Thin Film Deposition

- Physical processes
  - Evaporation: Thermal, E-beam, Laser, Ion-plating.
  - Sputtering: DC, RF, Magnetron, Reactive.
  - Spray: Flame, Plasma.
- Chemical processes
  - Chemical Vapor Deposition (CVD): Thermal, MOCVD, PECVD.
  - Plating: Electroplating, Electroless.
  - Solgel
  - ALD
- Molecular Beam Epitaxy

Epitaxial Growth

Epitaxial films take on a lattice structure and orientation identical to those of the substrate.

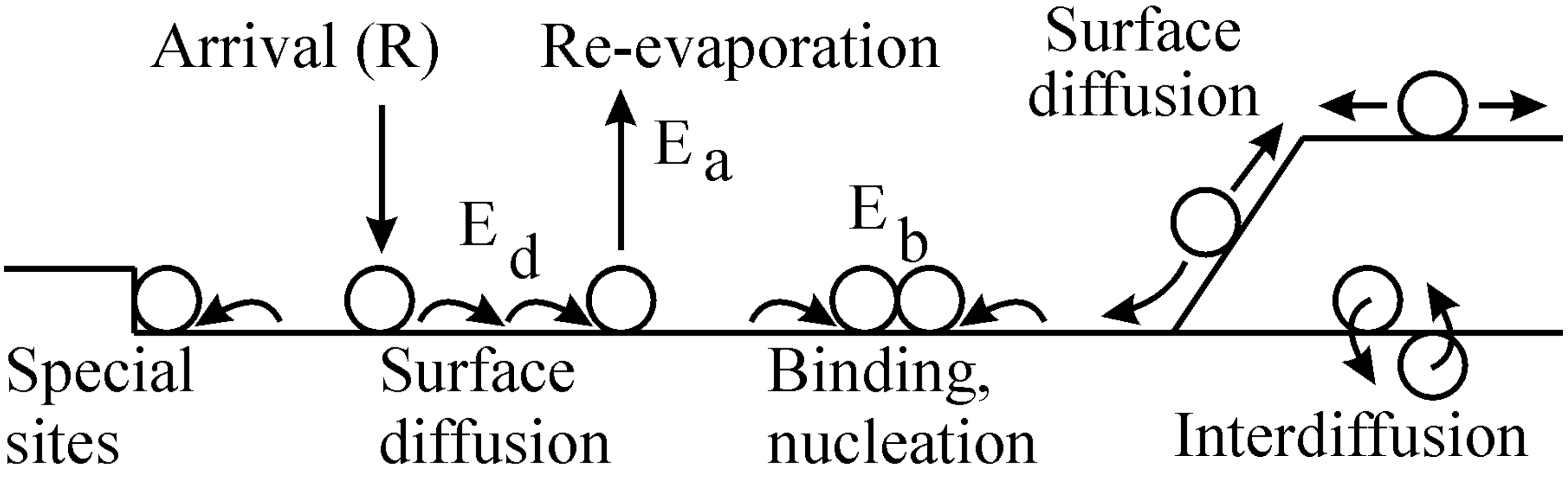
- **Homoepitaxy:** a crystalline film is grown on a substrate or film of the same material.
- **Heteroepitaxy:** a crystalline film grows on a crystalline substrate or film of a different material.

Physical growth kinetics

- Schematic description: particles are deposited on a surface and become adsorbed (adatoms). They diffuse around the surface and can be bound to the surface. Vice versa, unbinding and desorption happens.
- The kinetics of epitaxial growth is determined by the surface diffusion and nucleation.

Diffusion → Nucleation → Growth

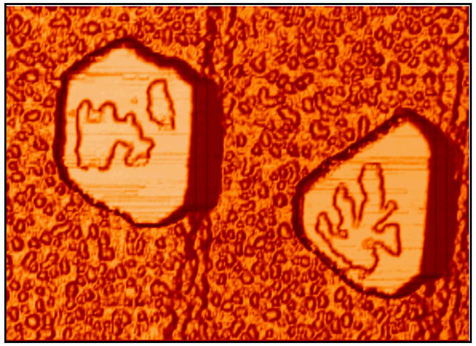
Atomic-level processes



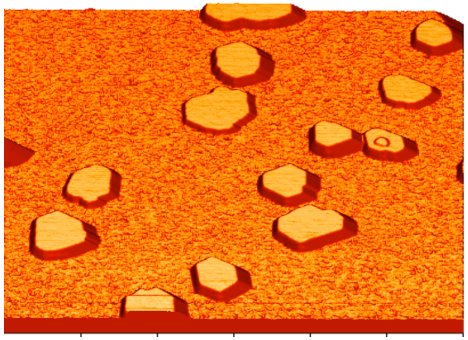
Variables: R (or F), T, time sequences (t)

Parameters: E_a, E_d, E_b, mobility, defects…

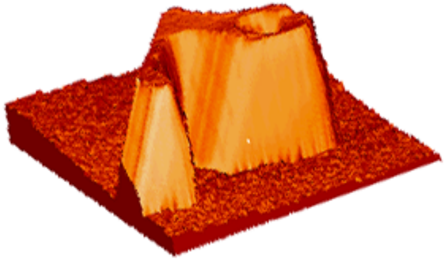
Growth modes at different temperature



Non-crystalline



2D islands

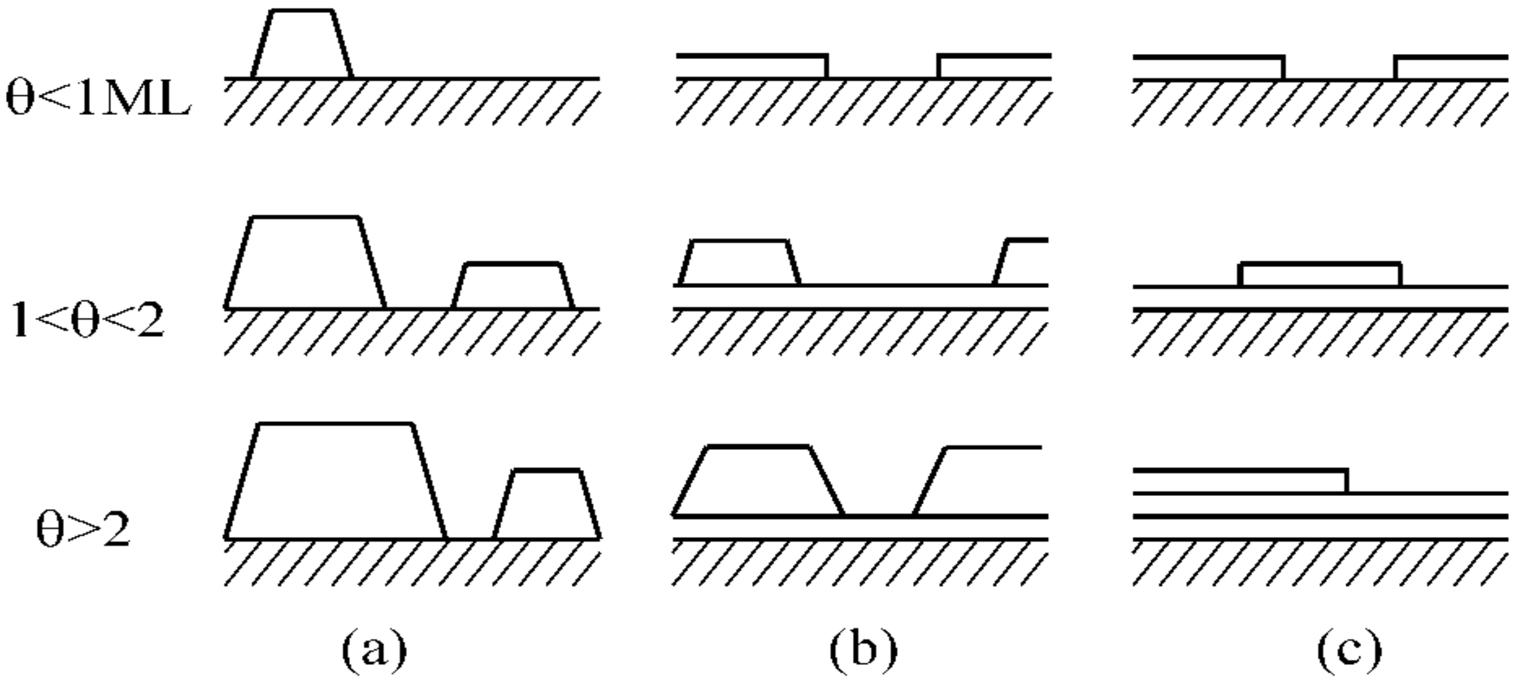


3D islands

150 K

300 K

Growth modes



Island
Volmer-Weber

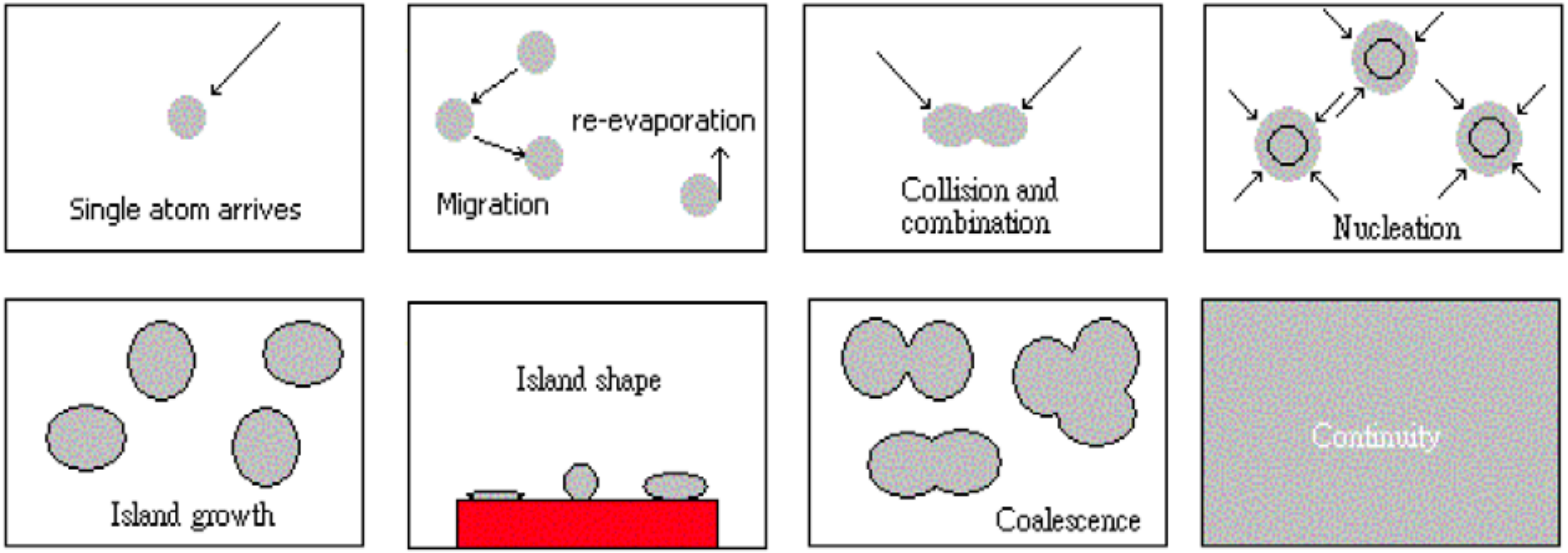
$$\gamma_s < \gamma_f + \gamma_i$$

Layer + Island
Stranski-Krastanov

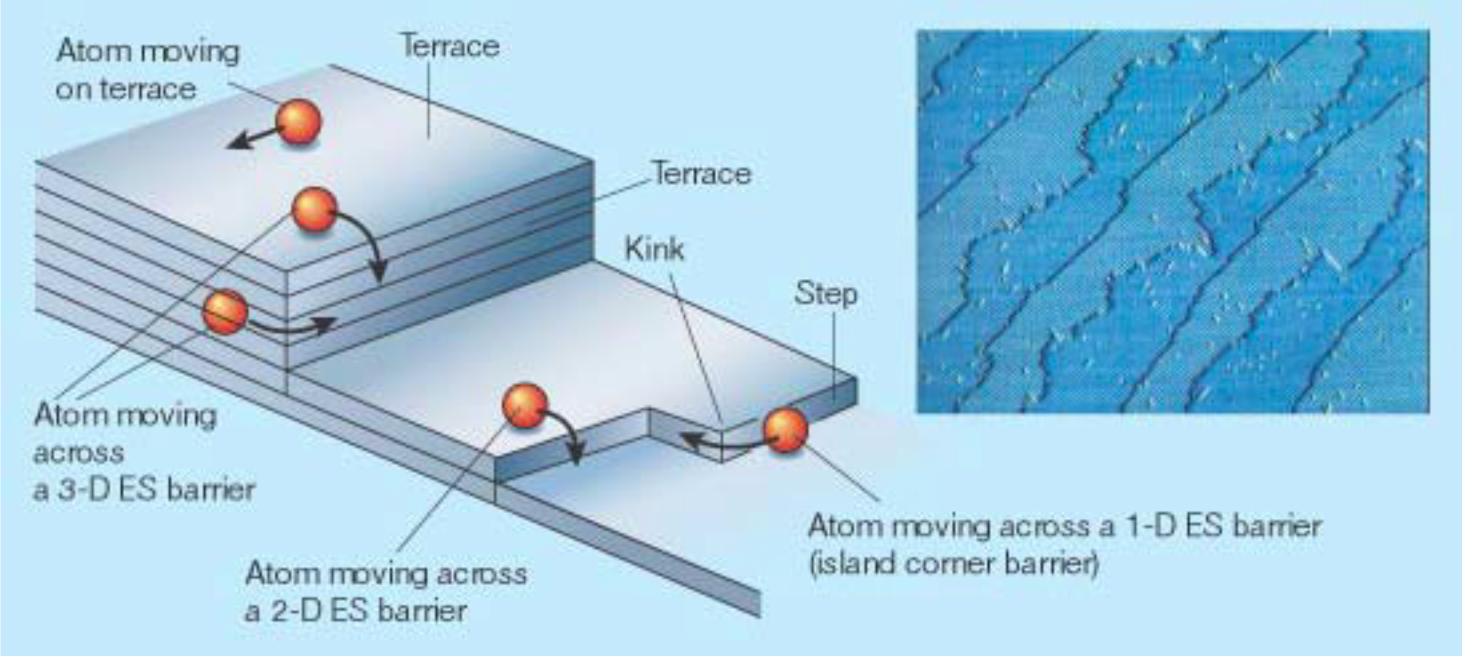
Layer
Frank-VdM

$$\gamma_s \geq \gamma_f + \gamma_i$$

Thin Film Growth Process



Atomistic Models for Crystalline Surfaces



Terrace Step Kink (TSK) model

Phase growth or transition simply involves the ***bond forming*** and ***bond breaking***

Vacuum Evaporation

- Heating a source material under vacuum until it evaporates or sublimates.
- The evaporant is deposited onto a substrate to form a film.
- Physical vapor deposition process.
- High deposition rate, simple, easy to use.
- Applied in conductor materials in electronic circuits and devices, dielectric and optical coatings.

Vacuum evaporation

Mean free path of atoms in the vapor > the distance from the source to the substrate.

The mean free path, λ_{mfp}, of particles in air at T = 25 ^{o}C

$$\lambda_{mfp} \approx \frac{5 \times 10^{-3}}{P(\text{torr})} \quad (\text{cm})$$

$$\lambda_{mfp} = \frac{1}{n\sigma}$$

$n = P/kT$

$$\lambda_{mfp} = \frac{kT}{P\sigma}$$

$$\sigma = \pi d^2$$

$$= \frac{411.24 \times 10^{-23}}{P\left(1.21 \times 10^{-18}\right)}$$

$$= \frac{3.40 \times 10^{-3}}{P} \quad (\text{cm})$$

For N_2 molecules

$d = 6.2$ Å

Vacuum evaporation

The flux of incident molecules is given by the Hertz-Knudsen equation

Flux , $\boldsymbol{F = P / (2\pi mkT)^{1/2}}$ [molecules m^{-2} s^{-1}]

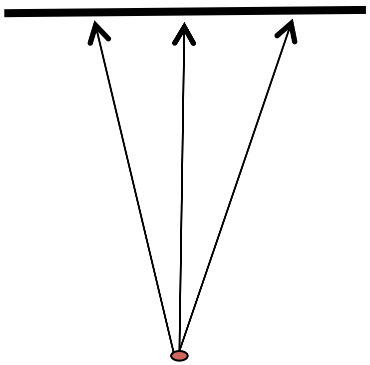
where

P - gas pressure [N m^{-2}]
m - mass of one molecule [kg]
T - temperature [K]

$F = nv/4$,
$n = P/kT$, $v = (8kT/\pi m)^{1/2}$

Vacuum evaporation

- Evaporation coefficient: Larger for clean surfaces, smaller for contaminated surfaces.
- Deposition rate: Greatly depends on the substrate-to-source geometry.
- Non-uniform thickness on surface: Due to the distance dependence.



Ranges of Vacuum

Low or Rough Vacuum	760 Torr to 1Torr
Medium Vacuum	1 Torr to 10^{-3} Torr
High Vacuum	10^{-5} to 10^{-8} Torr
Ultra-high Vacuum (UHV)	Below 10^{-9} Torr

High vacuum pumps

1) Oil diffusion pumps (gas transfer)

10^{-3} to 10^{-10} torr

2) Turbomolecular pumps (gas transfer)

10^{-4} to 10^{-10} torr

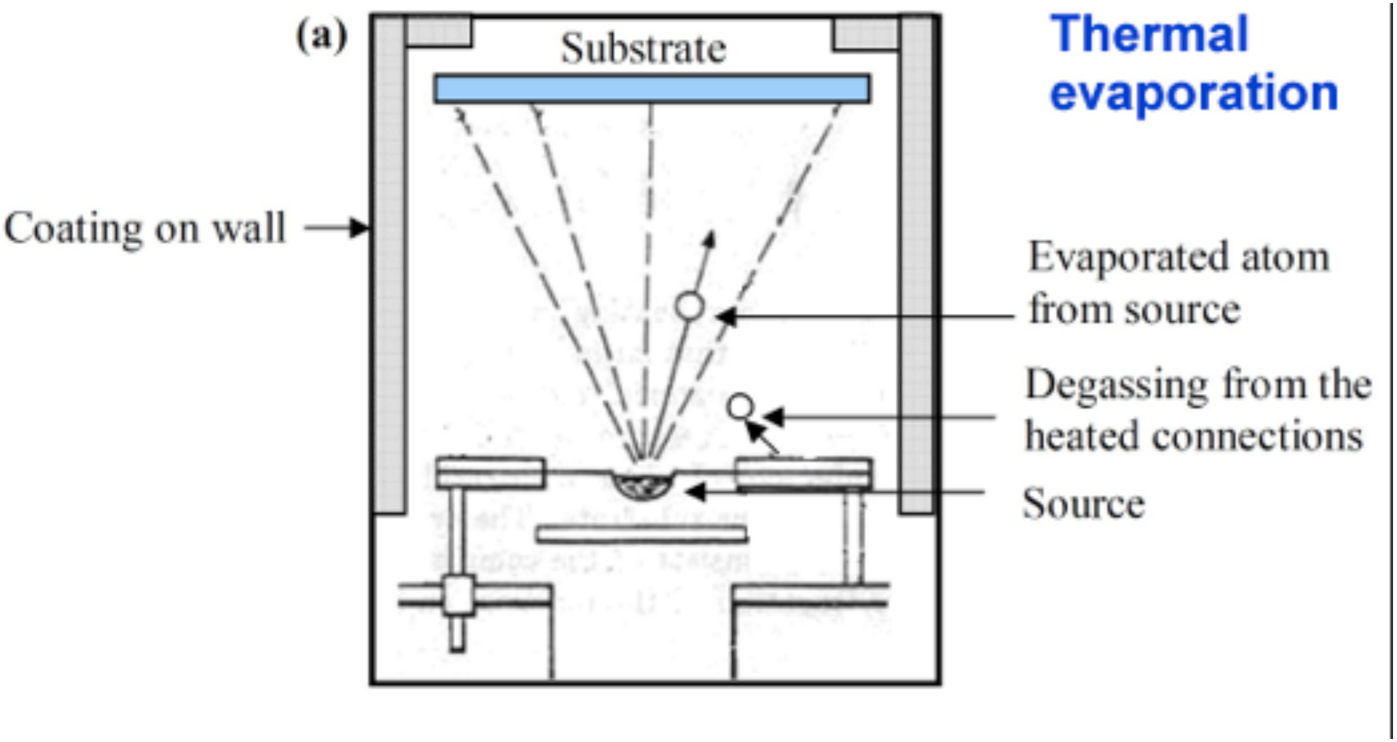
3) Gas capture pumps

ion pumps

must operate in conjunction
with other high vacuum pumps

to 10^{-11} torr

Thermal Evaporation

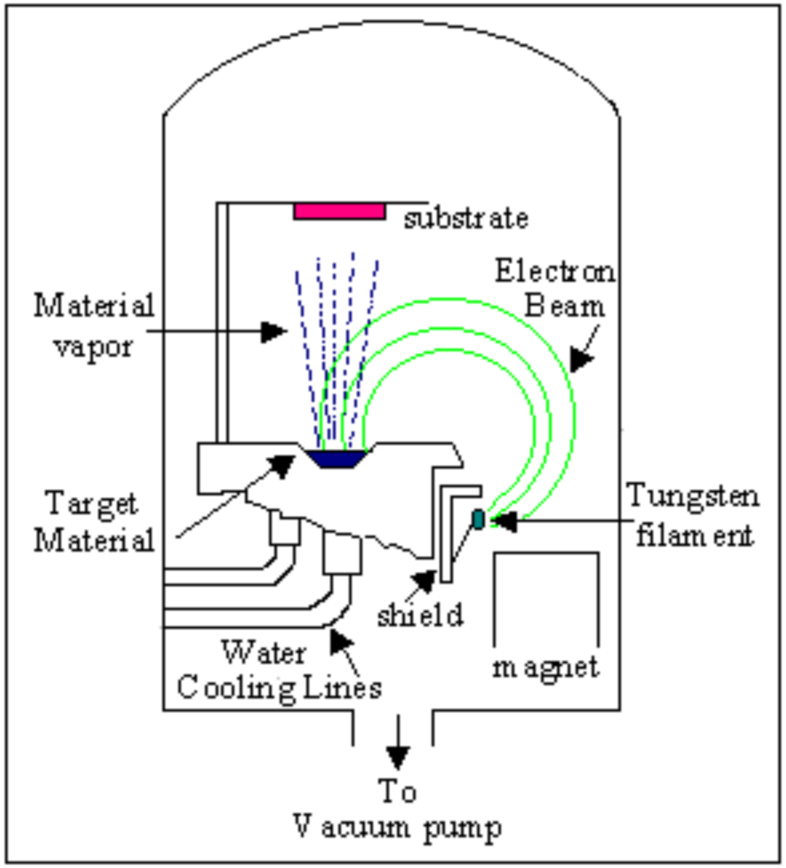


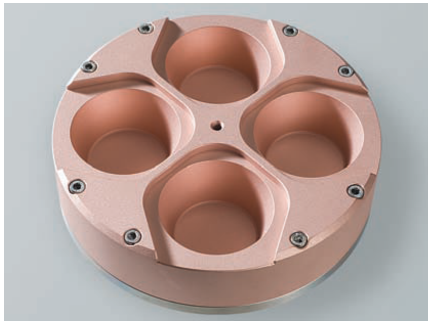
Thermal evaporation

- Difficulties: High melting point materials, uniformly heating, rapidly change of deposition rate, reactions between the source and the heating container.

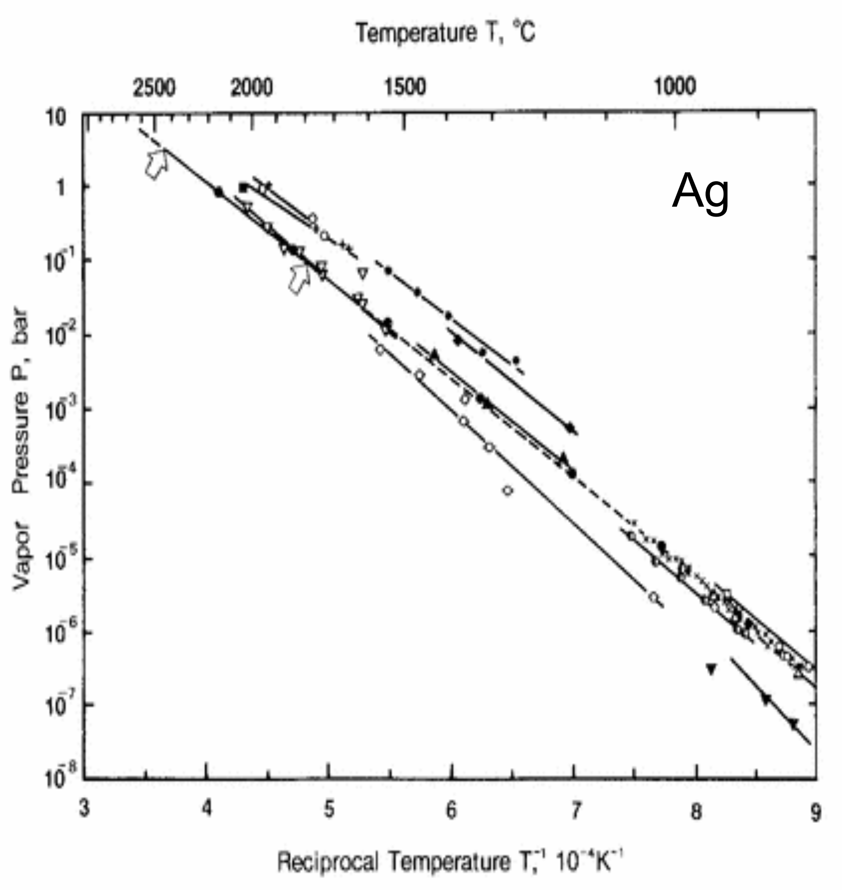
E-beam evaporation

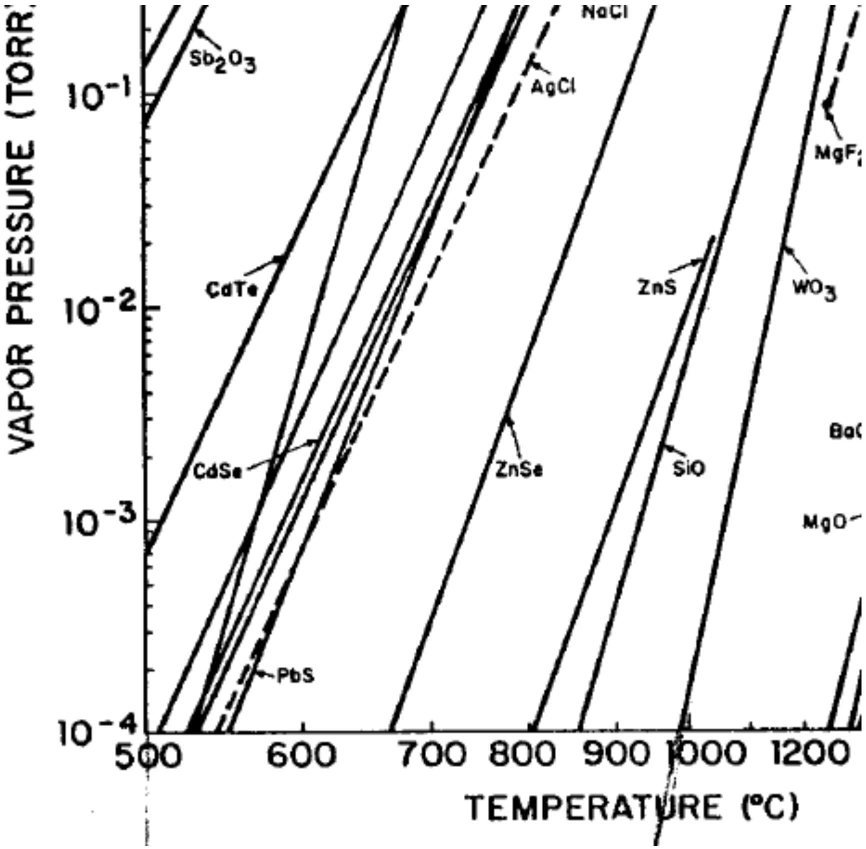
- High energy focused electron beam to heat the source material at a small area.
- Larger deposition rate.
- Water-cooled container (cavity or hearth): No source-container reaction.
- Sweeping or oscillating the e-beam to heat the source material uniformly.
- Multiple hearth sources: Different source materials.





Vapor pressure



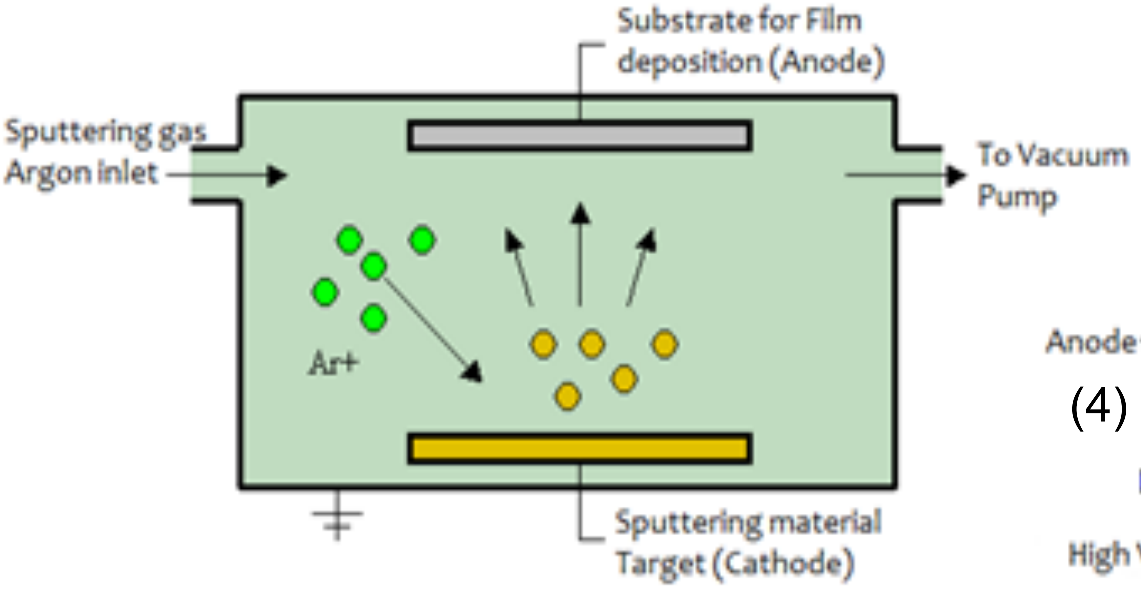


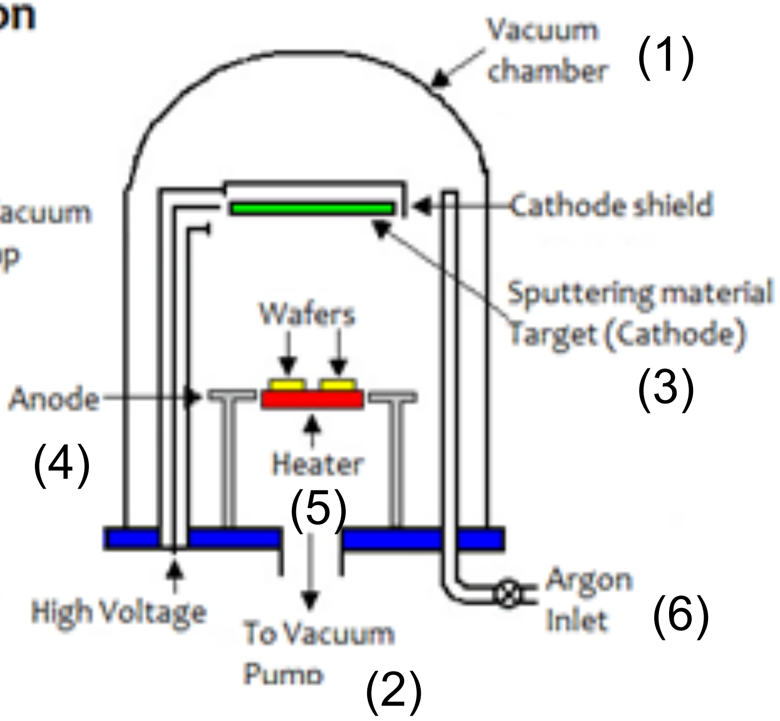
Sputter deposition

- PVD process.
- Bombardment and removal of the cathode material with positive ions from a rare gas discharge.
- Originally developed to deposit refractory metals.
- Now the sputter deposition is able to deposit most materials.

Sputter deposition system

Sputter deposition

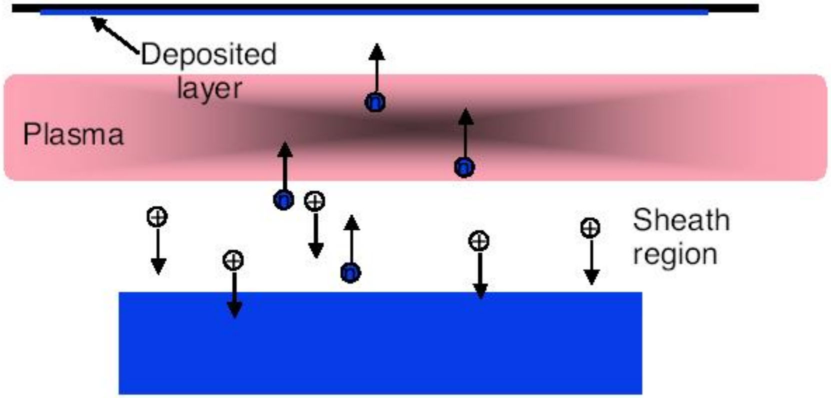


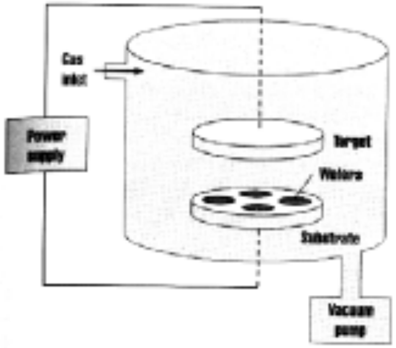


1) vacuum chamber
2) pumping system
3) sputter sources
4) substrate Anode
5) Heater
6) Gas flow supply

Sputtering Deposition Process

- **Sputtering**
  - Ions are accelerated into target
  - Some of the surface atoms are sputtered off of the target.
  - These sputtered atoms “flow” across the chamber to where they are deposited



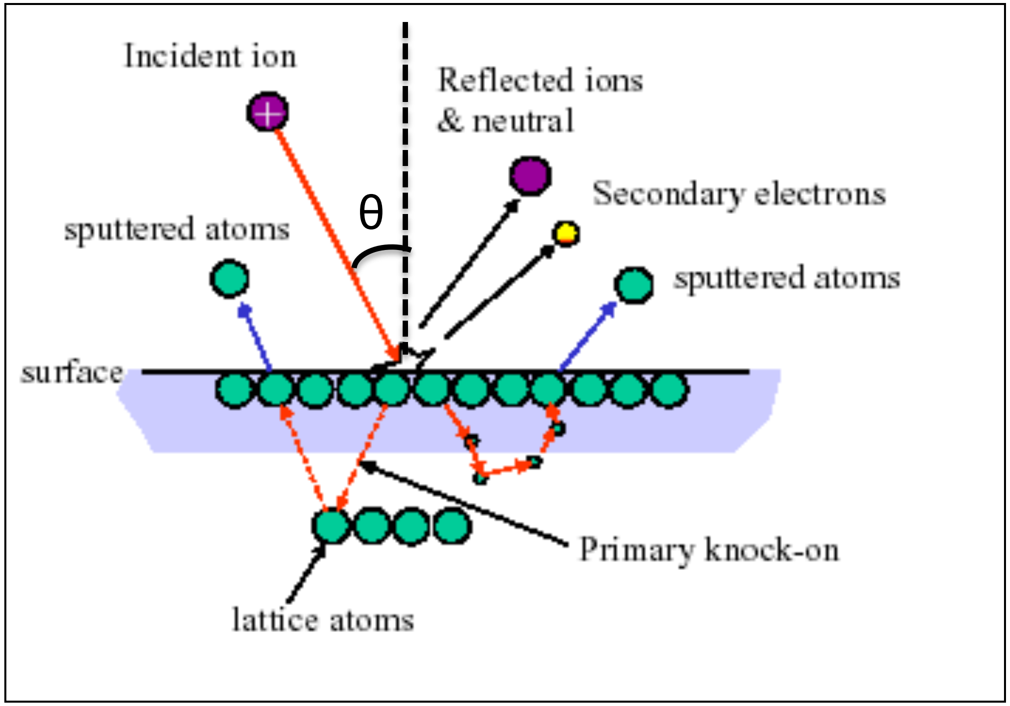


Sputtering chamber

http://www.utdallas.edu/~goeckner/plasma_sci_class/Plasma%20Process%203%20Types.pdf

Mechanism of Sputtering

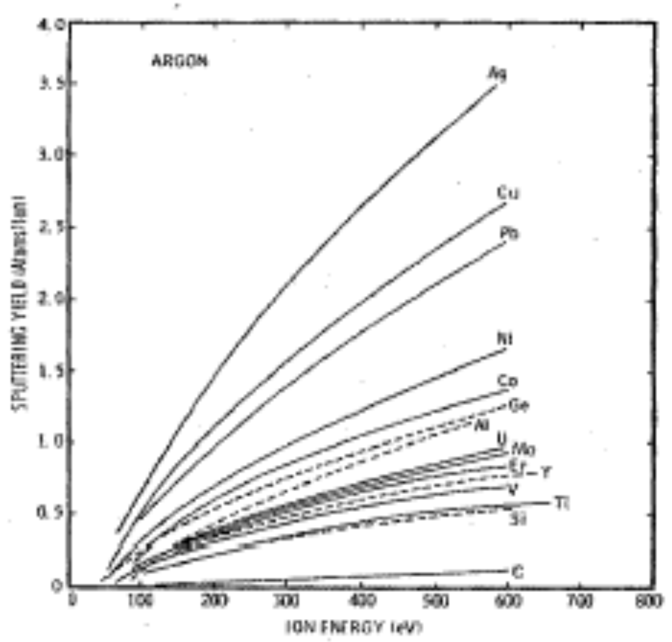
Sputtering involves the collisions of energetic ions with a target surface and the process usually leads to ejection of target atoms.



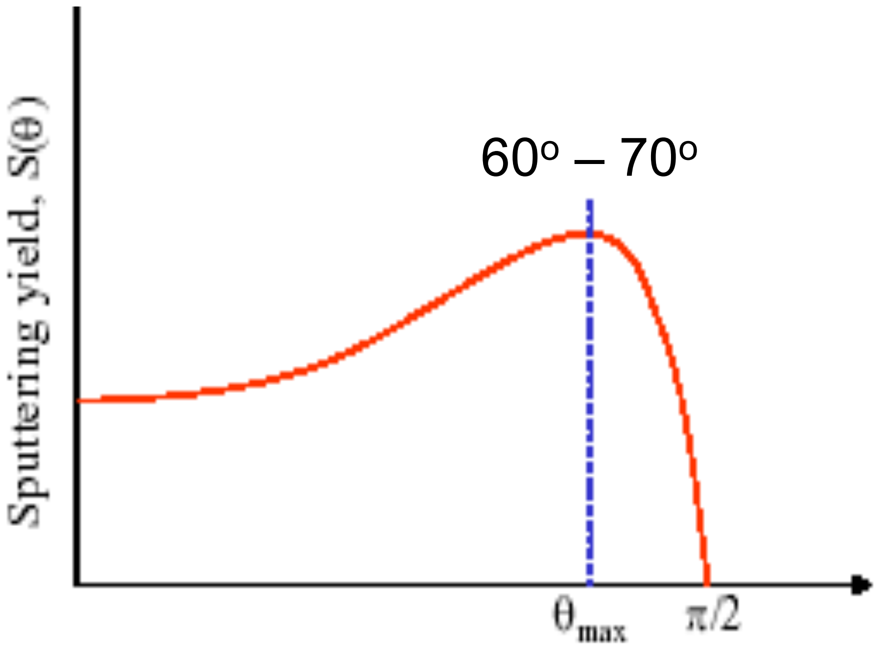
Sputtering process is characterized by sputter yield, S, which is typically in the range of 0.01 and 4 and increase with the mass of metals and energy of the sputtering gas.

Sputter Yield

The sputter yield depends on: (a) the energy of the incident ions; (b) the masses of the ions and target atoms; (c) the binding energy of atoms in the solid and (d) the incident angle of ions.



5.5: Variation of sputtering yield with ion energy at nor
of incidence. Data from R.V. Stuart and G.K. Wehner, J. A



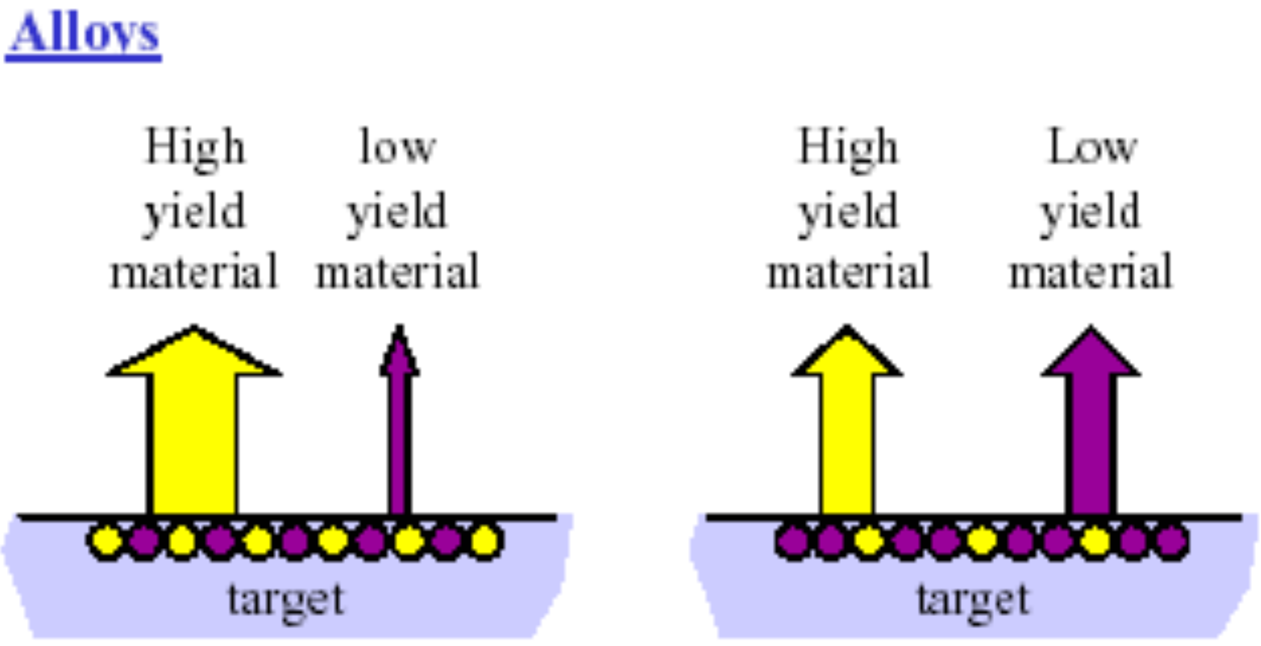
http://www.postech.ac.kr/mse/tfxs/2003_2/chapter3.pdf

Sputtering Alloy Targets

composition of alloy in film is approximately the same as alloy in target (unlike evaporation)

slow diffusion mixing in solids (sputtering)

- target reaches steady state
- surface composition balances sputter yield



Before surface equilibrium

After surface equilibrium

http://www.postech.ac.kr/mse/tfxs/2003_2/chapter3.pdf

Advantages of sputter deposition

- **Elements, alloys and compounds can be sputtered and deposited.**
- **The sputtering target provides a stable, long-lived vaporization source.**
- **In some configurations, reactive deposition can be easily accomplished using reactive gaseous species that are activated in plasma.**
- **The source and substrate can be spaced close together.**
- **The sputter deposition chamber can have a small volume.**

http://www.pfonline.com/articles/069901.html

Disadvantages of Sputter Deposition

- **Sputtering rates are low compared to those that can be attained in thermal evaporation.**
- **Sputtering targets are often expensive.**
- **Most of the energy incident on the target becomes heat, which must be removed.**
- **In reactive sputter deposition, the gas composition must be carefully controlled to prevent poisoning the sputtering target.**

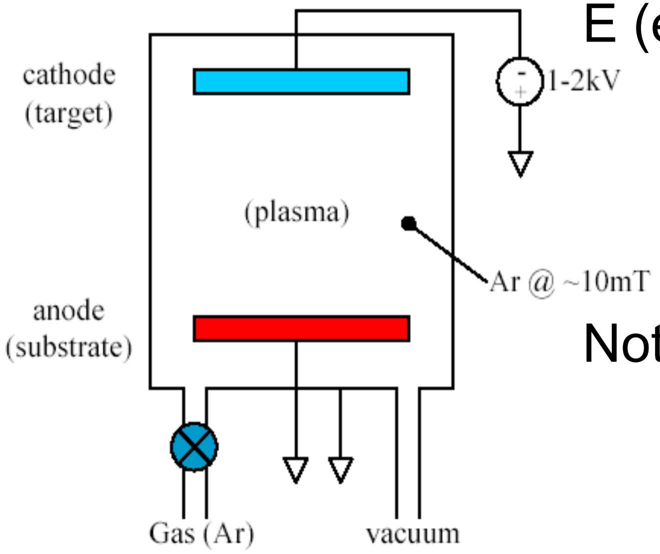
http://www.pfonline.com/articles/069901.html

Basic Techniques

- **DC (diode) sputtering**
- **RF (radio frequency) sputtering**
- **Magnetron sputtering**
- **Reactive sputtering**

DC Sputtering

The simplest sputtering technology



E (e-) < 2eV - no ionization, elastic collisions only
E (e-) > 2eV - inelastic collisions add energy to Ar

- ➢ ionization (highest energy process, ~15eV)

$$Ar + e^- \rightarrow Ar^+ + 2e^-$$

Note: mass (e-)/mass(Ar) ~ 10^{-5}

- energy transfer small
- e- gain energy via elastic collisions until E>15eV for ionization
- #ions ~ #neutrals ~ 3 x 10^9 cm^{-3} @ 10mT

http://www.glue.umd.edu/~ddev/me489f/slides/2b_deposition_x6.pdf

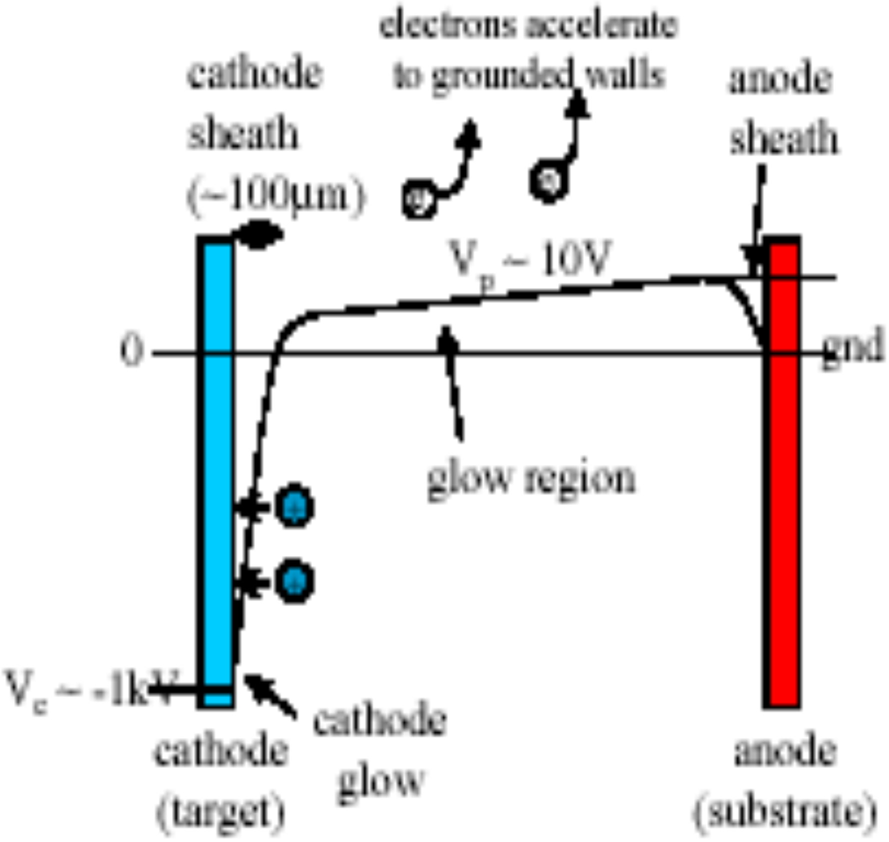
DC Sputtering (Cont.)

Light e- pulled towards walls faster than ions, leaving slightly more ions in glow region

Light e- move away from cathode faster than ions, leading to a large field, high acceleration of ions into cathode

high-E ions (10keV to 1 MeV) knock target material loose resulting plume of neutrals

new electrons from impact reactions replenish the plasma



http://www.glue.umd.edu/~ddev/me489f/slides/2b_deposition_x6.pdf

Operating Pressure for DC sputtering

Operating pressure limitations are imposed by the requirement of both the glow discharge and of film deposition.

Optimum deposition rate around 0.1 Torr

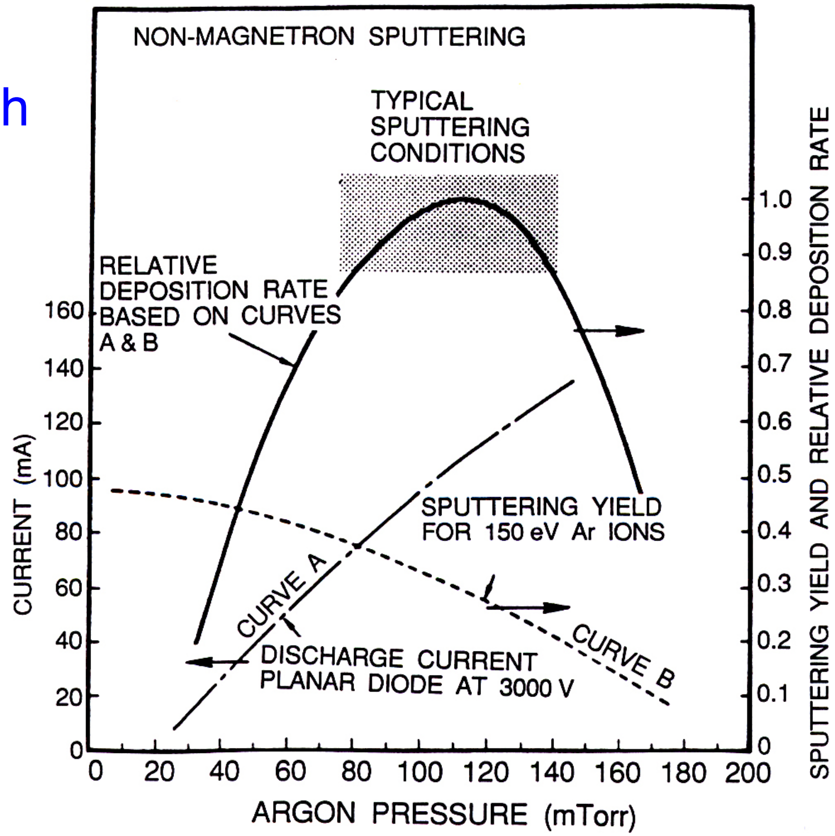


Figure 3-18. Influence of working pressure and current on deposition rate for nonmagnetron sputtering. (From Ref. 23).

Milton Ohring, *Materis Science of Thin Film*, second Edition, P208

Parameters for DC Sputtering

- **Sputter voltage**
  - typically -2 to -5 kV
- **Substrate Bias Voltage**
  - substrate is being bombarded by electrons and ions from target and plasma
    - sputtering film while you deposit
  - neutral atoms deposit independently
  - put negative bias on the substrate to control this
  - can significantly change film properties
- **Deposition rate**
  - changes with Ar pressure
  - increases with sputter yield
    - usually increases with high voltage

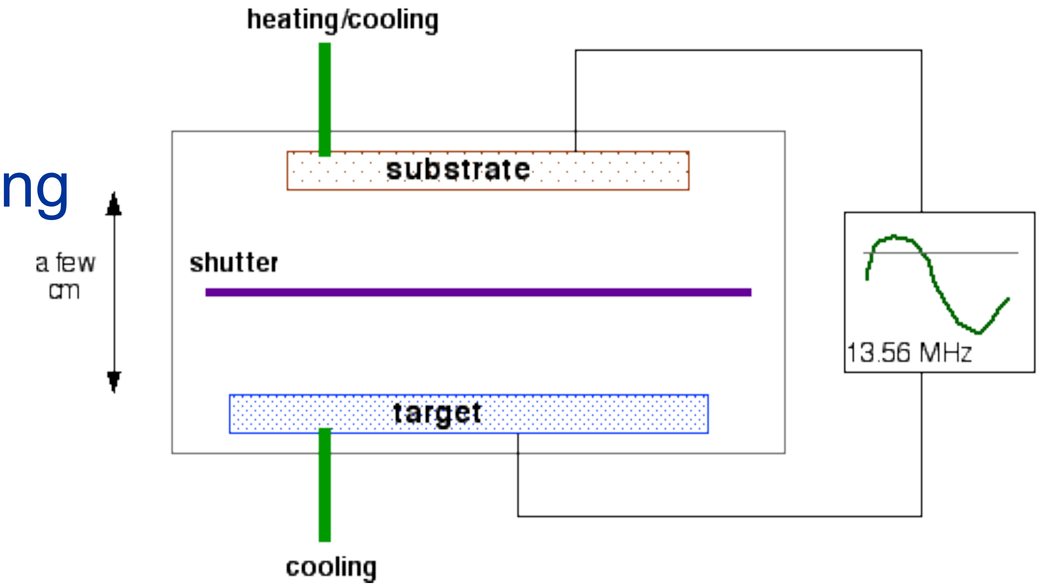
http://www.uccs.edu/~tchriste/courses/PHYS549/549lectures/sputtertech.html

RF Sputtering

- DC sputtering - what about dielectrics?
  - in DC systems, positive charge builds up on the cathode (target) need 10^{12} volts to sputter insulators !!

    avoid charge build up by alternating potential

RF sputtering



http://www.uccs.edu/~tchriste/courses/PHYS549/549lectures/sputtertech.html

RF Sputtering

- frequencies less than about 50 kHz
  - electrons and ions in plasma are mobile
    - both follow the switching of the anode and cathode
  - basically DC sputtering of both surfaces
- frequencies above about 50 kHz
  - ions (heavy) can no longer follow the switching
  - enough electrons to ionize gases (5~30MHz)

Typically 13.56 MHz is used

Advantages of RF Sputtering

- It works well with insulating targets
- High efficiency

  easier to keep plasma going → can operate at lower Ar pressures (1-15 mTorr) → fewer gas collisions → more line of sight deposition

http://aultimut.com/aultimut/details.asp?itemid=11

Magnetron Sputter Deposition

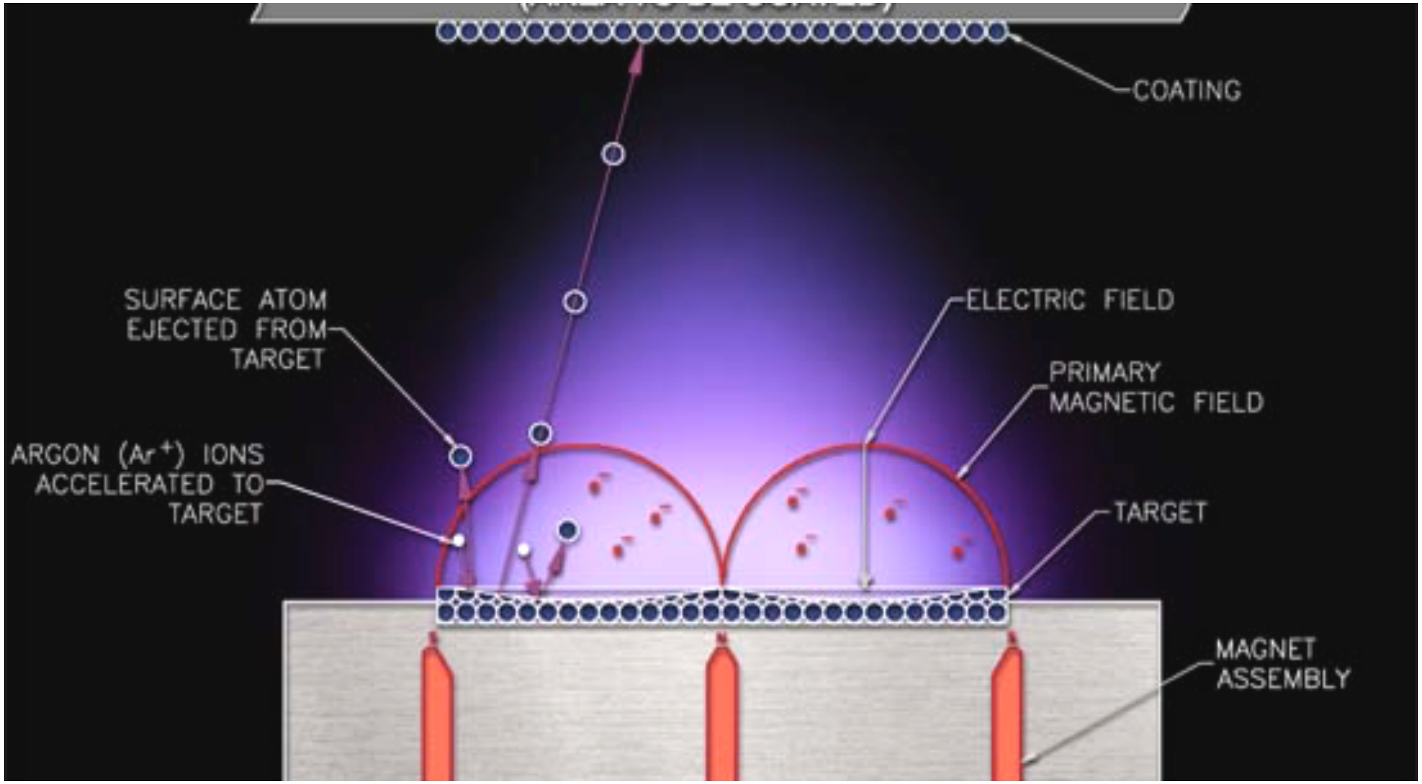
- ❖ Use with DC or RF
- High sputtering efficiency

  increase ionization of Ar

  - Why? Higher sputter rates at lower Ar pressures (down to 0.5 mTorr)

    fewer gas collisions - more line of sight
  - How ? increase probability of electrons striking Ar
    - increase electron path length
    - use electric and magnetic fields

Magnetron Sputtering Principle



This technology uses powerful magnets to confine the "glow discharge" plasma to the region closest to the target plate. That vastly improves the deposition rate by maintaining a higher density of ions, which makes the electron/gas molecule collision process much more efficient.

http://www.angstromsciences.com/technology/sputtering.htm

Advantages of Magnetron Sputtering

- High deposition rate
- Reducing electron bombardment of substrate
- Extending the operating vacuum range
  - ability to operate at lower pressures

The most widely commercially practiced sputtering method

Parameters for Magnetron Sputtering

- **Deposition pressure : 10^{-3} to 0.1 Pa (10^{-5} to 10^{-3} torr)**

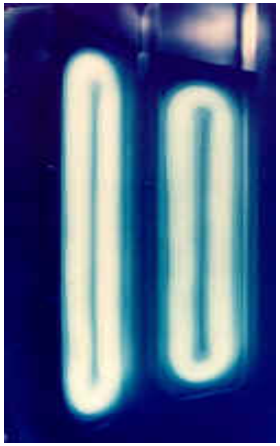
- **Deposition rate : 0.2 ~ 2 µm/min (10 times higher than conventional sputtering)**

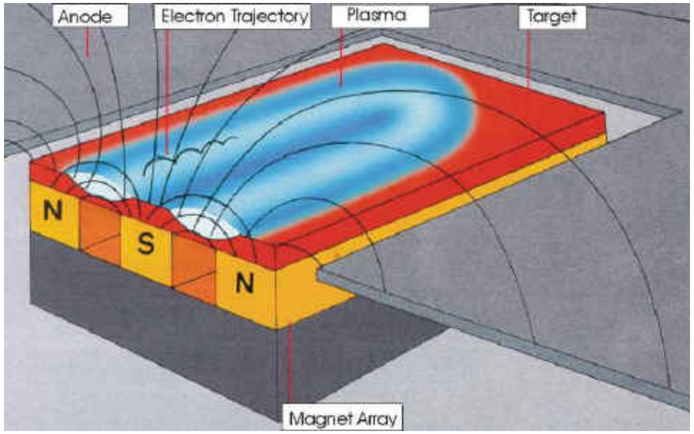
- **Deposition temperature : 100 to 150 ^{o}C**

http://engineering.dartmouth.edu/other/microeng/courses/es194/student/jiaying/sem/II.2.p4.html

Disadvantages for Magnetron Sputtering

- An erosion track in the target
  - This leads to poor efficiency of sputtering yield versus target volume compared to non-magnetron sputtering
- Non-uniform removal of particles from target result in non-uniform films on substrate





http://www.mse.ncsu.edu/WideBandgaps/classes/MAT%20751%20S03/Sputtering/Magnetron_Ihlefeld.pdf

Reactive Sputtering

Sputtering metallic target in the presence of a reactive gas mixed with inert gas (Ar)

- *A mixture of inert +reactive gases used for sputtering*

oxides – Al_2O_3, SiO_2, Ta_2O_5 (O_2)
nitrides – TaN, TiN, Si_3N_4 (N_2, NH_3)
carbides – TiC, WC, SiC (CH_4, C_2H_4, C_3H_8)

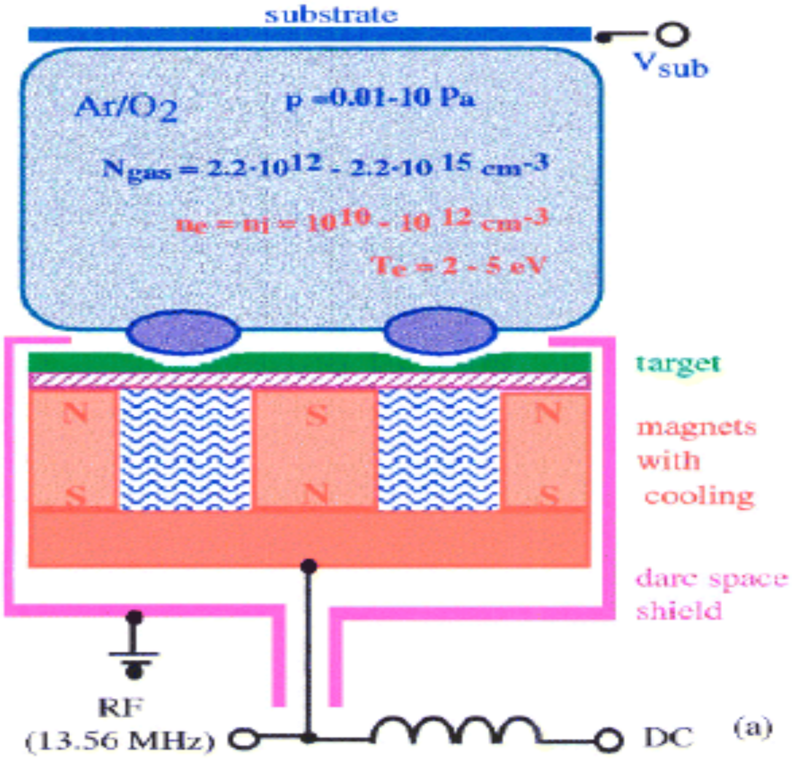
Reactive Sputtering (Cont.)

- chemical reaction takes place on substrate and target
- can poison target if chemical reactions are faster than sputter rate
- adjust reactive gas flow to get good stoichiometry without incorporating excess gas into film

Reactive Magnetron Sputtering
Zinc Oxide Thin films

- Zinc oxide is one of the most interesting II/IV compound semiconductors It has been investigated extensively because of its interesting electrical, optical and piezoelectric properties

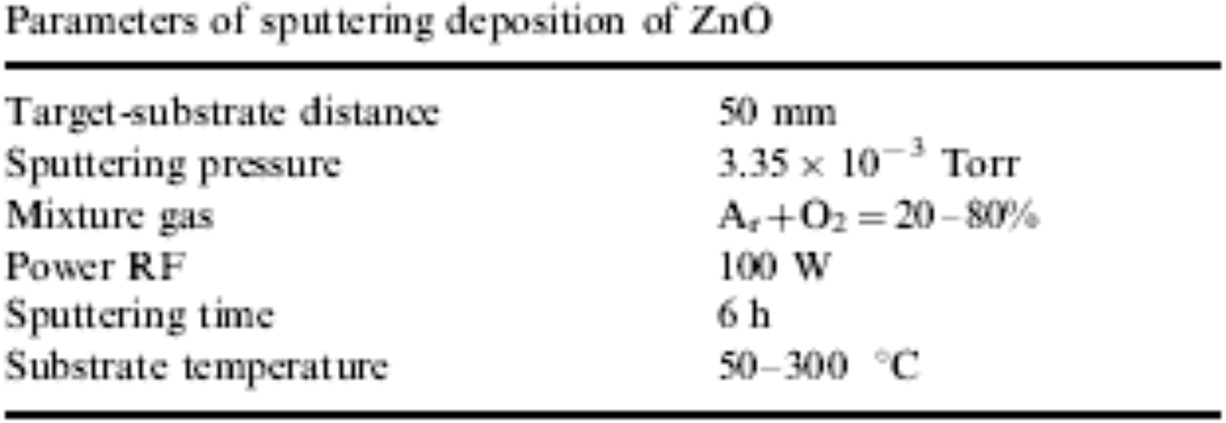
Reactive sputtering is the best technique for Zinc Oxide deposition.



R. Ondo-Ndong , F. Pascal-Delannoy, A. Boyer, A. Giani, A. Foucaran, Materials Science and Engineering B97 (2003) 68 /73

Process Parameters

Quality of the film dependents on deposition conditions, such as substrate temperature, deposition power, deposition pressure and argon–oxygen flow.



Parameters of sputtering deposition of ZnO

Target-substrate distance	50 mm
Sputtering pressure	3.35×10^{-3} Torr
Mixture gas	$A_r + O_2 = 20-80\%$
Power RF	100 W
Sputtering time	6 h
Substrate temperature	50–300 °C

Walter Water, Sheng-Yuan Chu,* Materials Letters 55 (2002) 67– 72

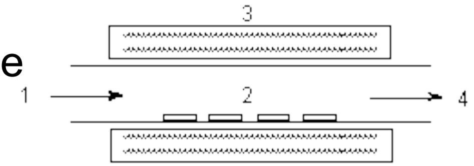
Energy sources and Reactor types

Thermal Energy

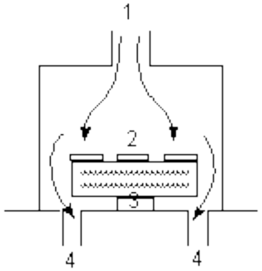
resistive heating - tube furnace
quartz tungsten halogen lamp (very good heat source) - radiant heating
radio-frequency - inductive heating
laser as thermal energy source

Photo Energy

UV-visible light
laser as photo energy source

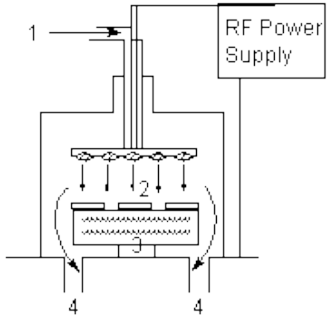


Horizontal Hot-Wall Reactor

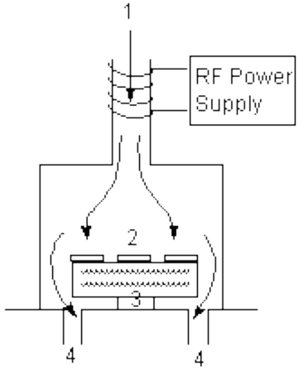


Vertical Cold-Wall Reactor

1: precursor in
2: substrates
3: heater or furnace
4: exhaust



Parallel Plate Plasma Reactor

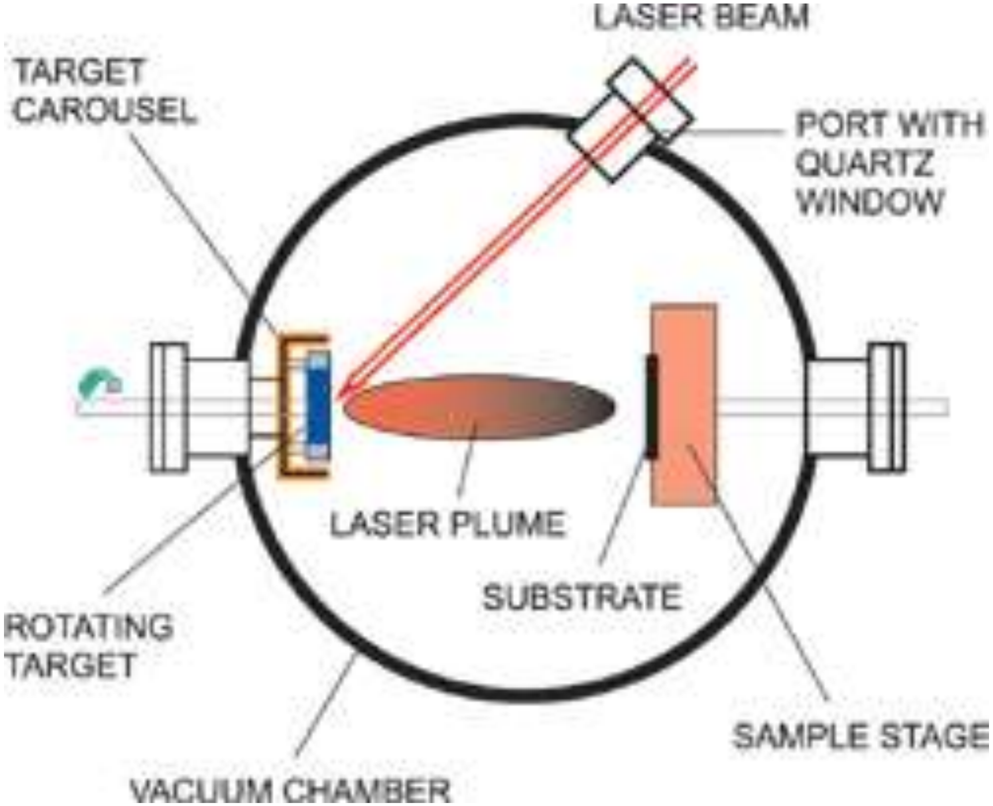


Inductive Tube
Remote-Plasma Reactor

Laser ablation

- Pulsed laser deposition (PLD).
- Ultraviolet (UV) light (~200 nm – 400 nm).
- High energy (> 1 J/cm^2).
- Pulsed, not continuous, laser beam.
- Excimer laser: Gas laser, F_2 (157 nm), ArF (193 nm), KrCl (222 nm), KrF (248 nm), XeCl (308 nm), XeF (351 nm).
- Nd^{3+} :YAG laser: Solid state laser, Nd ions, yttrium aluminum garnet (YAG), 1064 nm, frequency doubled to 532 nm, mixed with 1064 nm to produce 355 nm or 266 nm.

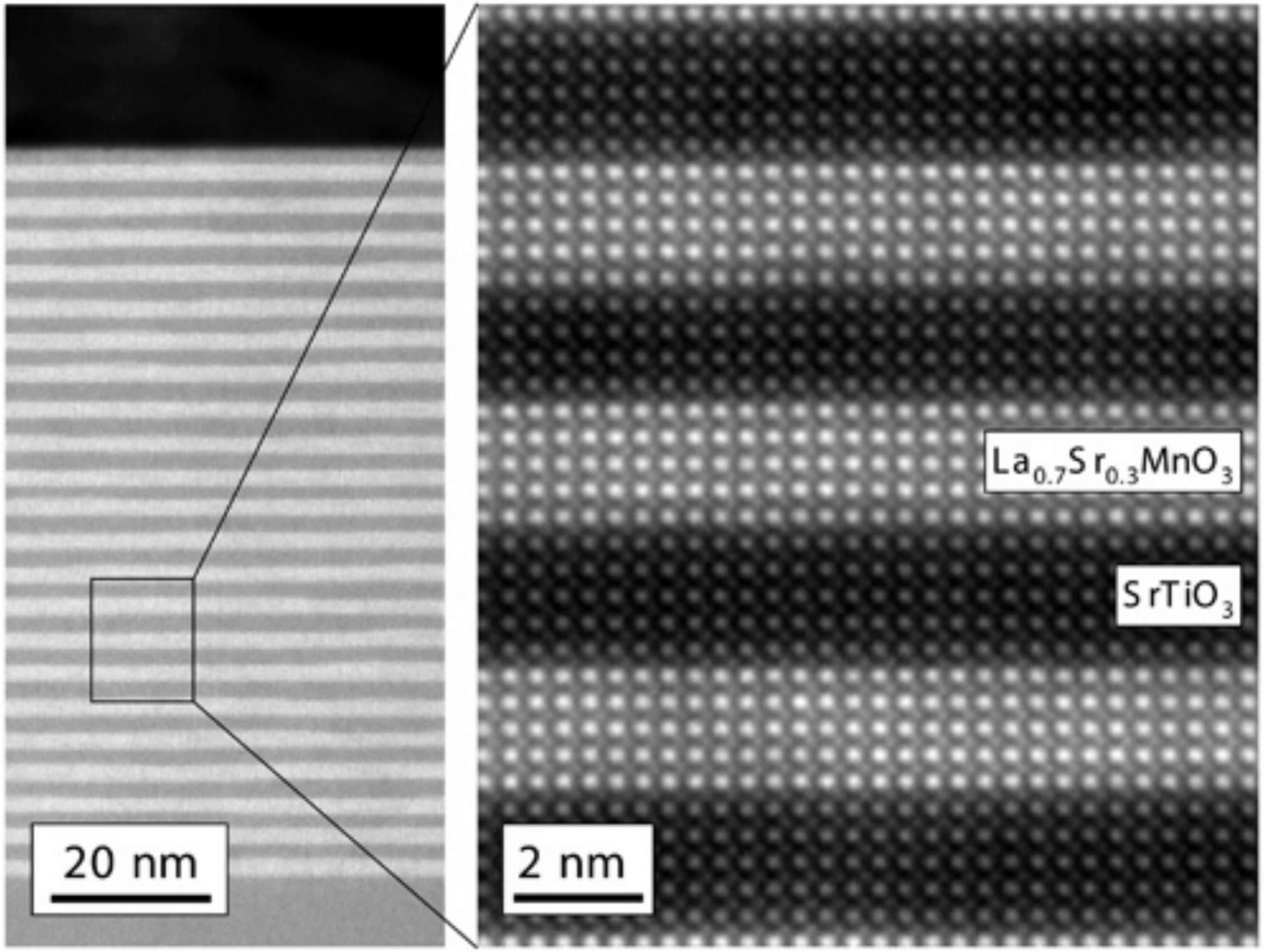
Pulsed Laser Deposition



PLD system

- Lasers: Excimer laser. 1 to 100 Hz repetition rates, 15 to 50 ns pulse duration.
- Optics: UV windows, mirrors, beam splitters.
- Vacuum chamber, pumps and gauges: High vacuum standard equipments.
- Gas flow: Oxygen.
- Target manipulation: Rotation.
- Substrate holder and heater.

LMO/STO superlattice



Chemical vapor deposition

- Reactive carrier gases.
- Transport precursors of desired materials to the substrate surface.
- Gases react with other gases or decompose to produce stable reaction products and deposit on the substrate.
- Most versatile deposition techniques.
- Wide range of chemical reactions, reactants, and applications.

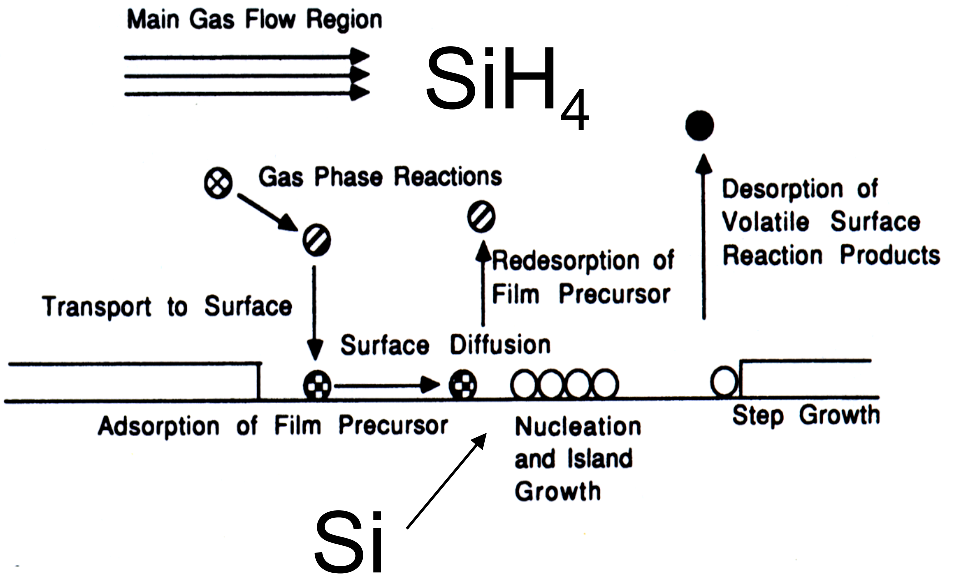
Films grown by CVD

- Single-crystalline thin films.
- Polycrystalline thin films.
- Amorphous thin films.
- Semiconductors (IV, III-V, II-VI), metals, dielectric, superconductors.
- Microelectronics, optoelectronics, hard and protective coatings.

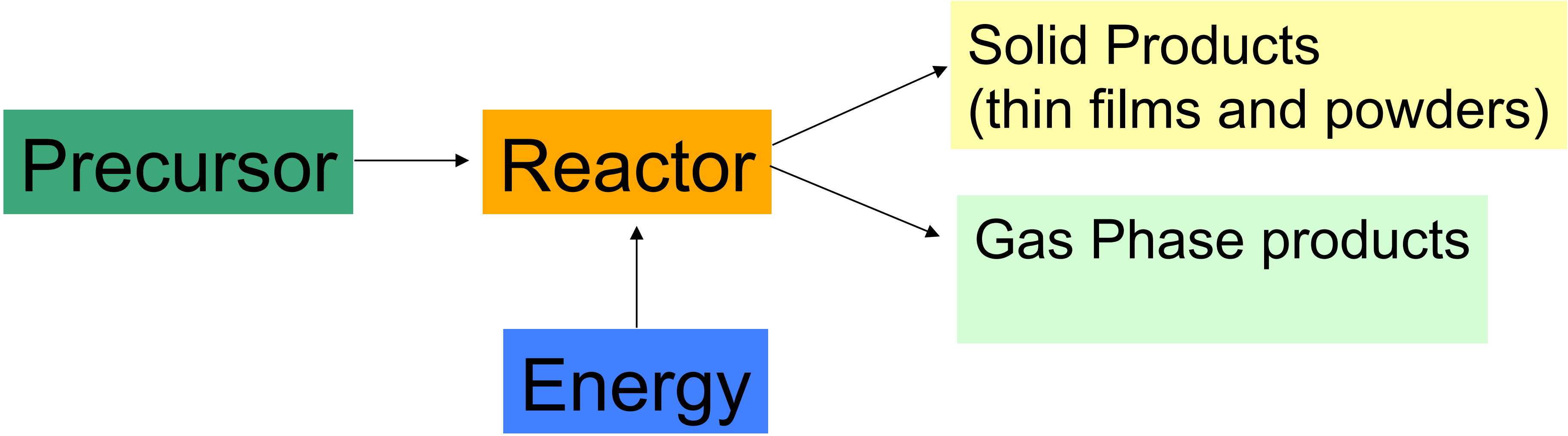
Chemical vapor deposition: reaction mechanisms

- Mass transport of the reactant in the bulk
- Gas-phase reactions (homogeneous)
- Mass transport to the surface
- Adsorption on the surface
- Surface reactions (heterogeneous)
- Surface migration
- Incorporation of film constituents, island formation
- Desorption of by-products
- Mass transport of by-produccts in bulk

CVD: Diffusive-convective transport of depositing species to a substrate with many intermolecular collisions-driven by a concentration gradient



Chemical Vapor Deposition



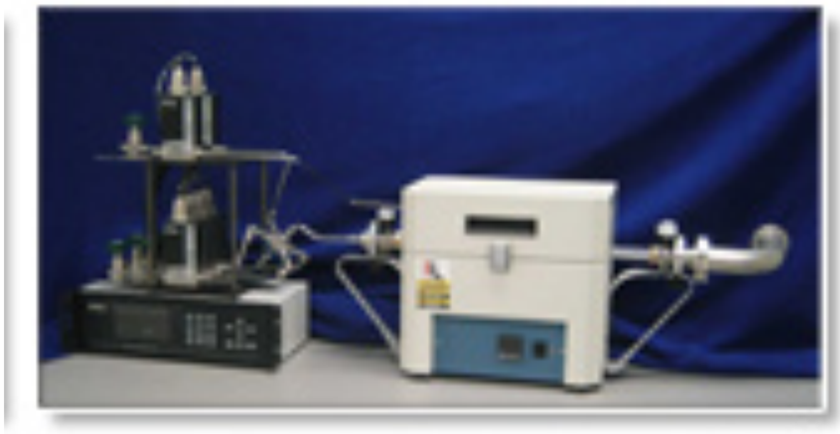
Precursor

Reactor

Energy

Solid Products
(thin films and powders)

Gas Phase products



Precursor Considerations

Volatility

vapor pressure - simple molecules with high vapor pressure are rare
determined by molecular weight and molecularity (degree polymerized) - result of structure and bonding
control - temperature, valving

Stability, Reactivity, and Safety

bond strength, bond dissociation energy - affects process temperature and film composition (purity)
thermal stability in storage and delivery into the reactor
reactivity of the precursor and byproducts towards other substances (including biological objects like us)

Single-Source Precursor

providing more than one element into the film
simpler delivery system
uniform elemental distribution at atomic level possible
limited composition range

Common Precursors

hydrides: MHx -
SiH4, GeH4, AlH3(NMe3)2, NH3, PH3 ...

halides: MXy -
TiCl4, TaCl5, MoF6, WF6, ...

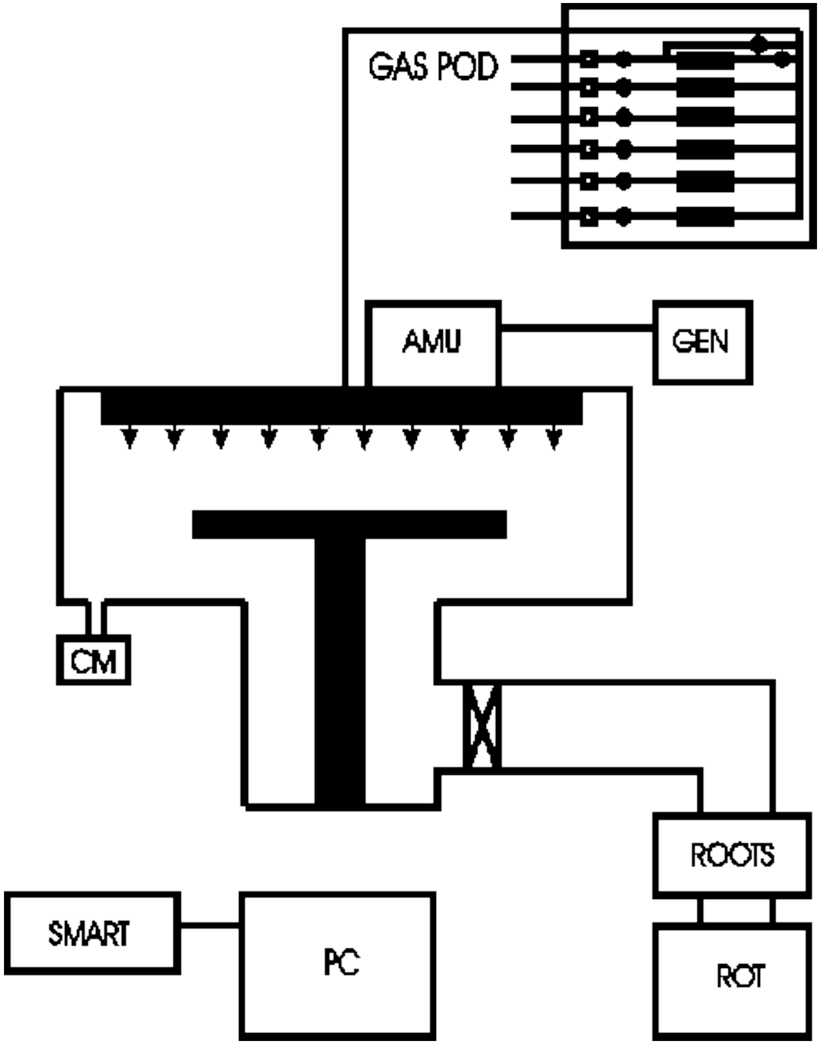
metal-organics -
metal alkyls: AlMe3, AliBu3, Ti(CH2tBu)4 ....
metal alkoxides: Ti(OiPr)4, [Cu(OtBu)]4 ....
metal dialkylamides: Ti(NMe2)4, Cr(NEt2)4 ....
metal diketonates: Cu(acac)2, Pt(hfac)2 ....
metal carbonyls: Fe(CO)5, Ni(CO)4 ....
others: complexes with alkene, allyl, cyclopentadienyl, ... ligands
many precursors have mixed ligands

http://chiuserv.ac.nctu.edu.tw/~htchiu/cvd/essential.html

Plasma-enhanced CVD

- Use plasma to ionize and dissociate gases.
- Enhance growth rate.
- Lower temperature, so SiO_2, Si_3N_4, etc. can be deposited at temperature <350^{o}C.
- Low pressure.

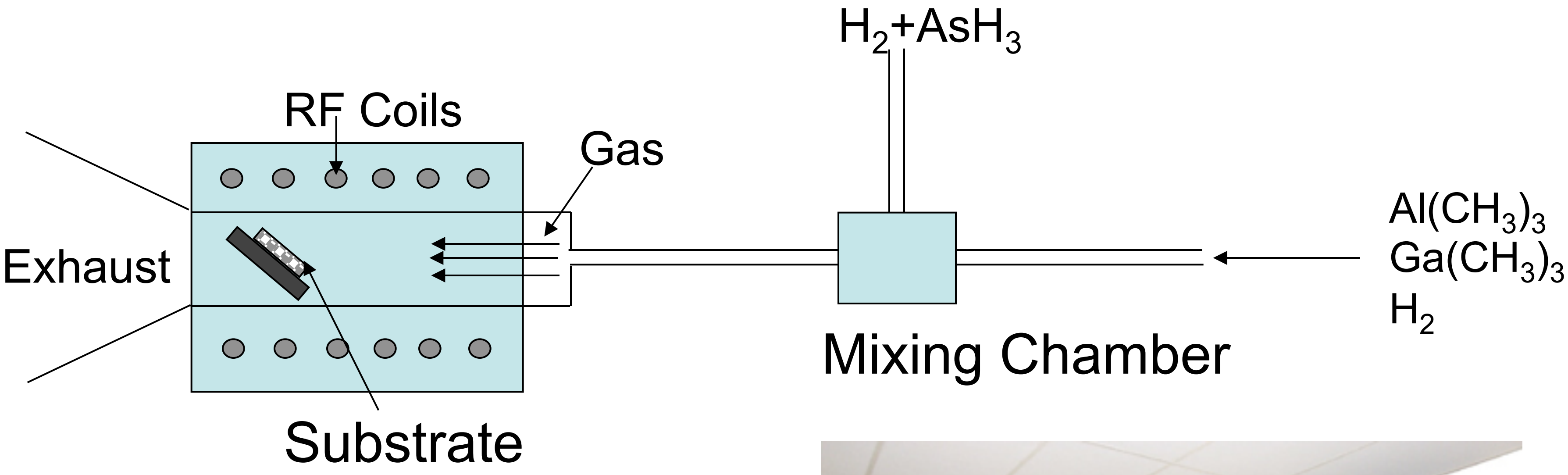
PECVD



MOCVD

- Thermal, glow discharge, ultraviolet radiation.
- Metalorganic compound (MO) gases or liquids.
- Epitaxial growth.
- Semiconductors (III-V, II-VI), high Tc superconductors, dielectric and metal films.

MOCVD



$$Ga(CH_3)_3 + AsH_3 \Rightarrow 3CH_4 + GaAs$$

Atomic Layer Deposition

- Surface controlled for epitaxial growth of single crystal.
- Originally designed for compound semiconductors, II-VI, III-V, oxides, nitrides.
- Epitaxy: Sequential saturated surface reactions to form a monolayer in each sequence.
- Release or exchange of ligands for saturation in each sequence.

ALD Process and Equipments

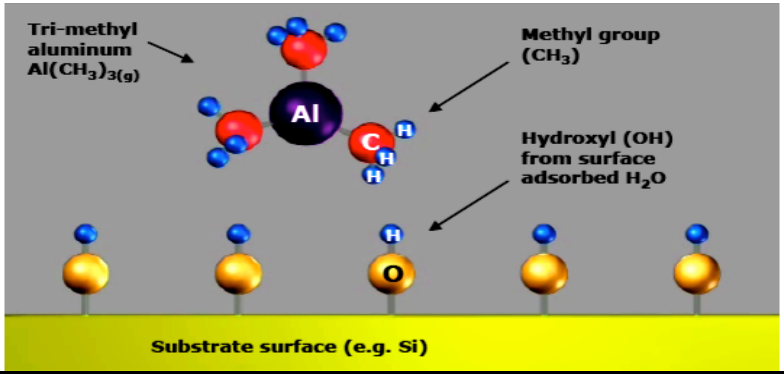
- Releases sequential precursor gas pulses to deposit a film one layer at a time.
- A first precursor gas is introduced into the process chamber and produces a monolayer of gas on the wafer surface. Then a second precursor of gas is introduced into the chamber reacting with the first precursor to produce a monolayer of film on the wafer surface.

Two fundamental mechanisms:

  - *Chemisorption saturation process*
  - *Sequential surface chemical reaction process*

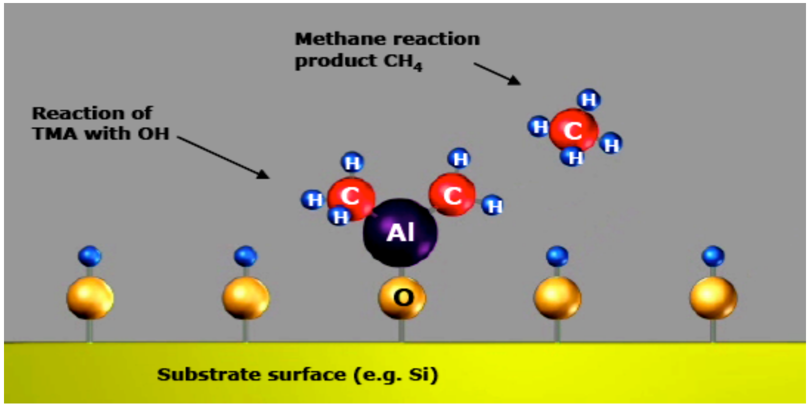
Ref: "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. <http://www.cambridgenanotech.com/>.

Example: ALD cycle for Al_2O_3 deposition



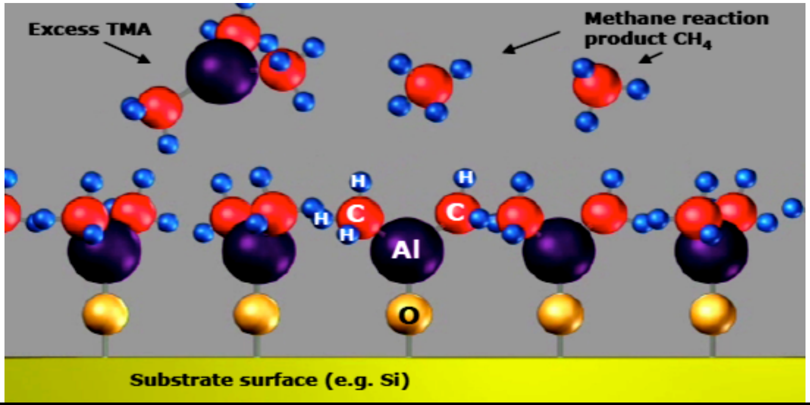
In air H_2O vapor is adsorbed on most surfaces, forming a hydroxyl group. With silicon this forms: $Si\text{-}O\text{-}H_{(s)}$

After placing the substrate in the reactor, Trimethyl Aluminum (TMA) is pulsed into the reaction chamber.

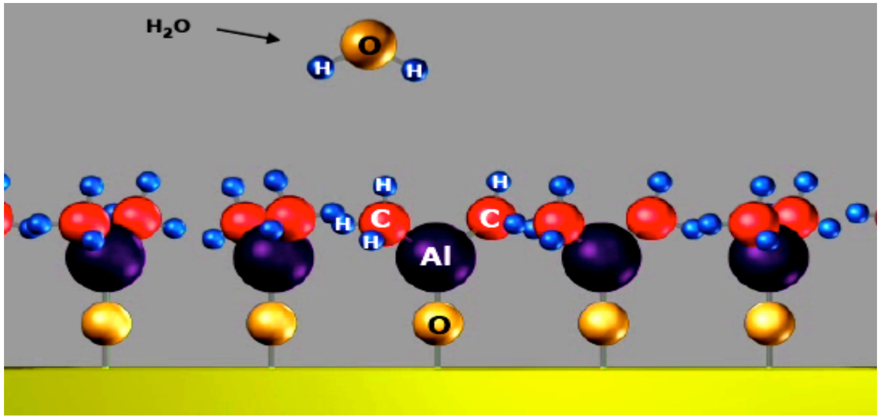


Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product

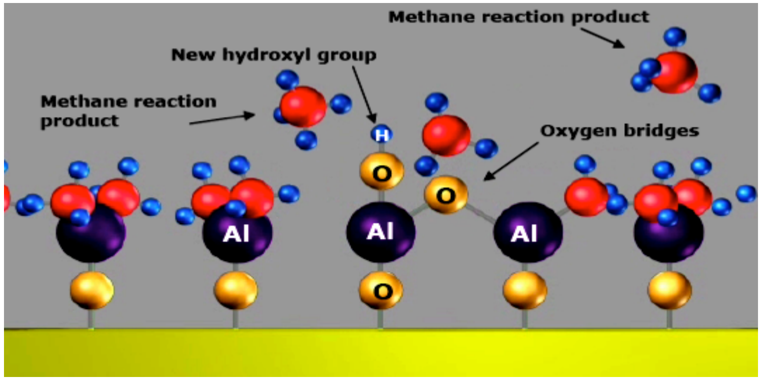
$$Al(CH_3)_{3\,(g)} + :Si\text{-}O\text{-}H_{\,(s)} \longrightarrow :Si\text{-}O\text{-}Al(CH_3)_{2\,(s)} + CH_4$$



Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, until the surface is passivated. TMA does not react with itself, terminating the reaction to one layer. This causes the perfect uniformity of ALD. The excess TMA is pumped away with the methane reaction product.

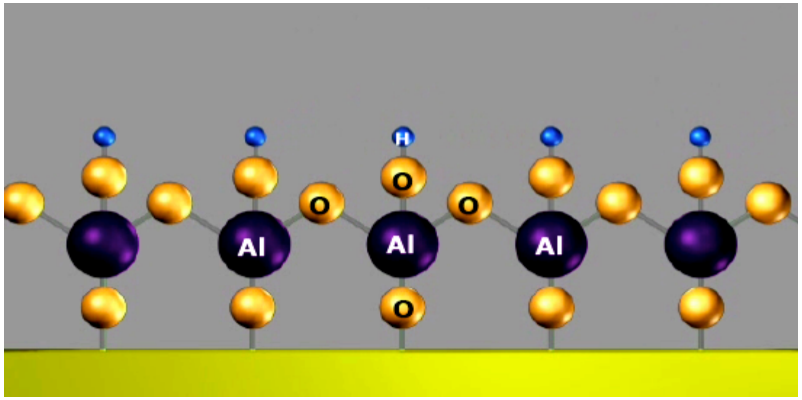


After the TMA and methane reaction product is pumped away, water vapor (H_2O) is pulsed into the reaction chamber.



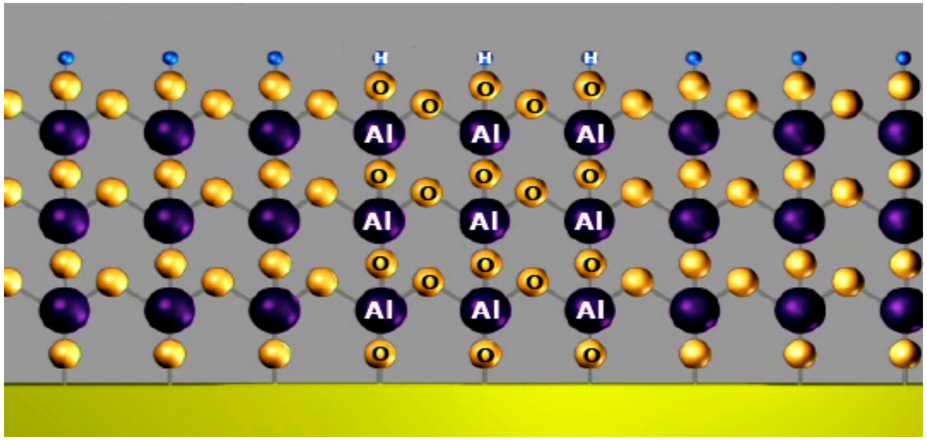
H_2O reacts with the dangling methyl groups on the new surface forming aluminum-oxygen (Al-O) bridges and hydroxyl surface groups, waiting for a new TMA pulse. Again metane is the reaction product.

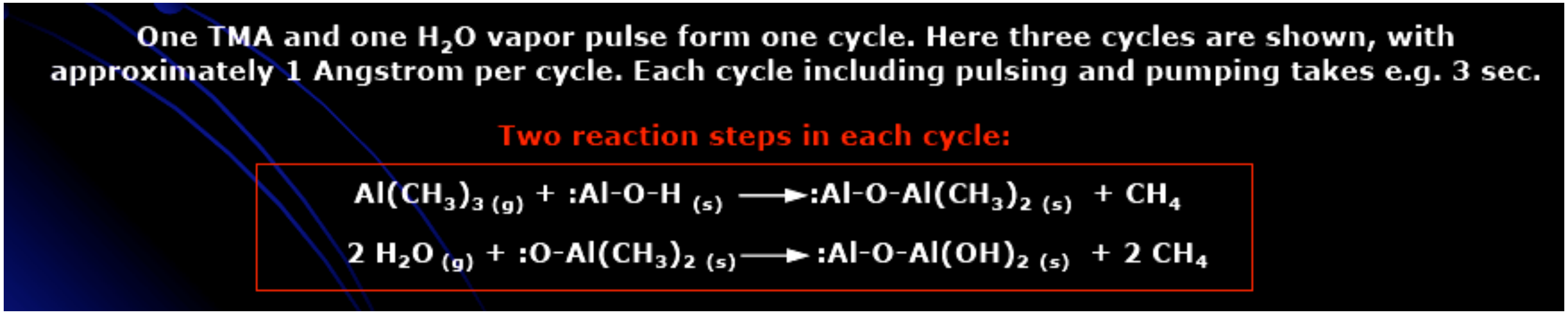
$$2\ H_2O_{(g)} + :Si\text{-}O\text{-}Al(CH_3)_{2\ (s)} \longrightarrow :Si\text{-}O\text{-}Al(OH)_{2\ (s)} + 2\ CH_4$$



The reaction product methane is pumped away. Excess H_2O vapor does not react with the hydroxyl surface groups, again causing perfect passivation to one atomic layer.

ALD cycle for Al_2O_3 deposition (after 3 cycles)





One TMA and one H_2O vapor pulse form one cycle. Here three cycles are shown, with approximately 1 Angstrom per cycle. Each cycle including pulsing and pumping takes e.g. 3 sec.

Two reaction steps in each cycle:

$$Al(CH_3)_{3\,(g)} + :Al\text{-}O\text{-}H_{\,(s)} \longrightarrow :Al\text{-}O\text{-}Al(CH_3)_{2\,(s)} + CH_4$$

$$2\,H_2O_{\,(g)} + :O\text{-}Al(CH_3)_{2\,(s)} \longrightarrow :Al\text{-}O\text{-}Al(OH)_{2\,(s)} + 2\,CH_4$$

Ref: "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. <http://www.cambridgenanotech.com/>.

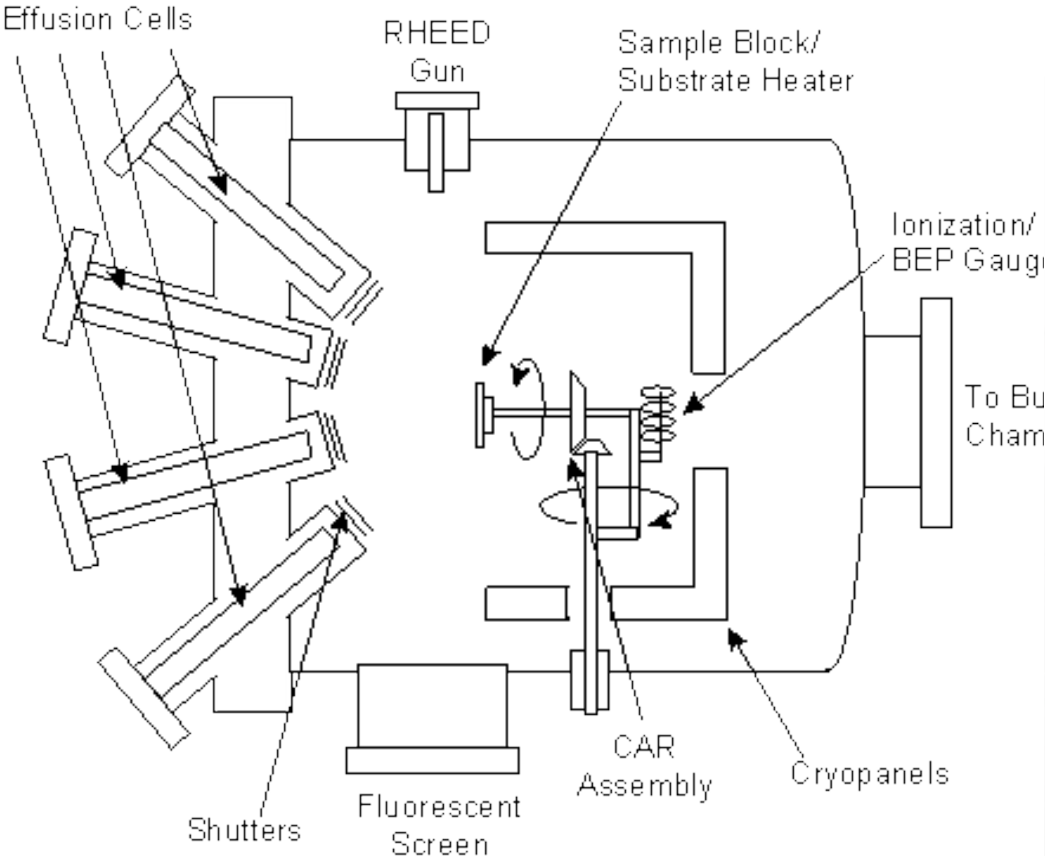
Atomic Layer Deposition

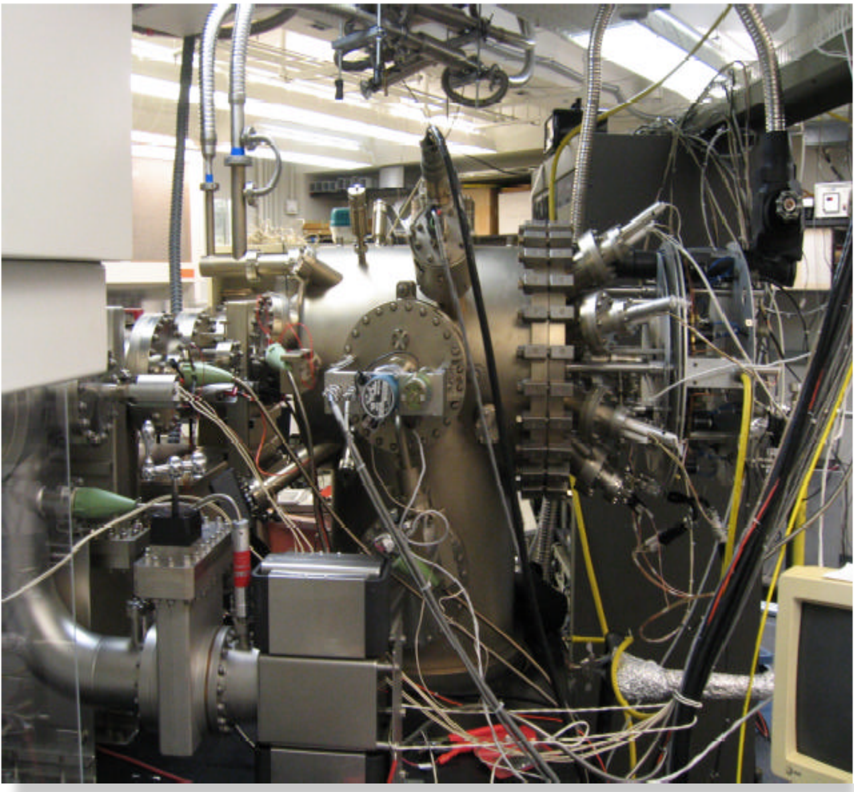
- Advantages
    - Stoichiometric films with large area uniformity and 3D conformality.
    - Precise thickness control.
    - Low temperature deposition possible.
    - Gentle deposition process for sensitive substrates.
- Disadvantages
    - Deposition Rate slower than CVD.
    - Number of different material that can be deposited is fair compared to MBE.

Molecular beam epitaxy

- Epitaxy: Continuation of crystal structure from the substrate to the film.
- Single crystalline contaminant-free film.
- Single atomic layer (monolayer) growth.
- Small mismatched lattice constant (<1%).
- Ultrahigh vacuum: $<5\times10^{-11}$ torr.
- Non-epitaxy films: amorphous or polycrystalline.

Molecular Beam Epitaxy





MBE deposition system

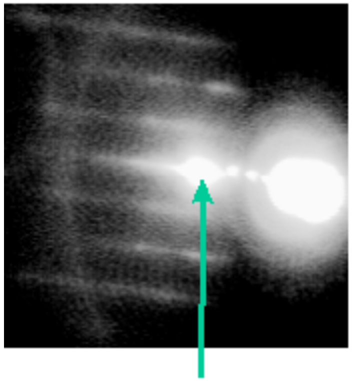
- Load lock for substrate loading & unloading.
- Liquid nitrogen shroud to cool the wall.
- Substrate heating: clean surface.
- Film growth: ultrahigh vacuum, shutters to control the flux, in-situ analysis and thickness monitor (RHEED) to control the deposition rate.

RHEED

- Reflection high energy electron diffraction.
- High energy: > 10 KeV.
- Small (grazing) angle incidence (<3°).
- Low depth penetration: < 100 A.
- Lateral ordered structure: Surface structure symmetry, lattice constant.

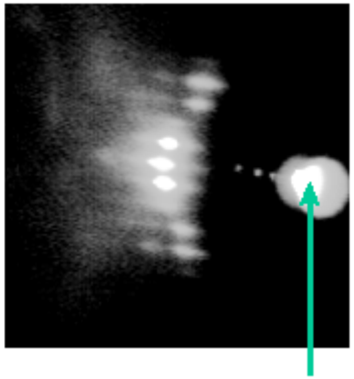
RHEED

‘2 x’ Pattern

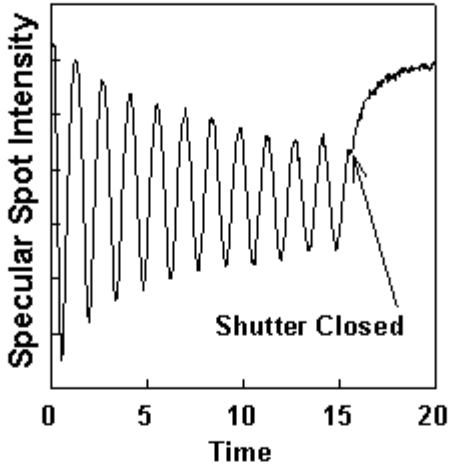


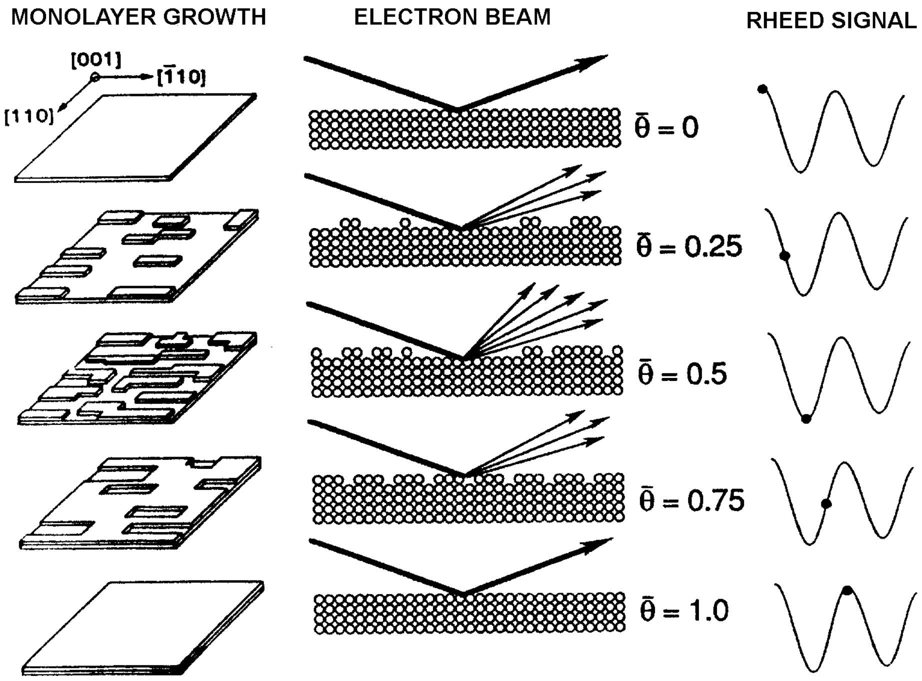
Specular Reflection

‘4 x’ Pattern



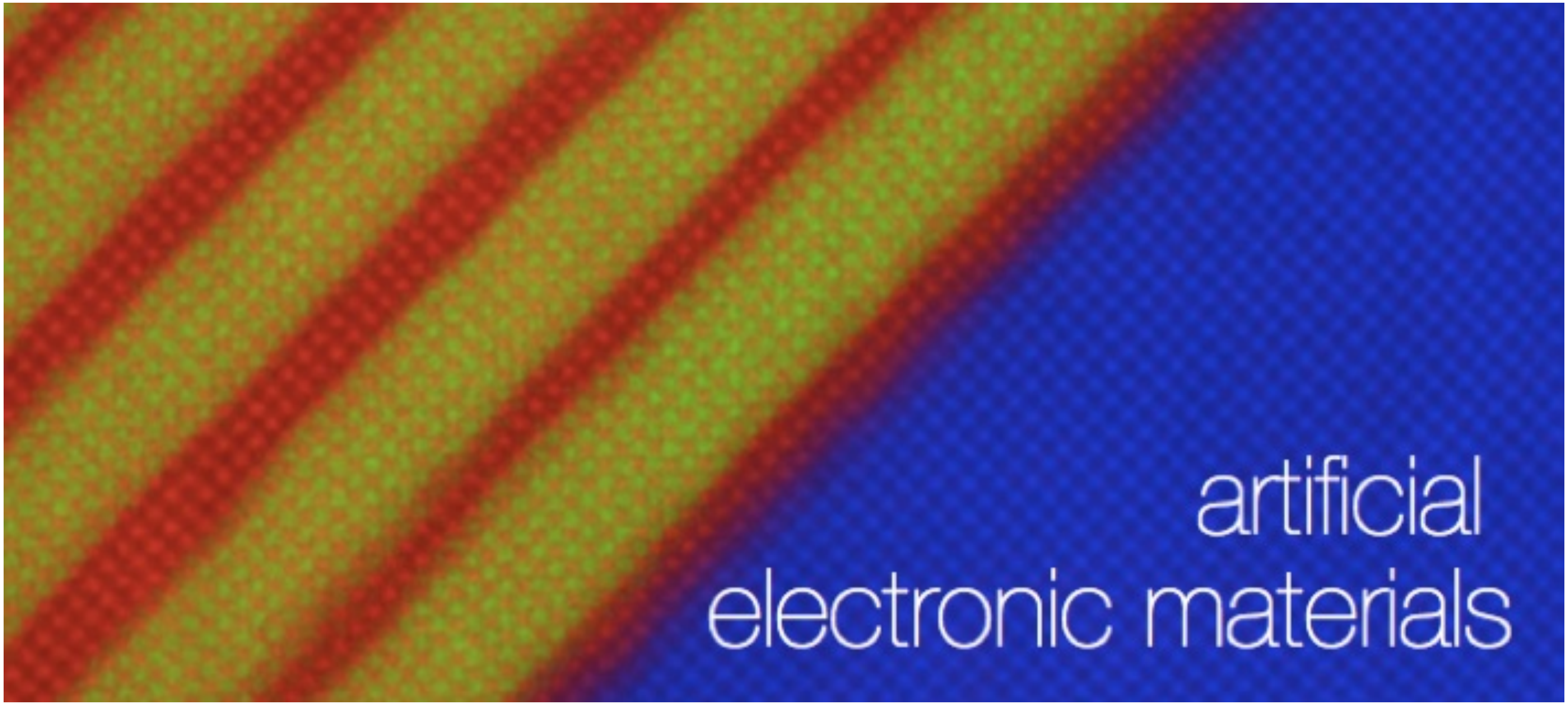
Straight-Through Beam





MBE film growth

- Single crystalline substrate with lattice matching to the film.
- Heating (500^{o}C to 550^{o}C for GaAs, 700^{o}C to 900^{o}C for Si) to remove the surface contamination.
- Layer by layer growth: controlled by high speed shutters and thickness monitor (or RHEED).


artificial
electronic materials