# Midterm 2 Review

Sputtering

- In sputtering, the target material and the substrate is placed in a vacuum chamber.
- A voltage is applied between them so that the target is the cathode and the substrate is attached to the anode.
- A plasma is created by ionizing a sputtering gas (generally a chemically inert, heavy gas like Argon).
- The sputtering gas bombards the target and sputters off the material we'd like to deposit.

-V

Target (cathode)

Plasma

Substrates

Anode

Sputtering gas
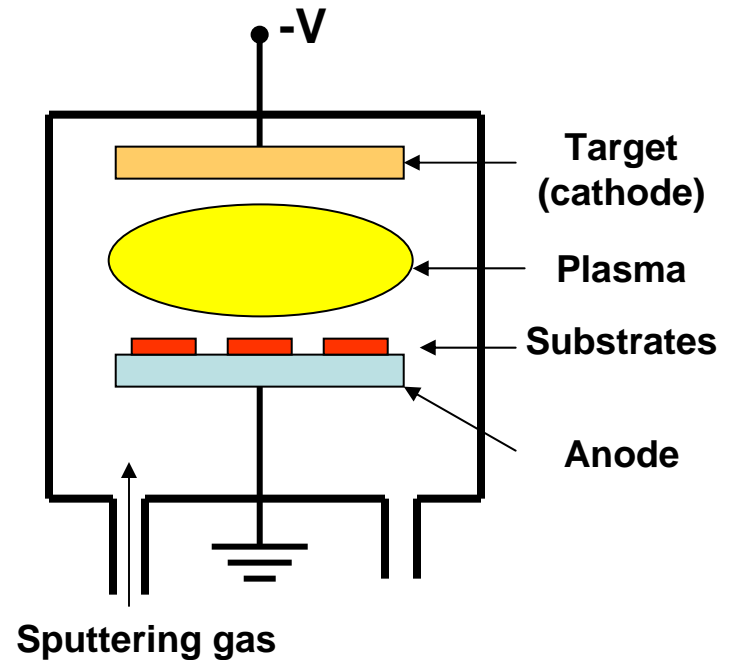
Generating and Controlling the Plasma

- Ions can be generated by the collision of neutral atoms with high energy electrons.
- The interaction of the ions and the target are determined by the velocity and energy of the ions.
- Since ions are charged particles, electric and magnetic fields can control these parameters.
- The process begins with a stray electron near the cathode is accelerated towards the anode and collides with a neutral gas atom converting it to a positively charged ion.
- The process results in two electrons which can then collide with other gas atoms and ionize them creating a cascading process until the gas breaks down.
- The breakdown voltage depends on the pressure in the chamber and the distance between the anode and the cathode.
- At too low pressures, there aren't enough collisions between atoms and electrons to sustain a plasma.
- At too high pressures, there so many collisions that electrons do not have enough time to gather energy between collisions to be able to ionize the atoms.

$$e^- + A \rightarrow 2e^- + A^+$$
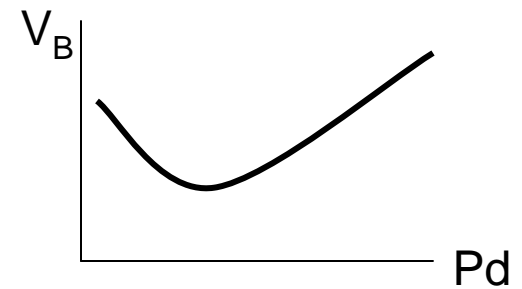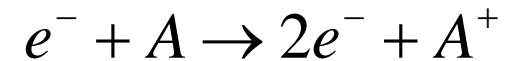
How Ions Sputter Atoms

- When ions collide with surface atoms on the target, the energy transfer can knock some of these atoms off the surface.

- The key principle is energy and momentum conservation.

- In any collision, momentum is conserved.

- If the collision is elastic, kinetic energy is also conserved.

- The energies required for sputtering are much higher than lattice bonding or vibrational energies (which are the causes of inelastic interactions), therefore sputtering collisions can be considered elastic.

Various Sputtering Regimes

- ## Single Knock-On
  - The initial ion-surface collision sets target atoms in motion. If enough energy is transferred, binding forces can be overcome. Typical threshold energies are in the 10 - 30 eV range.

- ## Linear Collision Cascade
  - At higher ion energies (100 eV - 10 keV) recoil is minimal and a cascading effect produces sputtering.
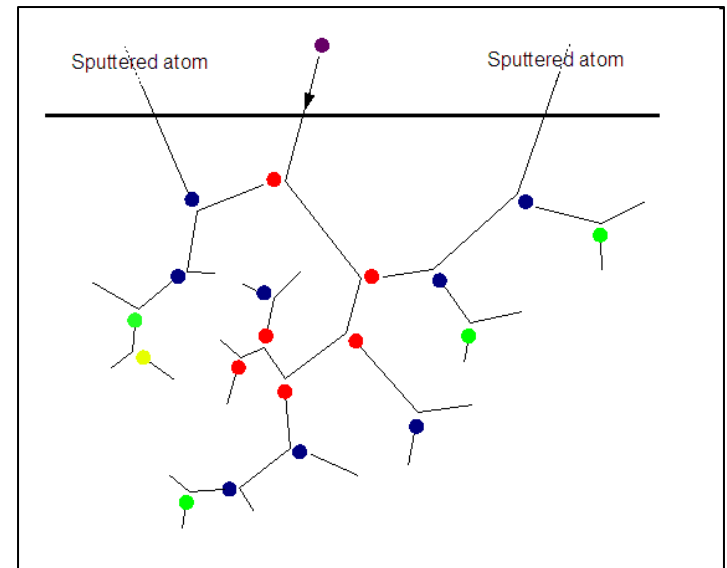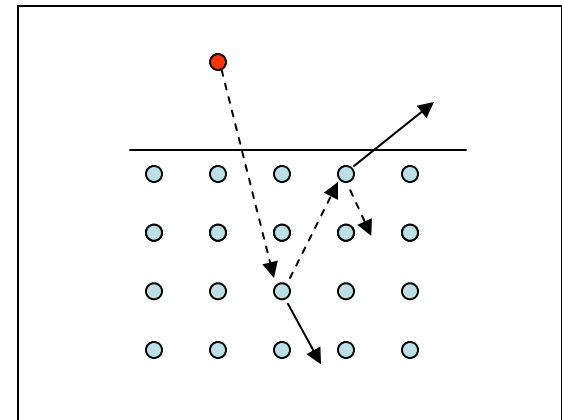
Sputter Yield

$$S = \frac{\text{Number of sputtered atoms}}{\text{Number of incident ions}}$$

- **S depends on**
  - type of target atom
  - binding energy of target atoms
  - relative mass of ions and atoms
  - incident ion energy
  - angle of incidence of ions
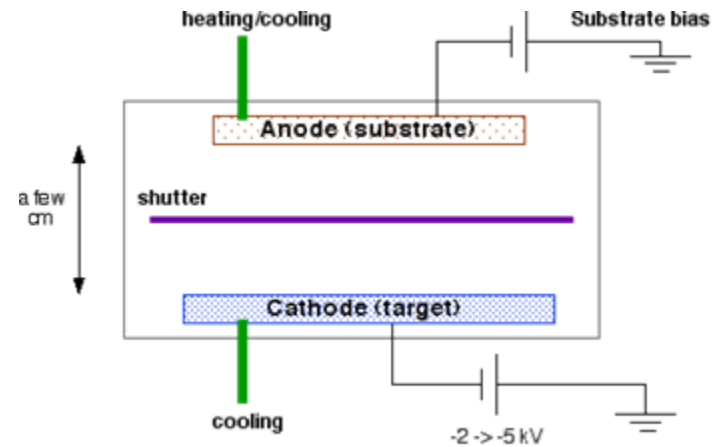- **S can range from 0.1 to 10**
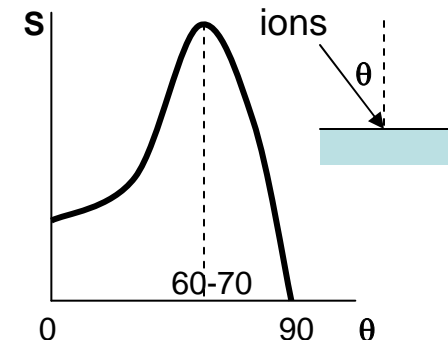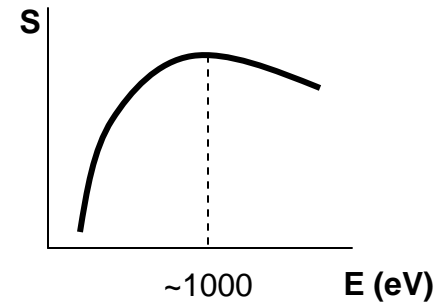
Deposition

- Sputtered atoms from the target make their way on to the substrate through diffusion.
- Ions and neutralized gas atoms may also embed on the substrate as impurities.
- The ions incident on the substrate may also re-sputter the surface.
- Chemical reactions may occur.
- The depostion rate is proportional to the sputtering yield.
- An optimum pressure exists for high deposition rates.
  - Higher pressure means more collisions and ions.
  - Lower pressure means less scattering.
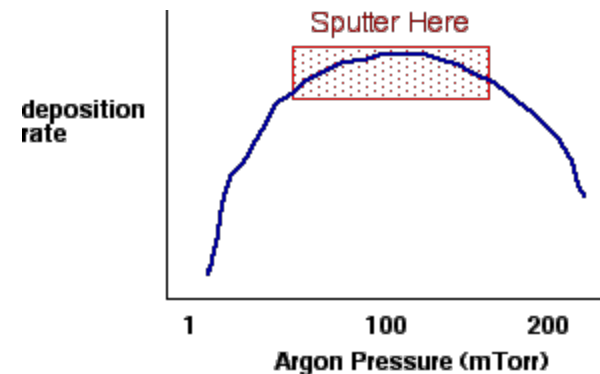
DC Sputtering

- Initially pump system down to 10^{-6} – 10^{-7} Torr for purity.
- Then let in controlled amount of the gas to be ionized (generally Argon).
- Eventually the chamber pressure will be around 1 – 100 mTorr.
  - This number is determined by the pressure required to have a sustainable plasma given the chamber dimensions.
- The main control is the energy of the ions.
  - They need to be in the right range for sputtering.

heating/cooling   Substrate bias

a few cm

shutter

Anode (substrate)

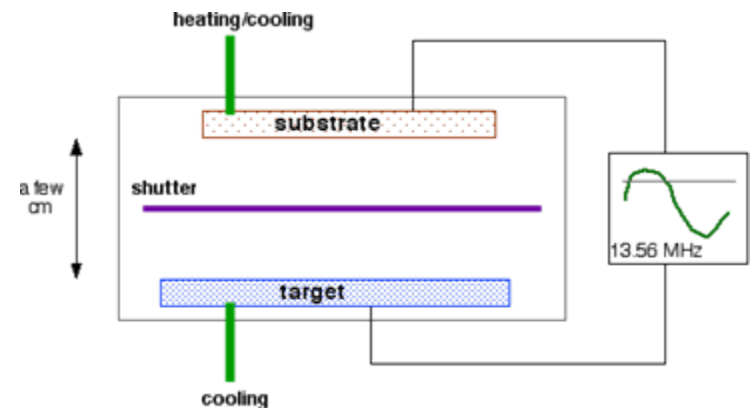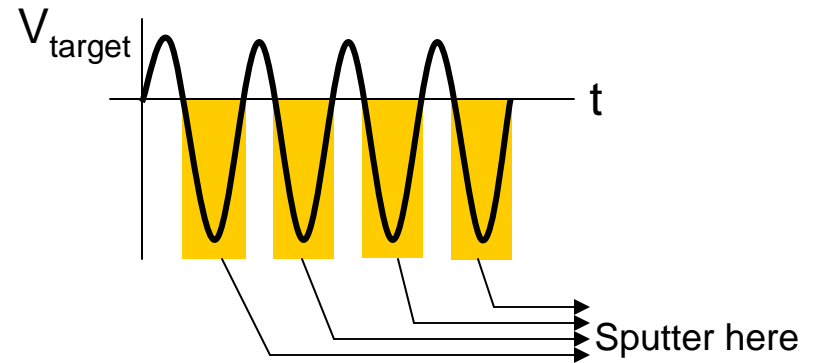Cathode (target)

cooling

-2 -> -5 kV

The Major Limitation of DC Sputtering

- Suppose instead of a metal, we want to sputter an insulator like quartz.

- Due to the high resistivity of the target running an appreciable current through would require an impossibly large voltage ($\sim 10^{12}$ V).

- The lack of a current will extinguish the plasma and stop the process.

- Practically this limits DC sputtering to materials of a resistivity less than 10^6 Ω.cm (no insulators).
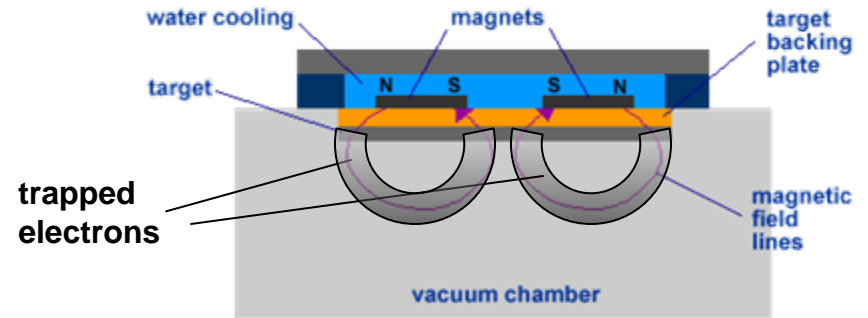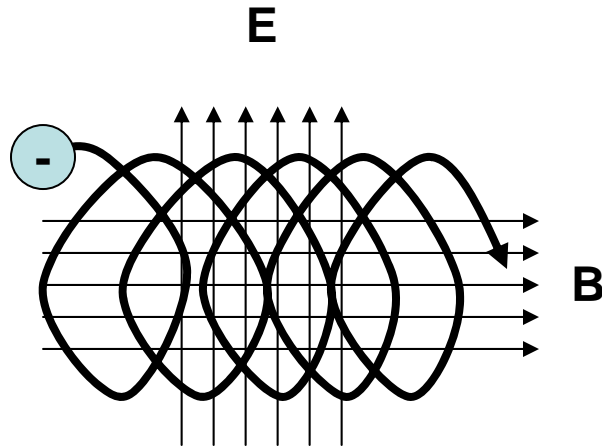
RF Sputtering

- Instead of applying a DC voltage to the cathode, apply a voltage oscillating at radio frequency (RF), typically around 13.5 MHz.
- At these frequencies, the impedance of the system is lower and the required voltage is lowered.
- Also electrons can react faster to these frequencies than the heavier ions and therefore electron flow through the anode is larger than ion flow through the cathode. This will cause the voltage to negatively self-bias. In practice, the voltage is negative ~99.9% of the time enabling sputtering.
- The RF peak to peak voltage is around 1000V, electron densities are around 10^9-10^{11} cm^{-3} and the chamber pressure is 0.5 - 10 mTorr
- On the positive cycle, electrons are attracted to the cathode, creating a negative bias (think of it as replenishing the negative charge on the target surface).
- On the negative cycle ion bombardment continues.

V_{target}

t

Sputter here

heating/cooling

substrate

a few cm

shutter

13.56 MHz

target

cooling

RF Sputtering Details

- By avoiding a constant negative voltage on the cathode, ion buildup is prevented for insulating targets.
- Can operate at lower pressures while still sustaining a plasma.
- RF plasmas tend to fill the chamber as opposed to DC plasmas which are confined to the cathode.
- Normally both the target and substrate should sputter. This can be overcome by making the target area small compared to the substrate.
- While any type of film can be RF sputtered, deposition rates are still low.
- Applying RF power is not so simple, power supplies are expensive and additional circuitry is needed.

The Magnetron

E

B

water cooling   magnets   target backing plate

target

trapped electrons

magnetic field lines

vacuum chamber

- Plasma generation is an inefficient process. If we can confine the electrons near the cathode, their high density will increase the plasma density and make for more efficient sputtering.
- If the electric and magnetic fields are crossed (perpendicular to each other), then the trajectory of the electron is a helix.
- A series of magnets with alternating polarity are attached to the back side of the target in a circular fashion.
- The magnets create curved magnetic field lines which confine the secondary electrons to them.
- The highly concentrated electron gas collides with the ions near the target and create a denser plasma without the need for higher pressures.
- Plasma densities can be increased by two orders of magnitude.

Reactive Sputtering

- A combination of physical and chemical deposition.
- Used to deposit compounds (oxides, nitrides).
- Add a reactive gas (oxygen, nitrogen) to the inert gas flow.
- The reactive gas goes in to a chemical reaction with the sputtered atoms.
- If the sputtering rate is faster than the chemical reaction rate, then the reaction will take place on the substrate.
- Adjust gas flow to get good stochiometry (chemical composition).
- Examples: Al_2O_3, AlN, TiO, TiN, SiO_2

Plasma Etching

- Most devices require patterning in addition to deposition.

- Plasma etching is the method of using a high energy plasma to selectively remove material from a surface.

- A mask provides the necessary pattern for the device.

UV Light

Mask
Resist
SiO_2
Si

Exposure
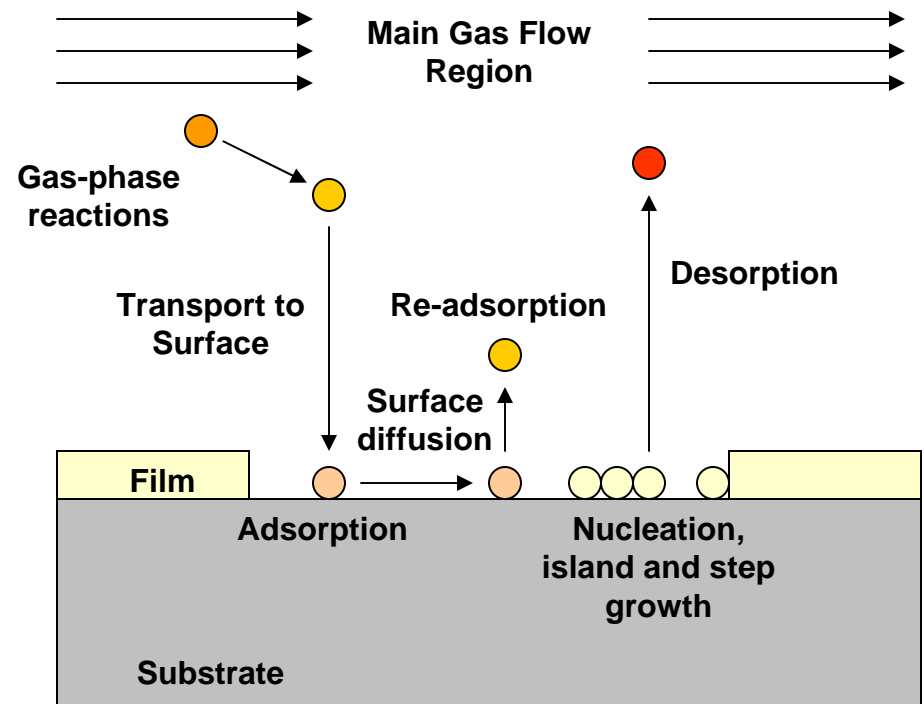
Development

Etching

Removal
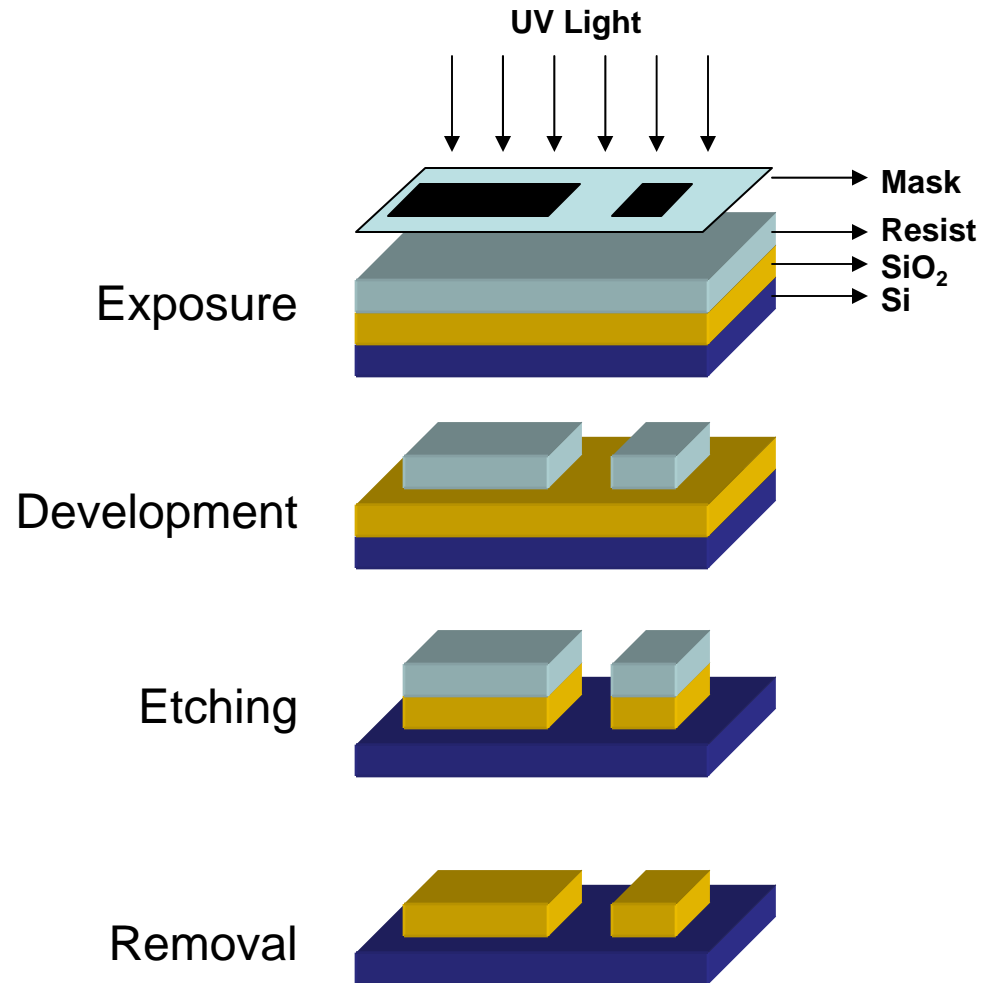
Chemical Vapor Deposition (CVD)

- Deposition can also take place due to a chemical reaction between some reactants on the substrate.

- In this case reactant gases (precursors) are pumped in to a reaction chamber (reactor).

- Under the right conditions (T, P), they undergo a reaction at the substrate.

- One of the products of the reaction gets deposited on the substrate.

- The by-products are pumped out.

- The key parameters are chemical (reaction rates, gas transport, diffusion).

Fundamental CVD Processes

1. Convective and diffusive transport of reactants to the reaction zone
2. Gas phase reactions
3. Transport of reactants to the substrate surface.
4. Chemical and physical adsorption
5. Surface reactions leading to film formation
6. Desorption of volatile by-products
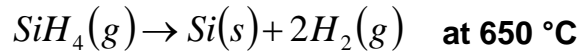7. Convective and diffusive transport of by-products away from the reaction zone

Main Gas Flow Region

Gas-phase reactions

Desorption

Transport to Surface

Re-adsorption

Surface diffusion

Film

Adsorption

Nucleation, island and step growth

Substrate

Choice of Chemical Reactions

- The precursors have to be volatile (gaseous).
  - Ex: SiH_4 (Silane) is a popular precursor to deposit Silicon.
- The chemical reactions need to be thermodynamically predicted to result in a solid film.
  - This means that there should be an energy advantage for the desired reaction to occur, meaning the Gibbs Free Energy (GFE) has to decrease.
  - T and P can be adjusted for $\Delta G < 0$.
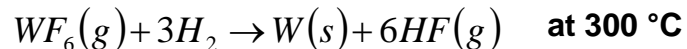- The by-products need to be volatile (gaseous).

CVD Reaction Types

- Pyrolysis
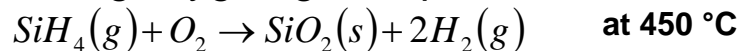 - Thermal decomposition of gaseous species on hot substrates.
    $$SiH_4(g) \rightarrow Si(s) + 2H_2(g)$$ **at 650 °C**
- Reduction
  - Use hydrogen gas to reduce halides, carbonyl halides and oxyhalides
    $$WF_6(g) + 3H_2 \rightarrow W(s) + 6HF(g)$$ **at 300 °C**
- Oxidation
  - Using oxygen gas to produce oxides.
    $$SiH_4(g) + O_2 \rightarrow SiO_2(s) + 2H_2(g)$$ **at 450 °C**
- Compound Formation
  - A variety of carbide, nitride and boride films can be formed.
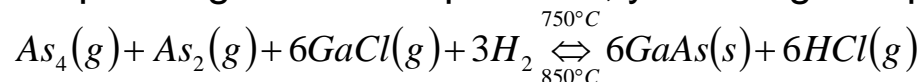 $$SiCl_4(g) + CH_4 \rightarrow SiC(s) + 4HCl(g)$$
- Disproportionation
  - A solid metal can be deposited when there exists two valence states for a metal with different stable temperatures.
 $$2GeI_2(g) \underset{600°C}{\overset{300°C}{\Leftrightarrow}} Ge(s) + GeI_4(g)$$
- Reversible Transfer
  - Depending on the temperature, you can get deposition or etching
    $$As_4(g) + As_2(g) + 6GaCl(g) + 3H_2 \underset{850°C}{\overset{750°C}{\Leftrightarrow}} 6GaAs(s) + 6HCl(g)$$
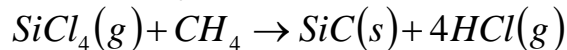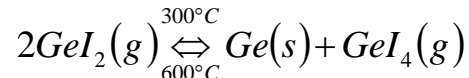
Boundary Layer

- While most flow in the chamber is laminar viscous flow, near the substrate surface the velocity of the gas has to go to zero.

- This creates a stagnant layer above the substrate.

- The thickness of this layer (δ) depends on the chamber conditions.

- The gas will move through the layer by diffusion.

Boundary Layer Gas Flow
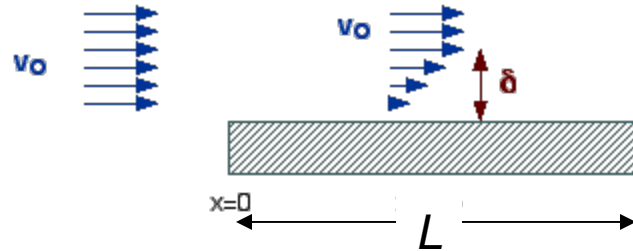
$$\bar{\delta} = \frac{10}{3}\frac{L}{\sqrt{\text{Re}_L}}$$

average width of stagnant layer

where Re is the Reynolds number of the flow tube and is a measure of the flow type.
For most CVD reactors: Re_L ~ few hundred
If flow is turbulent: Re_L ~ few thousand

$$D = D_0 \frac{P_0}{P}\left(\frac{T}{T_0}\right)^n$$
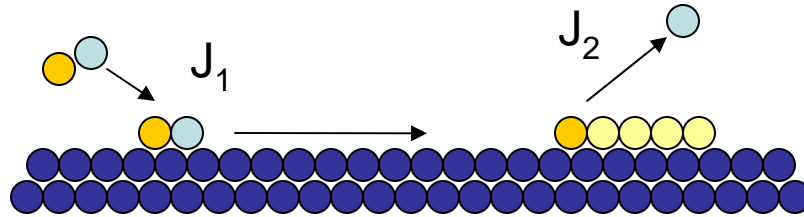
diffusion constant

where n is experimentally found to be 1.8 and D_0 is the diffusion constant at T_0 and P_0.

$$J_i = -\frac{D(P_g - P_s)}{\delta RT}$$

gas flow rate

where P_g is the vapor pressure in bulk gas and P_s is the vapor pressure is the substrate surface.

Deposition Rate

J_2

J_1

h_g: Gas phase mass transport coefficient
k_s: Surface reaction rate

$$J_1 = h_G\left(C_g - C_s\right)$$

$$J_2 = k_S C_s$$

In steady state $J_1 = J_2$ $\longrightarrow$

$$v = \frac{C_g}{\dfrac{1}{h_G} + \dfrac{1}{k_S}}$$

: deposition rate

$h_G \gg k_S$: Reaction Limited Growth

- growth controlled by processes on surface
- k_S is highly temperature dependent (increases with T)
- common limit at lower temperatures
- often preferred, slow but epitaxial growth
- temperature and reactant choices are important

$k_S \gg h_G$: Transport Limited Growth

- growth controlled by transfer to substrate
- h_G is not very temperature dependent
- common limit at higher temperatures
- non-uniform film growth
- gas dynamics and reactor design are important

Tube Reactors
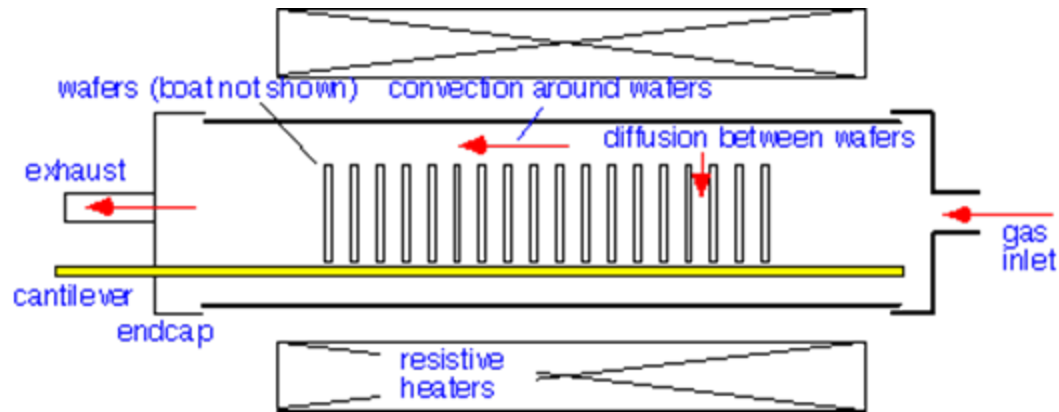
- Hot wall design (the reactor walls are heated).
- Can be horizontal or vertical.
- Batch processing of wafers
- Good radial uniformity of films
- Axial uniformity more suspect
- Need to slow down deposition rates for axial uniformity.

Showerhead Reactors

- Cold wall design (only substrate is heated)
- Better suited for plasma enhanced processing.
- Generally a single wafer design.
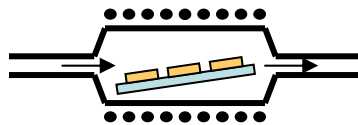- Good heater design is needed for radial uniformity.
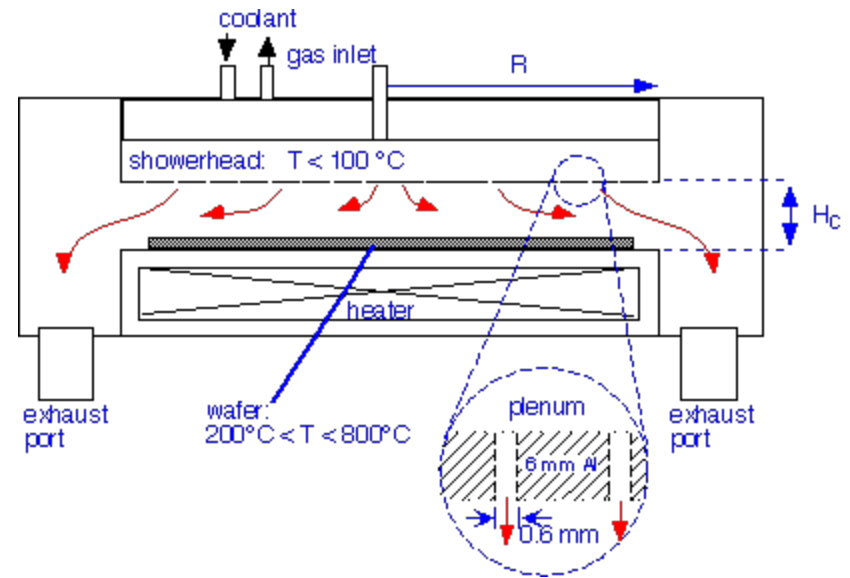
Atmospheric Pressure CVD

- High Temperature APCVD
  - Used to deposit epitaxial Si and compound films (cold wall reactors) or hard metallurgical coatings like TiC and TiN (hot wall reactors).
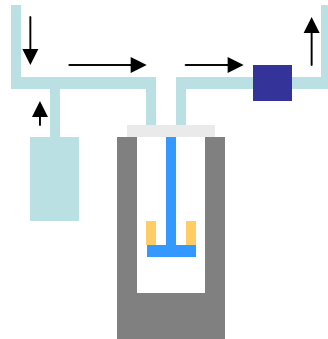
Cold Wall Reactor
• wafers tilted for uniform deposition

Hot Wall Reactor

- Low Temperature APCVD
  - Many insulating film layers (SiO_2, BPSG glasses) need to be deposited at low temperatures.
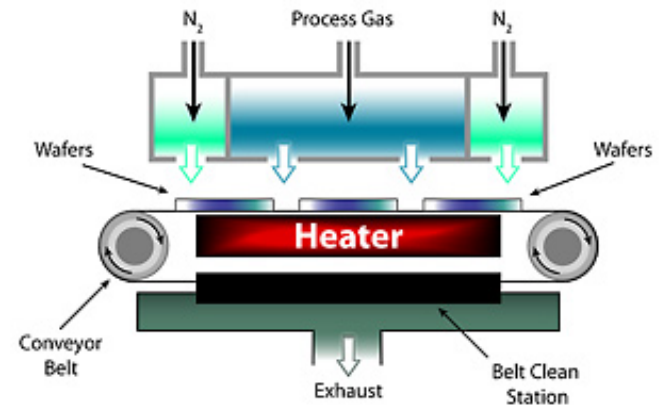
APCVD Reactor

N_2 Process Gas N_2

Wafers   Wafers

Heater

Conveyor Belt

Exhaust   Belt Clean Station

Conveyor Belt Reactor

Low Pressure CVD

- Classify by gas pressure:
  - For 100 torr > P > 1 torr, we have reduced pressure CVD (RPCVD)
  - For 10 mtorr > P > 1 mtorr, we have LPCVD
  - At UHV (~10^{-7} torr), we have UHV/CVD.
- Higher gas concentrations to compensate for lower pressure.
- Higher diffusivity of gas to the substrate
- Often reaction rate limited growth
- Due to lower pressures, there are fewer defects.
- Better step coverage, better film uniformity.

Pressure sensor

3-zone furnace

Wafers

Pump

Quartz tube

Gas inlet

Load door
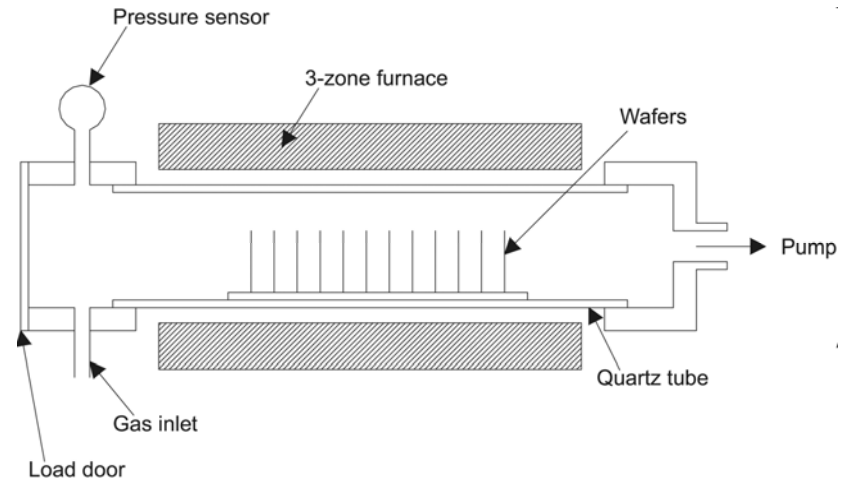
Hot wall reactor

Plasma Enhanced CVD Processes

- Create a plasma (RF or DC) in the vicinity of the substrate.
- As in sputtering, the energetic ions impart their energy and momentum on the reactant gas molecules and atoms.
- The energy transfer breaks up the molecules and aids the chemical reactions.
- The "helping hand" of the plasma allows for lower temperatures and pressures and improves film quality.
- For example, TiC would not normally form below 1200 °C (from GFE consideration) but with PECVD, it is possible to deposit it at 700 °C.
- The imparted momentum allows for better step coverage.
- Reactors can be direct or indirect.
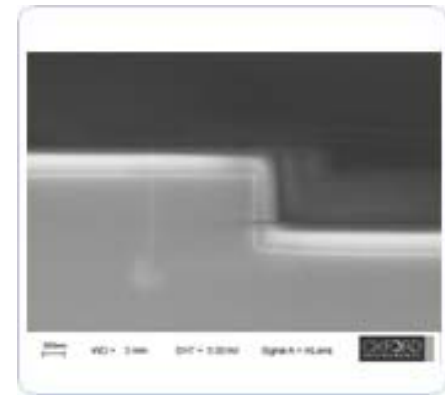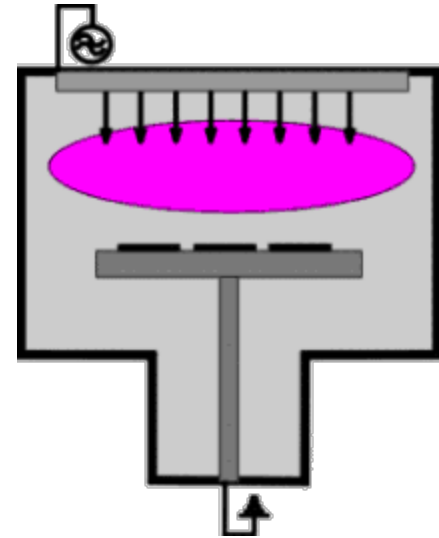
Step coverage in PECVD

Plasma Enhanced CVD (PECVD)

- The "helping hand" of the plasma allows for lower temperatures and pressures and improves film quality.
- For example, TiC would not normally form below 1200 °C (from GFE consideration) but with PECVD, it is possible to deposit it at 700 °C.
- The lower temperatures are especially useful when depositing metal contact layers (eg. Al) between dielectric (insulating) layers (eg. SiO_2).
- The higher temperatures of plain LPCVD would melt the metal and the alternate layers would interact.
- The imparted momentum allows for better step coverage.
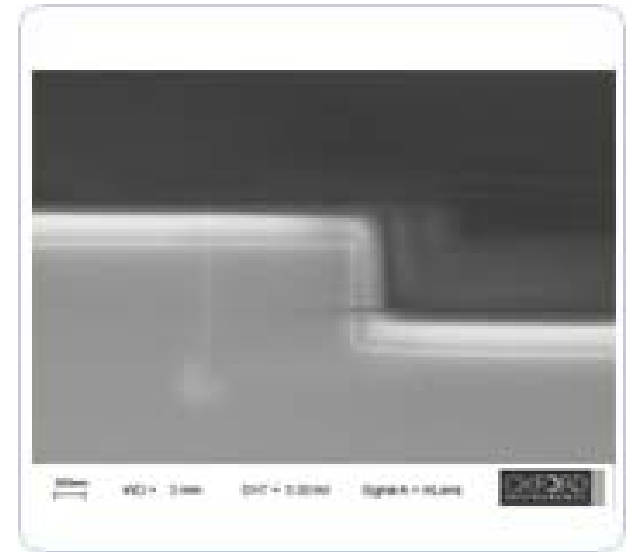
Step coverage in PECVD

Steps of Thin Film Growth

1. Absorption (physisorption)
2. Surface diffusion
3. Chemical bond formation (chemisorption)
   - Molecule-molecule
   - Substrate-molecule
4. Nucleation
5. Microstructure formation
   - Crystal structure
   - Defects
6. Bulk changes
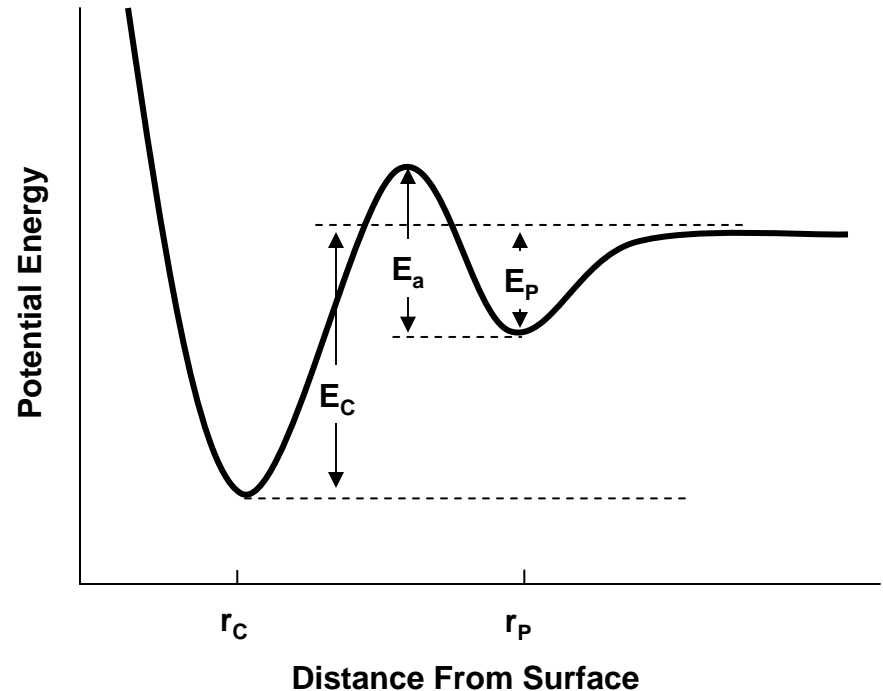   - Diffusion
   - Grain growth
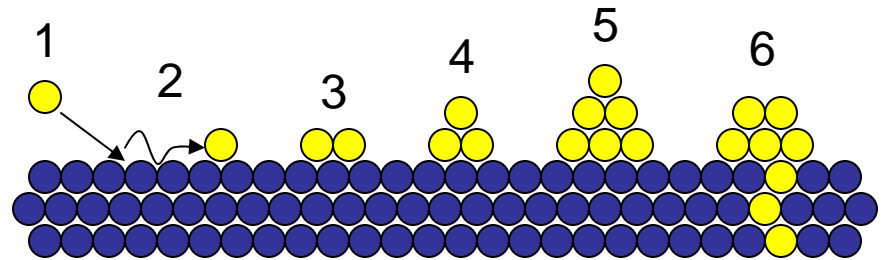
Energy Barriers

- Once physisorbed, the atom can be chemisorbed or desorbed (ejected).

- Both physisorption and chemisorption have to overcome local energy barriers.

$$k_r = v \exp\left(\frac{-E_b}{kT}\right)$$

$$\tau_r = \frac{1}{k_r} = \frac{1}{v} \exp\left(\frac{E_b}{kT}\right)$$


- E_P ~ 0.25 eV
- E_C ~ 1 - 10 eV

Nucleation

- For a stable film, nuclei at a critical size are needed.

- For "embryos" smaller than this, the surface energy is too large and the overall reaction is thermodynamically unfavorable.

- A stable embryo is one which adding more molecules decreases the Gibb's free energy.

Nucleation Types

- ## Homogeneous (undesirable)
  - The free energy of the atoms in free standing (gas) form is smaller when they nucleate.
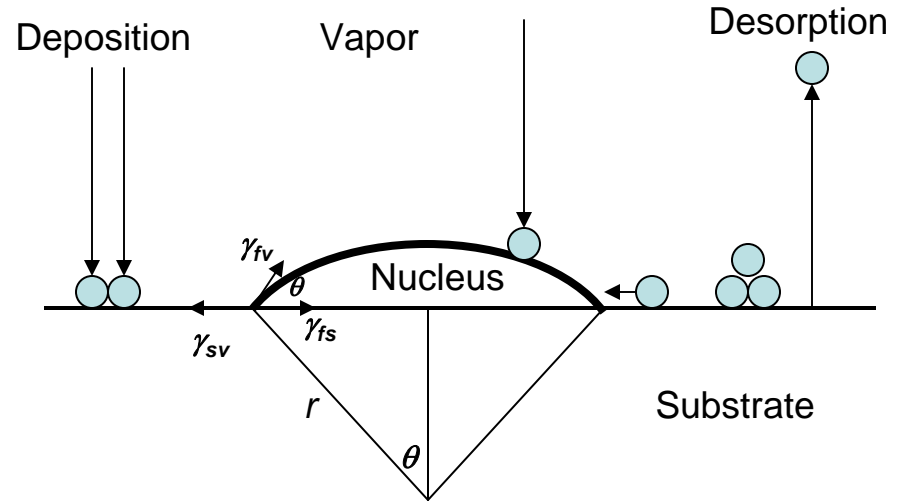
$$\Delta G_{total} = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$
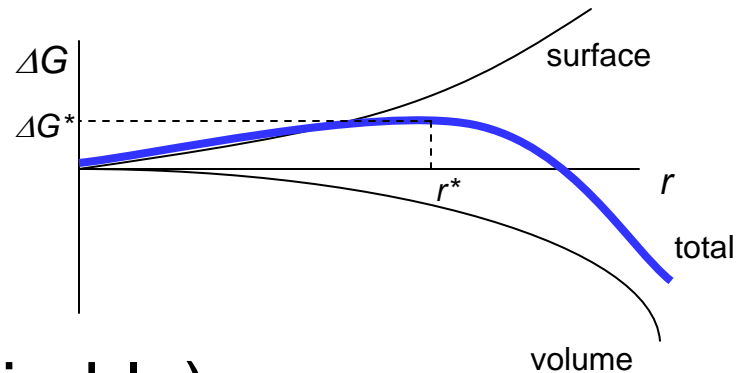
- ## Heterogeneous (desirable)
  - Nucleation on the substrate surface in solid form reduces the surface energy by reducing the surface area.

Heterogeneous Nucleation

- Nucleation depends on the relative surface energies of the various interfaces:
  - Substrate-vapor
  - Film-substrate
  - Film-vapor

$$\Delta G_{total} = a_3 r^3 \Delta G_v + a_1 r^2 \gamma_{fv} + a_2 r^2 \gamma_{fs} - a_2 r^2 \gamma_{sv}$$

- It has a barrier behavior similar to homogeneous nucleation with a critical radius and energy.

$$r^* = \frac{-2(a_1 \gamma_{fv} + a_2 \gamma_{fs} - a_2 \gamma_{sv})}{3 a_3 \Delta G_v}$$

$$\Delta G^* = \frac{16\pi (\gamma_{fv})^3}{3(\Delta G_v)^2} \left\{ \frac{2 - 3\cos\theta + \cos^3\theta}{4} \right\}$$

Dependence of Nucleation on Growth Parameters

- Substrate Temperature
  - The critical nuclei size increases with temperature.
  - The barrier for nucleation is greater with increasing temperature.
- Deposition Rate
  - The critical nuclei size decreases with increasing deposition rate.
  - The barrier for nucleation is smaller with increasing deposition rate.

Growth Types

Layered Growth

- If the substrate-vapor surface energy is larger than the other two combined.
- A smooth film will form.
- Layered growth will occur.
- The film wets the surface to lower surface energy.

Island Growth

- The total surface energy of the film interfaces is larger than that of the substrate-vapor interface.
- The material balls up to minimize interface with the substrate.
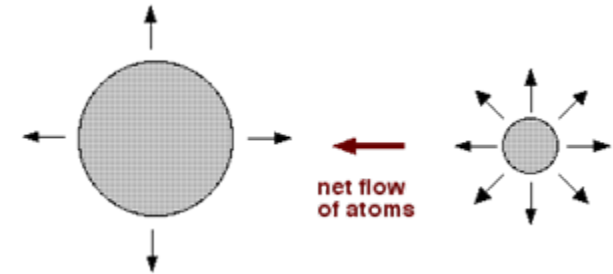- Uneven growth.
- Slow diffusion.

Mixed Growth

- Initial layer growth.
- Changes into island growth after a few monolayers.
- The initial layer is strained to match the substrate. After a few layers, the strain is relaxed.
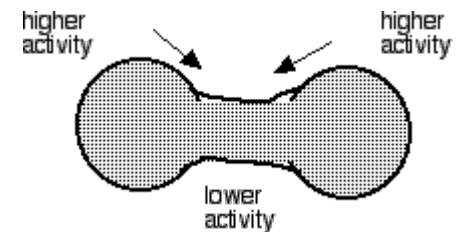
Nuclei Combination

- Ostwald Ripening
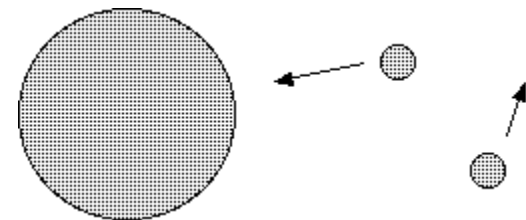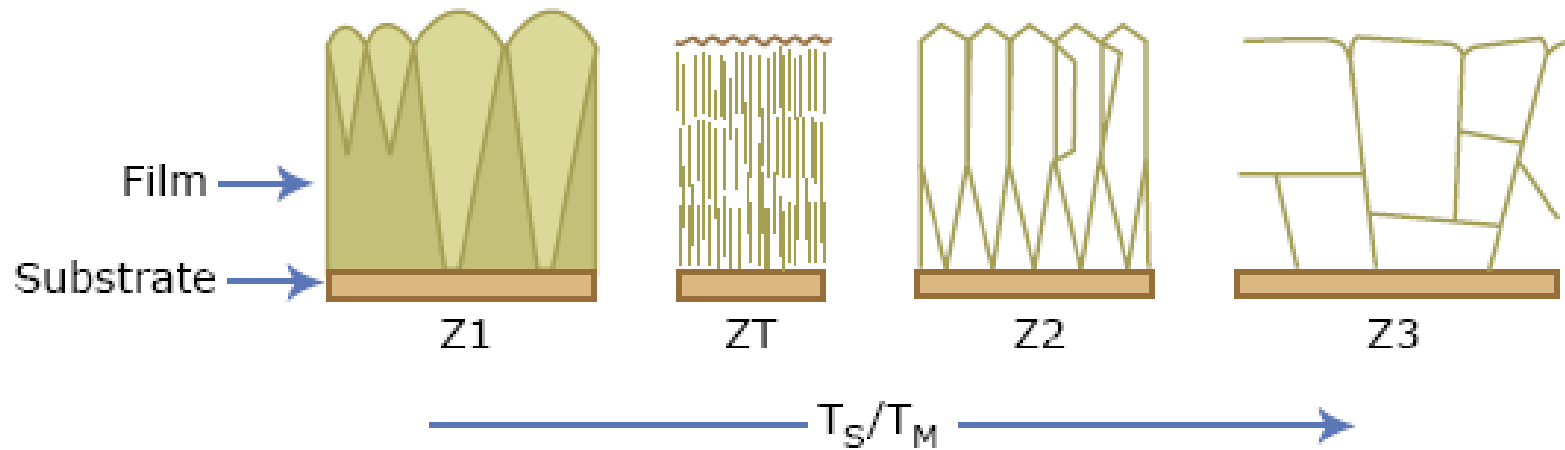 - Small particles shrink, large ones grow.

- Sintering
  - A neck forms between two growing nuclei.
  - The neck's curvature allows for faster growth and merging.

- Cluster Coalescence
  - Nuclei also undergo surface diffusion
  - When it is chemically favorable for two nuclei to align and stay permanently at a location, they merge.

Film Morphology

Film →

Substrate →

Z1   ZT   Z2   Z3

T_S/T_M

Types of Epitaxy

- Homoepitaxy
  - The film and the substrate are the same material.
  - Often used in Si on Si growth.
  - Epitaxially grown layers are purer than the substrate and can be doped independently of it.

- Heteroepitaxy
  - Film and substrate are different materials.
  - Eg: AlAs on GaAs growth
  - Allows for optoelectronic structures and band gap engineered devices.

Lattice Strains

- For many applications nearly **matched** lattices are desired to minimize defects and increase electron mobility.

- As the mismatch gets larger, the film material may **strain** to accommodate the lattice structure of the substrate. This is the case during the early stages of film formation (pseudomorphic growth) and with materials of the same lattice structure. The Si-Ge system is an example.

- If strain accommodation is not possible then dislocation defects at the interface may form leading to **relaxed** epitaxy and the film returns to its original lattice structure above the interface.

- **Lattice misfit** is defined as:

$$\underline{f} = \left[a_0(s) - a_0(f) \right] / a_0(f)$$

where $a_0(s/f)$ are the lattice constants of the substrate and the film.

Matched

Strained

Relaxed
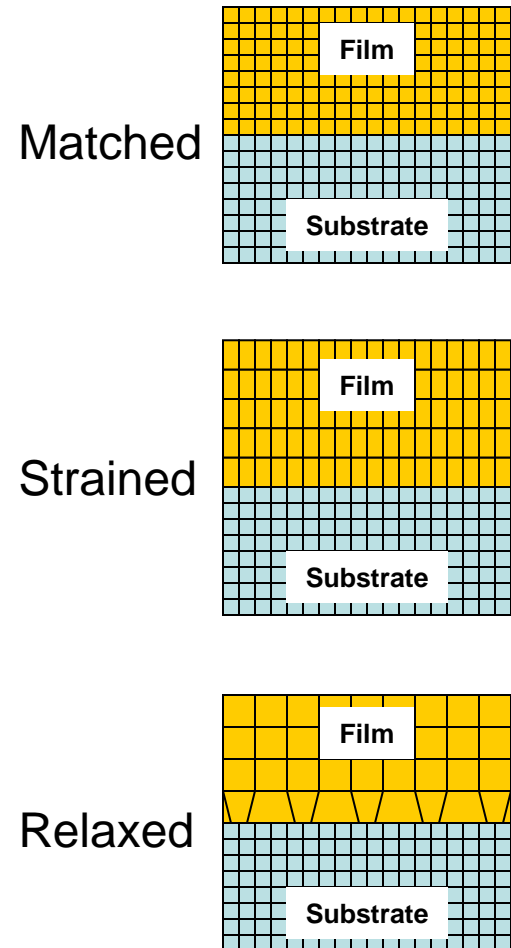
Lattice Misfits and Defects

- If the lattice mismatch is less than ~9%, the initial layers of film will grow pseudomorphically.
- Therefore very thin films strain elastically to have the same inter-atomic spacing as the substrate.
- As film thickness increases, the rising strain will eventually cause a series of misfit dislocations separated by regions of relatively good fit. As such they are equilibrium theories.
- There is a critical film thickness, d_c, beyond which dislocations are introduced.
- In most cases pseudomorphic growth occurs until

$$\underline{f} d_c = b/2$$,where b is the size of the film unit cell.

Formation of Misfit Dislocations

- They generally originate from threading dislocations at the film-substrate interface.

- The dislocation pierces through the substrate and the film.

- As it grows, it glides and bends in a slip plane.

- Above the critical thickness (d_c) the increasing strain allows a break and the film dislocation separates from the originating defect, leaving behind a stable misfit dislocation.

Properties of Compound Semiconductors

- For direct gap semiconductors, the band gap energy determines the wavelength (color) of the light that will be emitted. Various III-V alloys are used to cover most areas from the UV (GaN) to the NIR (GaAs) to the IR (InSb).
- The various alloys also offer a spectrum of lattice constants for lattice matching. GaAs and AlAs interfaces have minimal misfit and negligible dislocations.
- Thermal expansion coefficients are also comparable.
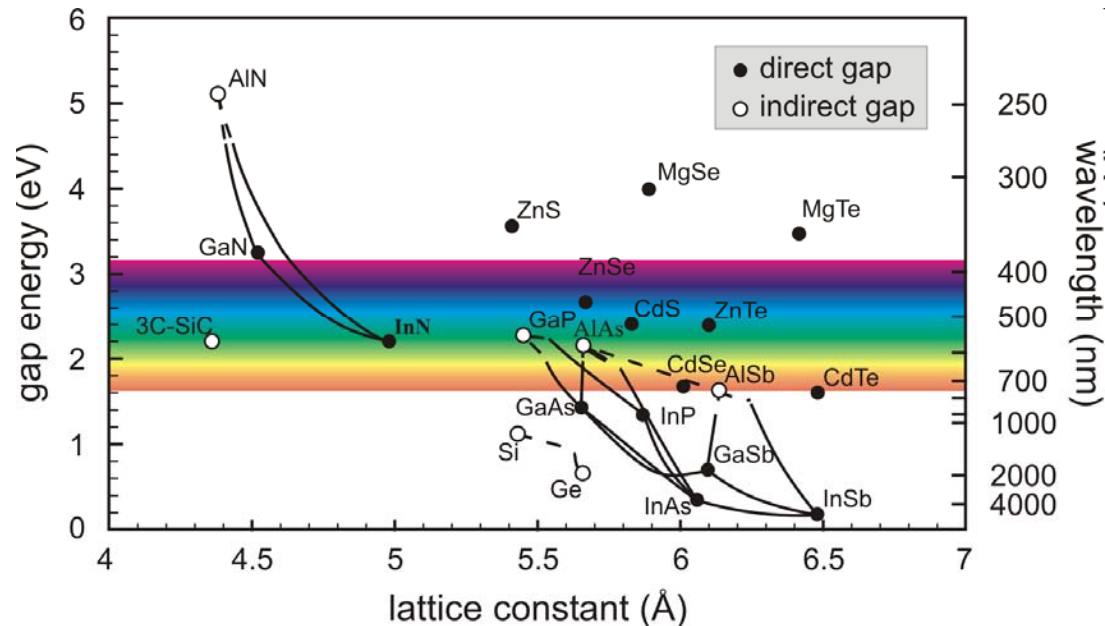
Liquid Phase Epitaxy (LPE)

- LPE involves the precipitation of a crystalline film from a supersaturated melt on to a substrate.
- The temperature is increased until a phase transition occurs and then reduced for precipitation.
- By controlling cooling rates the kinetics of layer growth can be controlled.
- Once can have either continuous reduction with the substrate (equilibrium cooling) or separate reduction in increments followed by contact with the substrate (step cooling).
- It is a low cost method yielding films of controlled composition, thickness and lower dislocation densities.
- Disadvantages are rough surfaces and poor thickness uniformity.
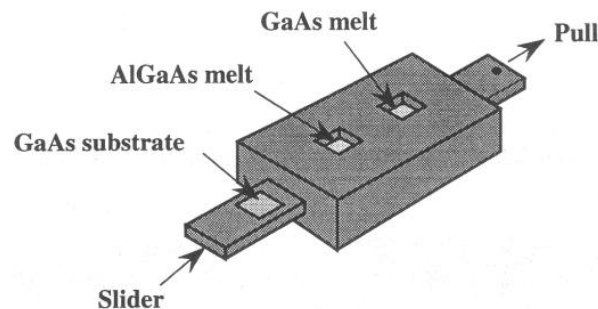
CVD Epitaxy (MOCVD)

- The CVD process is carried out a pressure around 0.5 – 760 torr and at temperatures hundreds of degrees lower than the substrate melt temperature.

- The precursors are metalorganic. The reactions can produce high quality epitaxial layers of III-V semiconductors with very good thickness control allowing quantum well structures to be manufactured.

- Examples:
  - TMGa + AsH_3 at 650 – 750 °C for GaAs.
  - TMGa + NH_3 at 800 °C for GaN.
  - TEIn + PH_3 at 725 °C for InP.

Wafer

Precursors

Heating ~600°C
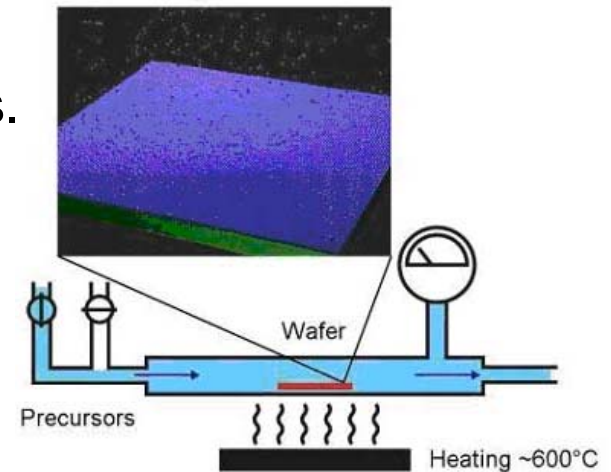
Molecular Beam Epitaxy (MBE)

- The environment is highly controlled ($P \sim 10^{-10}$ torr).
- One or more evaporated beams of atoms react with the substrate to yield a film.
- For epitaxial growth the surface diffusion-incorporation time has to be less than one layer's deposition time. This limits the technique to being a low temperature one.
- Semiconductor and dopant sources are arrayed around the substrate. Each source and the substrate can be individually heated. Shutters control exposure to each species.
- The sources can be solid source (for arsenide compounds) or gas source (for phosphorus compounds).

RHEED electron gun
main shutter
substrate holder (rotating)
cryopanel (liquid N$_2$)
ion gauge
valve
effusion cells
transfer rod
shutter
window
RHEED screen
port for pumps
motor