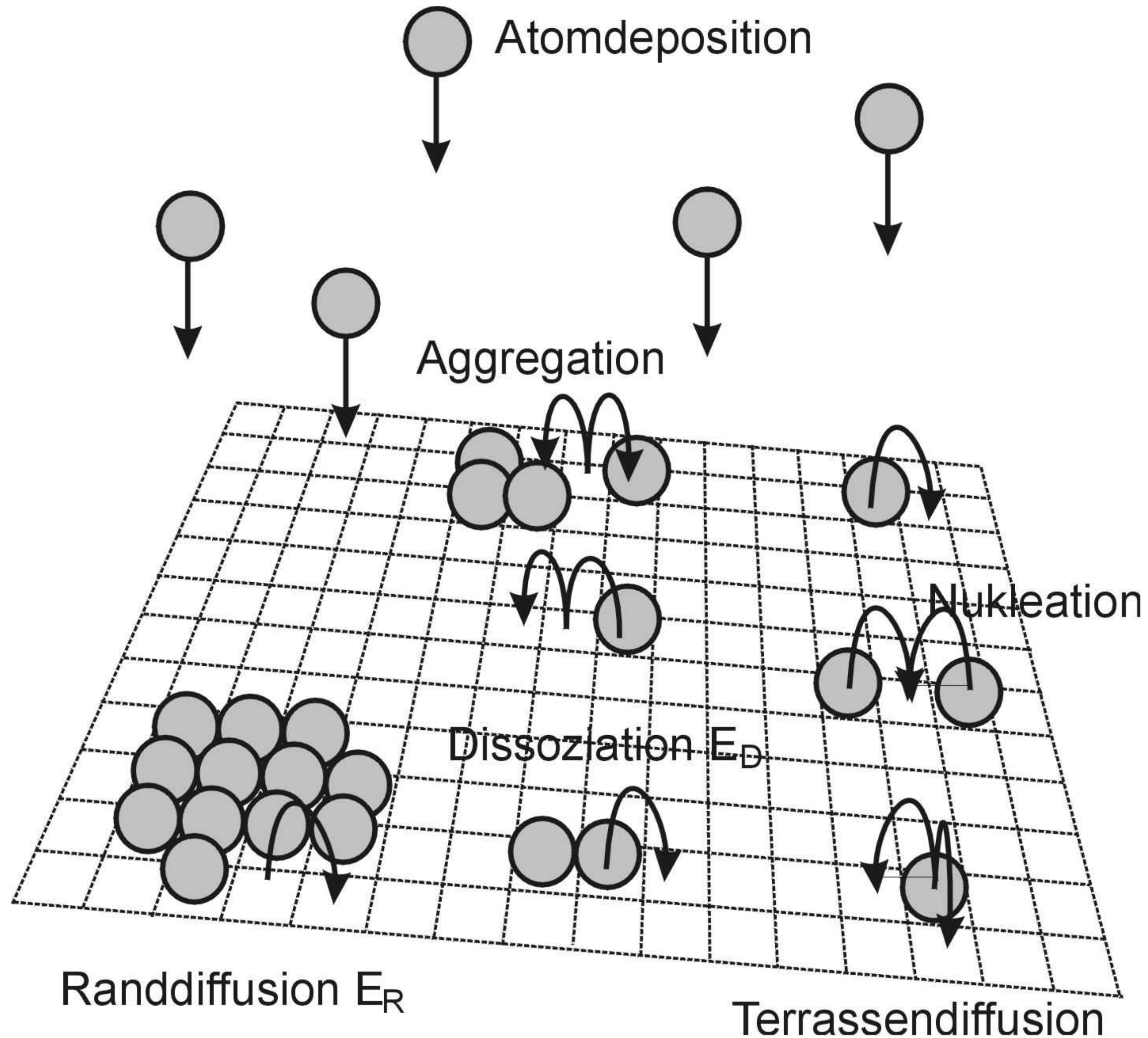
# Crystal growth in the thermodynamic equilibrium



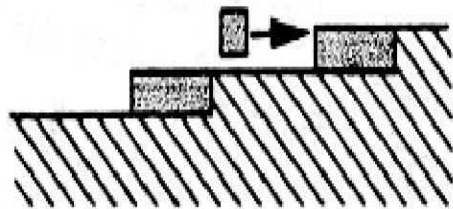



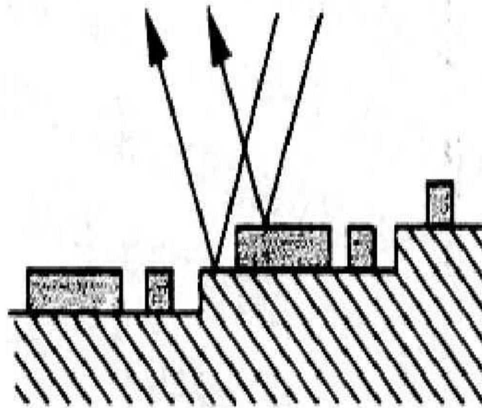



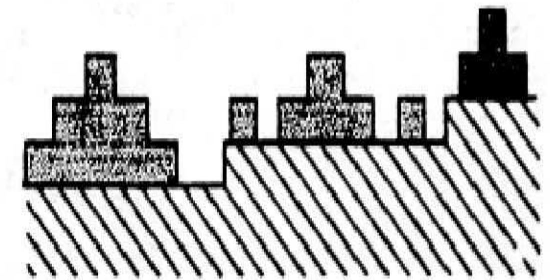
# Atomic processes during the crystal growth



# Growth under non equilibrium conditions



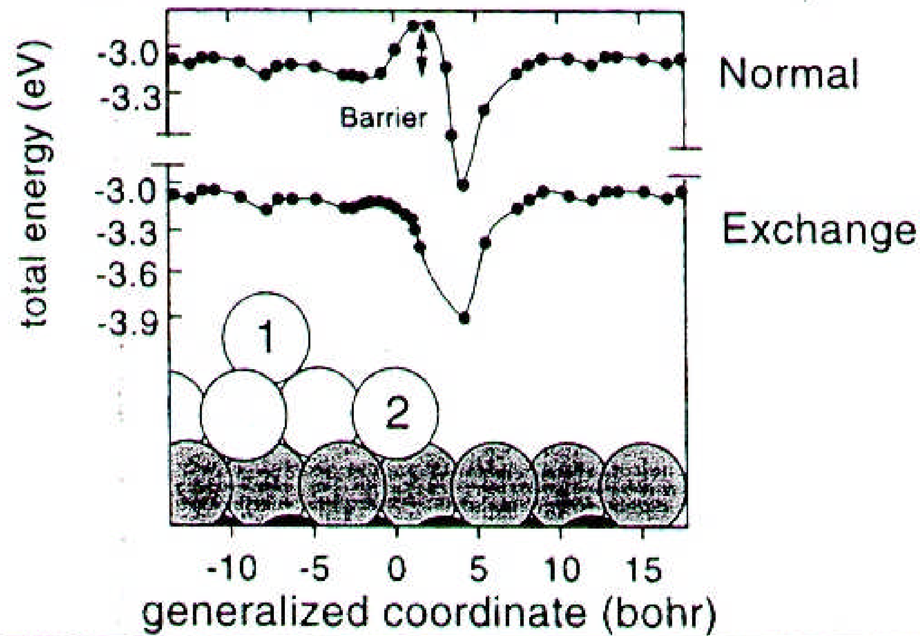




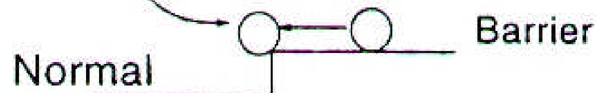
hohe Temperatur
niedrige Depositionsrate
hohe Stufendichte

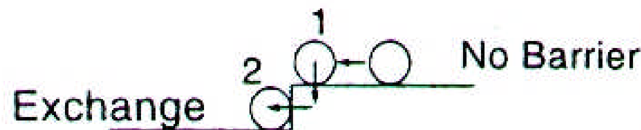
niedrige Temperatur
hohe Depositionsrate
niedrige Stufendichte

# Diffusion barrier at edges (Ehrlich-Schwoebel Barrier)

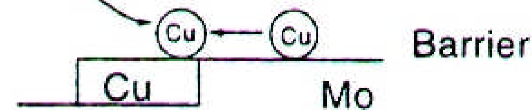



Less Bonding (Coordination)




Less Bonding (Cu-Cu versus Cu-Mo)

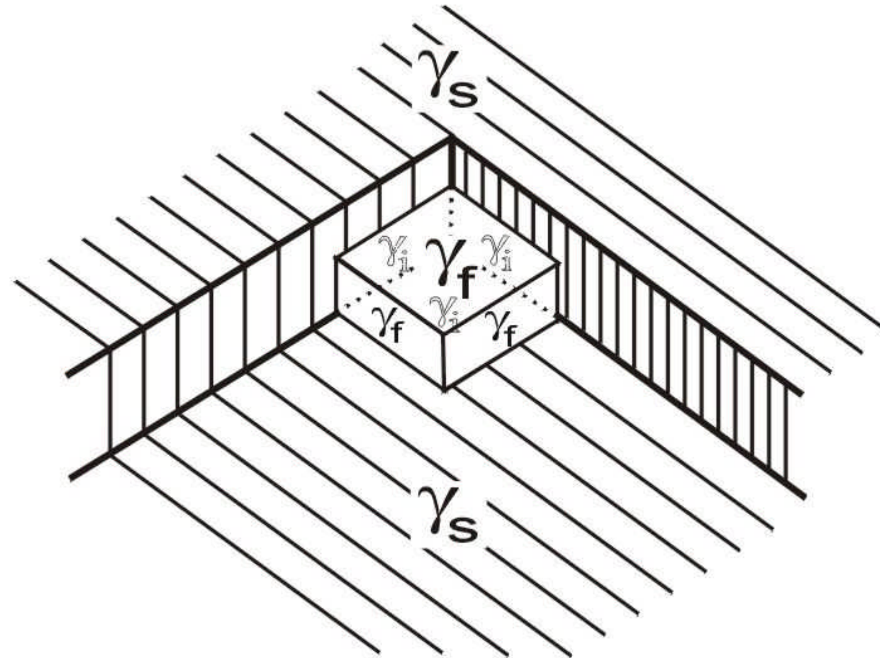



Self-Diffusion

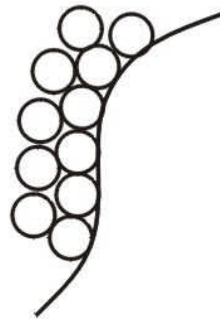
Adsorbate Diffusion

# Seed crystal formation in corner

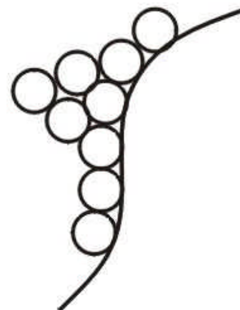
a)



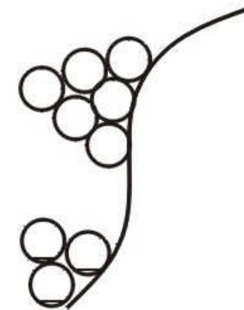

b)



Reihe-für-Reihe Wachstum

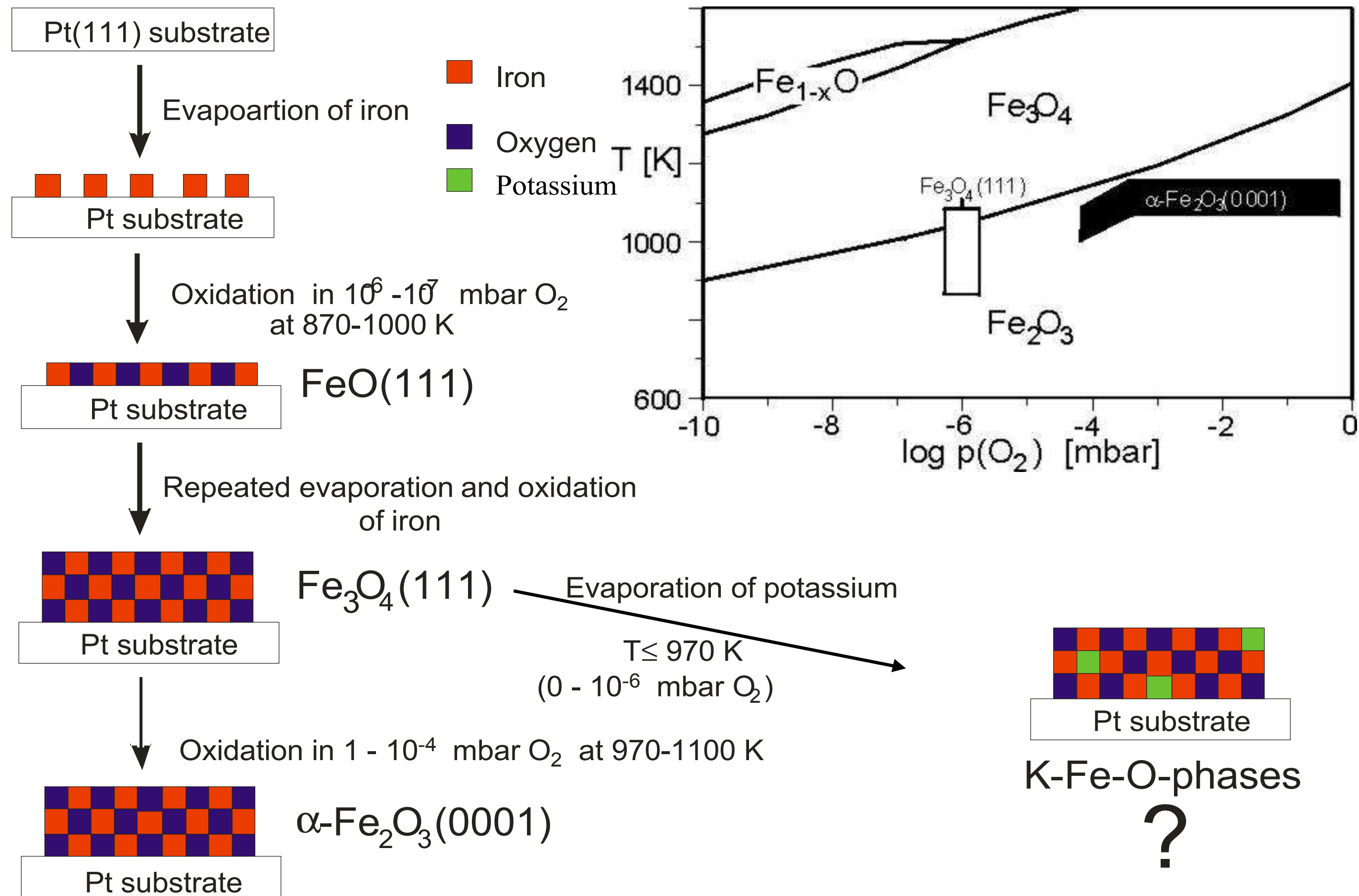


erst n Reihen, dann ML-hohe Inseln



Wachstum von ML-hohen Inseln

# Example: iron oxides preparation



# Film thickness estimation using a quartz crystal

Change of thickness, changes the resonance frequency

$$\frac{\Delta f}{f_0} = \frac{\Delta d}{d_0} = \frac{\Delta m}{\rho_q A d_0}$$

$f_0$ : *resonance Frequency of the quarz crystal*

$d_0$ : *thickness of the quarz crystal*

$\rho_q$ : *density of the quarz crystal*

$A$ : *area of the quarz crystal*

$\Delta m$ : *mass of the film*

$\varphi$ : *mass occupancy*

$N$ : *frequency const.*

$\rho_s$ : *density of the film*

Using:

$$\varphi = \frac{\Delta m}{A}, \qquad N = f_0 d_0$$

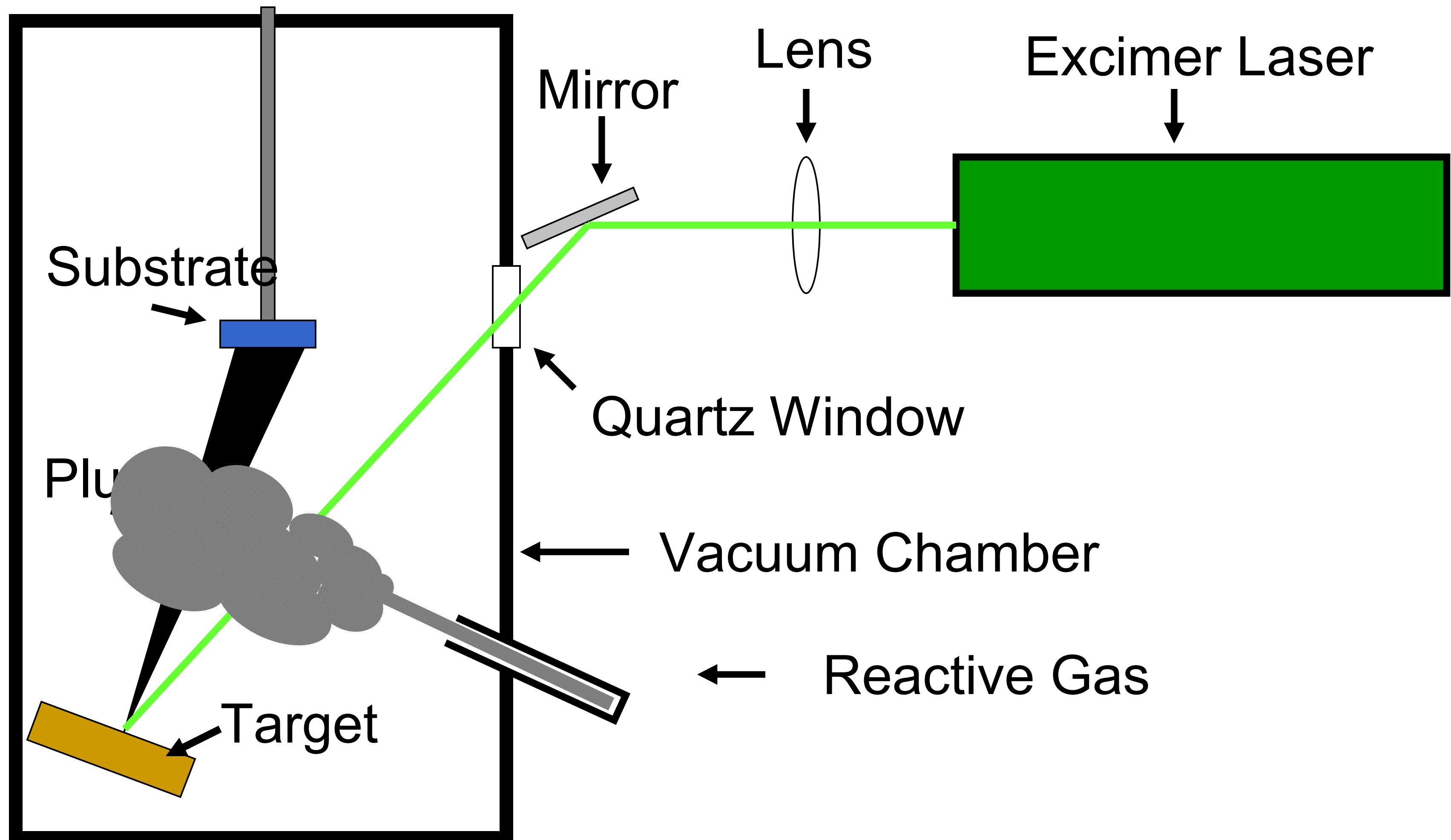
One gets:

$$\Delta f = -\frac{f_0 \varphi}{d_0 \rho_q} = -\frac{f_0^2}{N \rho_q}\varphi \quad when \quad \Delta m << m_q$$

The filmthickness d=Δd can be calculated:

$$d = \frac{\Delta m}{\rho_s A} \qquad \text{or} \qquad d = \frac{N \rho_q \Delta f}{f_0^2 \rho_s}$$

# Set up of pulsed laser deposition



# Pulsed laser deposition

## Advantages

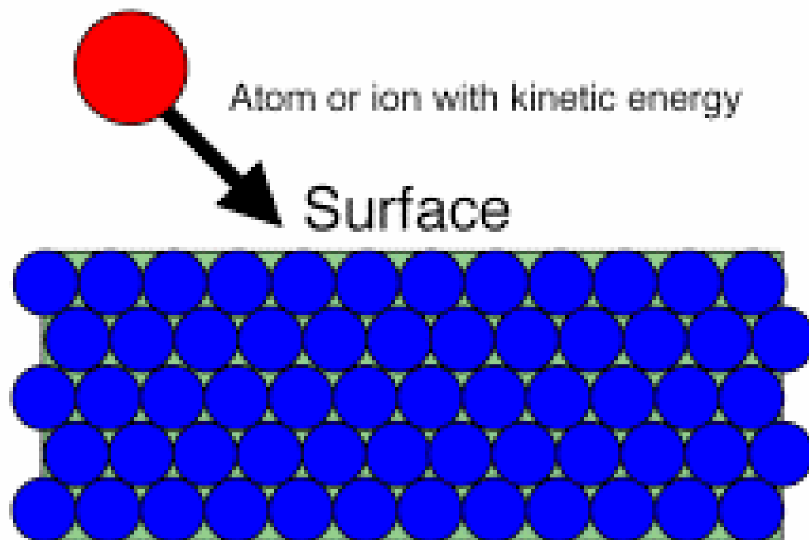
- Almost any material
- Laser outside chamber
- Reactive gases can be used
- Fast and Directional Plume
- Can be done at high pressures (~1 torr)

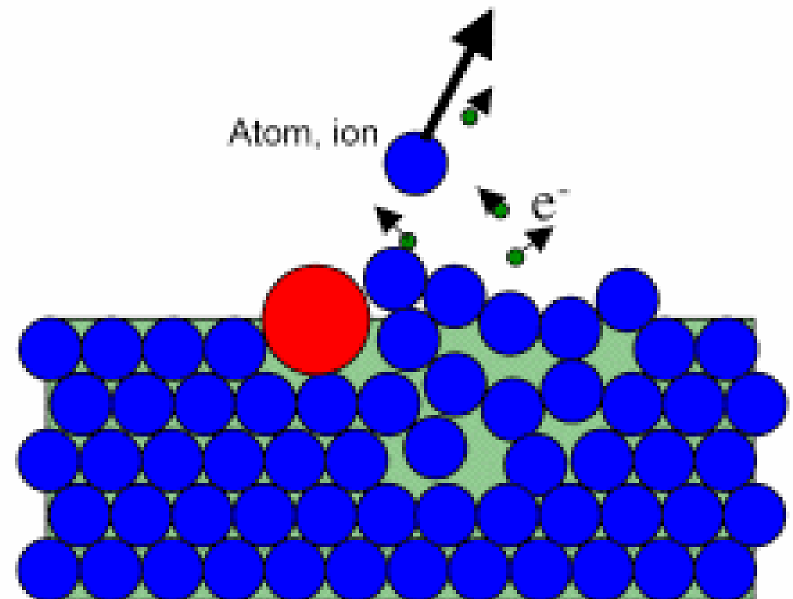
## Disadvantages

- Splashing causes micron-sized particulates
- Plume highly directional
    - Uniform only over a small area
    - Mass production hindered
- Extremely complex models eliminates theory based improvements

# sputtering

glow discharge on an inert gas (0.05 mbar) by putting a negative voltage on the target, ions impact the target and remove material, reactive sputtering



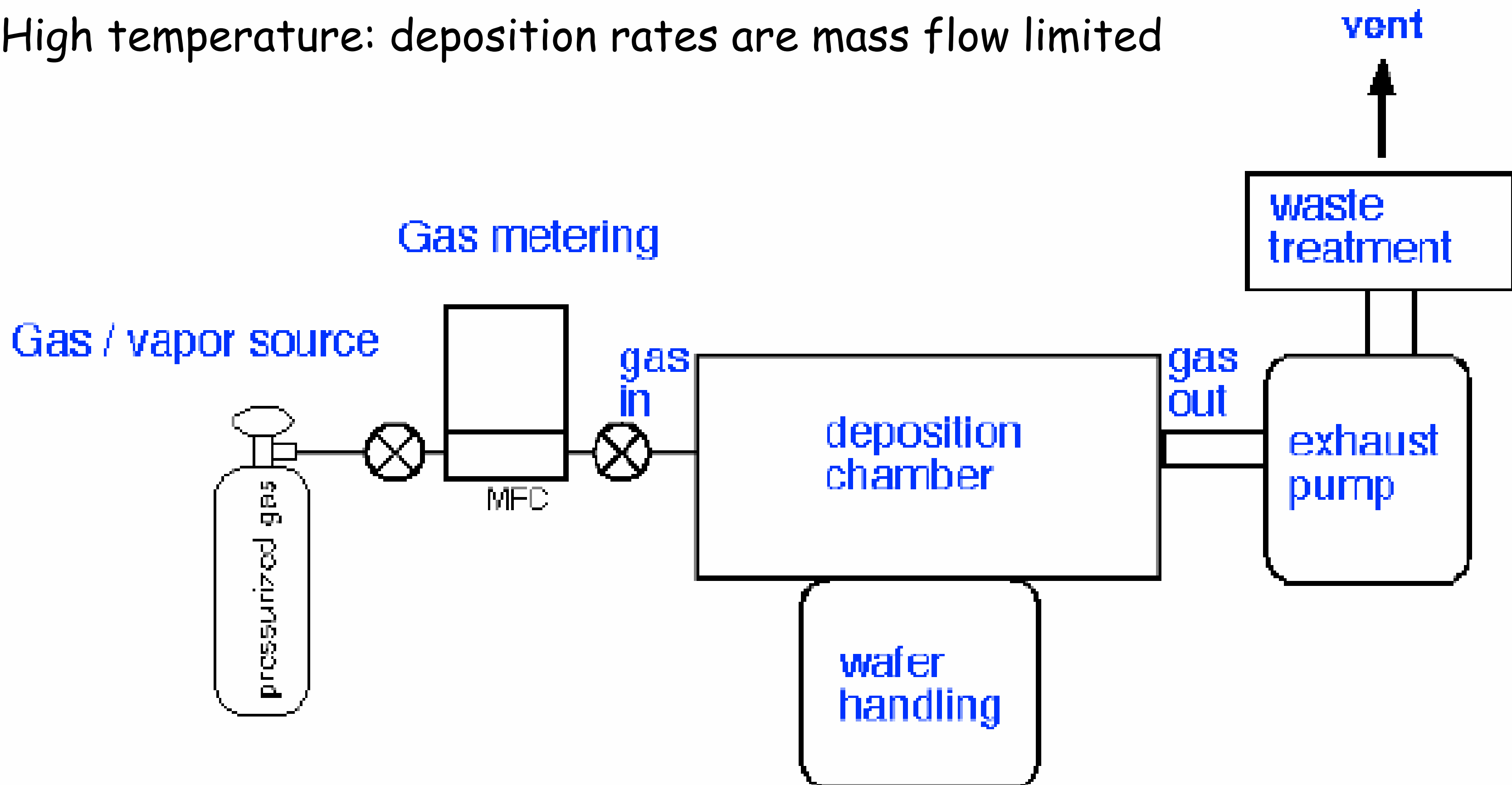



# Generic CVD reactor

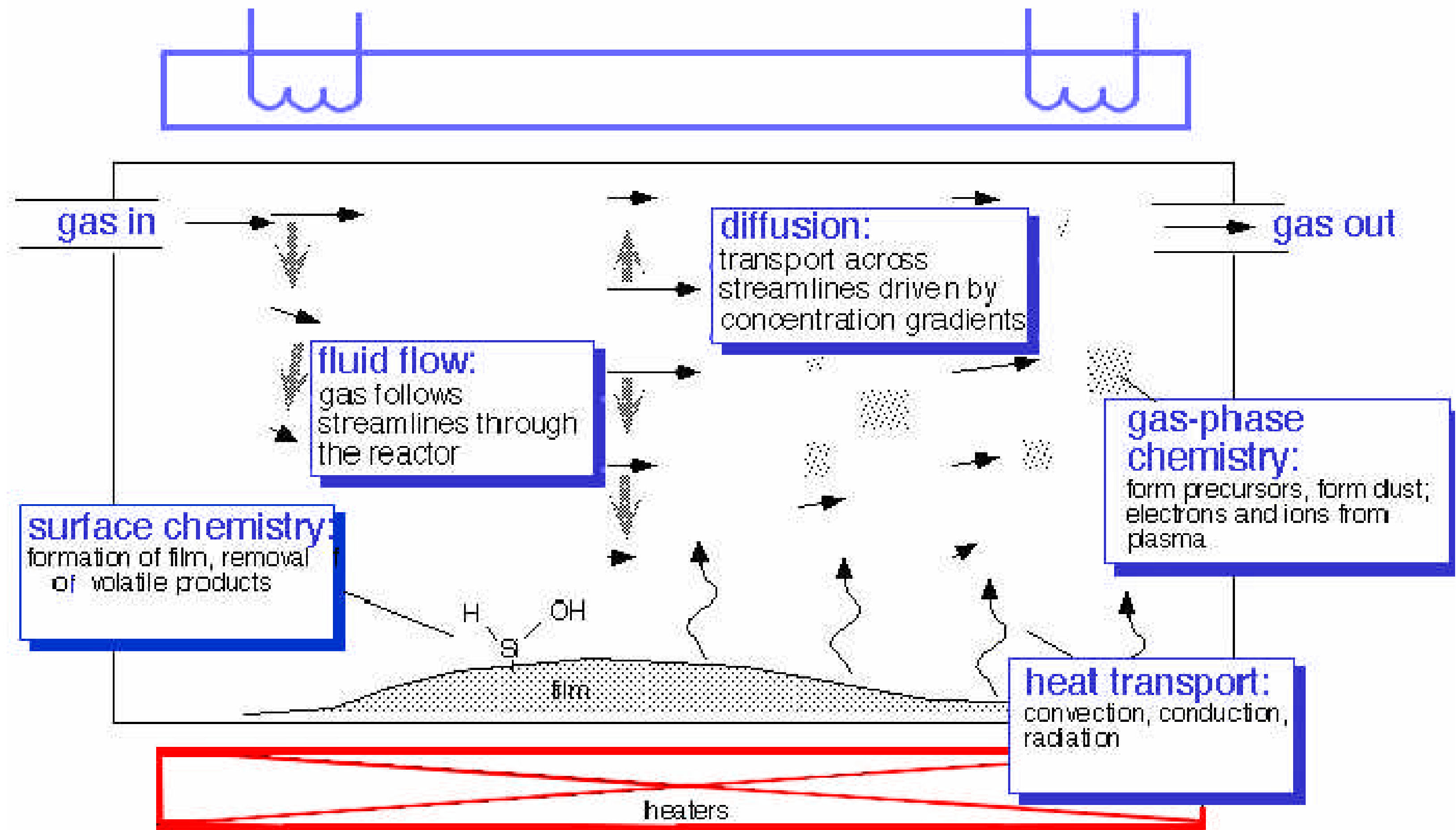
Deposition of solid material from gaseous phase

Low temperature: deposition rates are surface reaction limited

High temperature: deposition rates are mass flow limited



# Close up of a deposition chamber



# Kinetic Theory Example

Molecules in an ideal gas have a Maxwell velocity distribution:

$$dw(\upsilon) = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m\upsilon^2}{2kT}}\upsilon^2 d\upsilon$$

T = 300 K [room temperature]
Nitrogen ($N_2$), M = 28 g/mol

| Pressure (Torr) | Density (molecules/cm$^3$) | Mean free path (μm) | Mean velocity (m/s) | Flux to surface (molecules/cm$^2$ s) | Growth rate (μm/min) |
|---|---|---|---|---|---|
| 0.1 | $3.2 \cdot 10^{15}$ | 500 | 470 | $3.8 \cdot 10^{19}$ | 10 |
| 10 | $3.2 \cdot 10^{17}$ | 50 | 470 | $3.8 \cdot 10^{21}$ | 1000 |
| 760 | $2.5 \cdot 10^{19}$ | 0.07 | 470 | $2.9 \cdot 10^{23}$ | 77000 |

the "growth rate" is the amount of solid material that would be formed if each molecule was incorporated into a solid on the surface

# Chemical vapour deposition

**Metal Organic CVD (MOCVD)**

$MR_n\,(v) + ER'_n\,(v) \rightarrow ME\,(s) + n\,RR'(v)$

M is a group II or group III metal

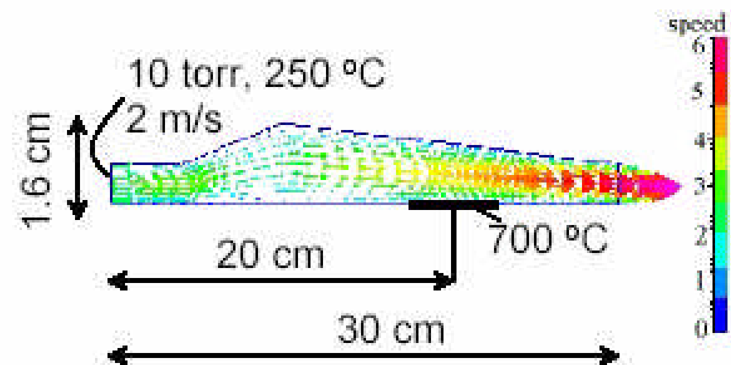
E is a group V or group VI element

R and R' alkyl radicals

## Advantages

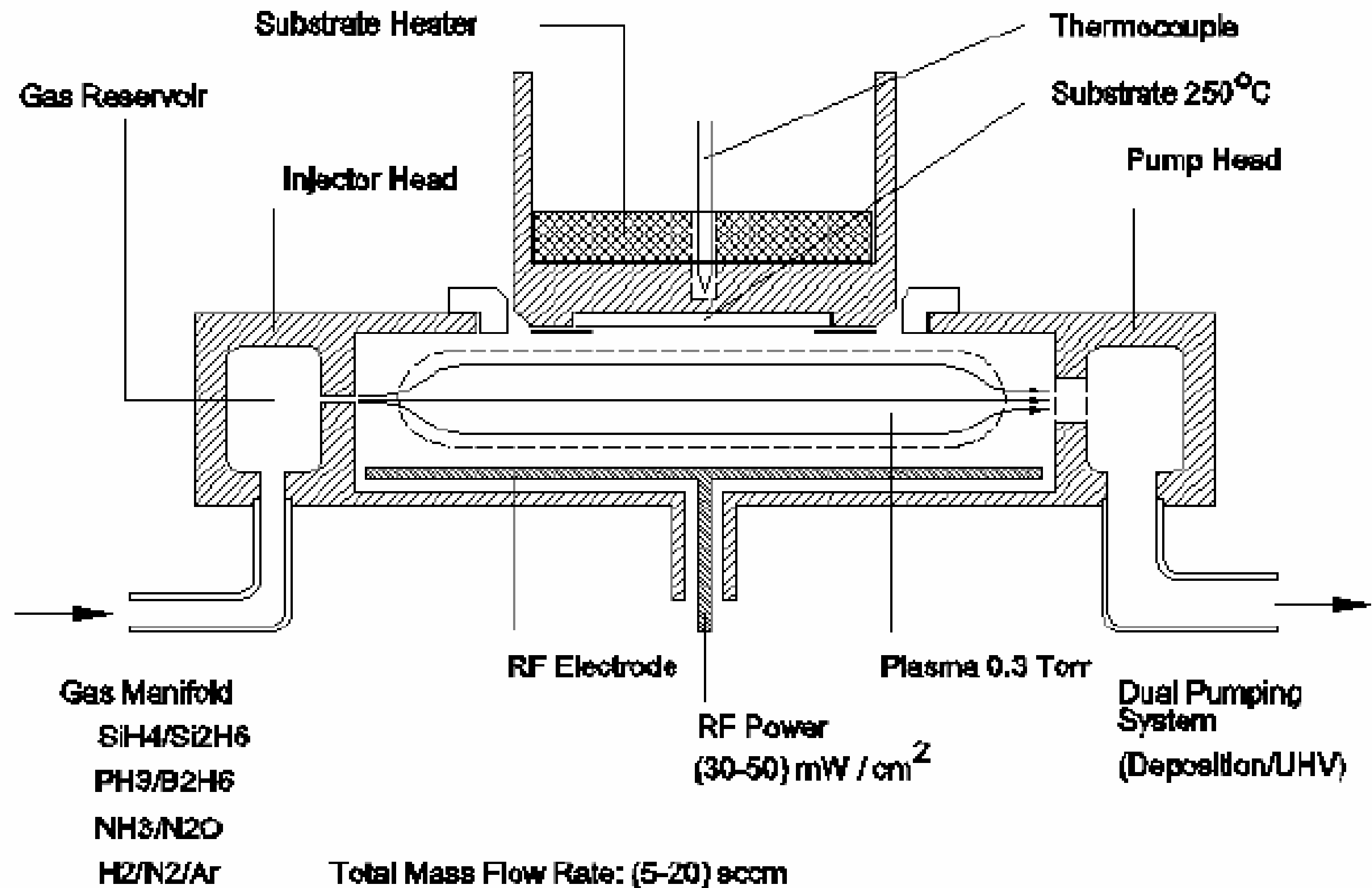
- Highly uniform thickness
- Excellent repeatability
- Low maintenance costs
- High throughput

**Schematic of a MOCVD reactor**

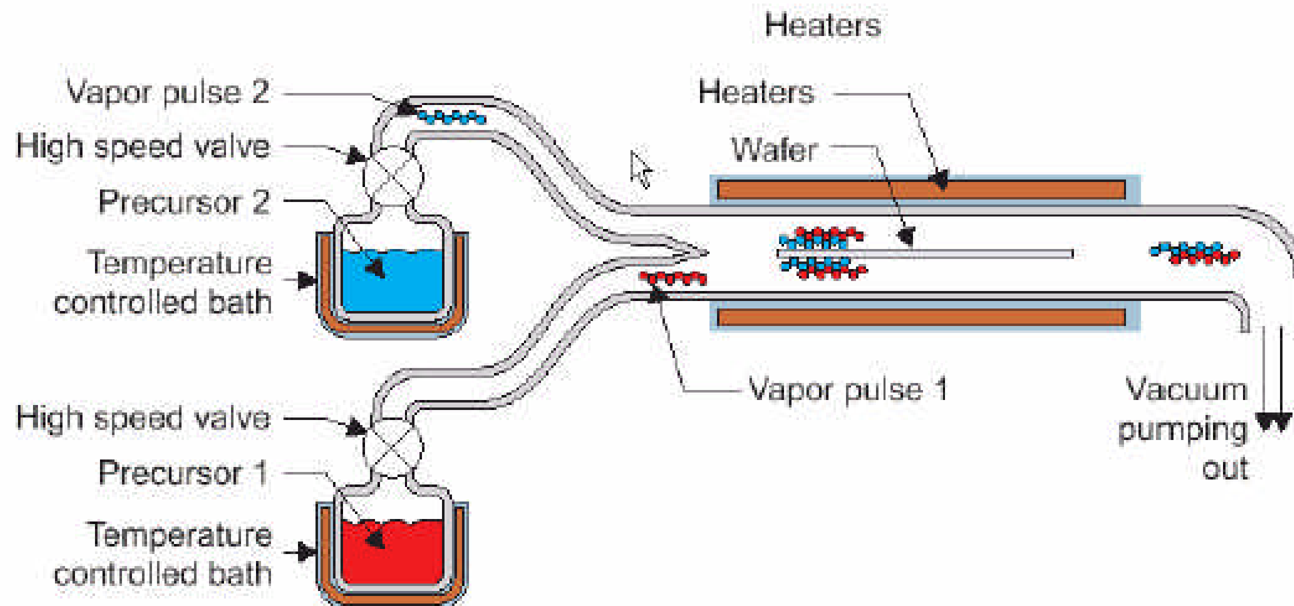



(Vertical size is exaggerated)

# Schematic of a PECVD reactor



# ALD reactors



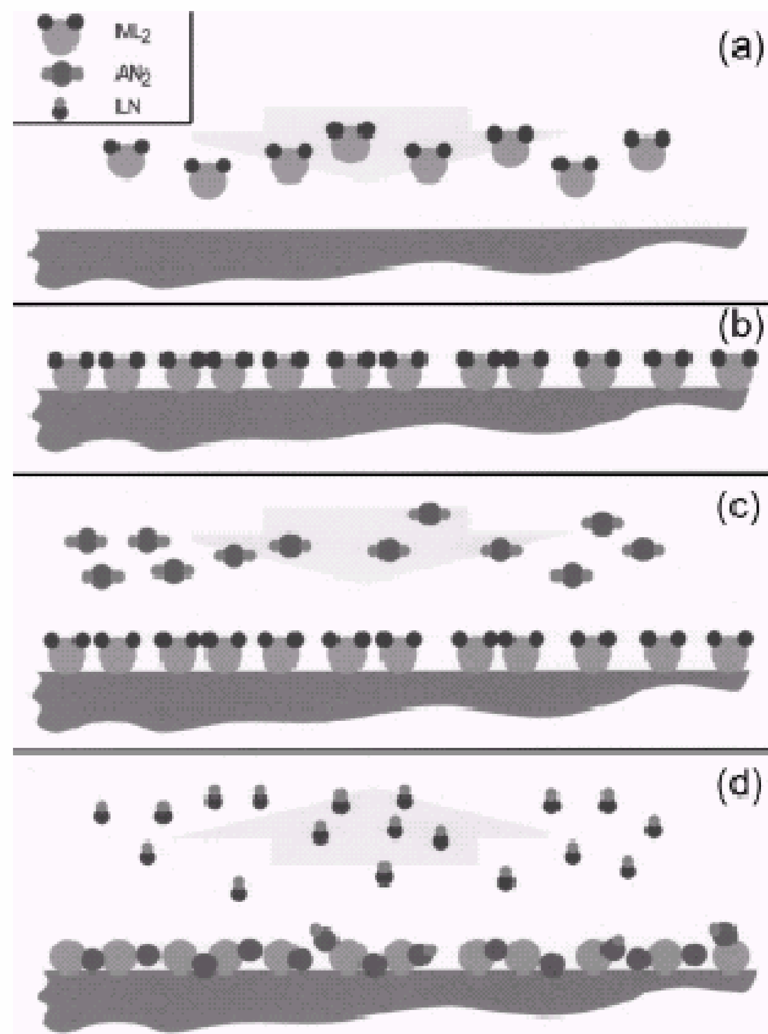

- Low impurities content
- Low process temperature
- Ultra thin film deposition with excellent thickness control
- Superior uniformity over large substrate area
- Excellent step coverage performance

# Chemisorption saturation process

- **Step 1**. Chemisorption of the first molecular precursor $ML_2$ on the substrate surface
- **Step 2**. The excess of the first precursor is purged out of the chamber to leave a monolayer of precursor $ML_2$
- **Step 3**. The second gas precursor ($AN_2$) is introduced. Exchange reactions take place between two precursors and by-products are formed:

$$ML_2 + AN_2 \rightarrow MA\ (film) + 2\ LN$$

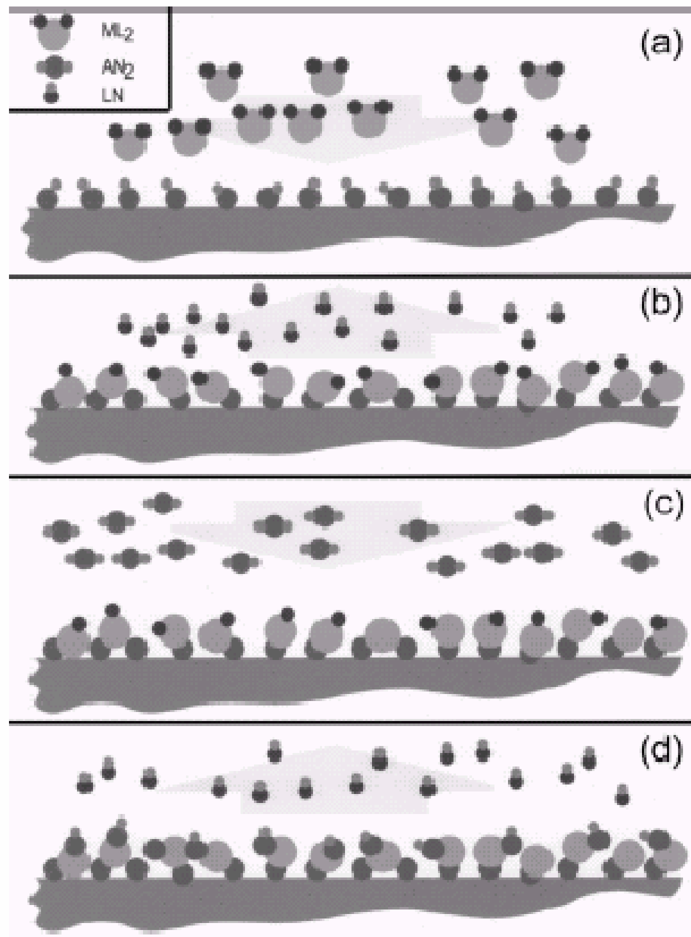
- **Step 4**. Unreacted material and by-product (LN) are purged out by purge gas




M=Al, W, Ta, Si, etc;   L=alkyl group, Cl, F

A= O, N, S ;   N=H

# Sequential chemical reaction process

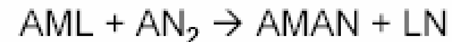



M = Al, W, Ta, Si, … A = O, N, S

- **Initial step.** The substrate surface is activated by AN groups
- **Step 1**. The surface is exposed to the first metal precursor $ML_2$

$$AN + ML_2 \rightarrow AML + LN$$

- **Step 2**. The first precursor and by-product (LN) are removed by purging with inert gas.
- **Step 3**. The second, usually non-metallic, precursor ($AN_2$) is introduced.



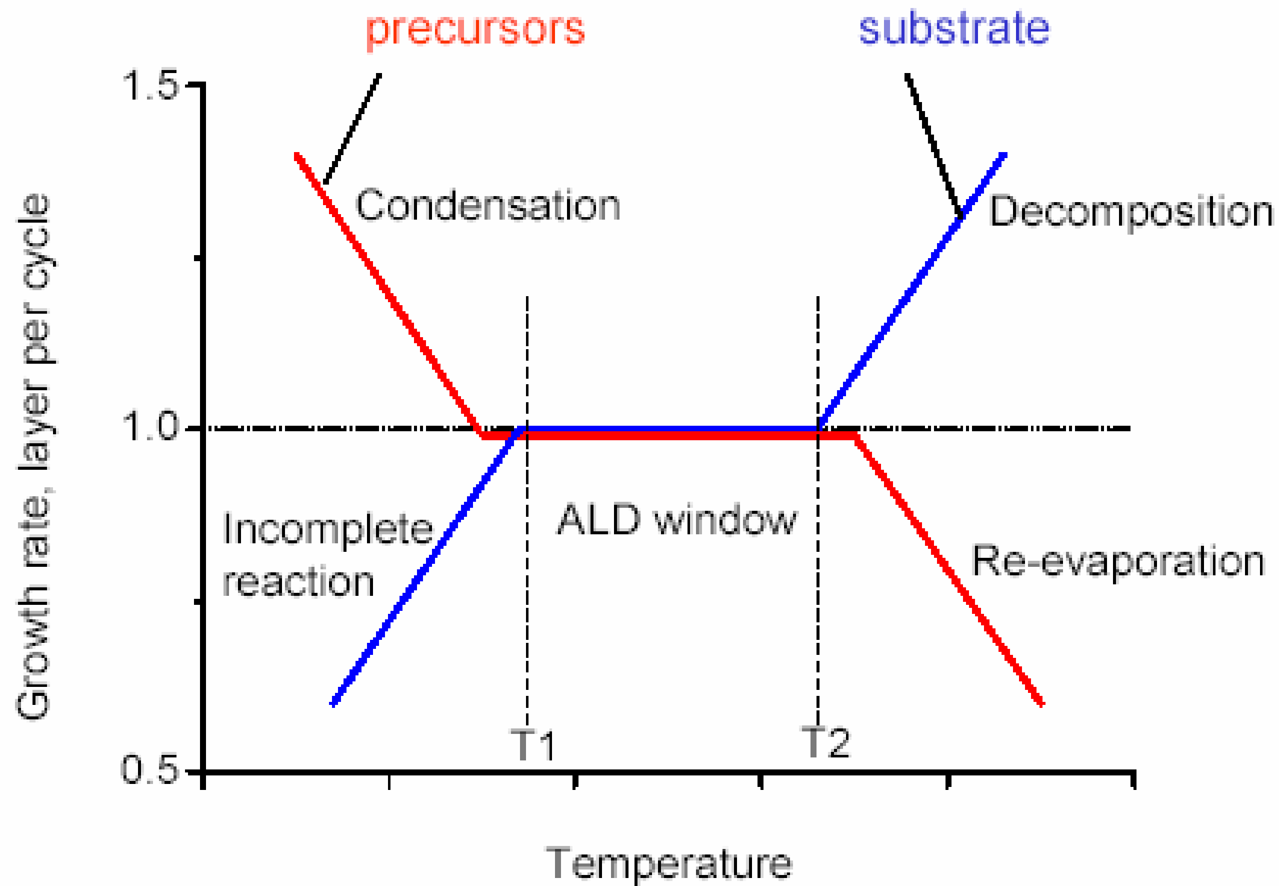
$$AML + AN_2 \rightarrow AMAN + LN$$

- **Step 4**. The second precursor and by-product (LN) are removed by purging with inert gas.

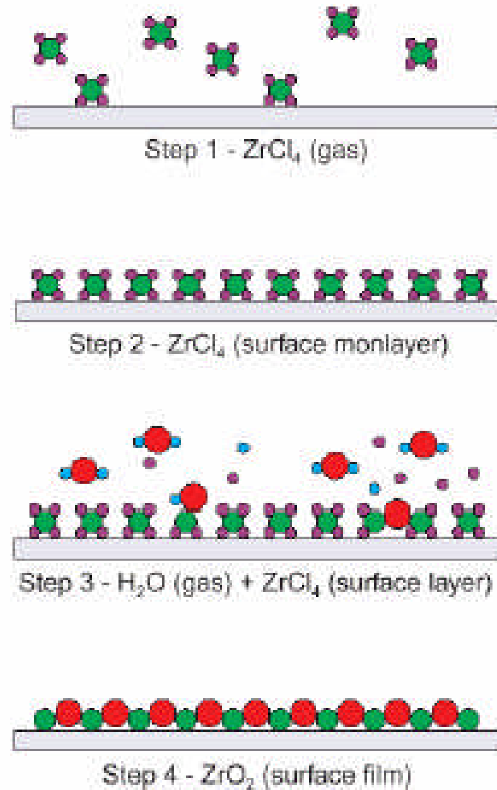
**Restoration of initial surface is the factor that differentiates RS-ALD from CS-ALD**

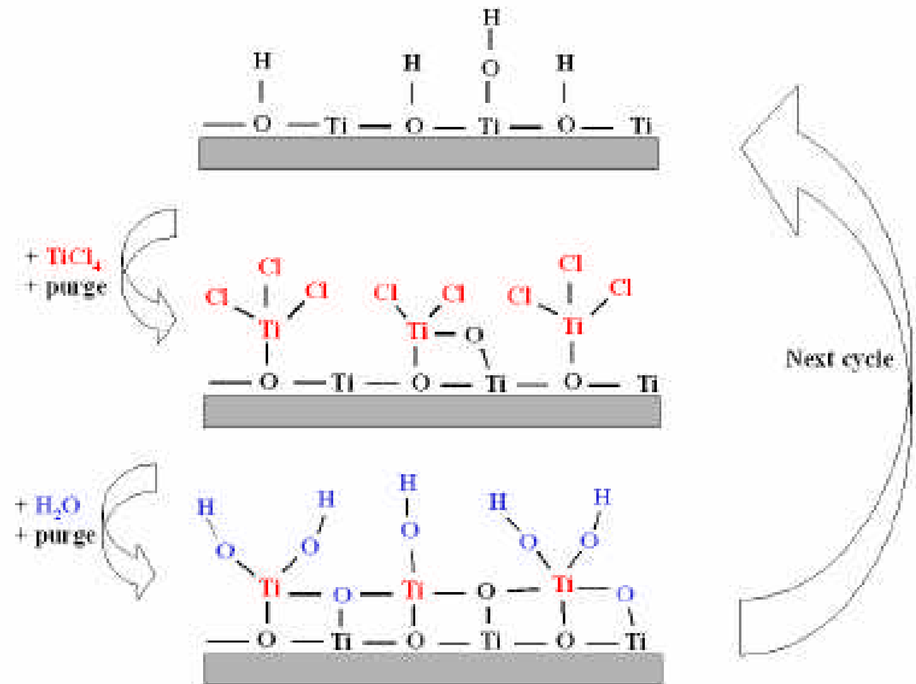
L= alkyl group, Cl, F, etc N=H

# Temperature window



# examples



# ALD precusor potential

…similar reactions are applicable to the deposition of materials containing elements in **blue**

| H | | | | | | | | | | | | | | | | | He |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |
| | | | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr | |

Compounds with appropriate reactivity and volatility are not currently known for the elements in **red**

# Characteristic features of ALD

| Characteristic feature of ALD | Inherent implication for coating deposition | Practical advantage |
|---|---|---|
| Self-limiting growth process | Film thickness is dependent only on the number of deposition cycles | Accurate thickness control |
| | No need for reactant flux homogeneity | Large-area capability |
| | | Excellent conformality |
| | | Excellent reproducibility |
| | Atomic level control of material composition | Sharp interfaces |
| Separate dosing of reactants | No gas phase reactions | Highly reactive towards each other precursors are used |
| | Sufficient time is provided to complete each reaction step | High-quality materials are obtained at low temperatures |
| Processing temperature windows are often wide | Processing conditions of different materials are readily matched | Capability to prepare multilayer·structures in a single process |

# Summary

Evaporation: target of the material to be deposit will be evaporated, creating of vapor steam, reaction with gases while moving from target to substrate to deposit oxides, nitrides...

Sputtering: glow discharge on an inert gas (0.05 mbar) by putting a negative voltage on the target, ions impact the target and remove material, reactive sputtering

Pulsed laser deposition process utilizes the plasma resulting form the interaction of focussed laser radiation pulses with the target surface to deposit coatings composed of one or several materials.

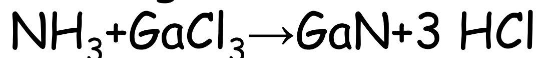
Molecular beam epitaxy (MBE) is based on molecular or atomic beams directed at a suitably heated single crystal sample to achieve epitaxial growth (1 micron/h) under UHV-conditions. The mean free path is several orders of magnitude greater than the distance source to sample. The surrounding of the sample is cooled. Precisely controled epitaxial film growth and compositon can be achived.

# Summary

Atmospheric pressure CVD: Multiport injection prevents mixing of the reactant gases until they are dispensed into the deposition region. Highly reactive miture such as silane and oxygen at atmospheric pressure can be used to get good film quality. Substrat is moved during the process.

Metal organic CVD: Very reactive, pure organometallic compounds (high vapor pressure of 1-100 Torr at RT) are used. The sources are introduced as vapor phase constituents into a reaction chamber at 200-250°C and are thermally decomposed at elevated temperature on the surface of a hot substrate to form the desired film.

Low pressure CVD: Comparing with APCVD produced coatings, LPCVD films have better thickness uniformity, fewer pinholes due to reduced pressure inhibiting gas-phase reactions. Traditional LPCVD tube reactors are hot wall reactors working in batch mode. GaN is synthesised by LPCVD process



$NH_3 + GaCl_3 \rightarrow GaN + 3\ HCl$

Plasma assisted CVD: Active species are created by the plasma generated by an RF field. Low pressure is used to create free electrons within the discharge region. PECVD has become the major thin film deposition technique. The kinetics is extremely complex, reactants can damage the film due to high energy

# Summary

Laser (assisted) CVD: Interaction of a laser beam with a reactive gaseous/vapor atmosphere and a substrate material. Film deposition occurs either by direct bond breaking in the precursor molecule due to resonant absorption of the laser radiation (photolytic LCVD) or by thermal decomposition of the reactant molecule at or near the surface of the laser heated substarte (pyrolytic LCVD). (extremely high deposition rate)

Photo CVD: new, low temperature, non surface damaging method. The precusors will be dissociated by photons, reactants are electrically neutral, free radicals, the choise of the wavelength will dedicated which chemical bond will be broken.