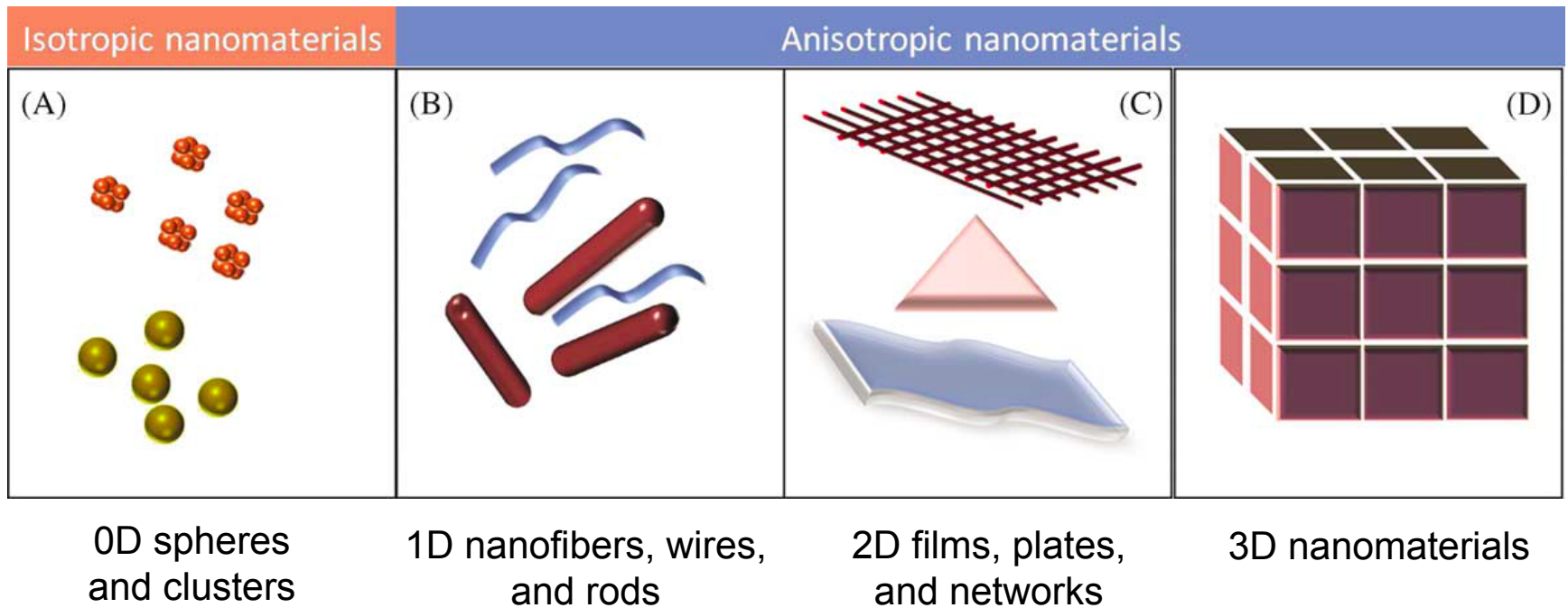


Growth of Nanostructures and Nanomaterials



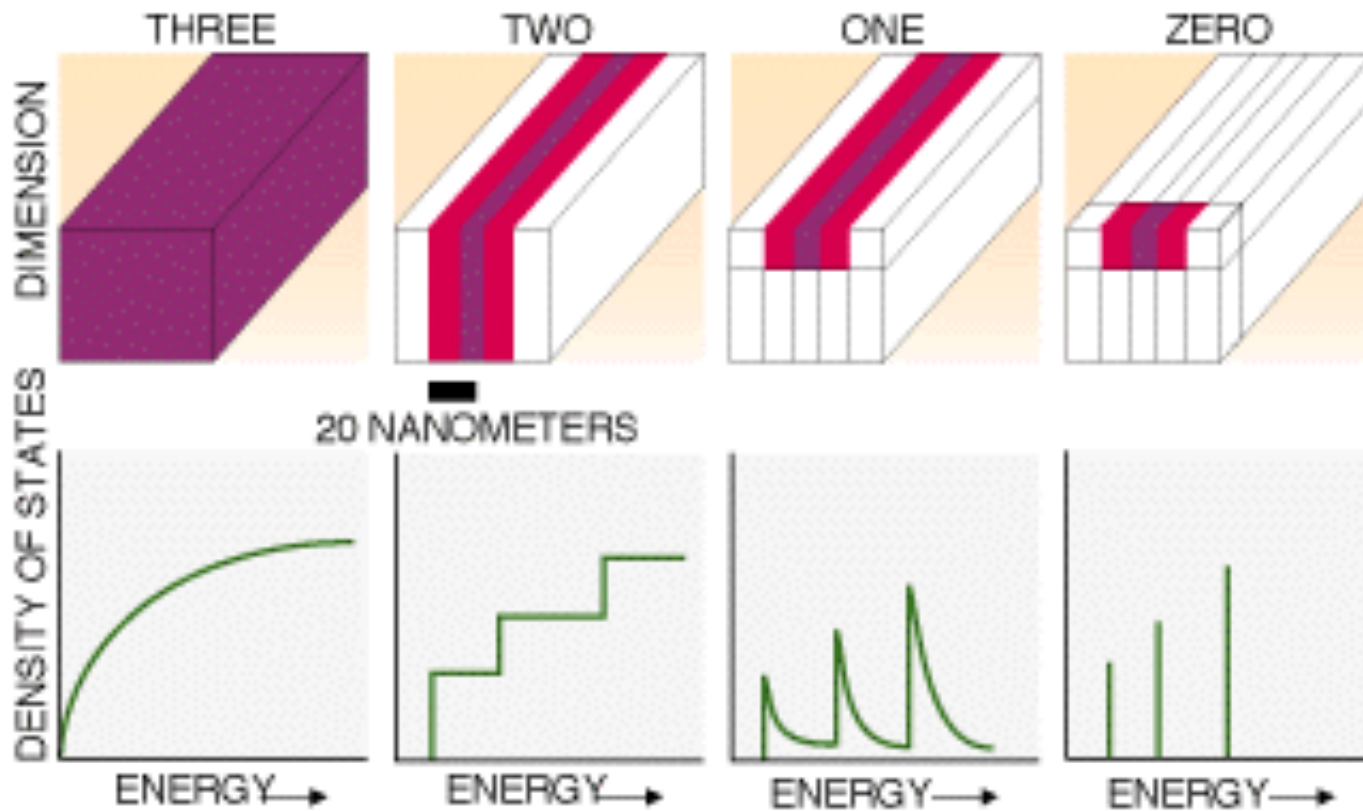
Various kinds of nanomaterials

Critical lengthes for Nanostructures

Nanostructured materials derive their special properties from having one or more dimensions made small compared to a length scale critical to the physics of the process.

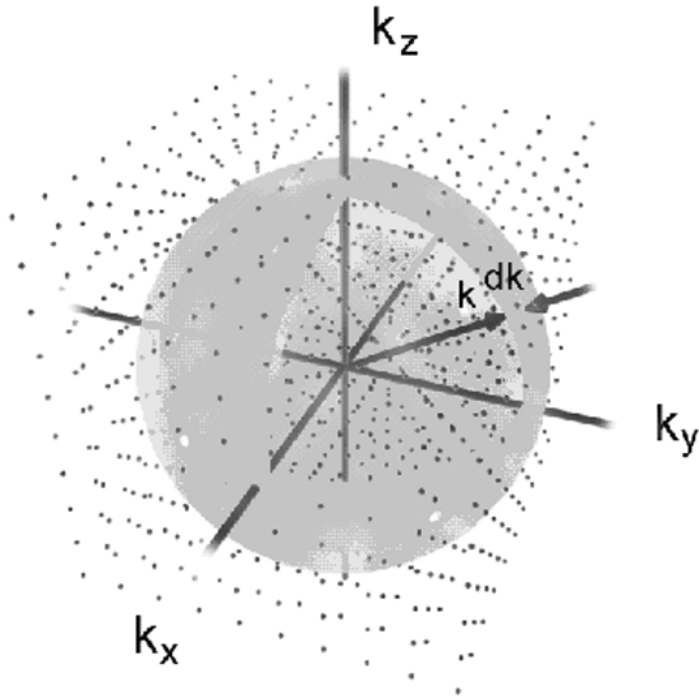
Phenomenon	Electronic Transport	Optical Interactions	Magnetic Interactions	Thermal	Fluidic Interactions
Physics	Fermi wavelength, λ_F Scattering length, ℓ	Wavelength of light in medium, $\lambda / 2n$	Range of exchange interactions, range of magnetic dipole interactions	Phonon mean free path	Boundary layers, molecular dimensions
Length scale	$\lambda_F \approx 1\text{\AA}$ $\ell \approx 10\text{-}100\text{ nm}$	100 – 300 nm	Exchange 1-100 $\text{\AA}$, Dipolar ca. microns	Hundreds of nm at 300K to very large at low T	Always in the low Reynolds number limit: Radius of gyration for dissolved molecules.

Quantum confinement



(Scientific American)

Size dependence of density of states



k-space is filled with an uniform grid of points each separated in units of $2\pi/L$ along any axis.

The volume (V_k) of k-space occupied by each point is:

$$\left(\frac{2\pi}{L} \right)^3$$

r-space:

$$\frac{4\pi r^2 dr}{V}$$

k-space:

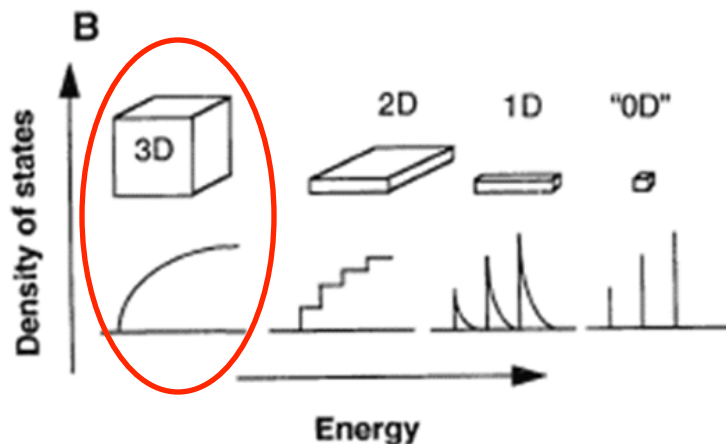
$$\frac{4\pi k^2 dk}{V_k} = \frac{4\pi L^3 k^2 dk}{8\pi^3}$$

3D DOS

Density of states in a volume V per unit wave vector: $\frac{dn}{dk} = \frac{Vk^2}{2\pi^2}$

For a free electron gas: $E = \frac{\hbar^2 k^2}{2m}$ $\frac{dE}{dk} = \frac{\hbar^2 k}{m}$

$$\frac{dn}{dE} = \frac{dn}{dk} \frac{dk}{dE} = \frac{Vk^2}{2\pi^2} \frac{m}{\hbar^2 k} = \frac{Vm}{\hbar^2 2\pi^2} \sqrt{\frac{2mE}{\hbar^2}} \propto E^{\frac{1}{2}}$$

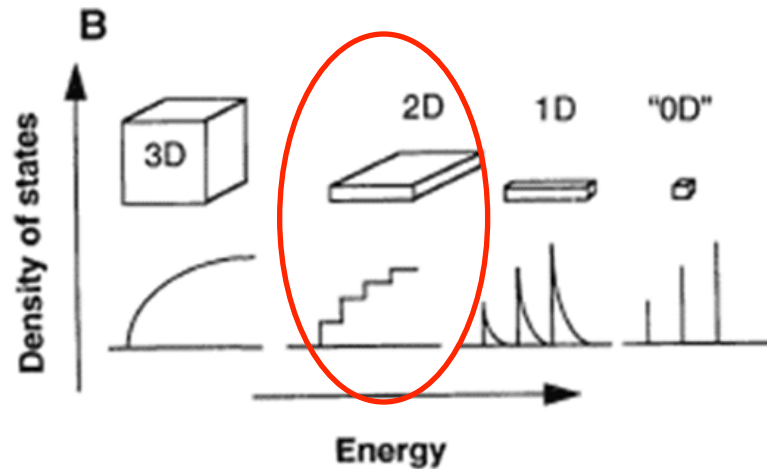


2D DOS

$$\frac{dn}{dk} = \frac{A2\pi k}{(2\pi)^2} \quad \frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

$$\frac{dn}{dE} = \frac{dn}{dk} \frac{dk}{dE} = \frac{Am}{2\pi\hbar^2}$$

Constant for each electronic band

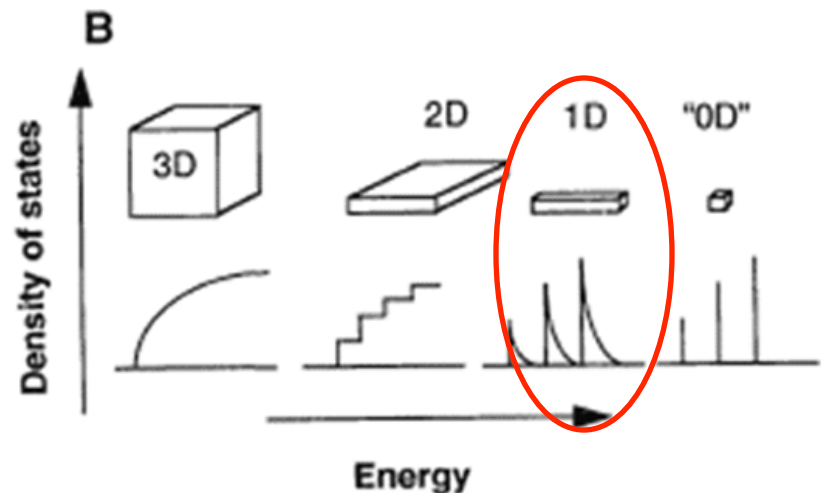


1D DOS

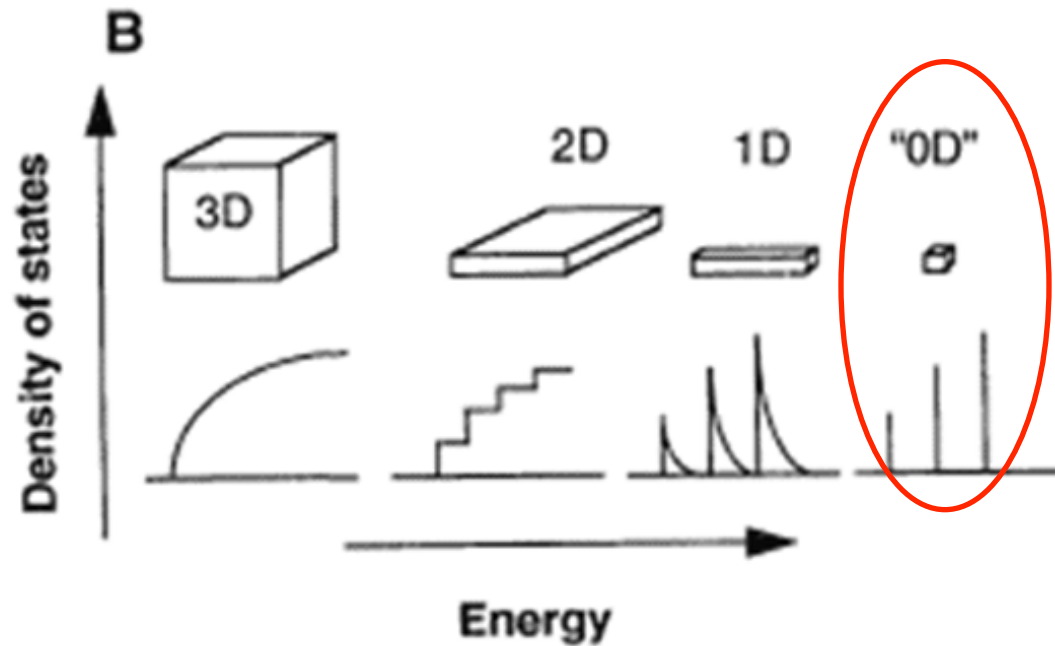
$$\frac{dn}{dk} = \frac{L}{2\pi} \quad \frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

$$\frac{dn}{dE} = \frac{Lm}{2\pi\hbar^2 k} \propto E^{-\frac{1}{2}}$$

At each atomic level, the DOS in the 1D solid decreases as the reciprocal of the square root of energy.

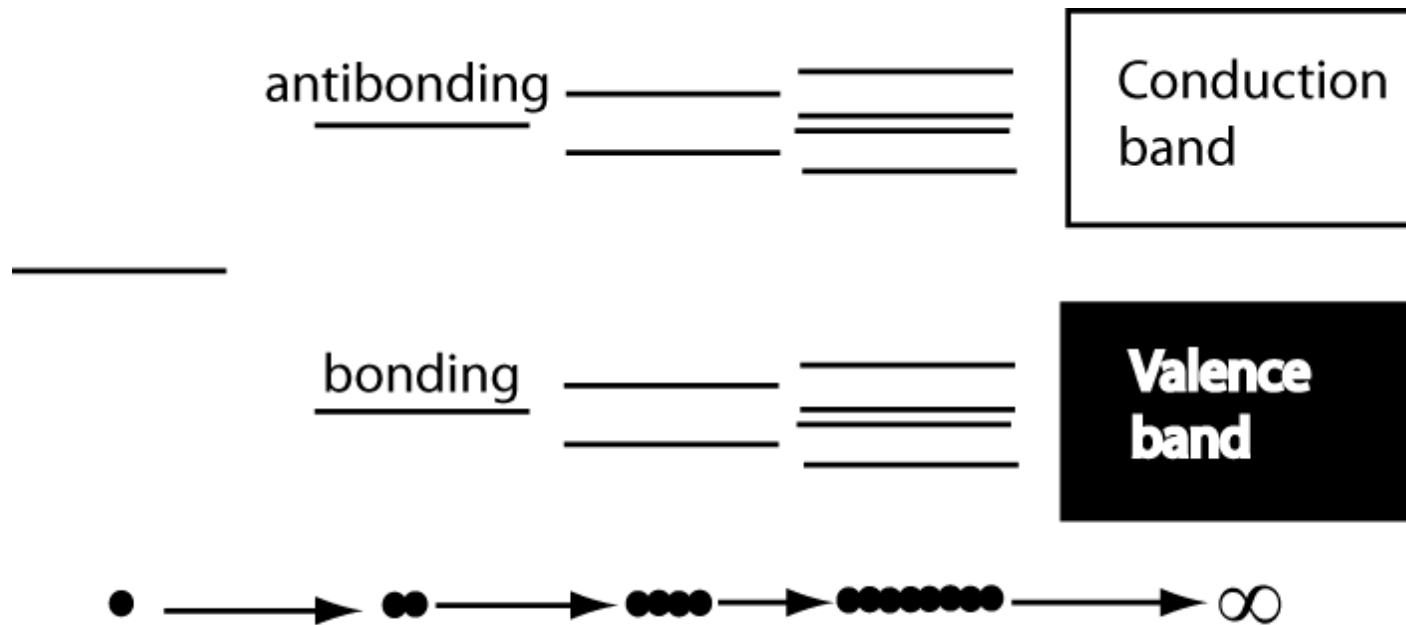


0 D DOS



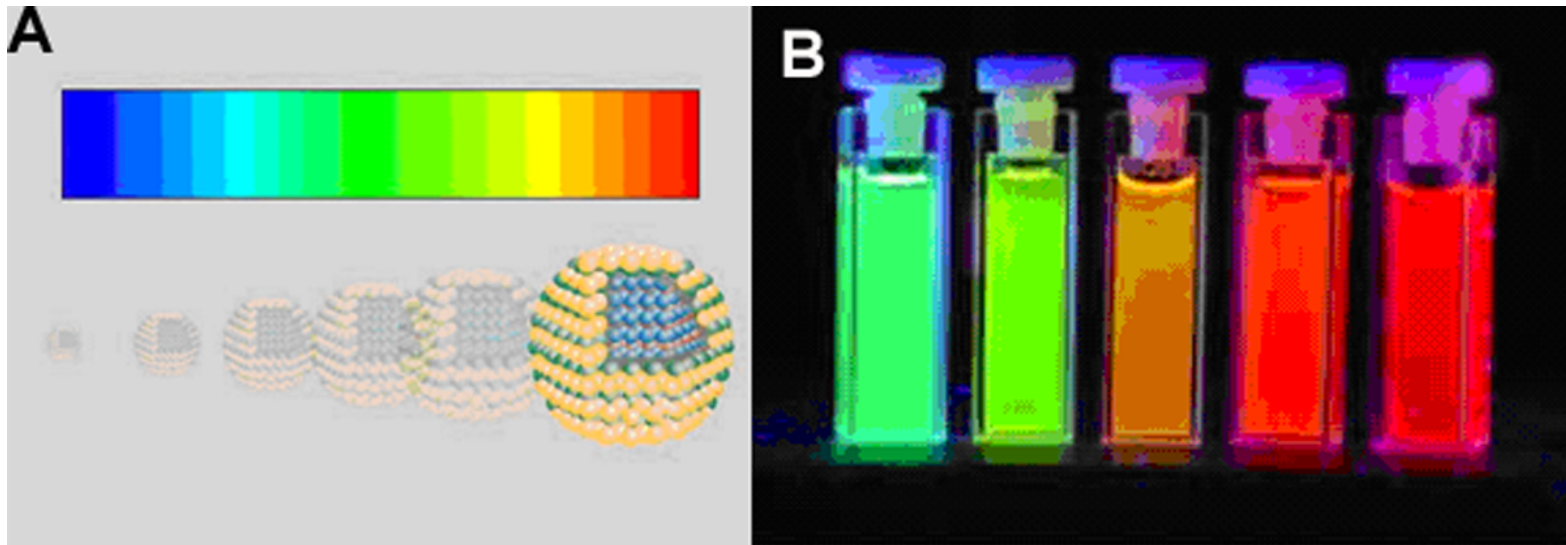
In zero dimensions the energy states are sharp levels corresponding to the eigenstates of the system.

Development of electronic properties as a function of cluster size



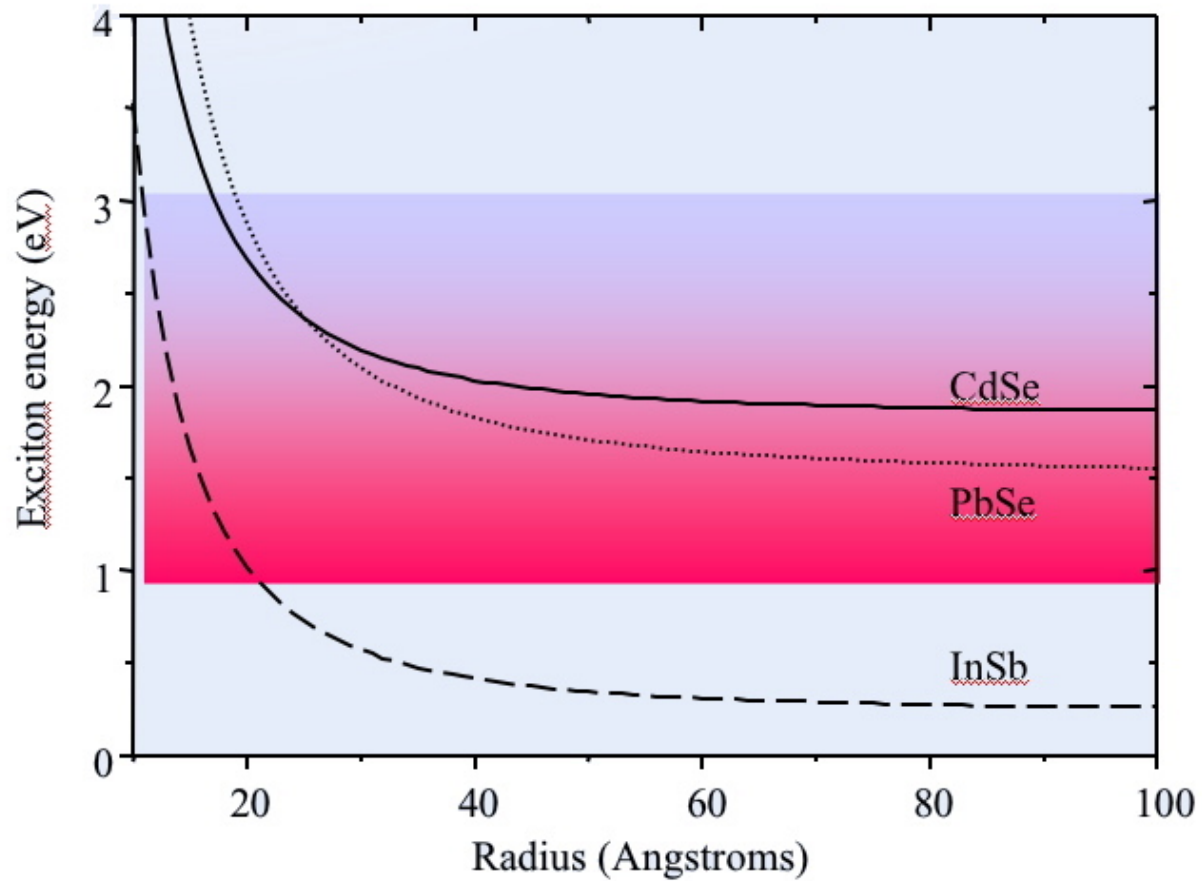
Each band has a width that reflects the interaction between atoms, with a bandgap between the conduction and the valence bands that reflects the original separation of the bonding and antibonding states.

0D Electronic Structures: Quantum Dots



Light incident on a semiconductor at an energy greater than the bandgap forms an exciton, i.e. an electron-hole quasiparticle, representing a bound state.

Exciton Energy



Nanostructure fabrications

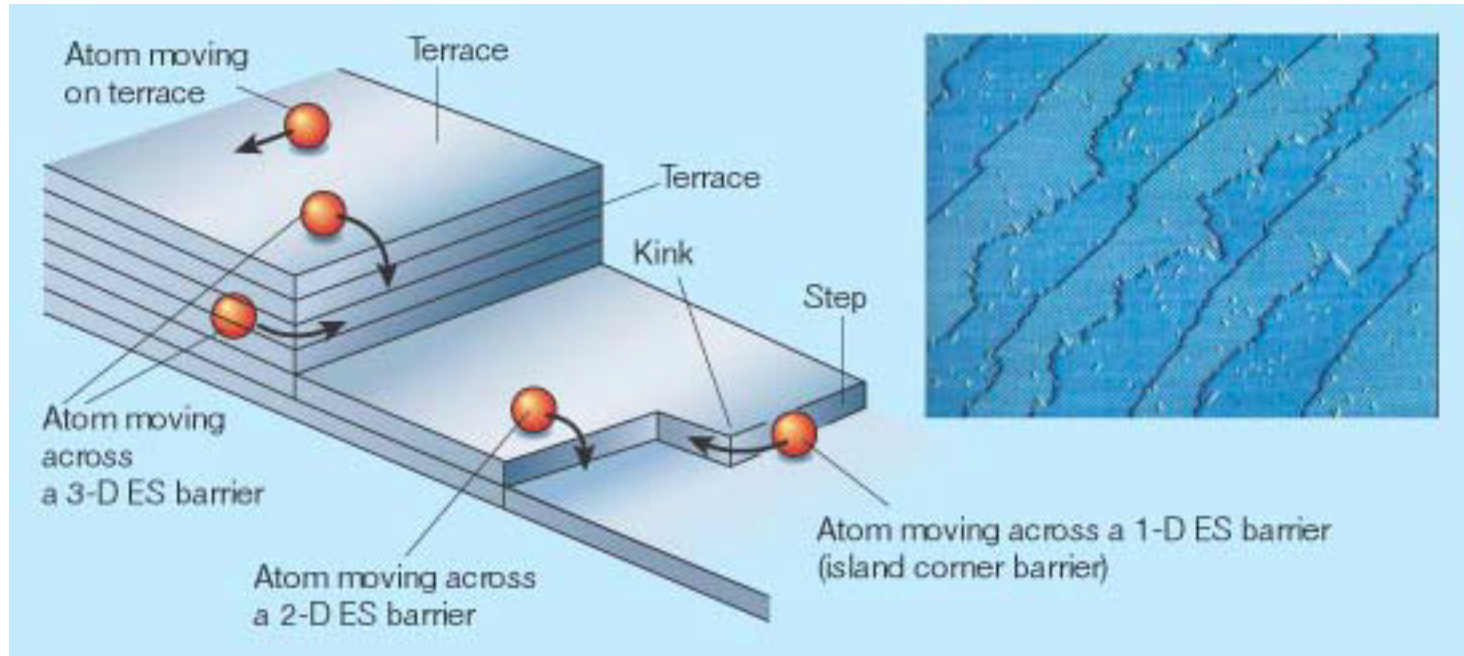
- Bottom-up approach: Growth and self-assembly to build nanostructures from atomic or molecular precursors.
- Top-down approach: Lithographic patterning to structure macroscopic materials at the nanoscale.

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.

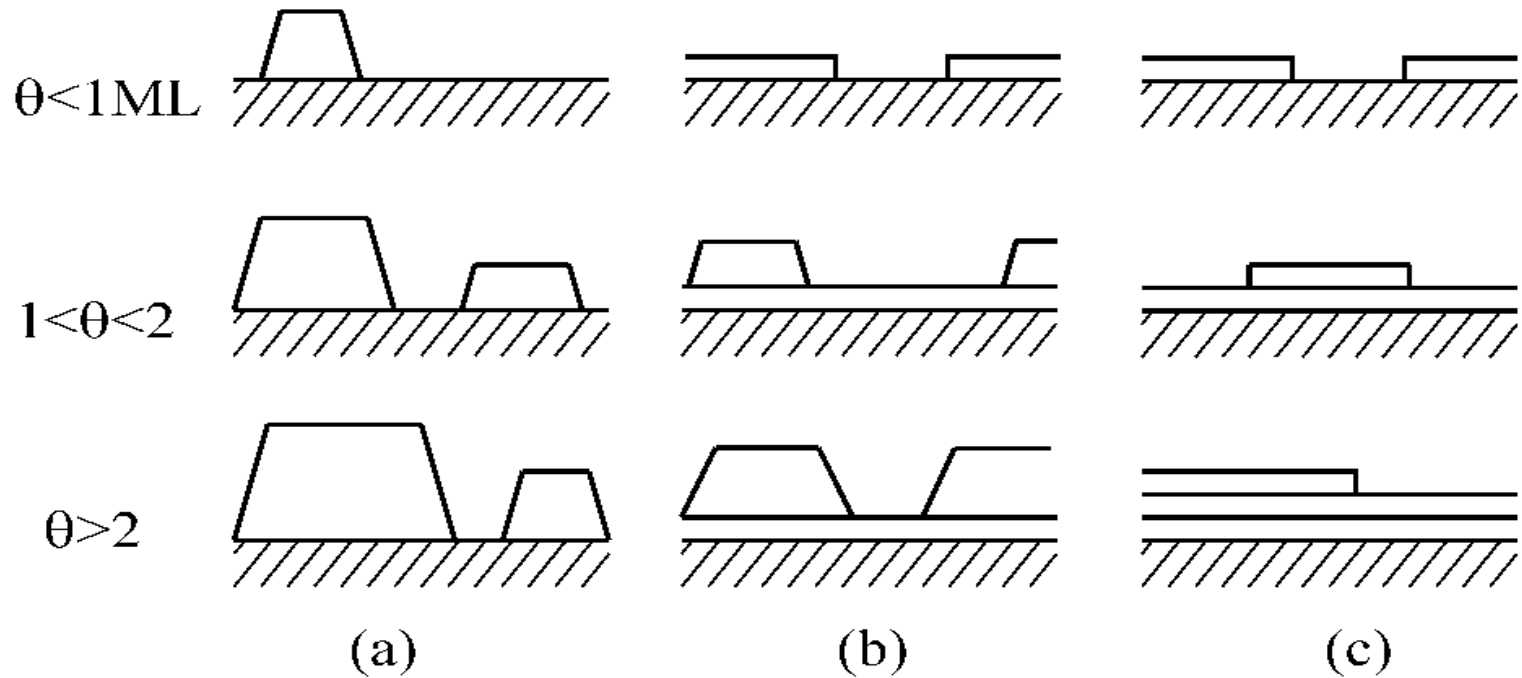
Atomistic Models for Crystalline Surfaces



Terrace Step Kink (TSK) model

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

Growth modes



Island

Volmer-Weber

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

Layer + Island

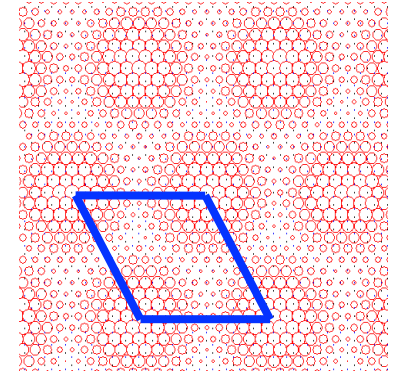
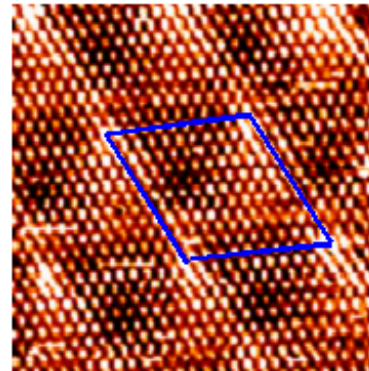
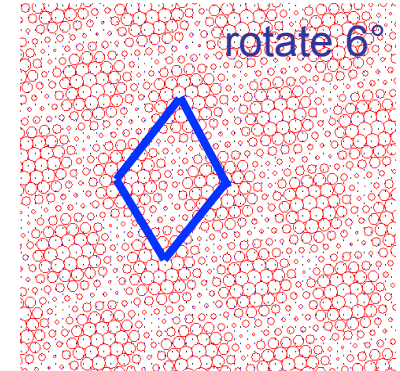
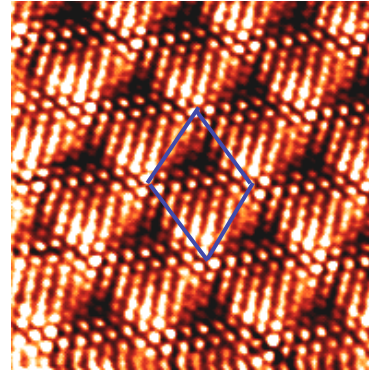
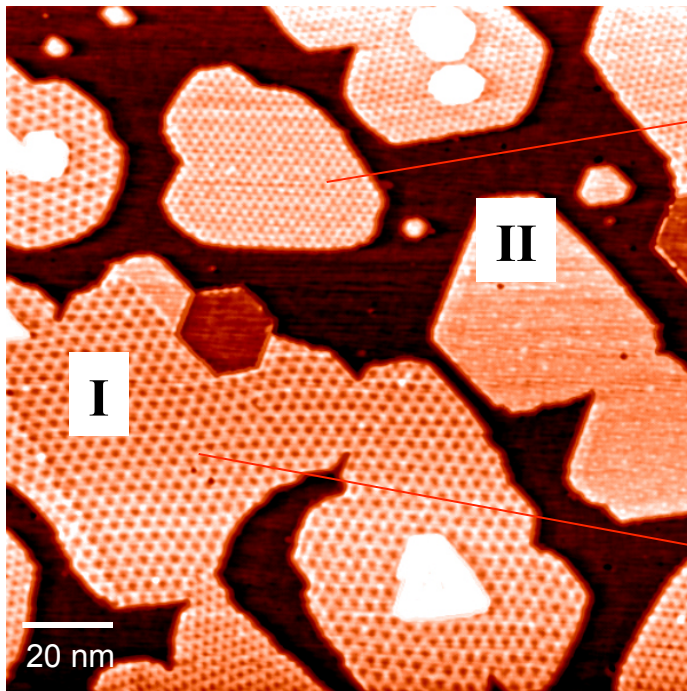
Stranski-Krastanov

Layer

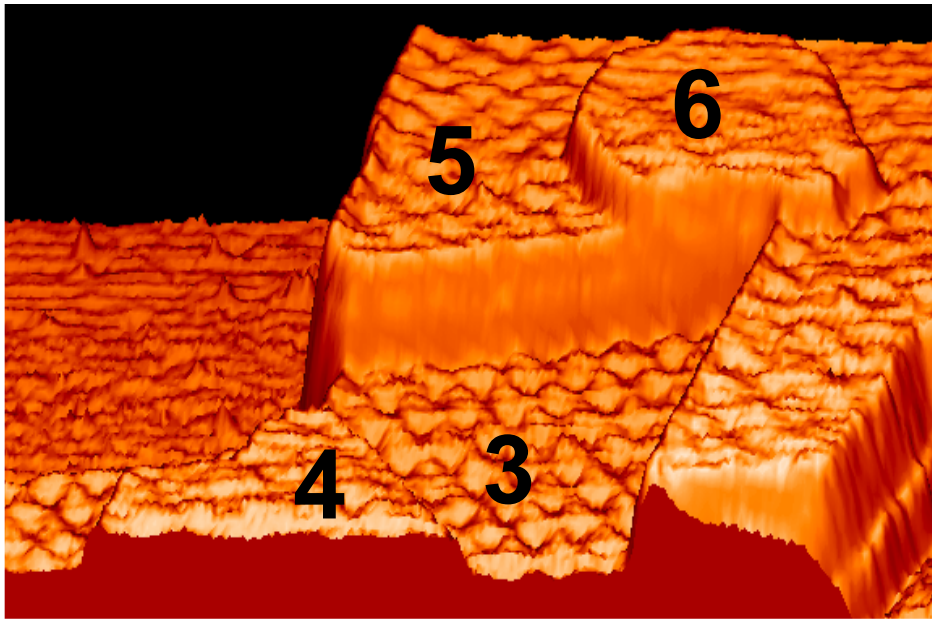
Frank-VdM

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

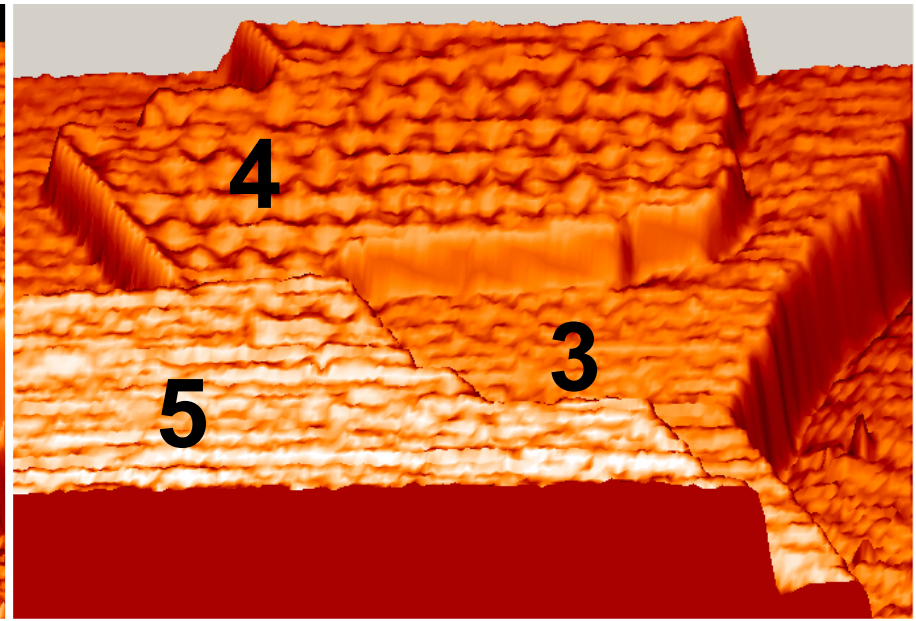
Superstructures of 2D islands



Characteristics of Pb island--- oscillatory and complementary contrast



Type I



Type II

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.

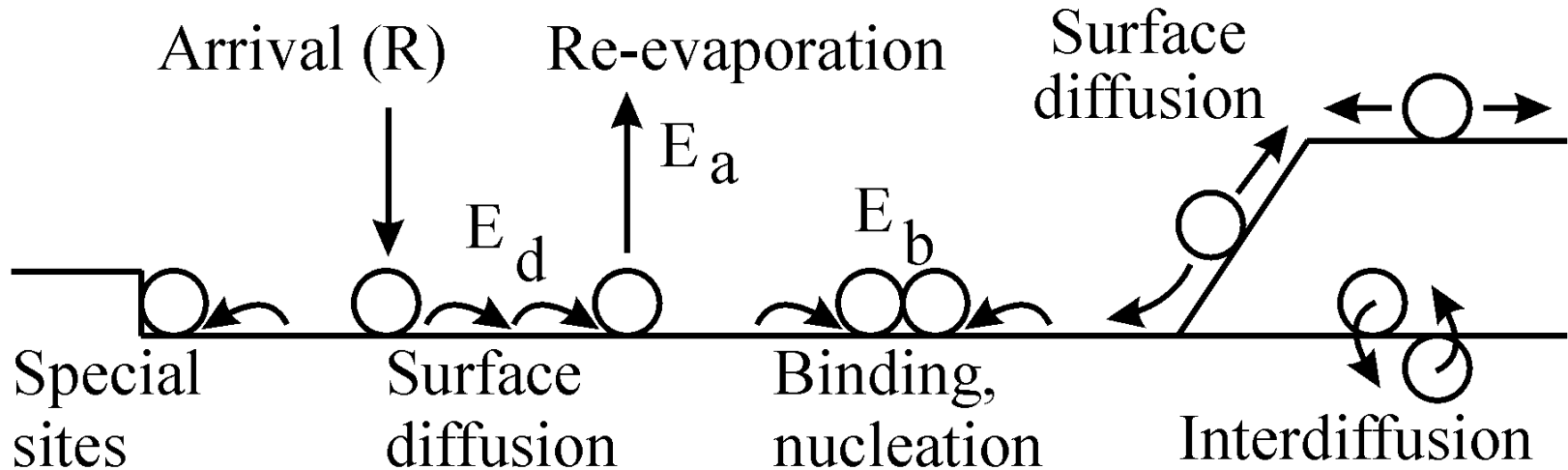
- **Homoepitaxy:** a crystalline film is grown on a substrate or film of the same material.
- **Heteroepitaxy:** a crystalline film grows on a crystalline substrate or film of a different material.

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

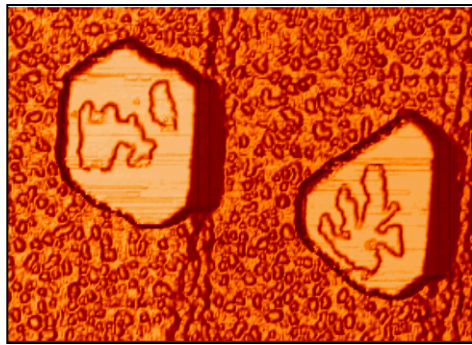
Atomic-level processes



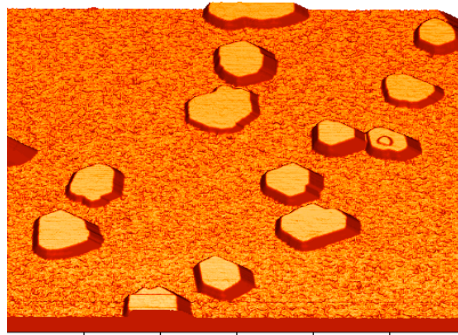
Variables: R (or F), T , time sequences (t)

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

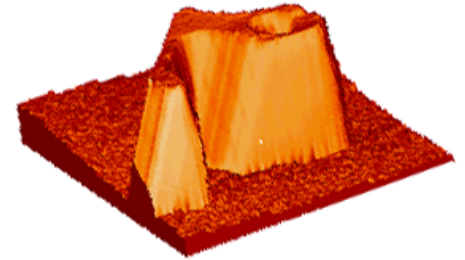
Growth modes at different temperature



Non-crystalline



2D islands



3D islands

150 K

300 K

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 $T = 25\text{ }^{\circ}\text{C}$

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

$$\lambda_{mfp} = \frac{1}{n\sigma} \quad n = P/kT$$

$$\lambda_{mfp} = \frac{kT}{P\sigma} \quad \sigma = \pi d^2$$

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

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

For N_2 molecules

$$d = 6.2 \text{ \AA}$$

Vacuum evaporation

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

$$\text{Flux, } \mathbf{F} = \mathbf{P} / (2\pi m k T)^{1/2} \text{ [molecules m}^{-2} \text{ s}^{-1} \text{]}$$

where

P - gas pressure [N m⁻²]

m - mass of one molecule [kg]

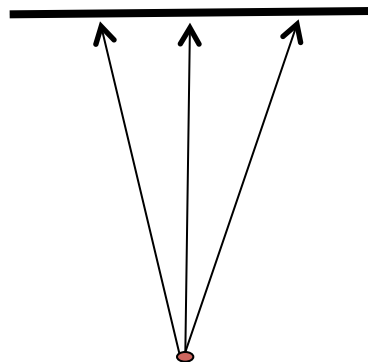
T - temperature [K]

$$F = nv/4,$$

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

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 1 Torr
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

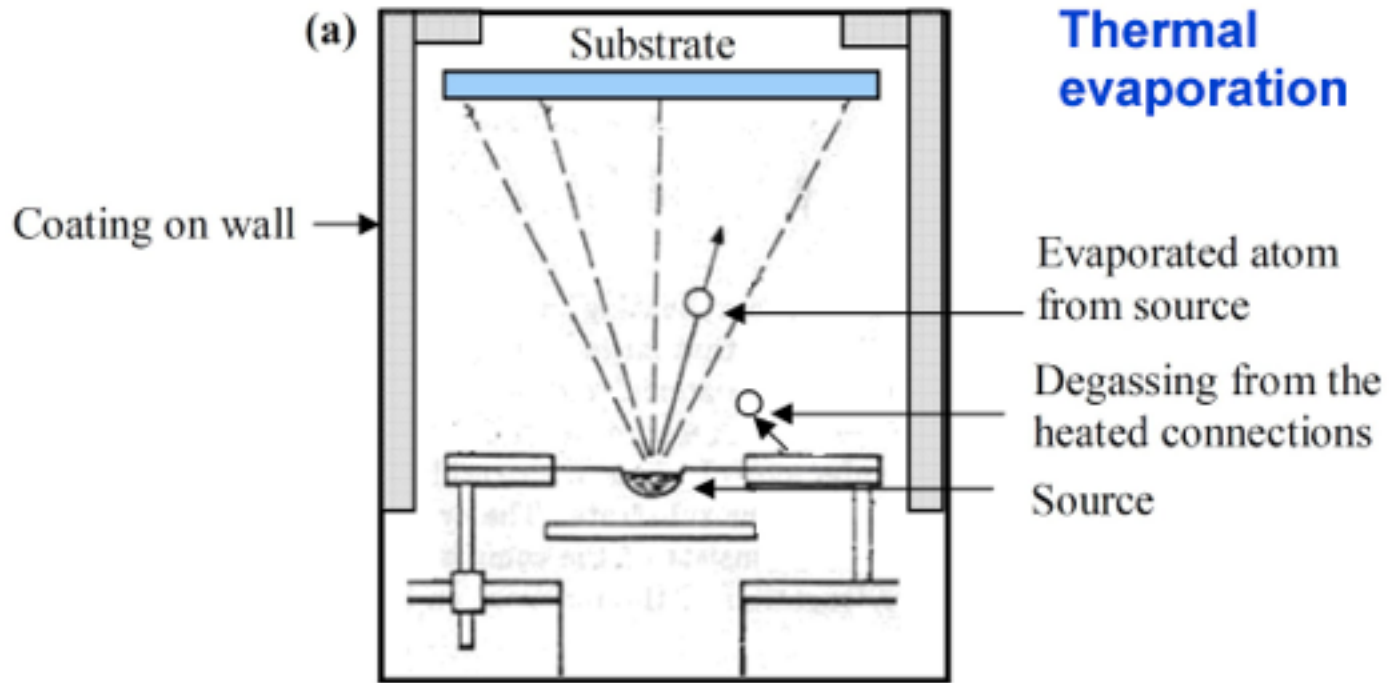
3) Gas capture pumps

ion pumps

must operate in conjunction
with other high vacuum pumps

to 10^{-11} torr

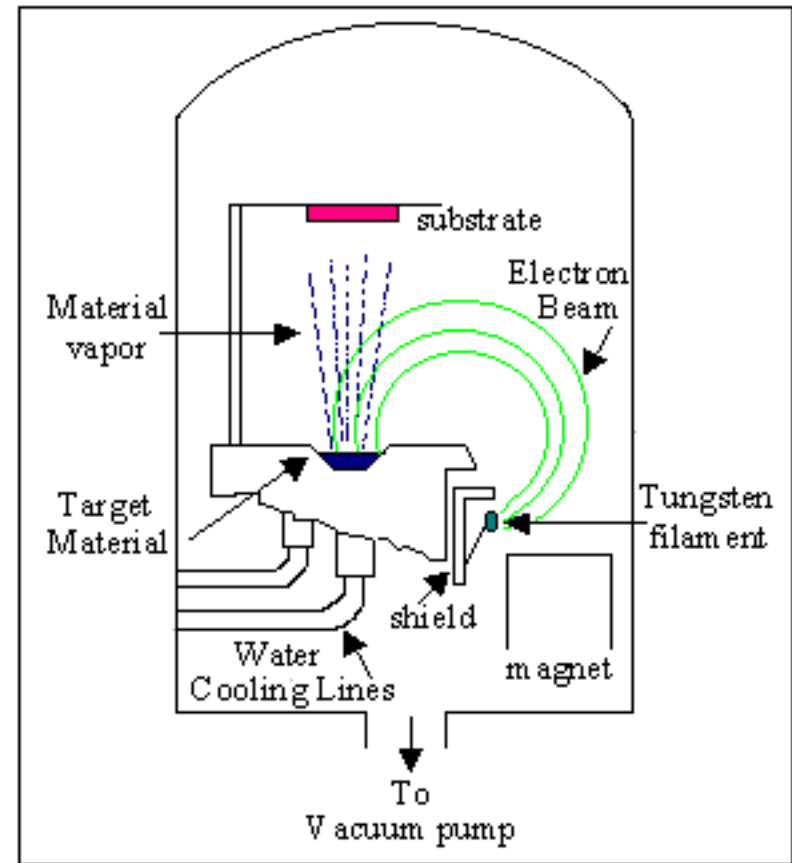
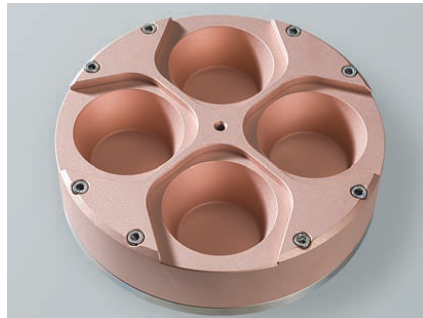
Thermal Evaporation



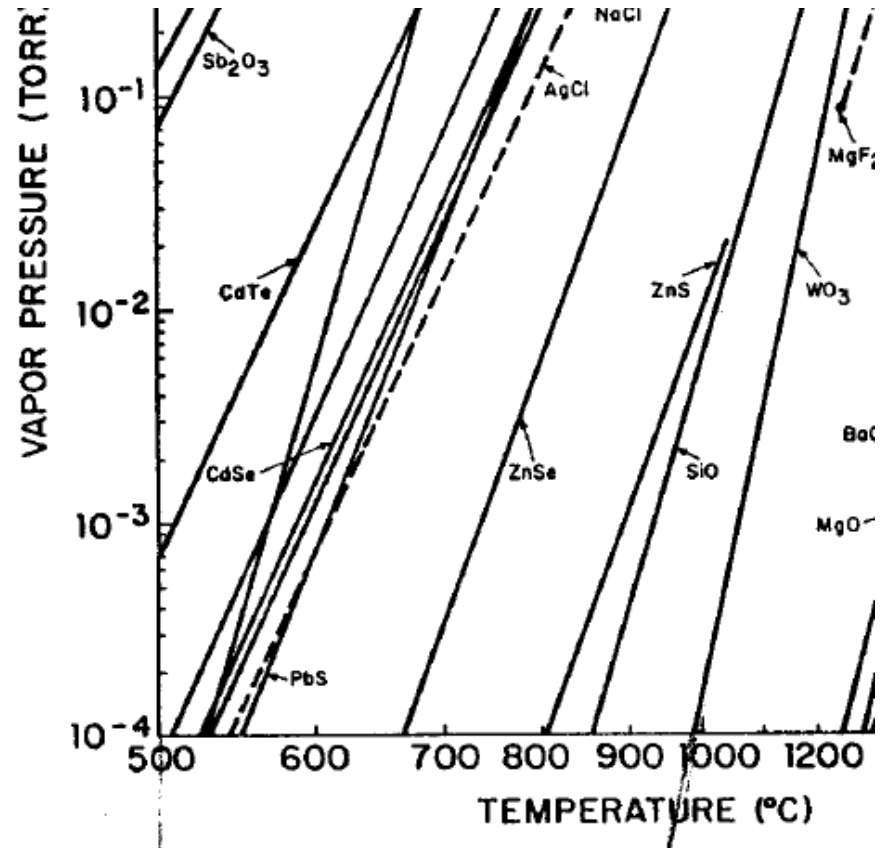
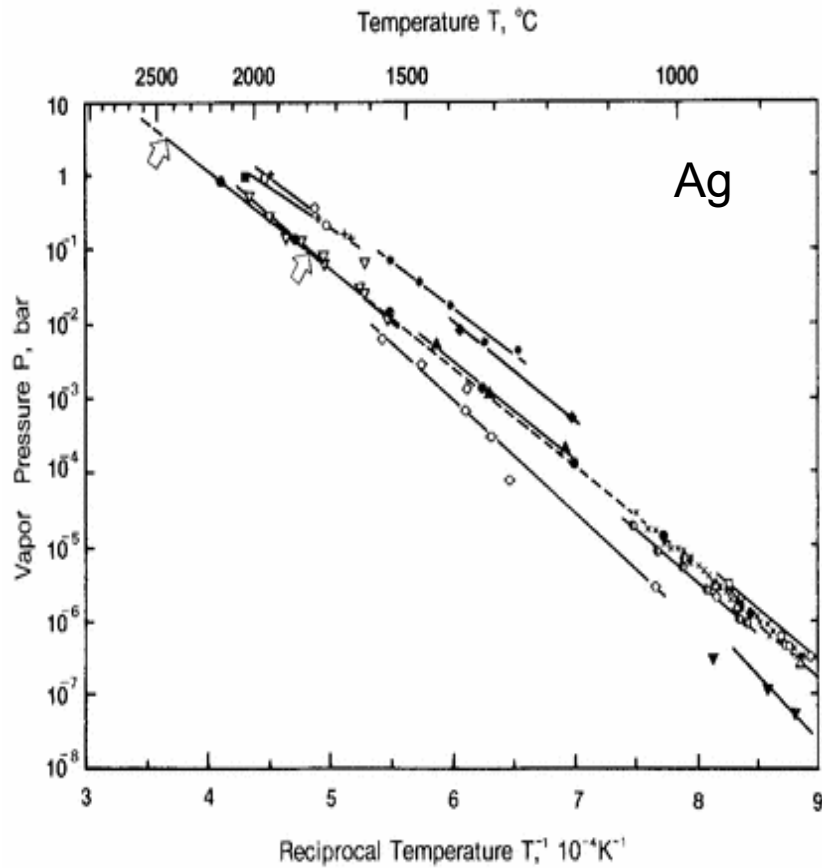
- Difficulties: High melting point materials, uniformly heating, rapidly change of deposition rate, reactions between the source and the heating container.

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.



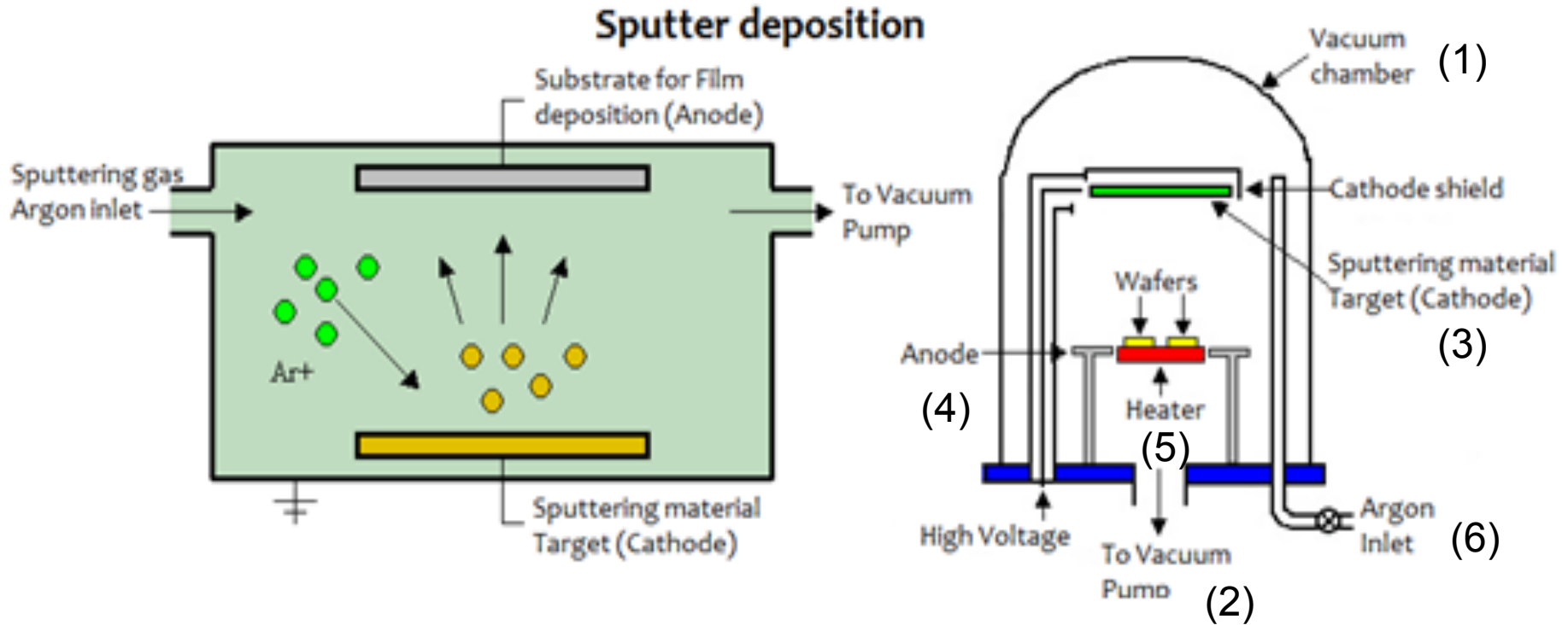
Vapor pressure



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.

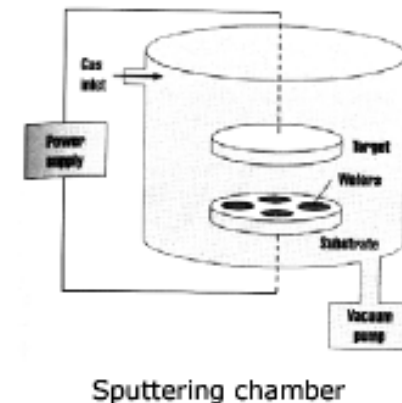
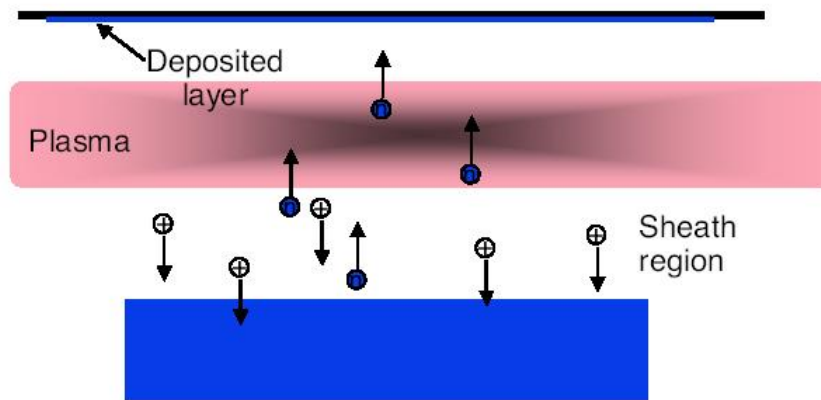
Sputter deposition system



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

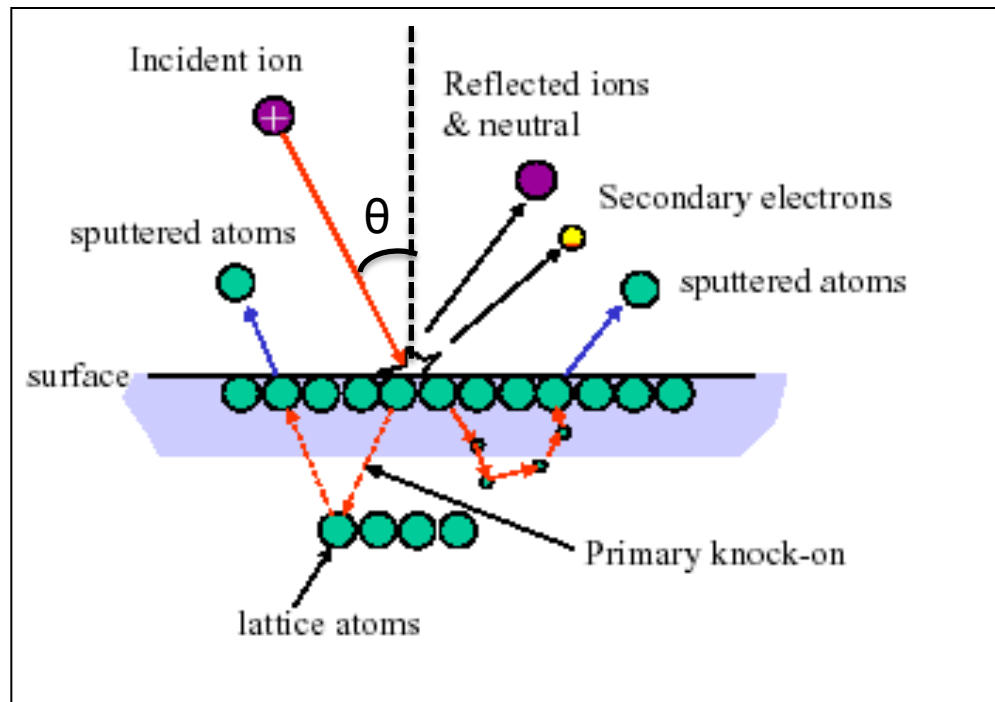
Sputtering Deposition Process

- **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



Mechanism of Sputtering

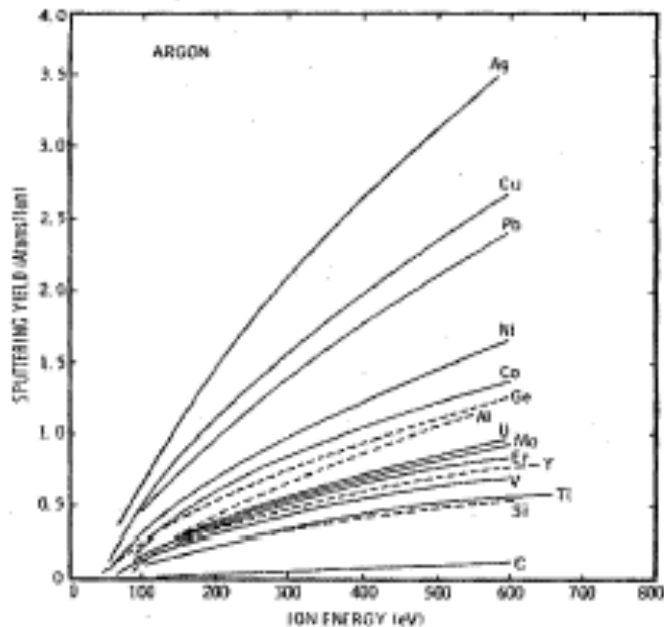
Sputtering involves the collisions of energetic ions with a target surface and the process usually leads to ejection of target atoms.



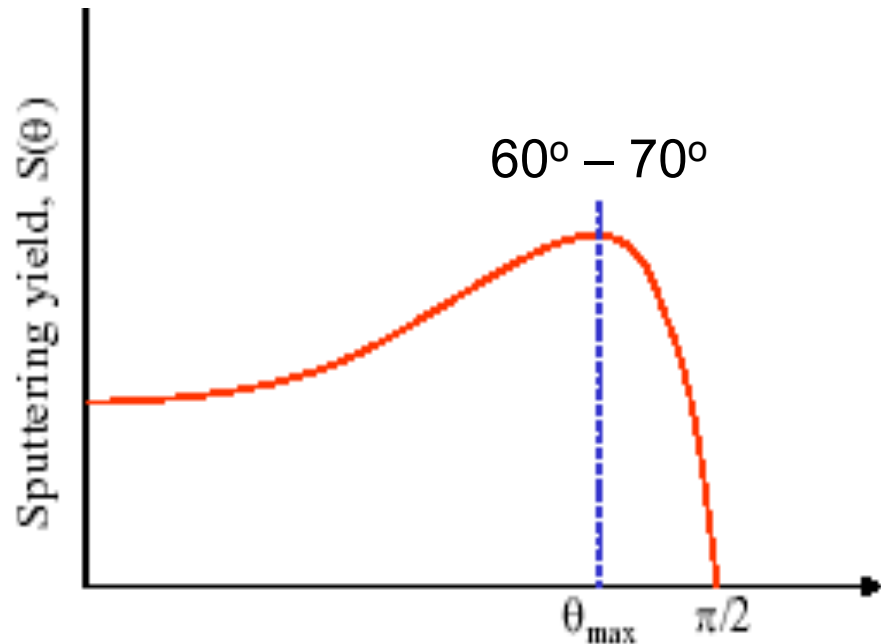
Sputtering process is characterized by sputter yield, S , which is typically in the range of 0.01 and 4 and increase with the mass of metals and energy of the sputtering gas.

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 normal incidence. Data from R.V. Stuart and G.K. Wehner, J. Appl. Phys.



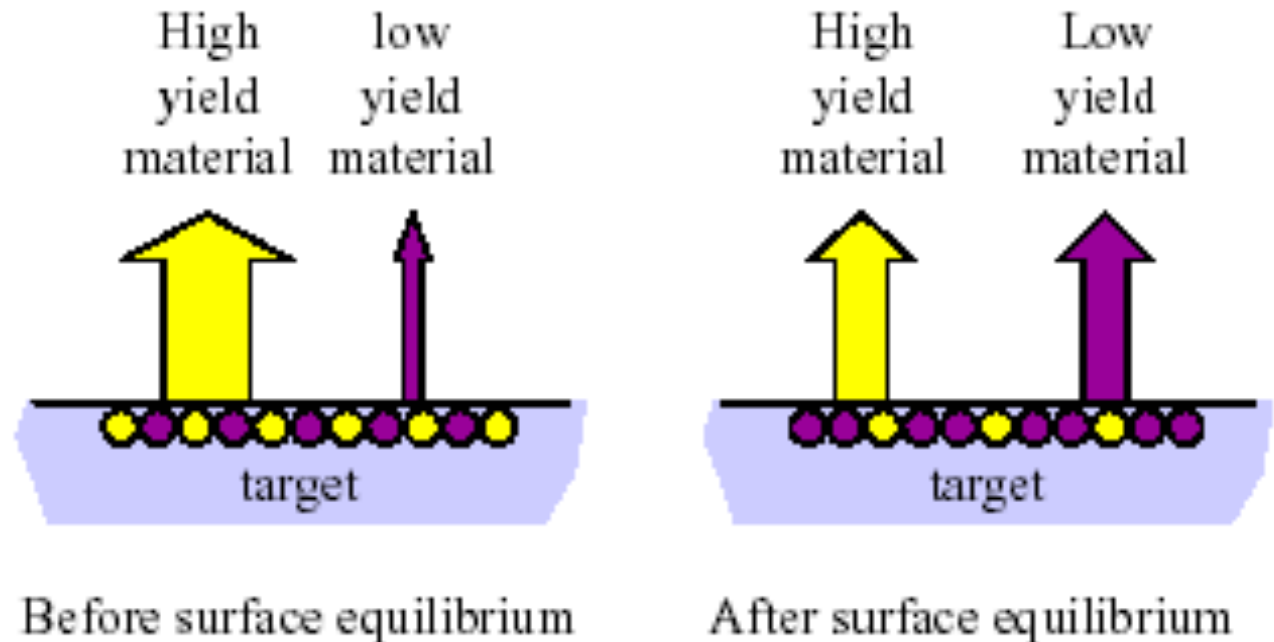
Sputtering Alloy Targets

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

Alloys



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.**

Disadvantages of Sputter Deposition

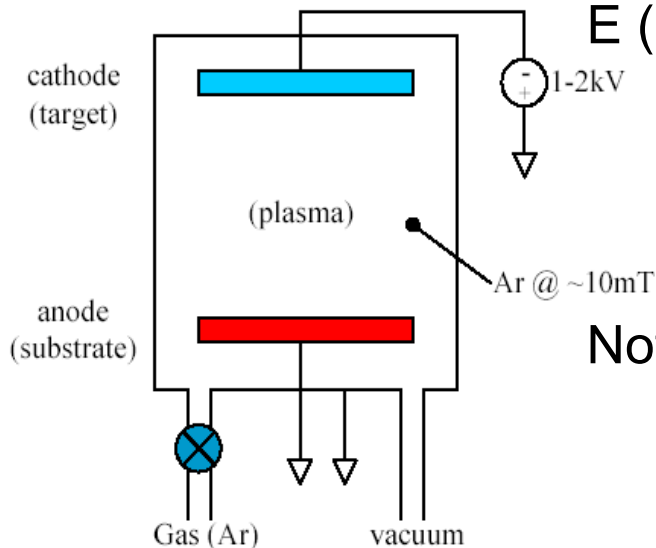
- **Sputtering rates are low compared to those that can be attained in thermal evaporation.**
- **Sputtering targets are often expensive.**
- **Most of the energy incident on the target becomes heat, which must be removed.**
- **In reactive sputter deposition, the gas composition must be carefully controlled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

Basic Techniques

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

DC Sputtering

The simplest sputtering technology



$E(e^-) < 2\text{eV}$ - no ionization, elastic collisions only
 $E(e^-) > 2\text{eV}$ - inelastic collisions add energy to Ar
➤ ionization (highest energy process, ~15eV)



Note: $\text{mass}(e^-)/\text{mass}(\text{Ar}) \sim 10^{-5}$

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

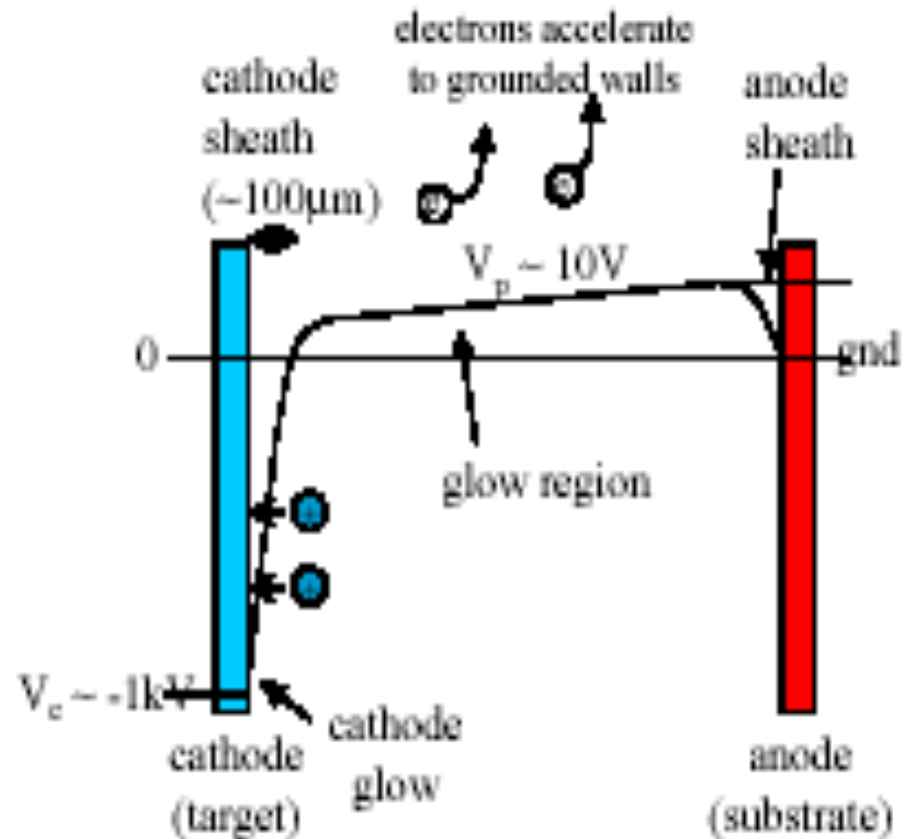
DC Sputtering (Cont.)

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



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

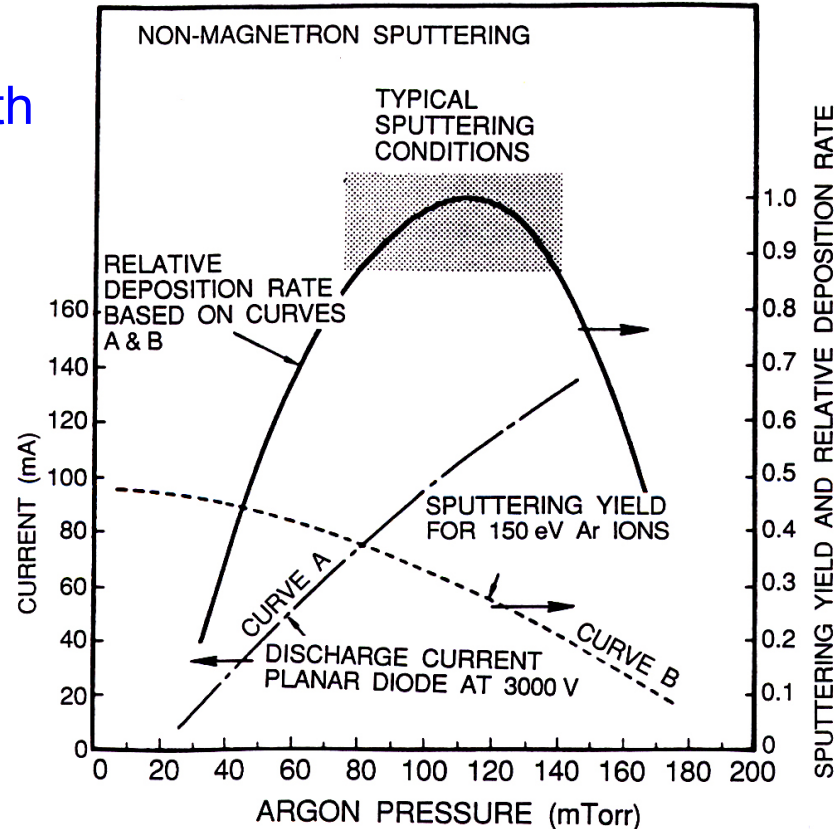


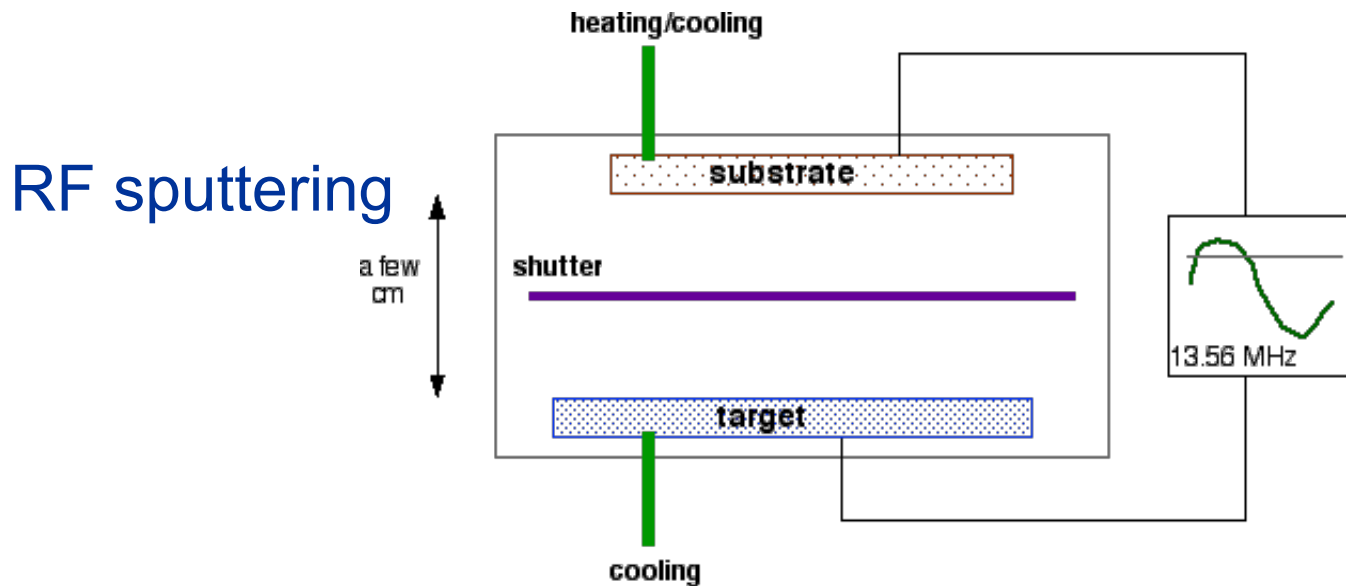
Figure 3-18. Influence of working pressure and current on deposition rate for nonmagnetron sputtering. (From Ref. 23).

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

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

- 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

Magnetron Sputter Deposition

❖ Use with DC or RF

- High sputtering efficiency

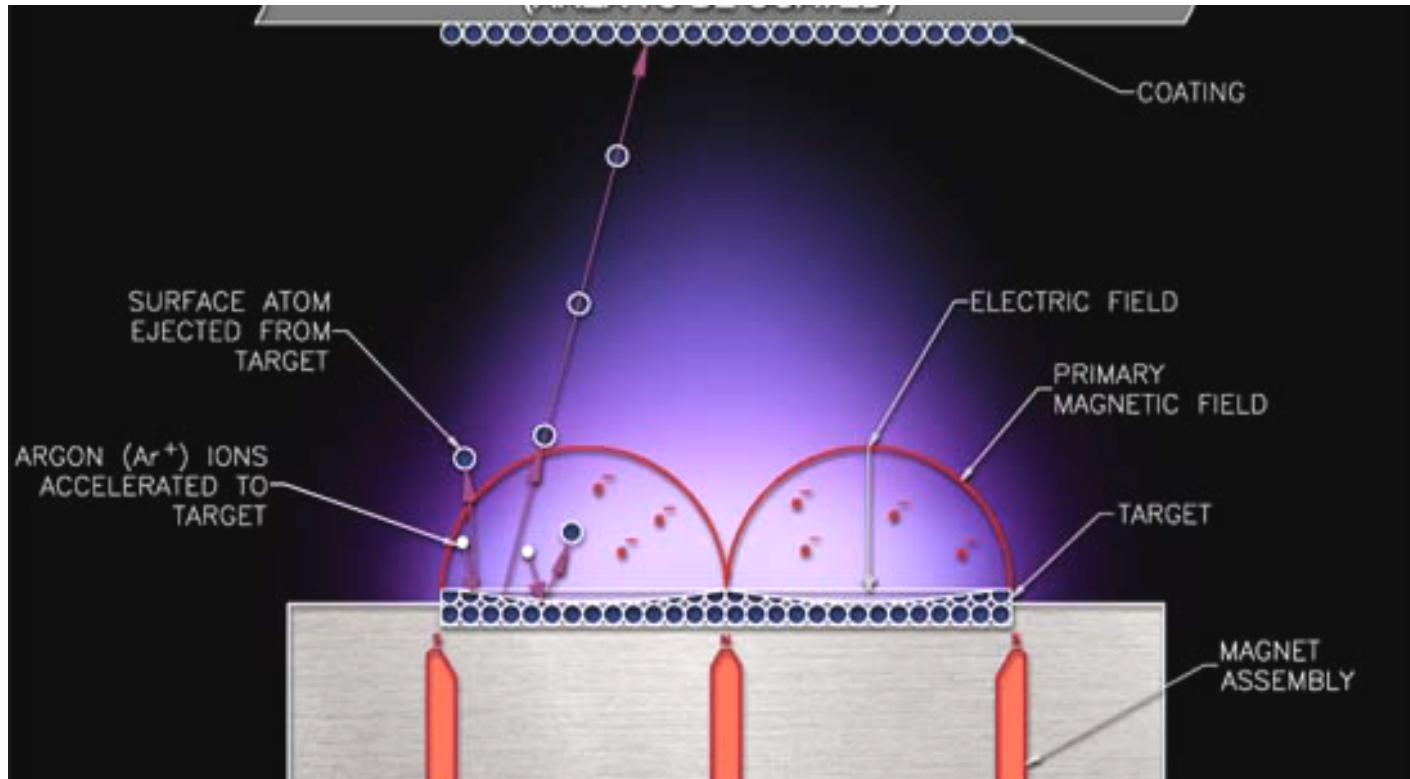
increase ionization of Ar

- 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.

Advantages of Magnetron Sputtering

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

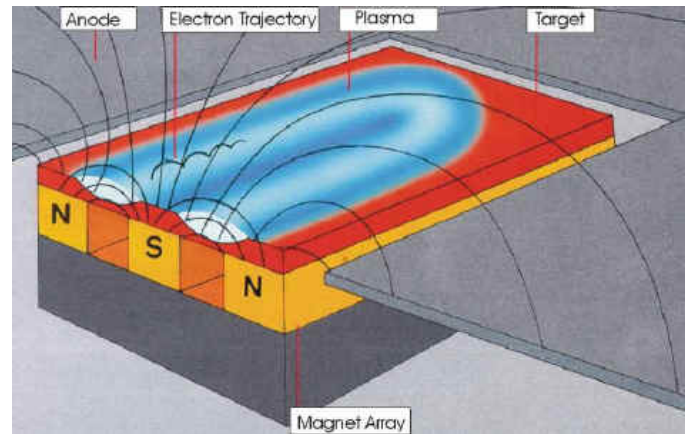
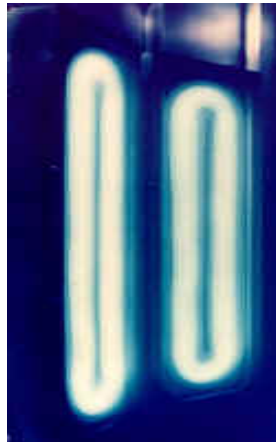
The most widely commercially practiced sputtering method

Parameters for Magnetron Sputtering

- **Deposition pressure : 10^{-3} to 0.1 Pa (10^{-5} to 10^{-3} torr)**
- **Deposition rate : 0.2 ~ 2 $\mu\text{m}/\text{min}$ (10 times higher than conventional sputtering)**
- **Deposition temperature : 100 to 150 $^{\circ}\text{C}$**

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



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.)

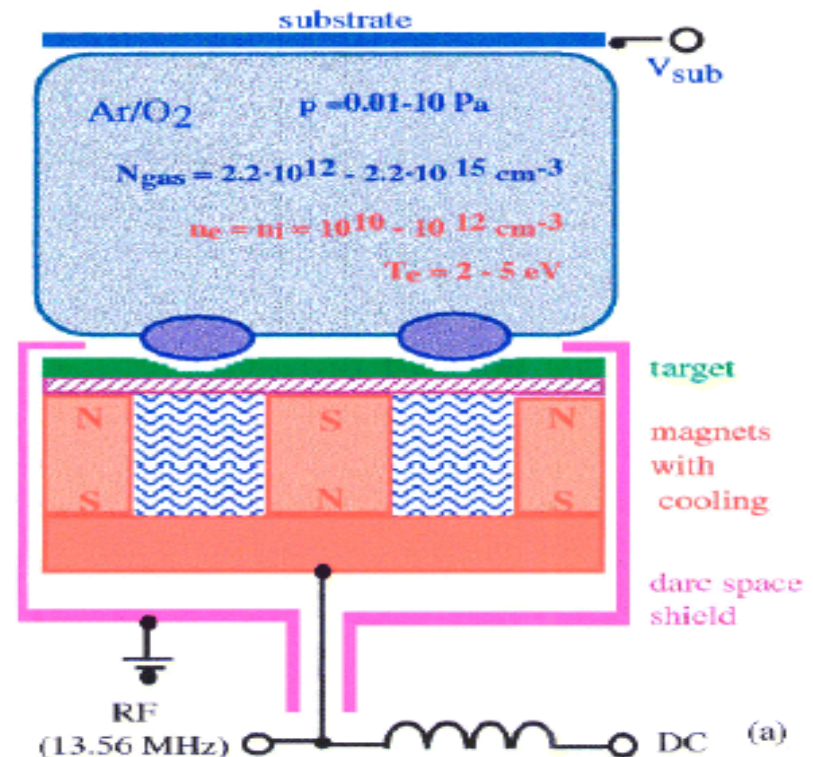
- **chemical reaction takes place on substrate and target**
- **can poison target if chemical reactions are faster than sputter rate**
- **adjust reactive gas flow to get good stoichiometry without incorporating excess gas into film**

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 depends 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	$\text{Ar} + \text{O}_2 = 20 - 80\%$
Power RF	100 W
Sputtering time	6 h
Substrate temperature	50–300 °C

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

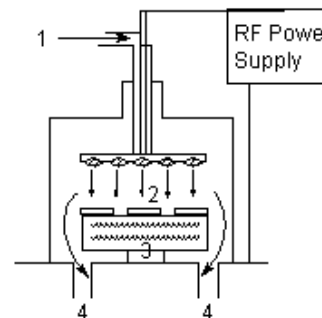
Photo Energy

UV-visible light

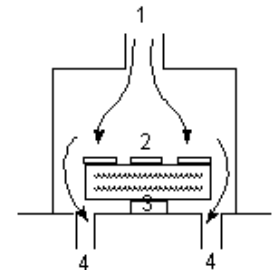
[laser](#) as photo energy source



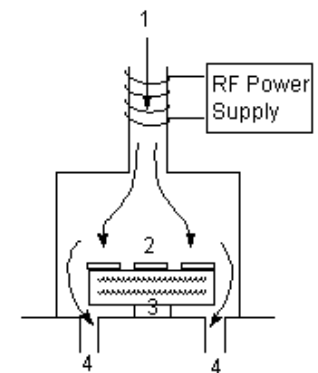
Horizontal Hot-Wall Reactor



Parallel Plate Plasma Reactor



Vertical Cold-Wall Reactor



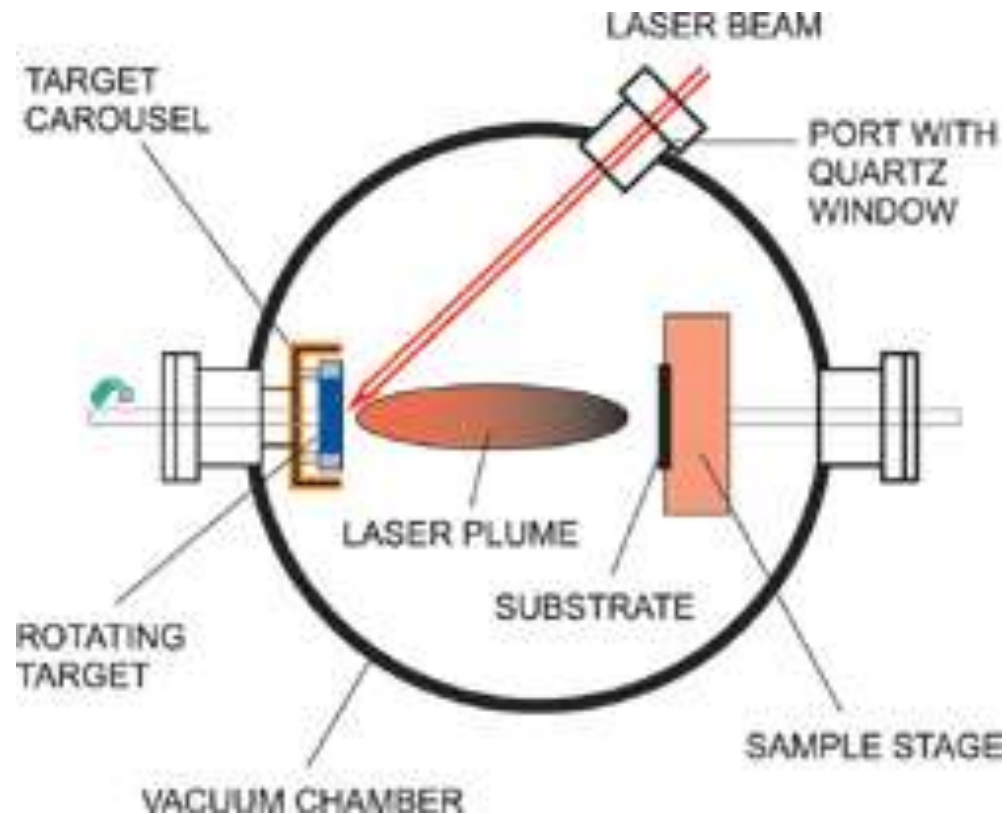
Inductive Tube
Remote-Plasma Reactor

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

Laser ablation

- Pulsed laser deposition (PLD).
- Ultraviolet (UV) light (~ 200 nm – 400 nm).
- High energy (> 1 J/cm²).
- Pulsed, not continuous, laser beam.
- Excimer laser: Gas laser, F₂ (157 nm), ArF (193 nm), KrCl (222 nm), KrF (248 nm), XeCl (308 nm), XeF (351 nm).
- Nd³⁺: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.

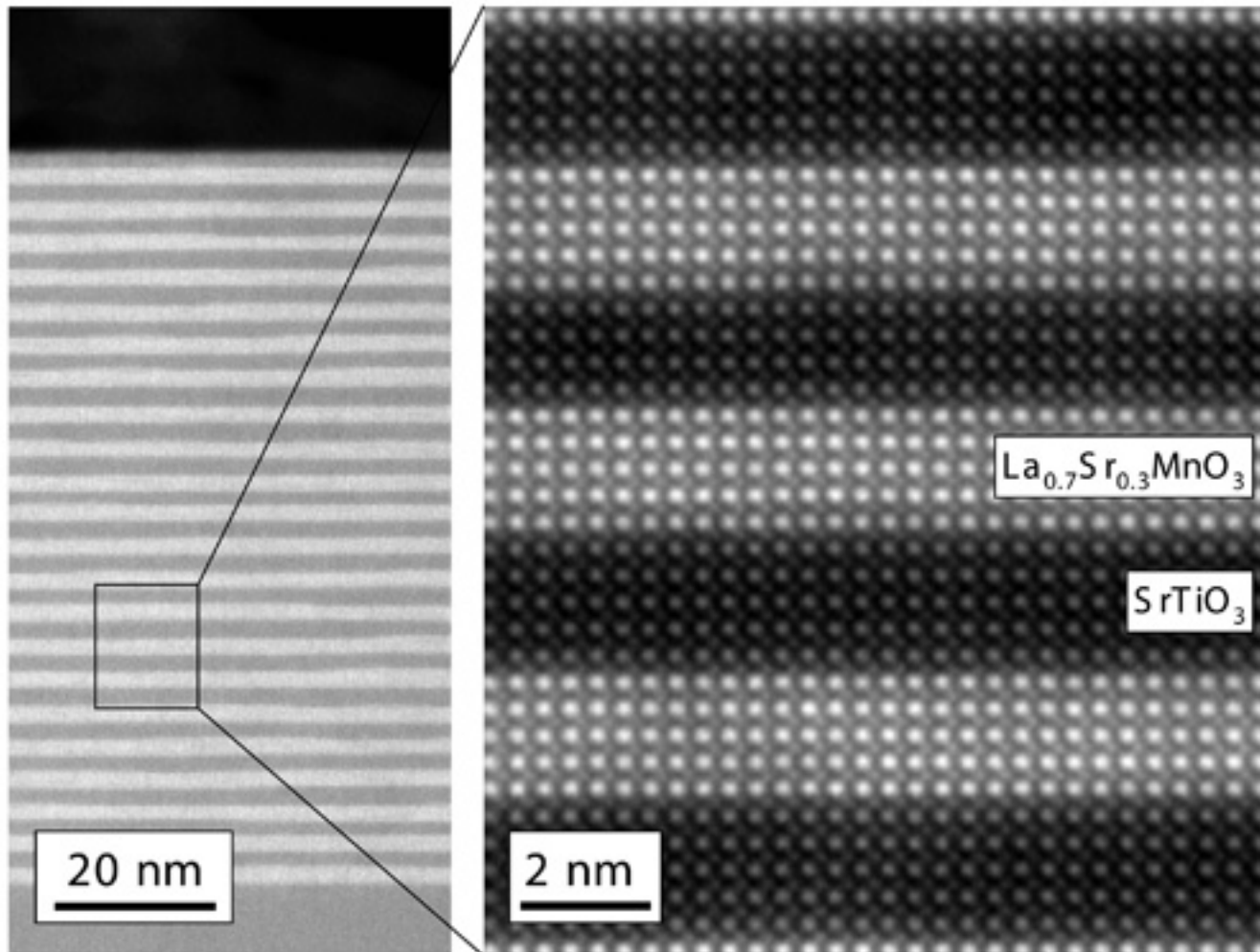
Pulsed Laser Deposition



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.

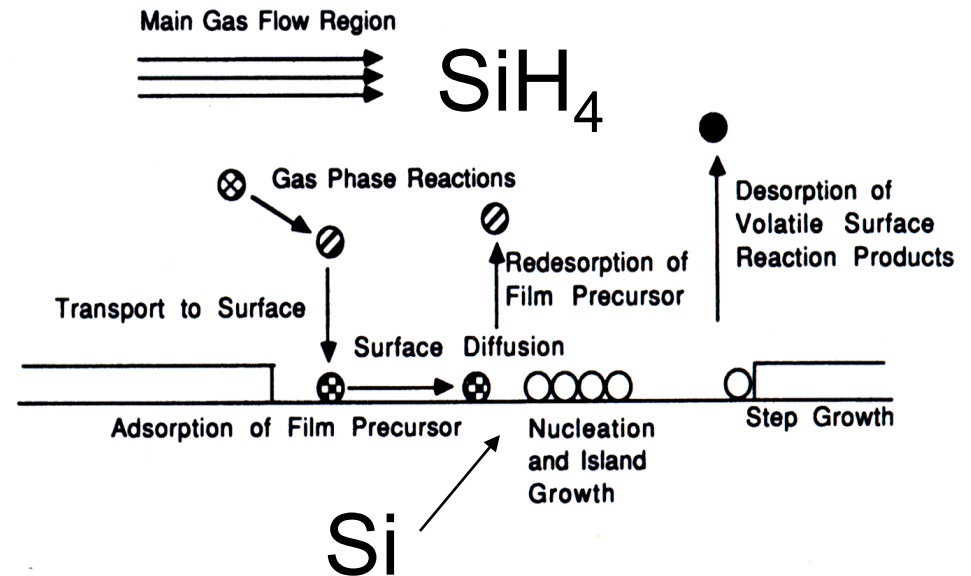
Films grown by CVD

- 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.

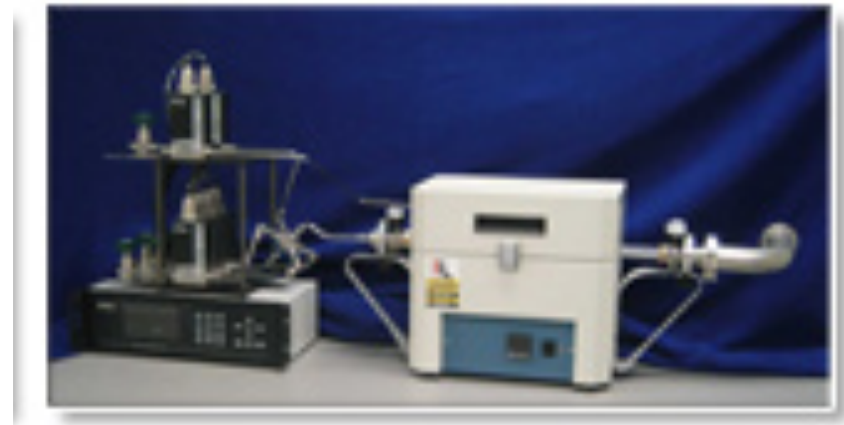
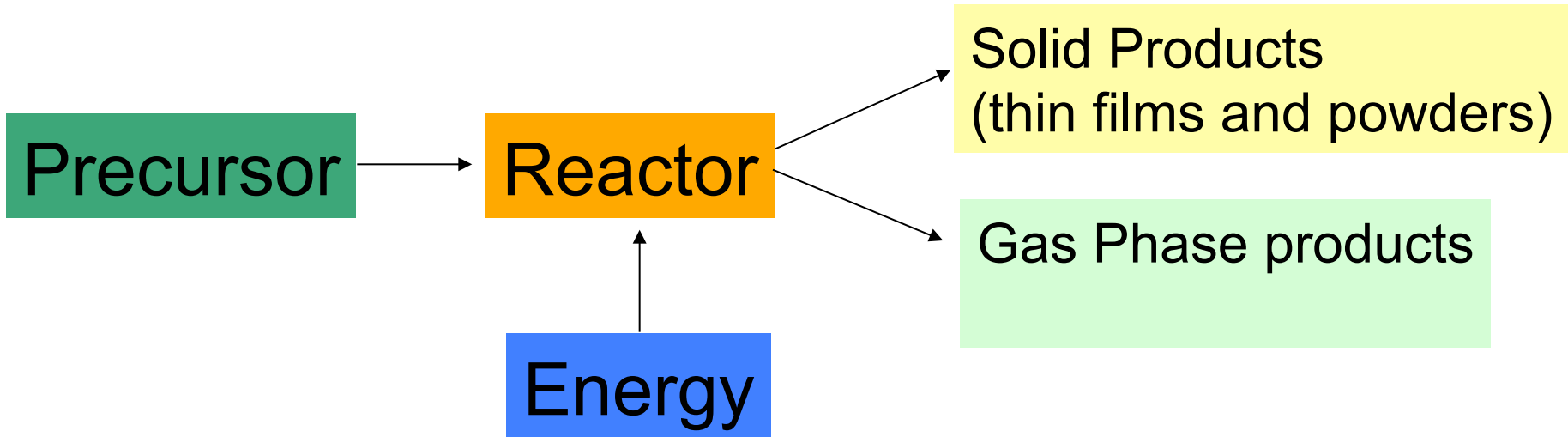
Chemical vapor deposition: reaction mechanisms

- 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-products 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 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: MH_x -
 SiH_4 , GeH_4 , $AlH_3(NMe_3)_2$, NH_3 , PH_3 ...

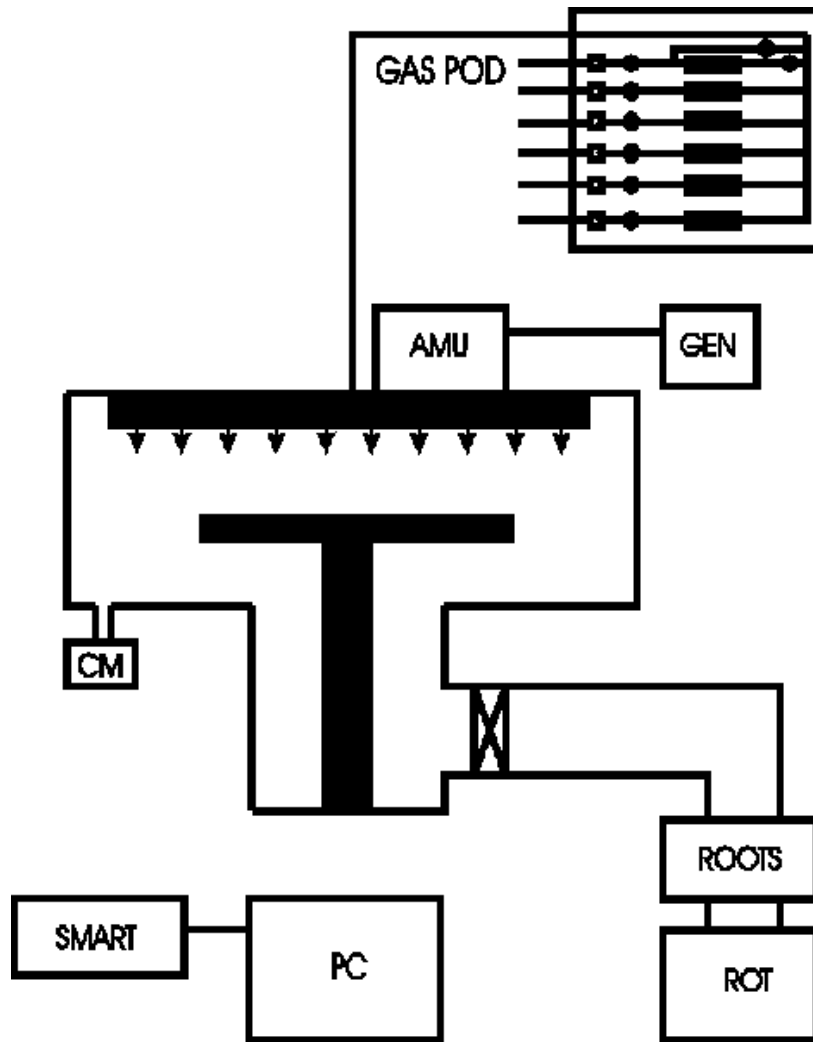
halides: MX_y -
 $TiCl_4$, $TaCl_5$, MoF_6 , WF_6 , ...

metal-organics -
metal alkyls: $AlMe_3$, $Al(iBu)_3$, $Ti(CH_2tBu)_4$
metal alkoxides: $Ti(OiPr)_4$, $[Cu(OtBu)]_4$
metal dialkylamides: $Ti(NMe_2)_4$, $Cr(NEt_2)_4$
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

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 $< 350^\circ\text{C}$.
- Low pressure.

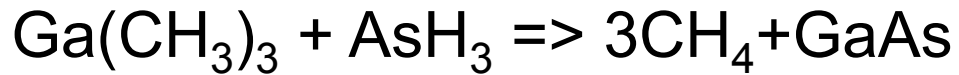
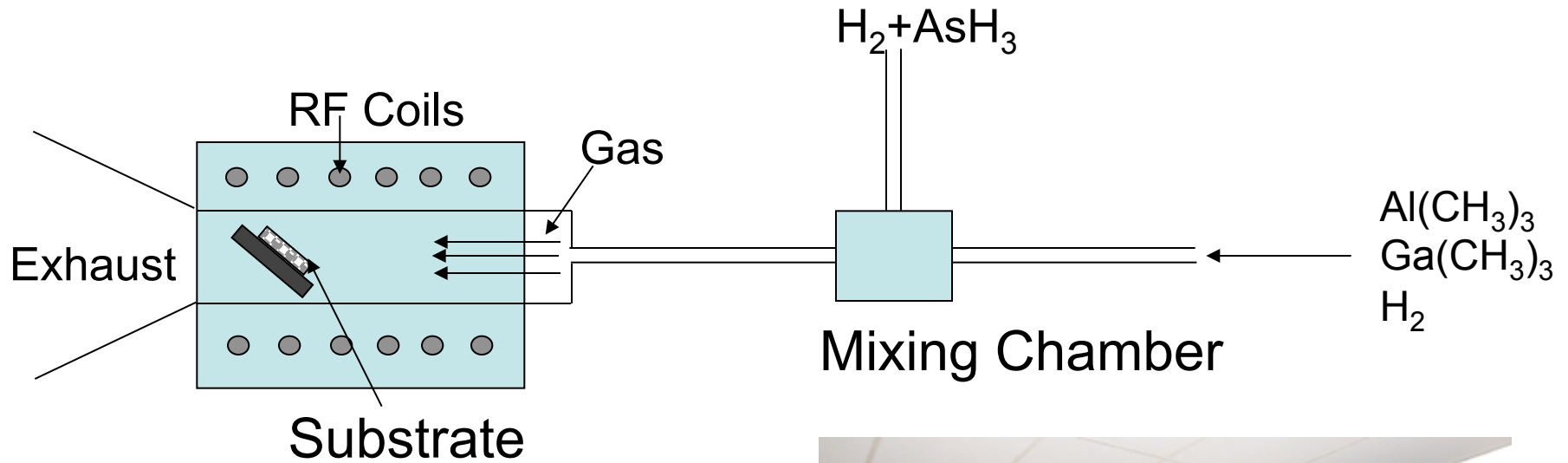
PECVD



MOCVD

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

MOCVD



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.

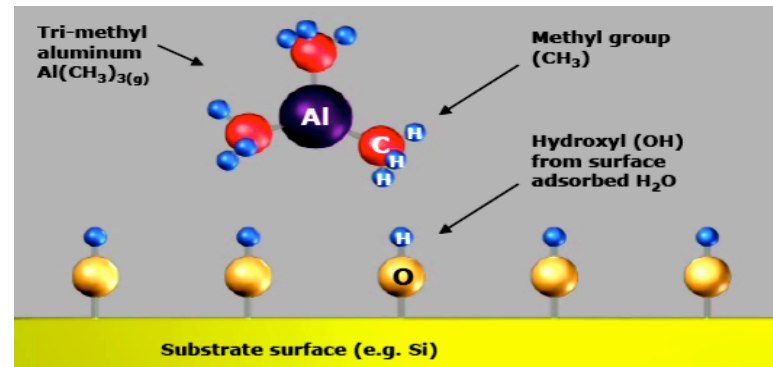
ALD Process and Equipments

- 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:

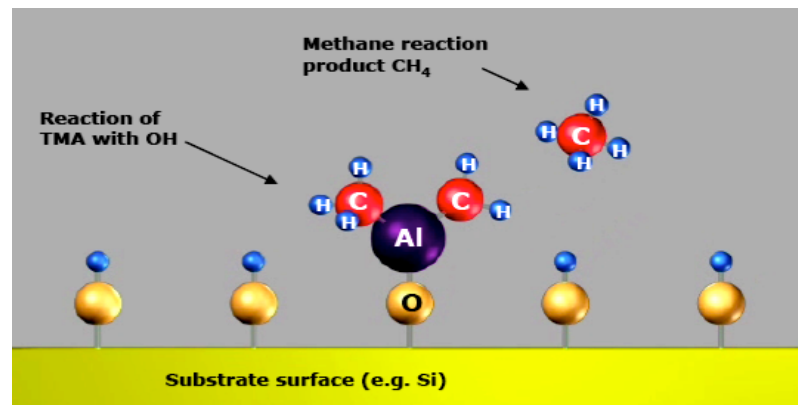
- *Chemisorption saturation process*
- *Sequential surface chemical reaction process*

Example: ALD cycle for Al_2O_3 deposition



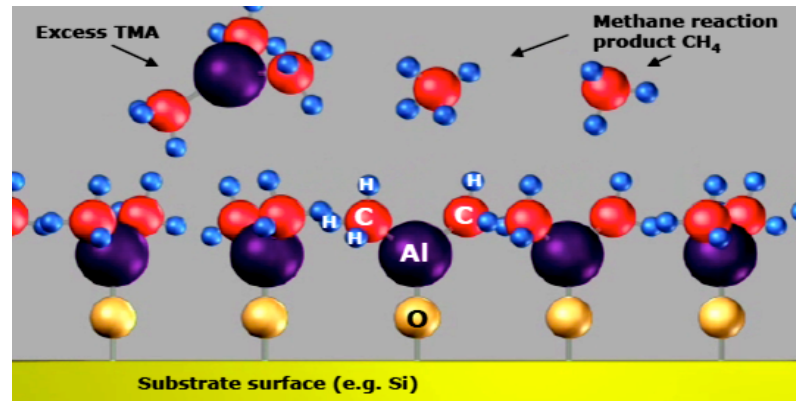
In air H_2O vapor is adsorbed on most surfaces, forming a hydroxyl group. With silicon this forms: $\text{Si-O-H}_{(\text{s})}$

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

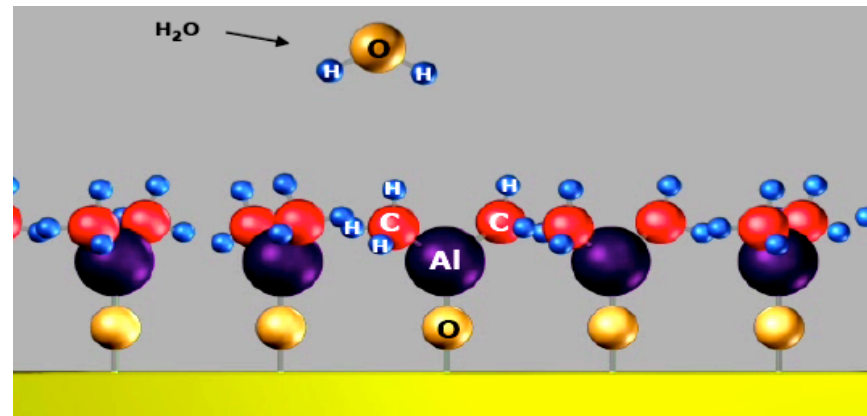


Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product

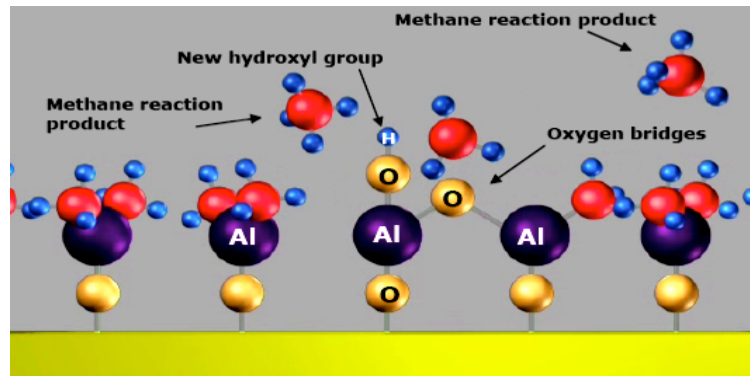




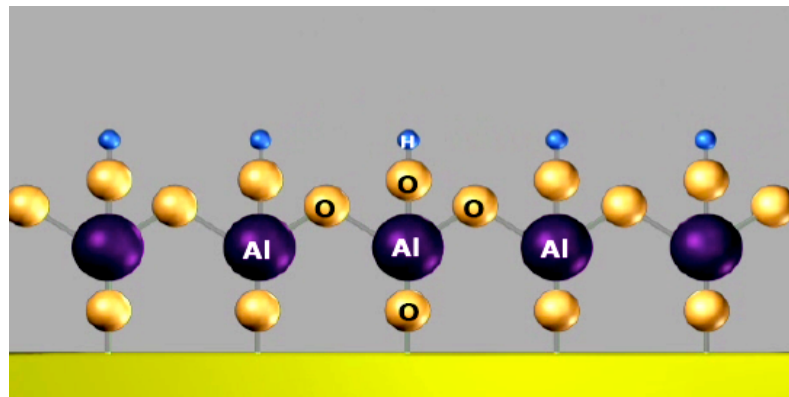
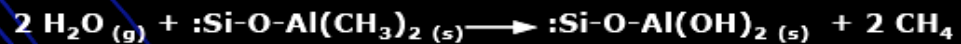
Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, until the surface is passivated. TMA does not react with itself, terminating the reaction to one layer. This causes the perfect uniformity of ALD. The excess TMA is pumped away with the methane reaction product.



After the TMA and methane reaction product is pumped away, water vapor (H₂O) is pulsed into the reaction chamber.

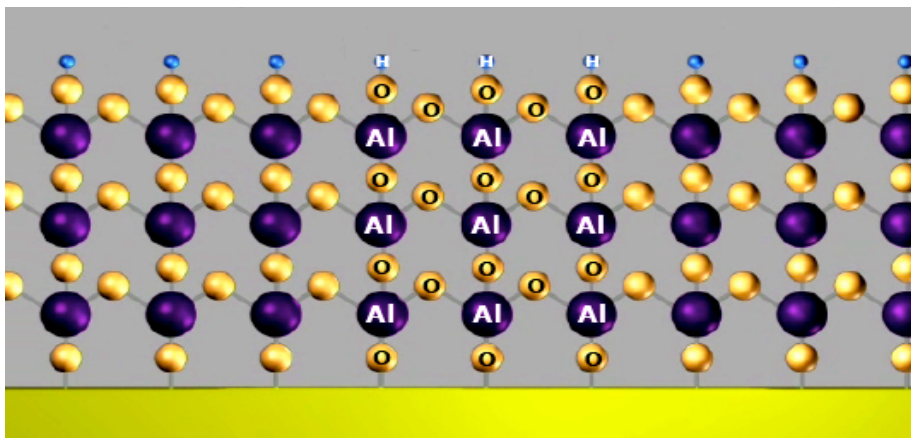


H₂O reacts with the dangling methyl groups on the new surface forming aluminum-oxygen (Al-O) bridges and hydroxyl surface groups, waiting for a new TMA pulse. Again methane is the reaction product.



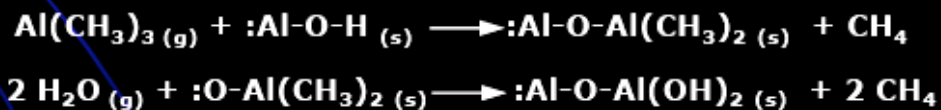
The reaction product methane is pumped away. Excess H₂O vapor does not react with the hydroxyl surface groups, again causing perfect passivation to one atomic layer.

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:



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.

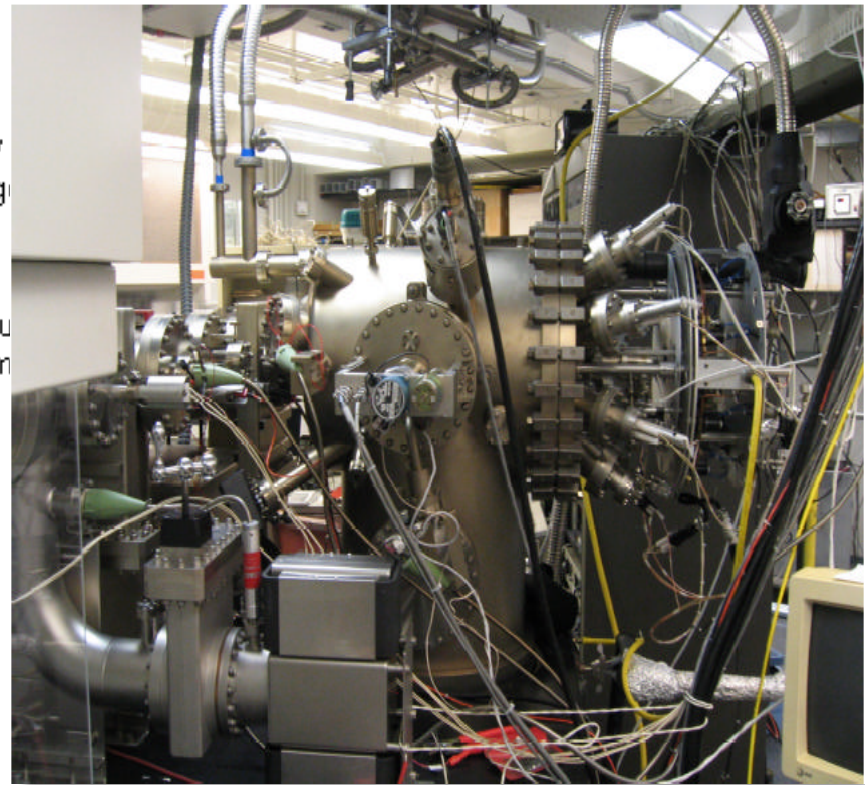
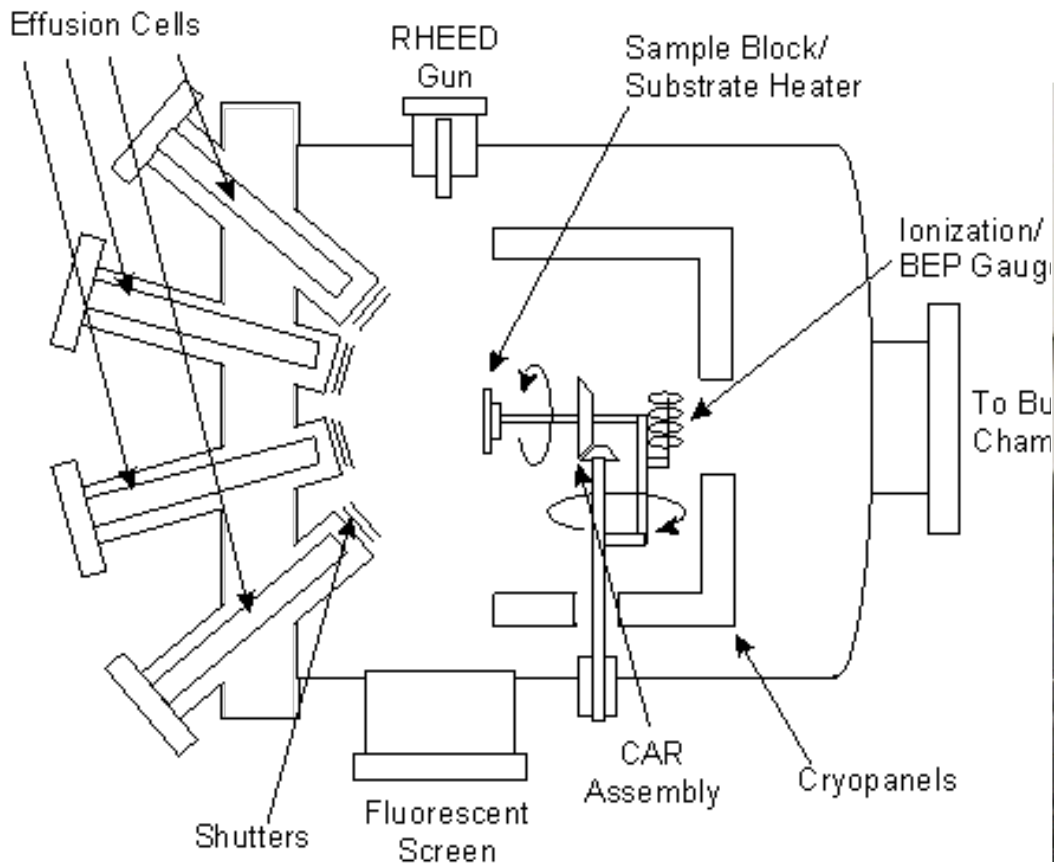
- Disadvantages

- 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: $<5 \times 10^{-11}$ torr.
- Non-epitaxy films: amorphous or polycrystalline.

Molecular Beam Epitaxy



MBE deposition system

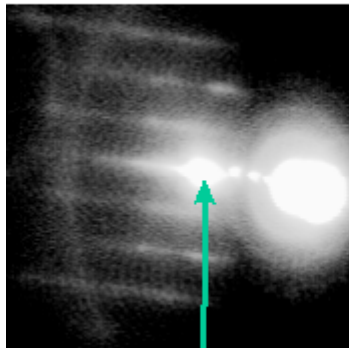
- Load lock for substrate loading & unloading.
- Liquid nitrogen shroud to cool the wall.
- Substrate heating: clean surface.
- Film growth: ultrahigh vacuum, shutters to control the flux, in-situ analysis and thickness monitor (RHEED) to control the deposition rate.

RHEED

- Reflection high energy electron diffraction.
- High energy: $> 10 \text{ KeV}$.
- Small (grazing) angle incidence ($< 3^\circ$).
- Low depth penetration: $< 100 \text{ \AA}$.
- Lateral ordered structure: Surface structure symmetry, lattice constant.

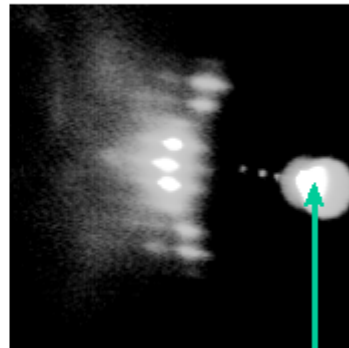
RHEED

'2 x' Pattern

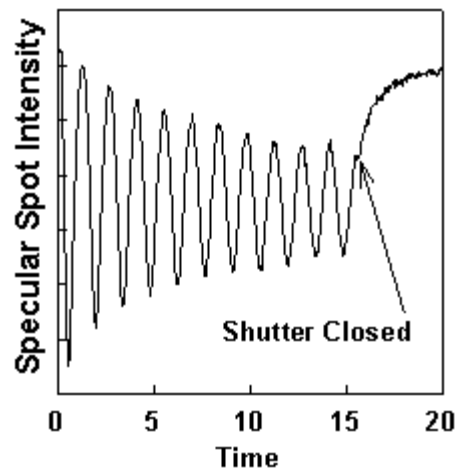


Specular Reflection

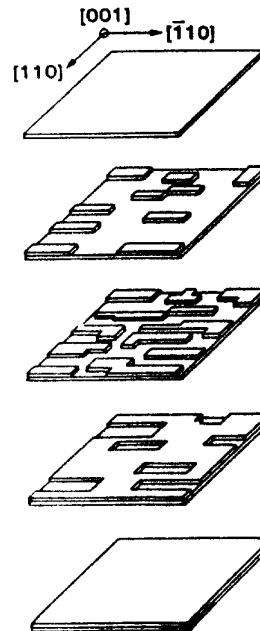
'4 x' Pattern



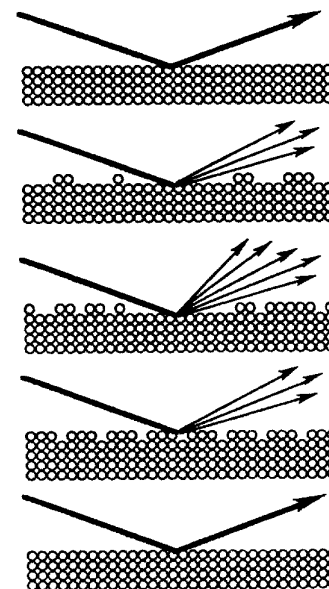
Straight-Through Beam



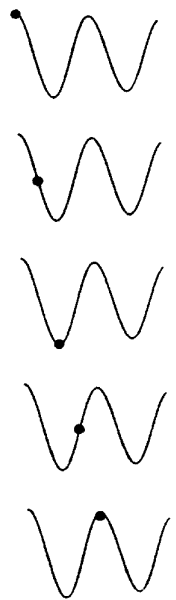
MONOLAYER GROWTH



ELECTRON BEAM

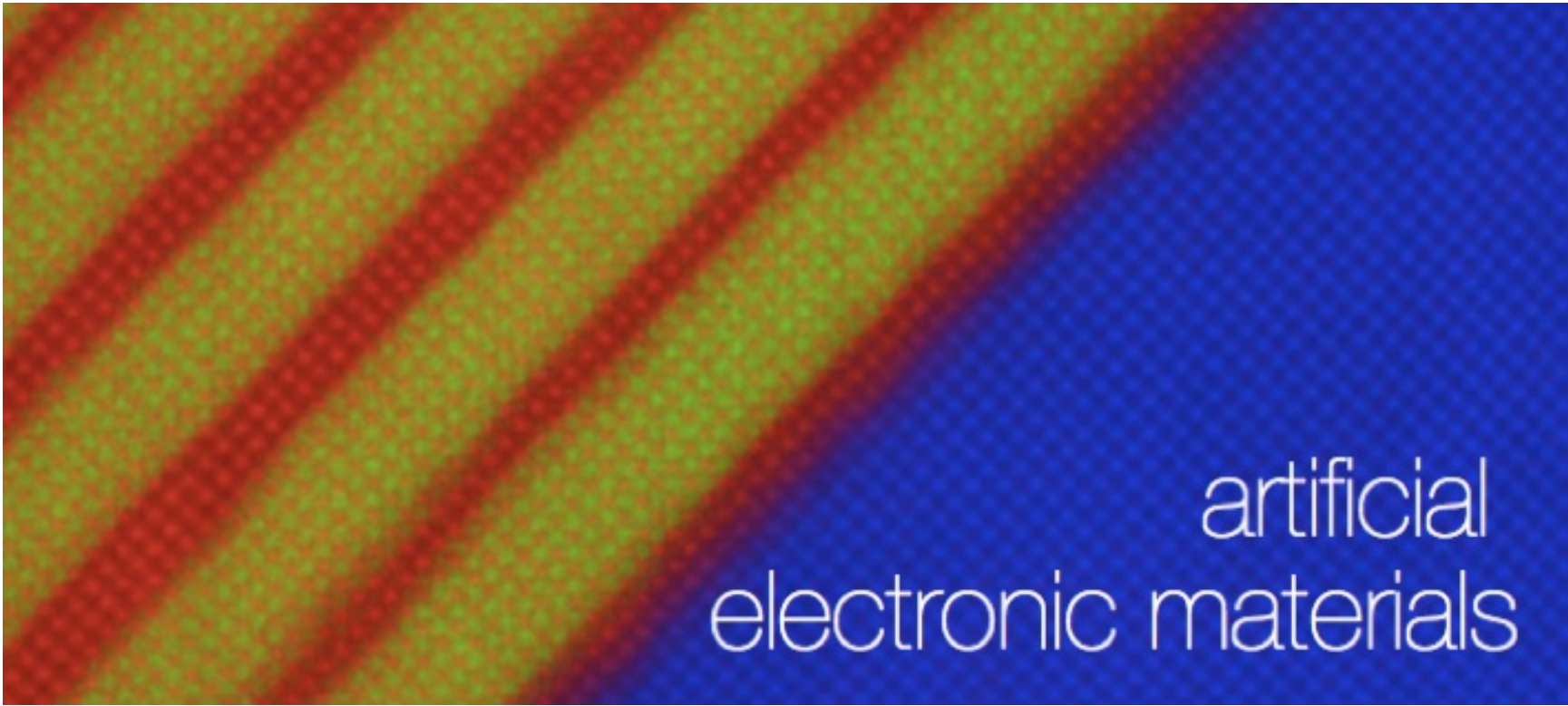


RHEED SIGNAL



MBE film growth

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

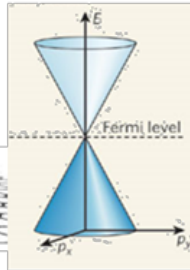
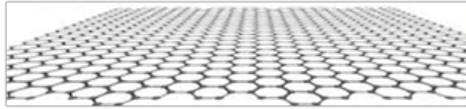


artificial
electronic materials

Diversity of 2D Atomic Layers

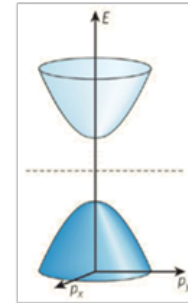
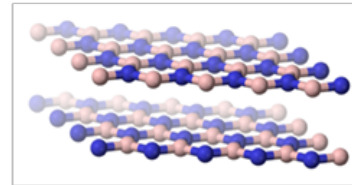
Semi-metal

Graphene



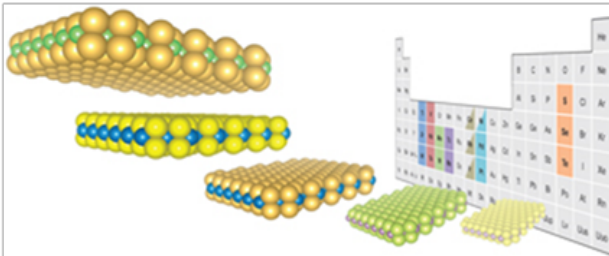
Insulator

Transition metal oxides
Boron nitride

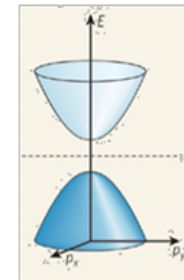


Semiconductor

Transition metal dichalcogenides (TMD)
e.g. MoS_2 , MoSe_2 , WS_2 , WSe_2 ...

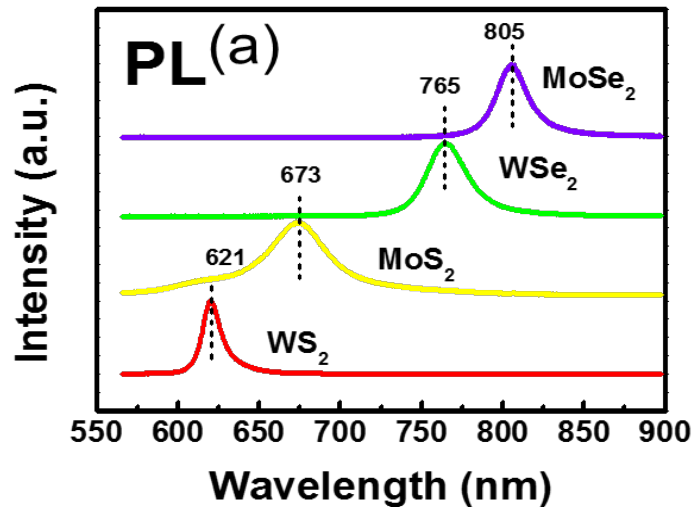


Black phosphorus



Ideal Bandgap

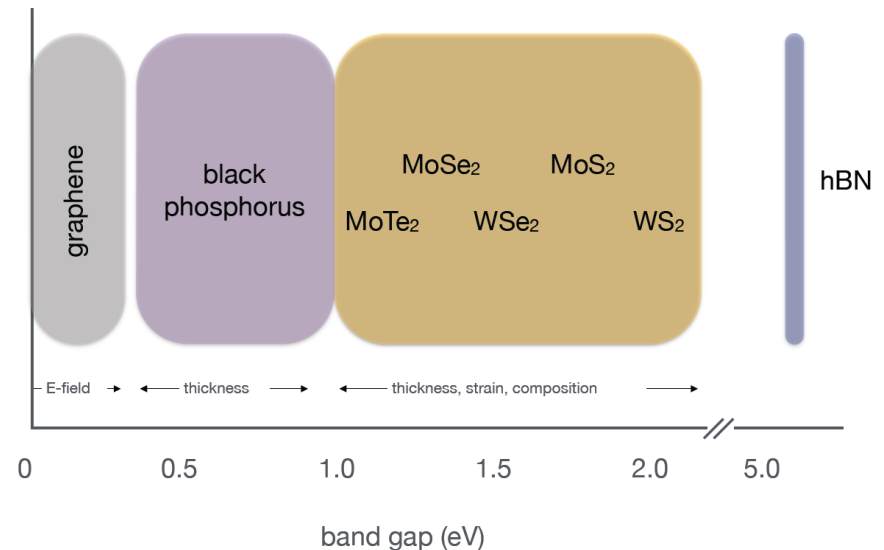
Direct Bandgap



Ref: Sam Yang, Y.H. Lee*, [VLSI](#) (2016)

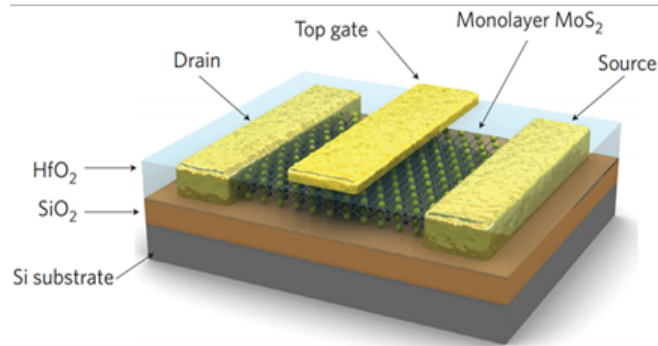
Bandgap Engineering

- Materials System
- Thickness
- Strain
- Composition



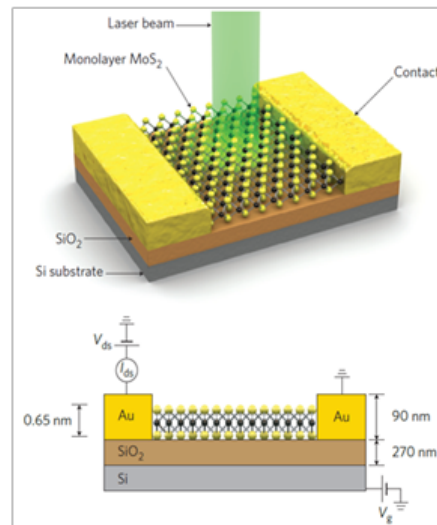
Prominent Properties

FET



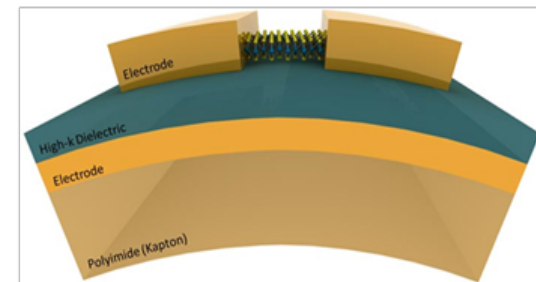
Nature Nanotech. **6**, 147–150 (2011).

Photodetector



Nature Nanotech. **8**, 497–501 (2013).

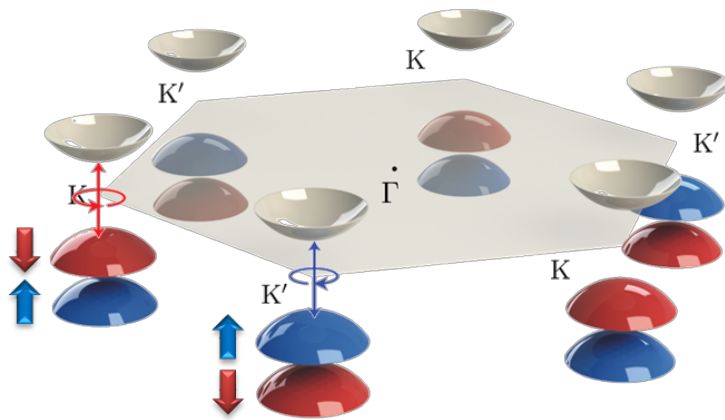
Flexible electronics device



ACS Nano. **2013**, **6**, 5446-5452

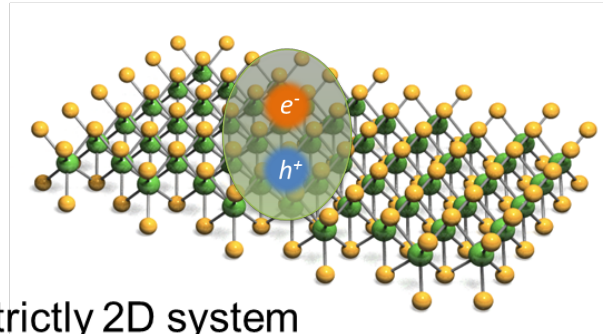
Novel Physics

Optically controlled
spin-valley states



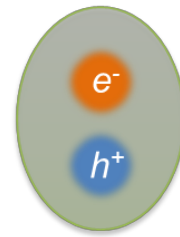
Spintronics and valleytronics

Many-body interactions



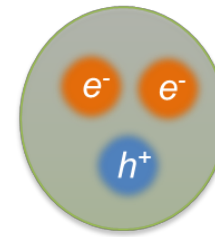
Strictly 2D system

→ strong Coulomb interactions



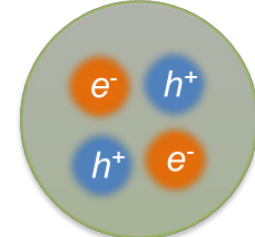
exciton

E_b : >500 meV
(Bolotin)



trion

>20 meV
(Heinz)



bi-exciton

>20 meV
(Gedik)

Nanowire preparations

- Specific substrate crystallographic structures.
- Catalytic growth by a liquid droplet in vapor-liquid-solid process.
- Template: Anodic aluminum oxides.
- Self-assembly.
- Lithography.

Techniques for making nanowires

- **Spontaneous growth:**
 - Evaporation condensation
 - Dissolution condensation
 - Vapor-Liquid-Solid growth (VLS)
 - Stress induced re-crystallization
- **Template-based synthesis:**
 - Electrochemical deposition
 - Electrophoretic deposition
 - Colloid dispersion, melt, or solution filling
 - Conversion with chemical reaction
- **Electro-spinning**
- **Lithography** (*top-down*)

General characters for spontaneous growth

- Anisotropic growth is required
- Crystal growth proceeds along one direction, where as there is no growth along other direction.
- Uniformly sized nanowires (i.e. the same diameter along the longitudinal direction of a given nanowire)

Vapor-Solid (VS) technique

- Nanowires and nanorods grown by this method are commonly single crystals with fewer imperfections
- The formation of nanowires or nanorods is due to the anisotropic growth.
- The general idea is that the different facets in a crystal have different growth rates
- There is no control on the direction of growth of nanowire in this method

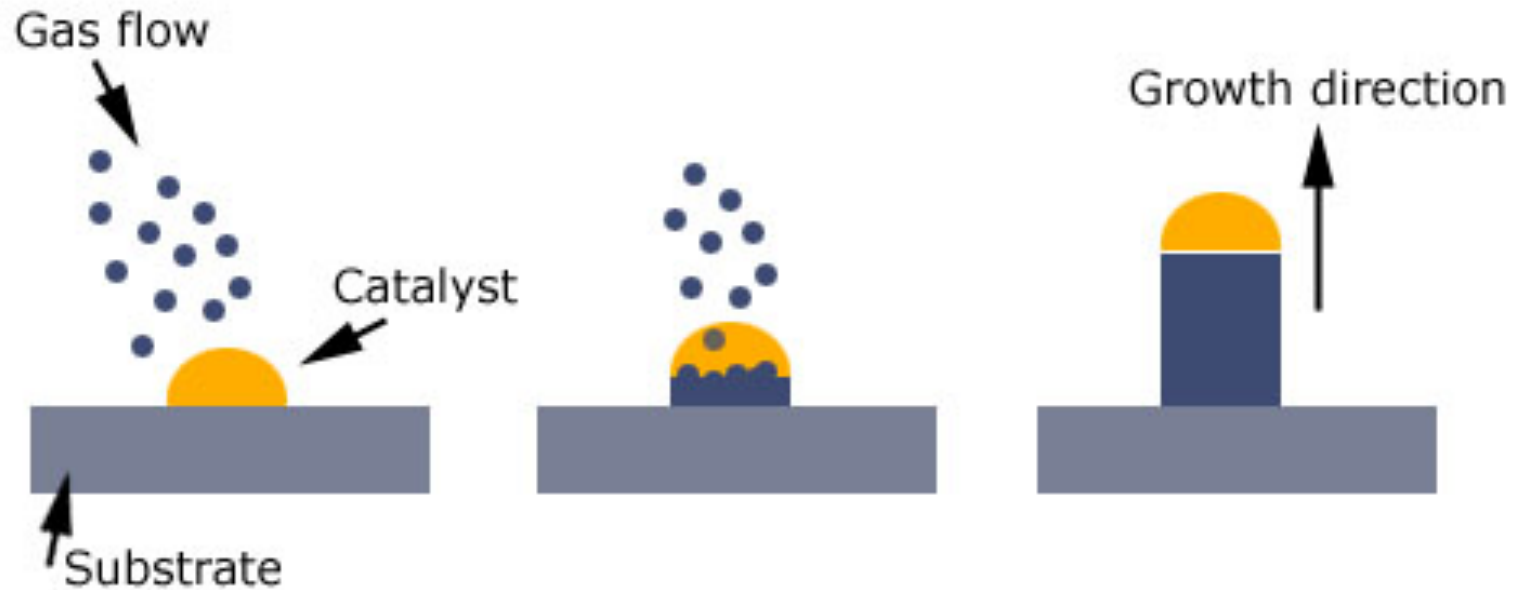
Vapor Liquid Solid Growth (VLS)

General Idea:

A second phase material, commonly referred to as ***catalyst***, is introduced to direct and confine the crystal growth on a specific orientation and within a confined area.

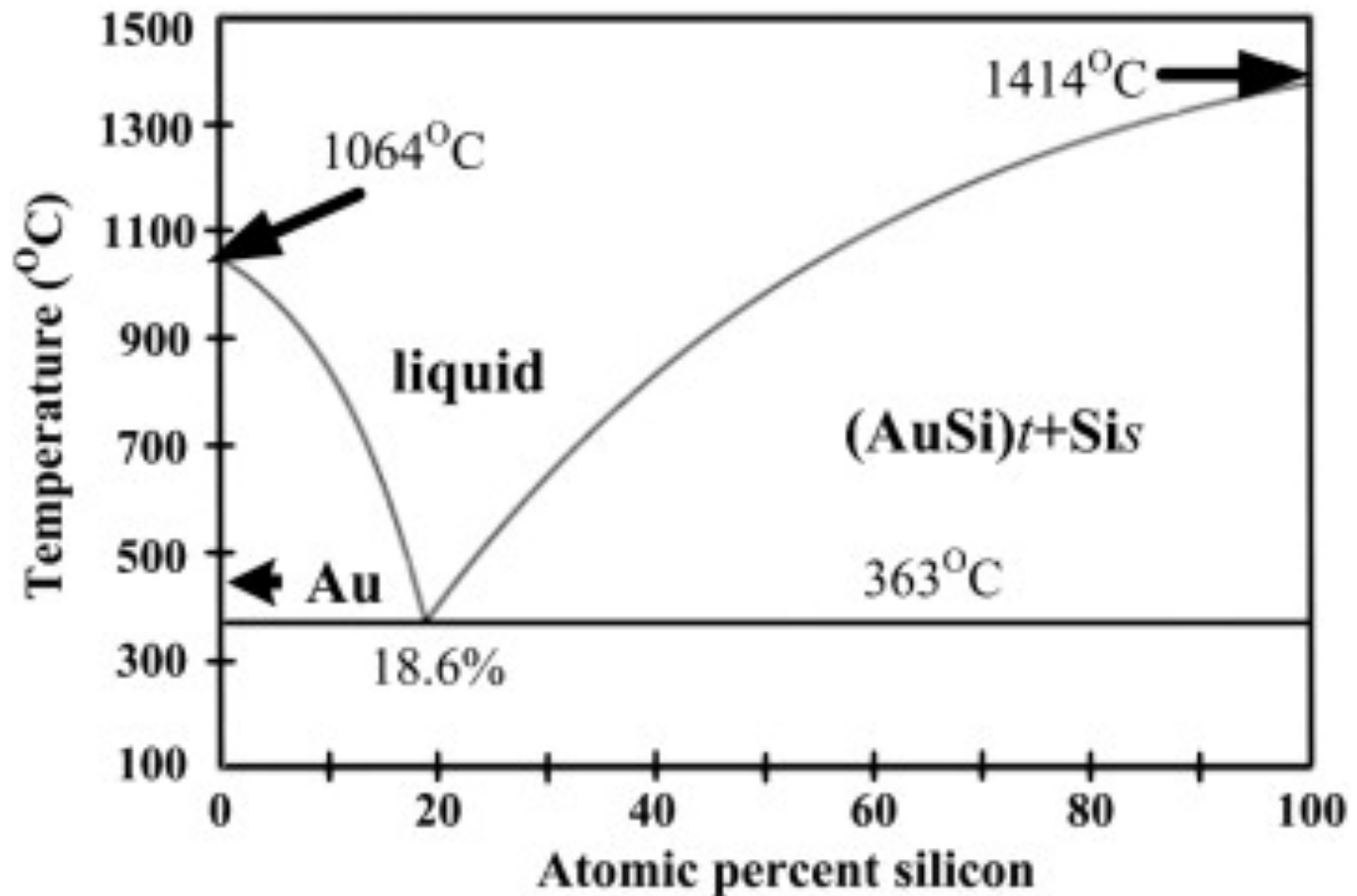
- Catalyst forms a **liquid droplet** by itself
- Acts as a trap for growth species
- The growth species is evaporated first and then diffuses and dissolves into a liquid droplet
- It precipitates at the interface between the substrate and the liquid

VLS Growth

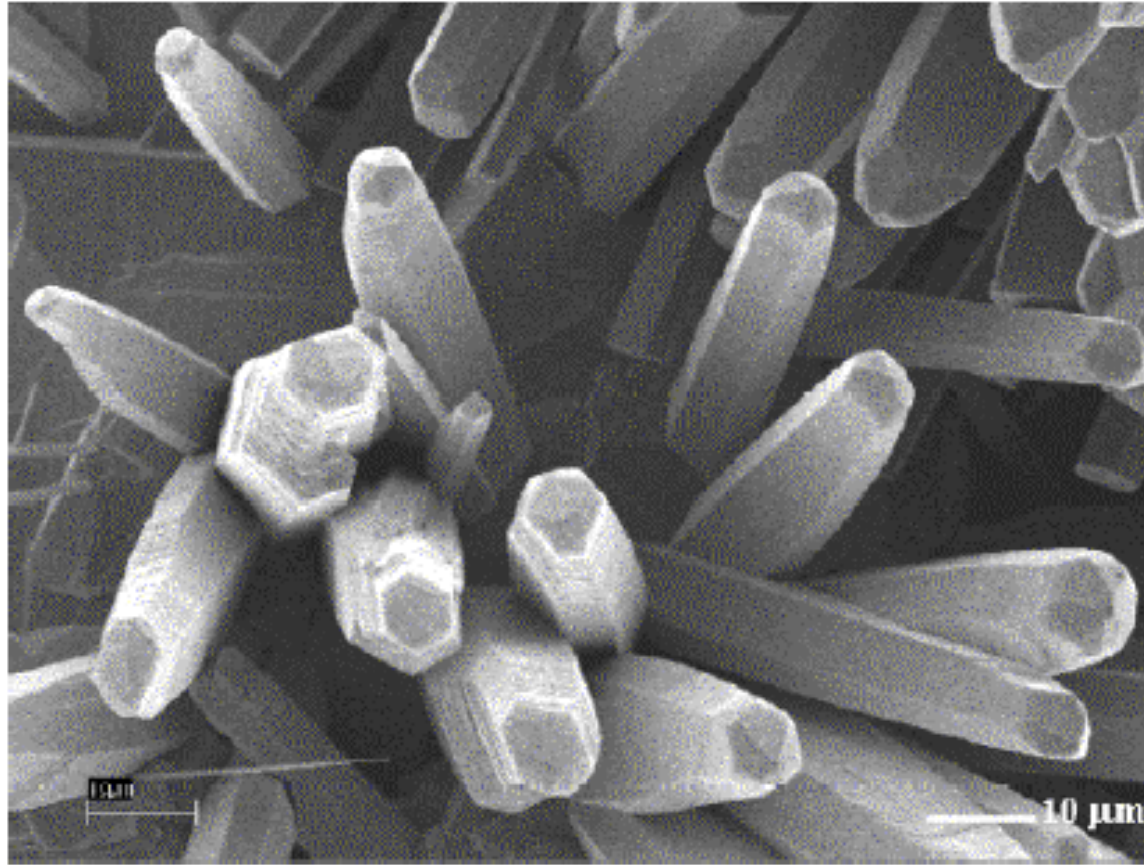


Growth species in the catalyst droplets subsequently precipitates at the growth surface resulting in the ***one-directional growth***

Phase diagram of AuSi

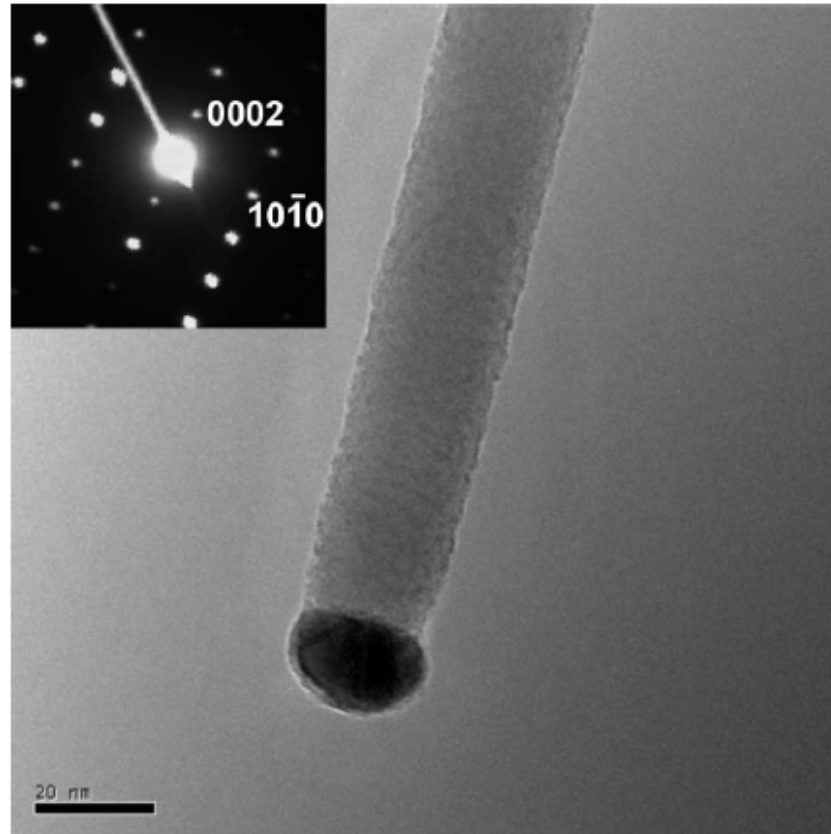


VLS Growth



“A Non-Traditional Vapor-Liquid-Solid Method for Bulk Synthesis of Semiconductor Nanowires,” Shashank Sharma, and Mahendra K. Sunkara

VLS Growth



TEM and selected area diffraction image of a single crystal ZnO nanorod.(~20 nm width).

“ZnO nanowire growth and devices,” Y.W. Heoa, D.P. Nortona, et al.

Laser Assisted Catalytic growth

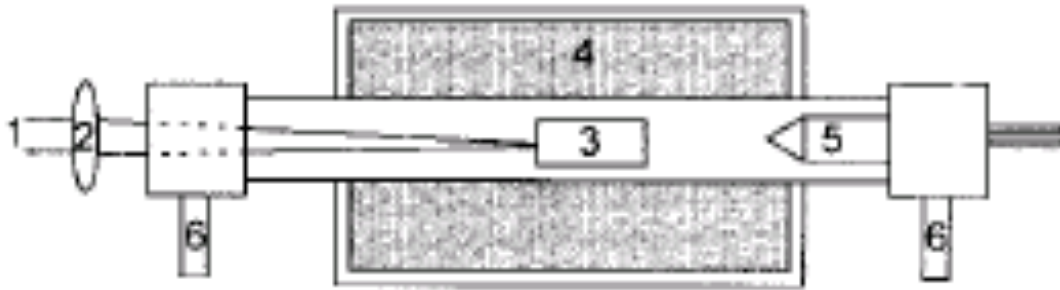


Fig. 2 Schematic of a nanowire growth set up using a combination of laser ablation and vapor-liquid- solid scheme

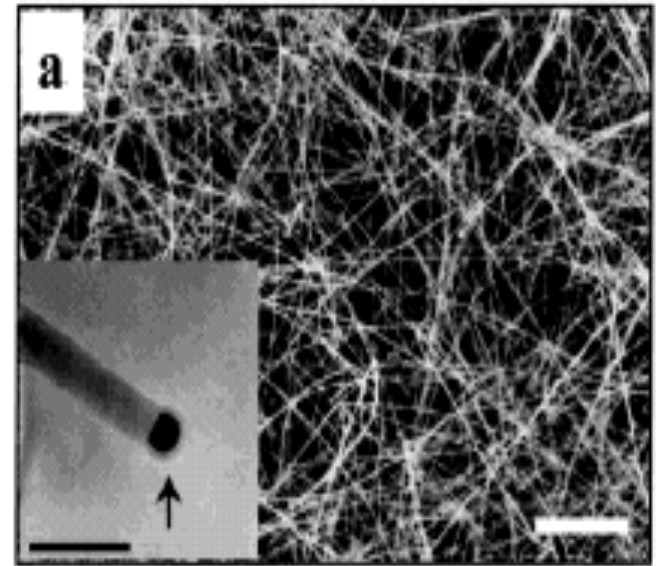
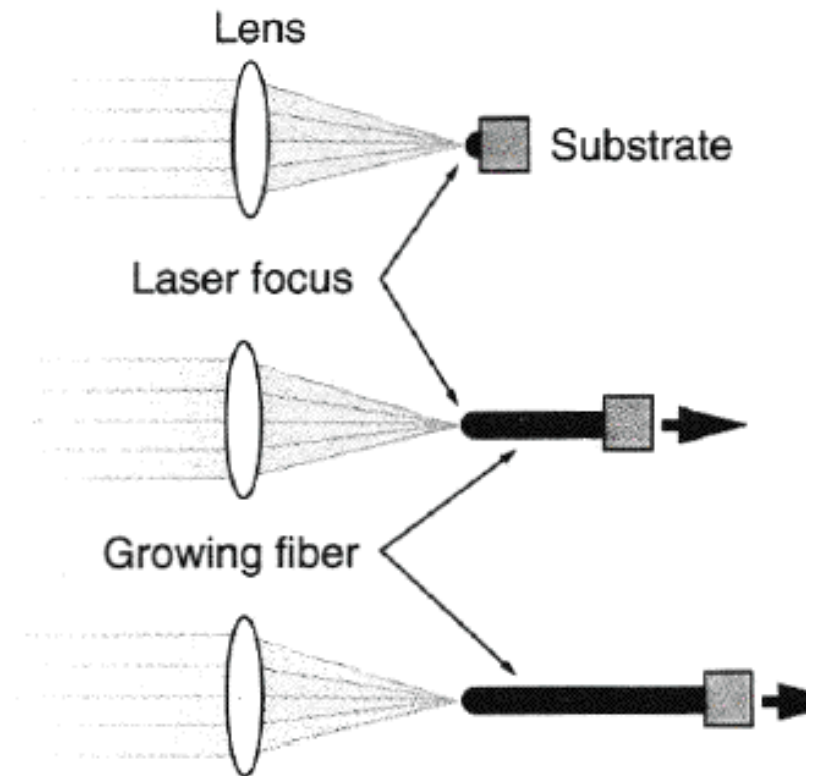


Fig.1 Semiconductor (GaAs) nanowires grown using laser assisted catalytic growth [1ref]. The scale bar corresponds to 50 nm.

Chemical vapor deposition (CVD) : L-CVD

- The L-CVD method is able to fabricate continuous thin rods and fibres by pulling the substrate away from the stationary laser focus at the linear growth speed of the material while keeping the laser focus on the rod tip, as shown in the Figure. LCVD was first demonstrated for carbon and silicon rods. However, fibers were grown from other substrates including silicon, carbon, boron, oxides, nitrides, carbides, borides, and metals such as aluminium. The L-CVD process can operate at low and high chamber pressures. The growth rate is normally less than $100\text{ }\mu\text{m/s}$ at low chamber pressure ($\ll 1\text{ bar}$). At high chamber pressure ($>1\text{ bar}$), high growth rate ($>1.1\text{ mm/s}$) has been achieved for small-diameter ($<20\text{ }\mu\text{m}$) amorphous boron fibers.



Nanoparticle preparation

- Vapor condensation: Metallic and metal oxide ceramic nanoparticles. Inert gas condensation, thin film deposition (sputtering, thermal evaporation, chemical vapor deposition etc.).
- Chemical synthesis: In a liquid medium composed of various reactants. Sol-gel, electrodeposition.
- Solid-state processes: Mechanical processes (Grinding or milling) of bulk materials.

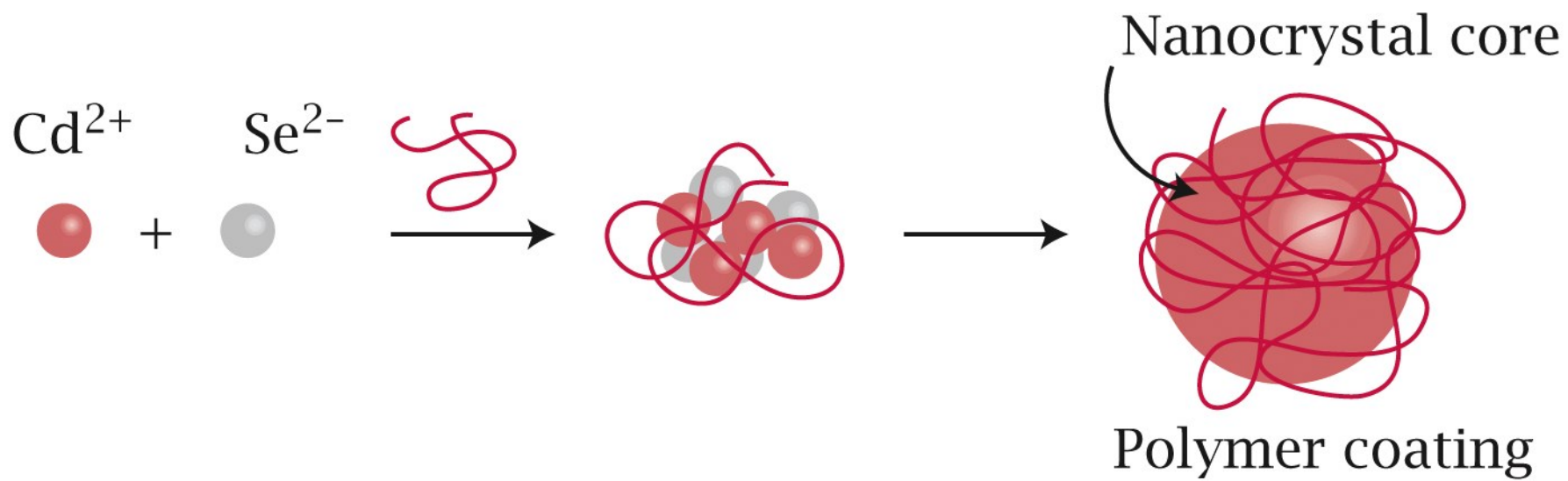


Figure 13.1 Introductory Nanoscience (© Garland Science 2012)

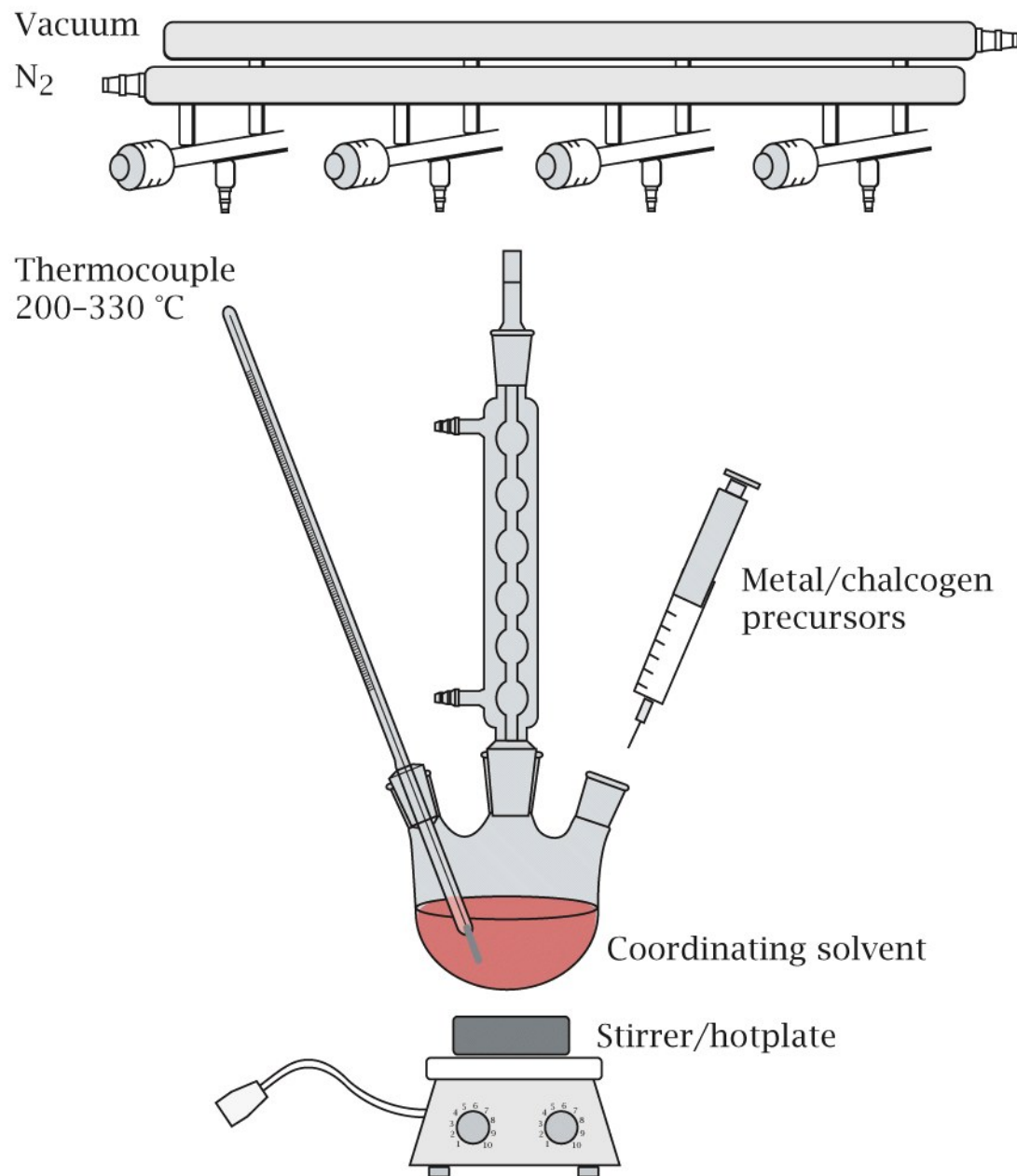


Figure 13.7 Introductory Nanoscience (© Garland Science 2012)

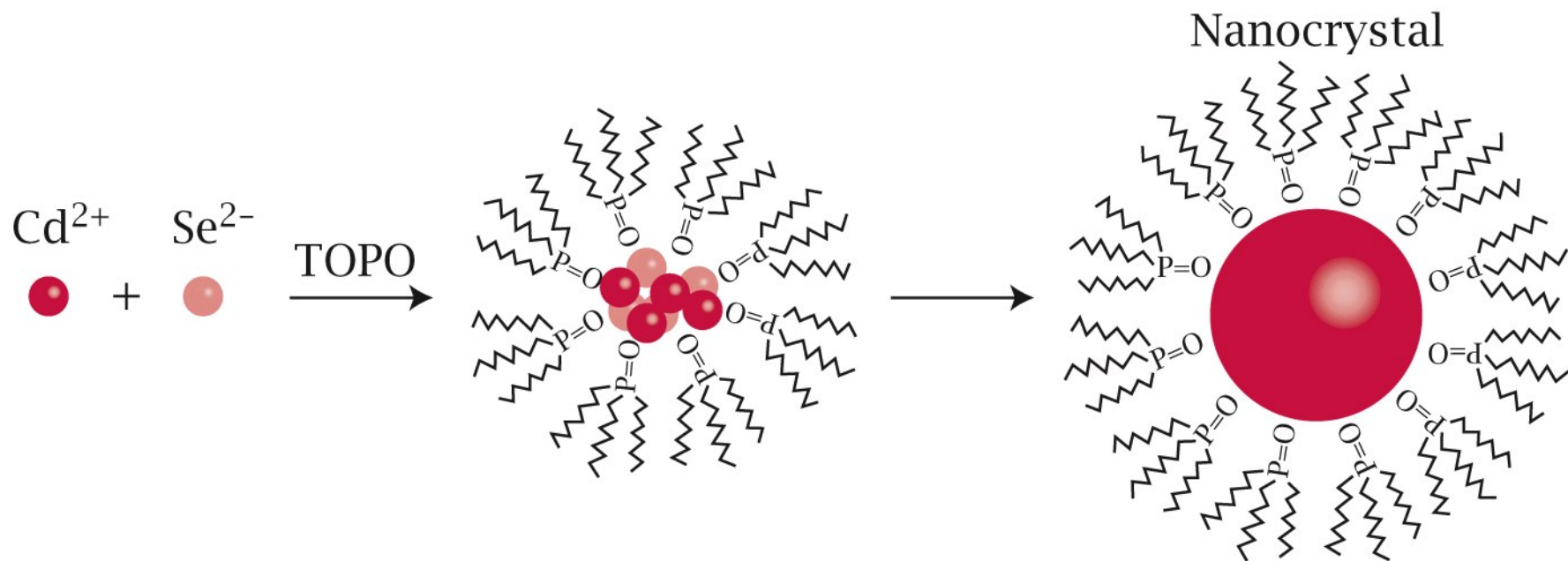


Figure 13.8 Introductory Nanoscience (© Garland Science 2012)

Surface Energy

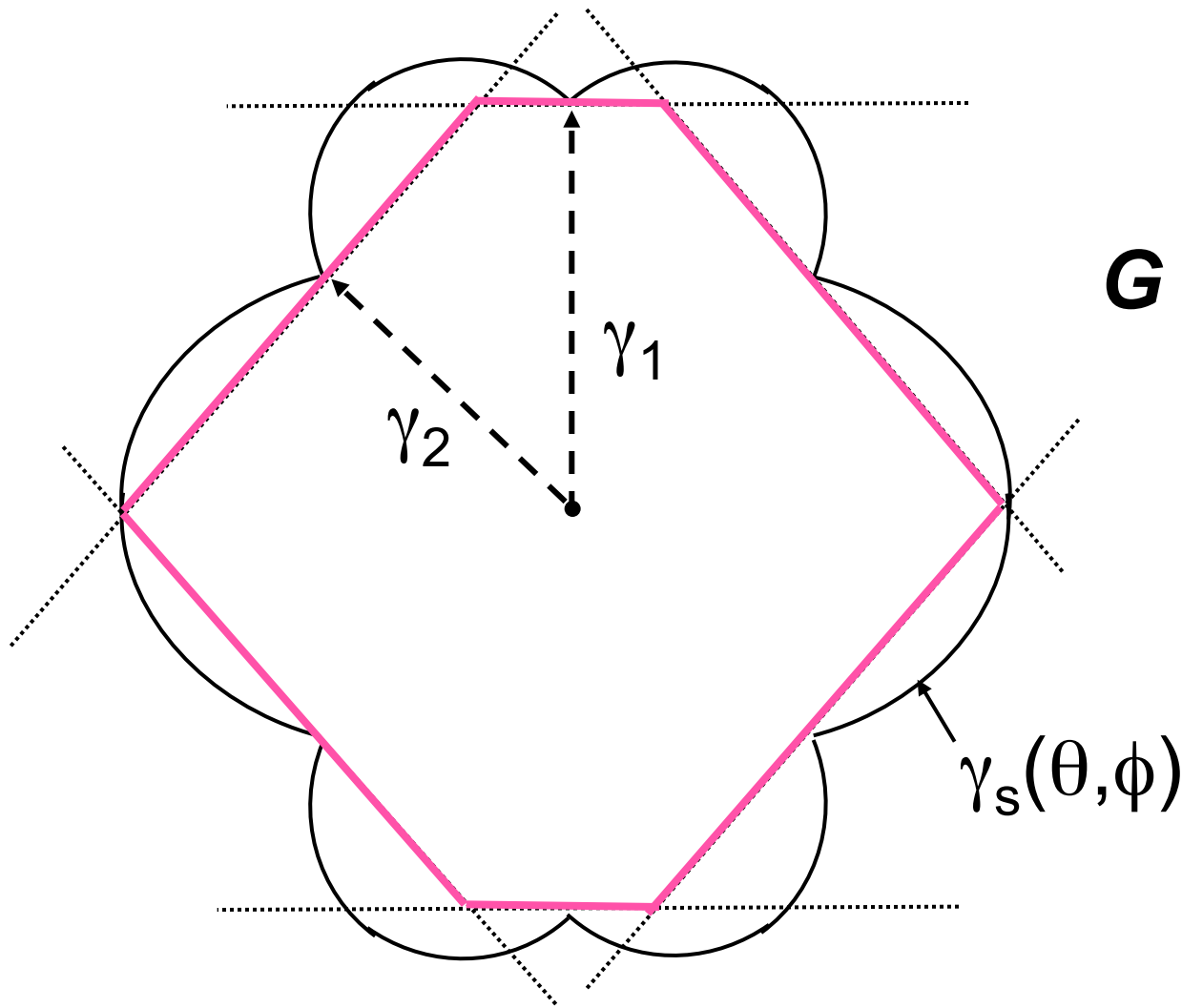
- Surface energy is given by

$$E(\Gamma) = \int_{\Gamma} \gamma \, dS$$

- Standard model for anisotropic surface free energy

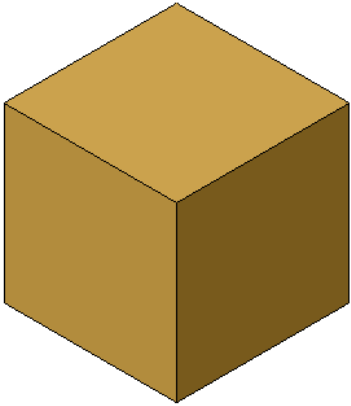
$$\gamma = \gamma_0(n)$$

Wulff construction

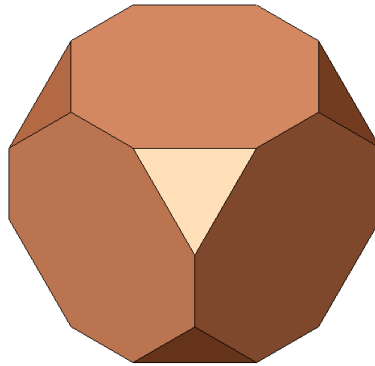


$$\mathbf{G} = \int \gamma_s(\theta, \phi) dA$$

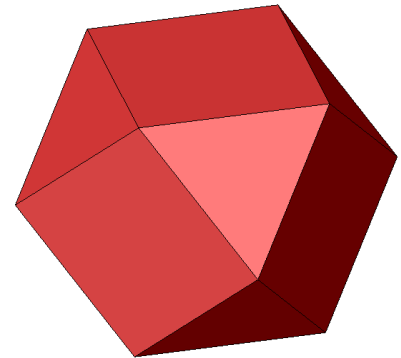
Single crystalline structures



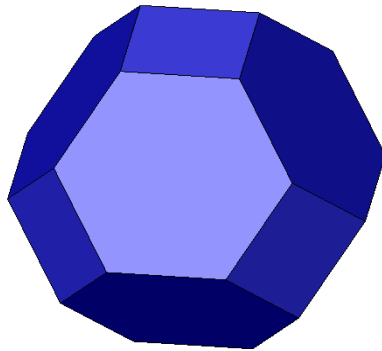
(a) cube



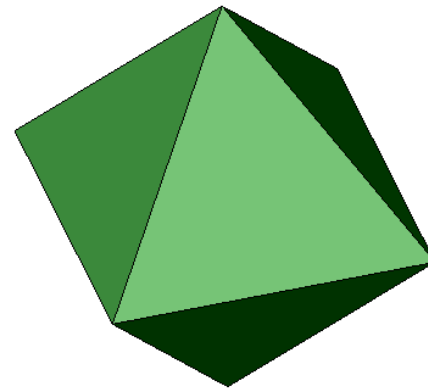
(b) truncated cube



(c) cuboctahedron

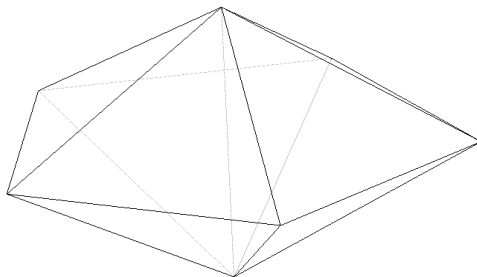
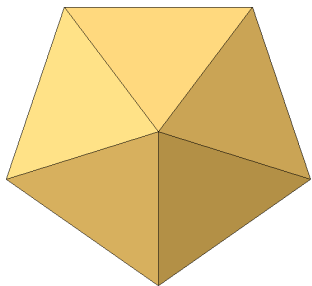


(d) truncated octahedron

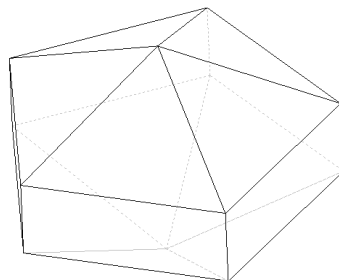
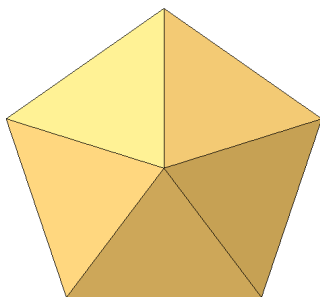


(e) octahedron

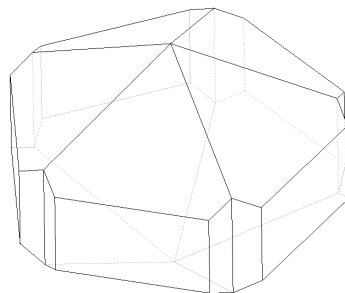
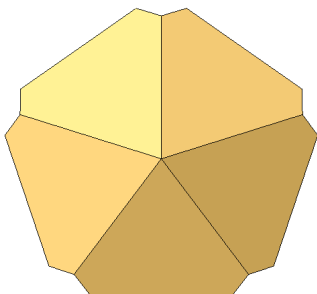
Decahedra



Classic

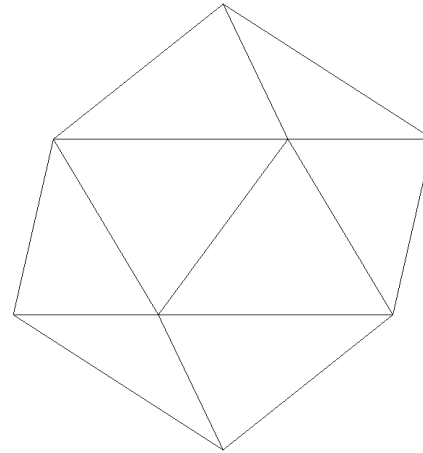
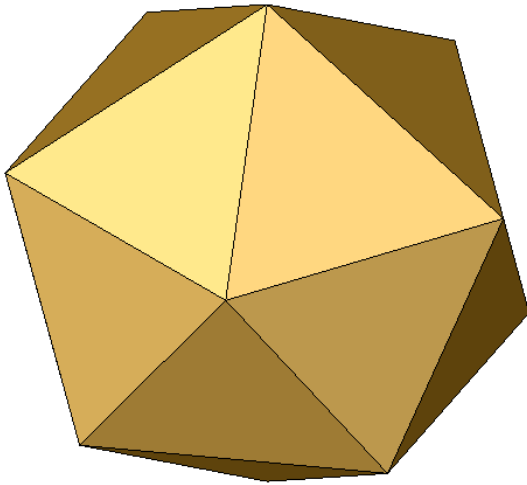


Ino's



Marks'

Icosahedra

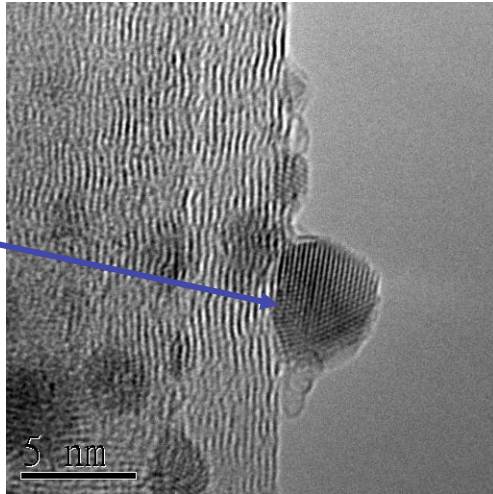


Size-dependent structures calculated for Ni clusters:
Icosahedra for 142 – 2300 atoms;
Marks' decahedra for 2300 – 17000 atoms;
Single crystal for > 17000 atoms.

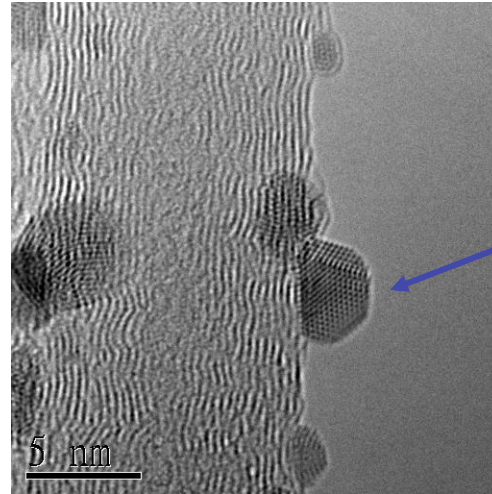
C.L. Cleveland and Uzi Landman, J. Chem. Phys. 94, 7376 (1991)

Varying structures of Ag clusters

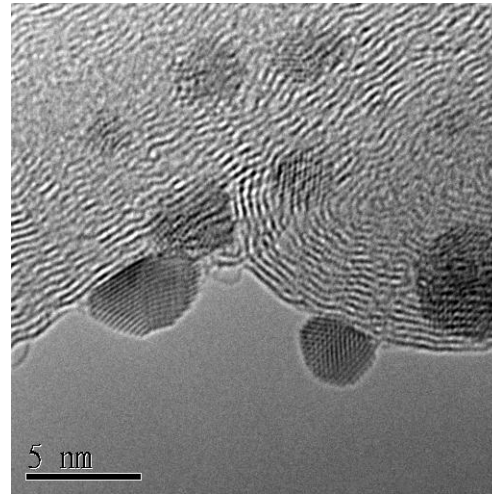
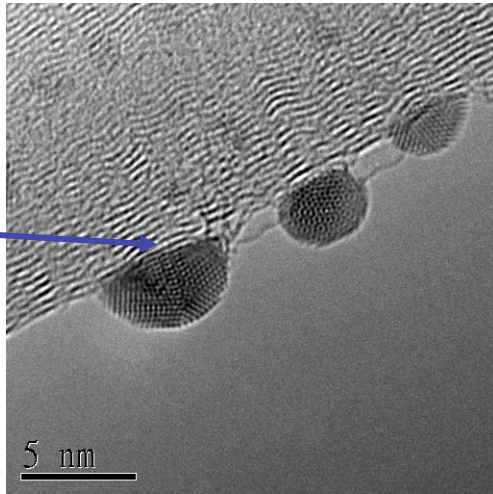
SC



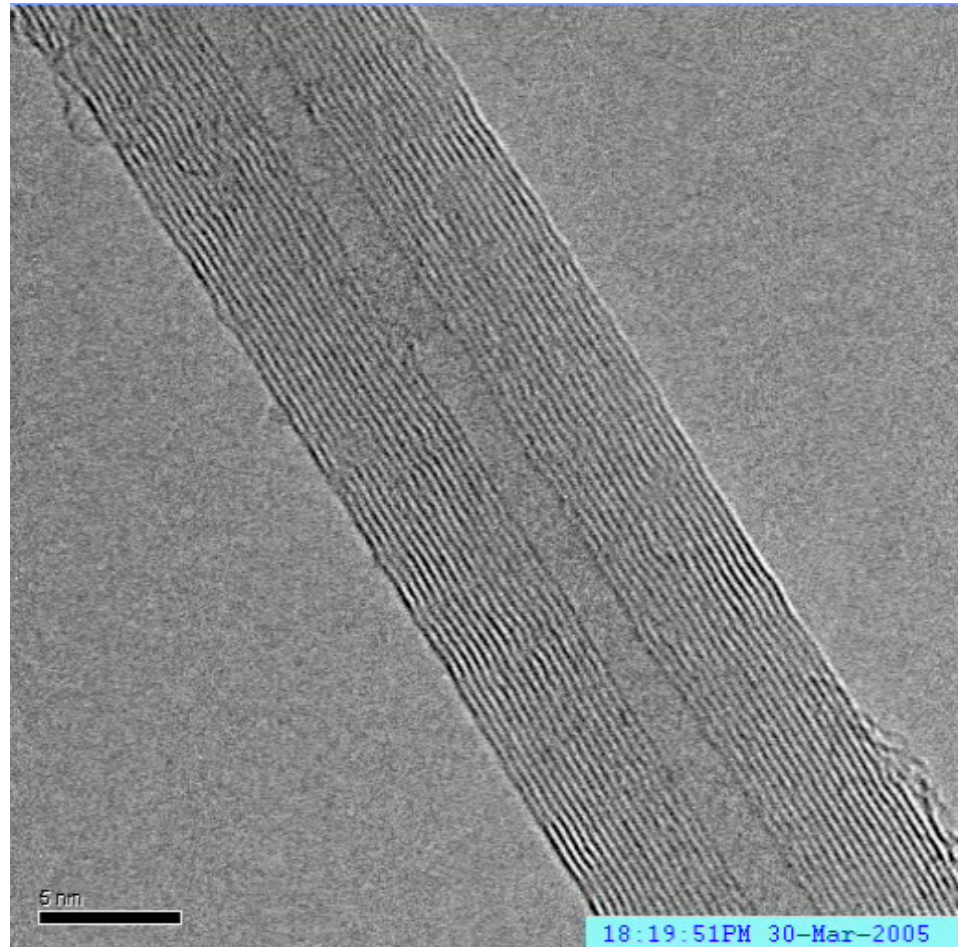
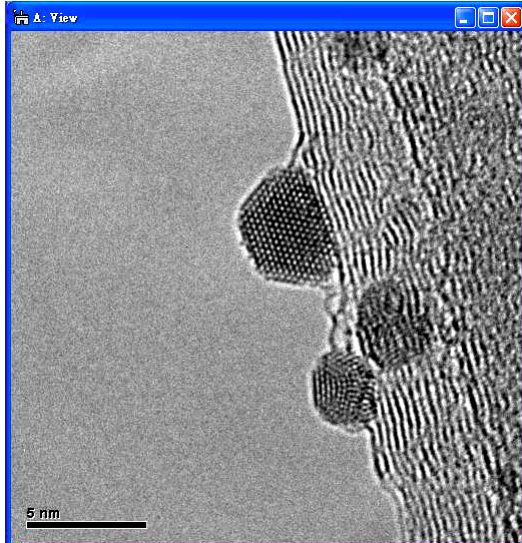
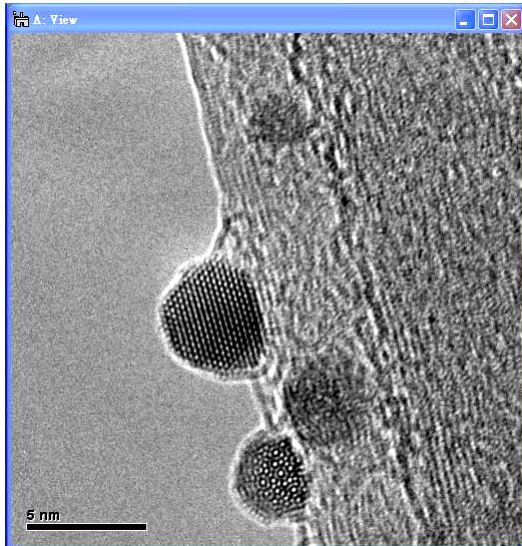
Dh



Ic

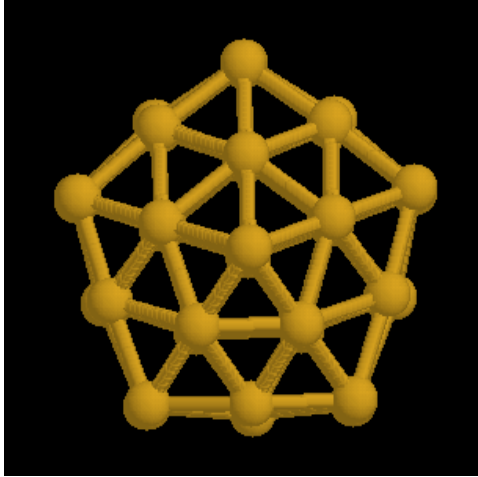


Atomic motion and recrystallization



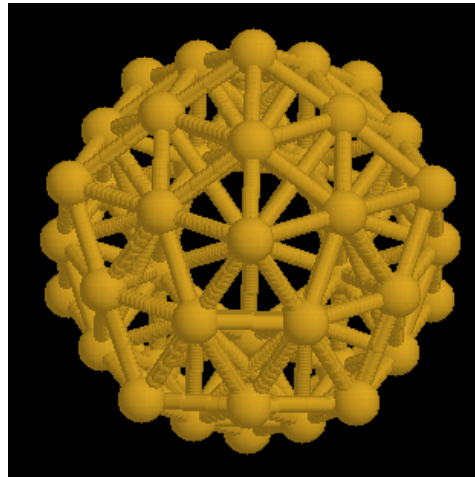
Room temperature

Possible shell structures of nano particles



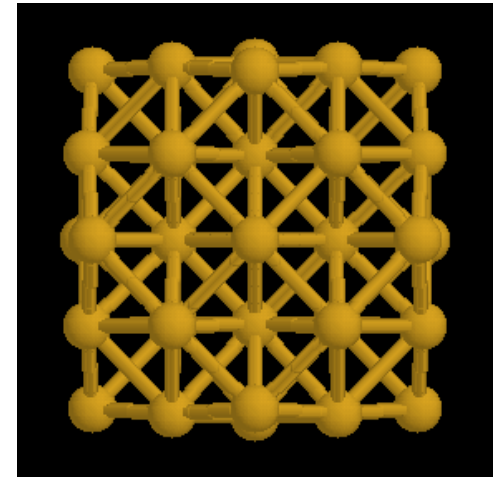
Decahedral:

10 (111) faces +
5 (100) faces



Icosahedral:

20 (111) faces



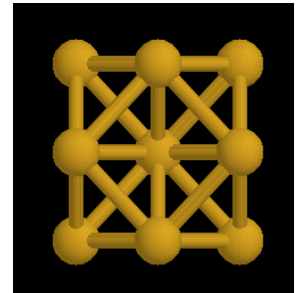
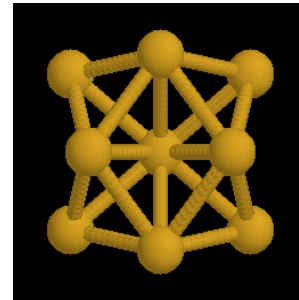
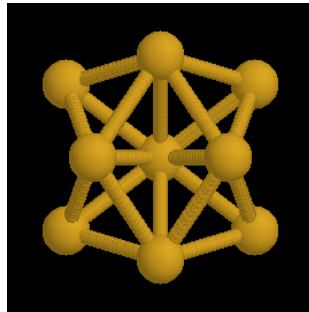
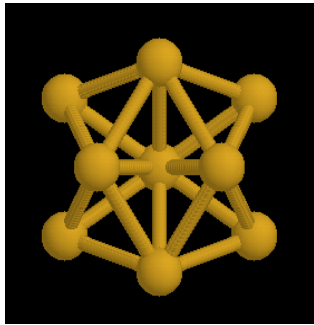
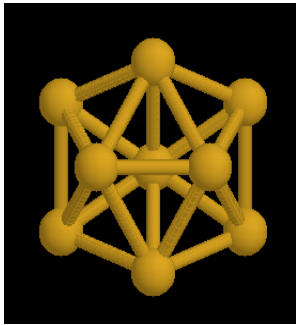
Cuboctahedral:

8 (111) faces +
6 (100) faces

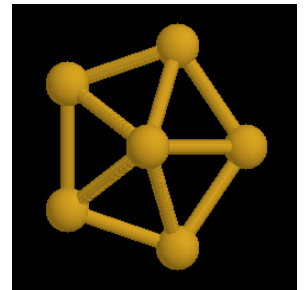
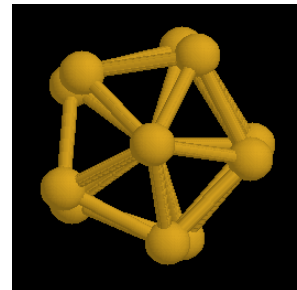
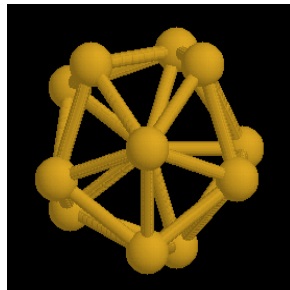
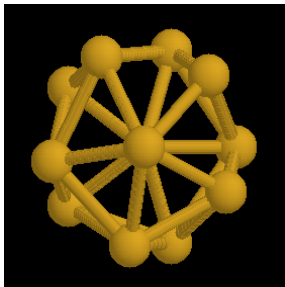
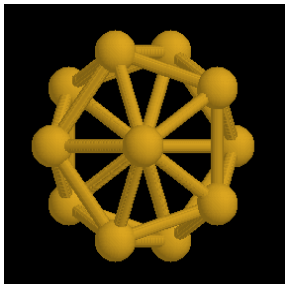
(Courtesy of C.M. Wei)

Structural phase transition

Icosahedral $\Leftrightarrow$ Cubotohedral

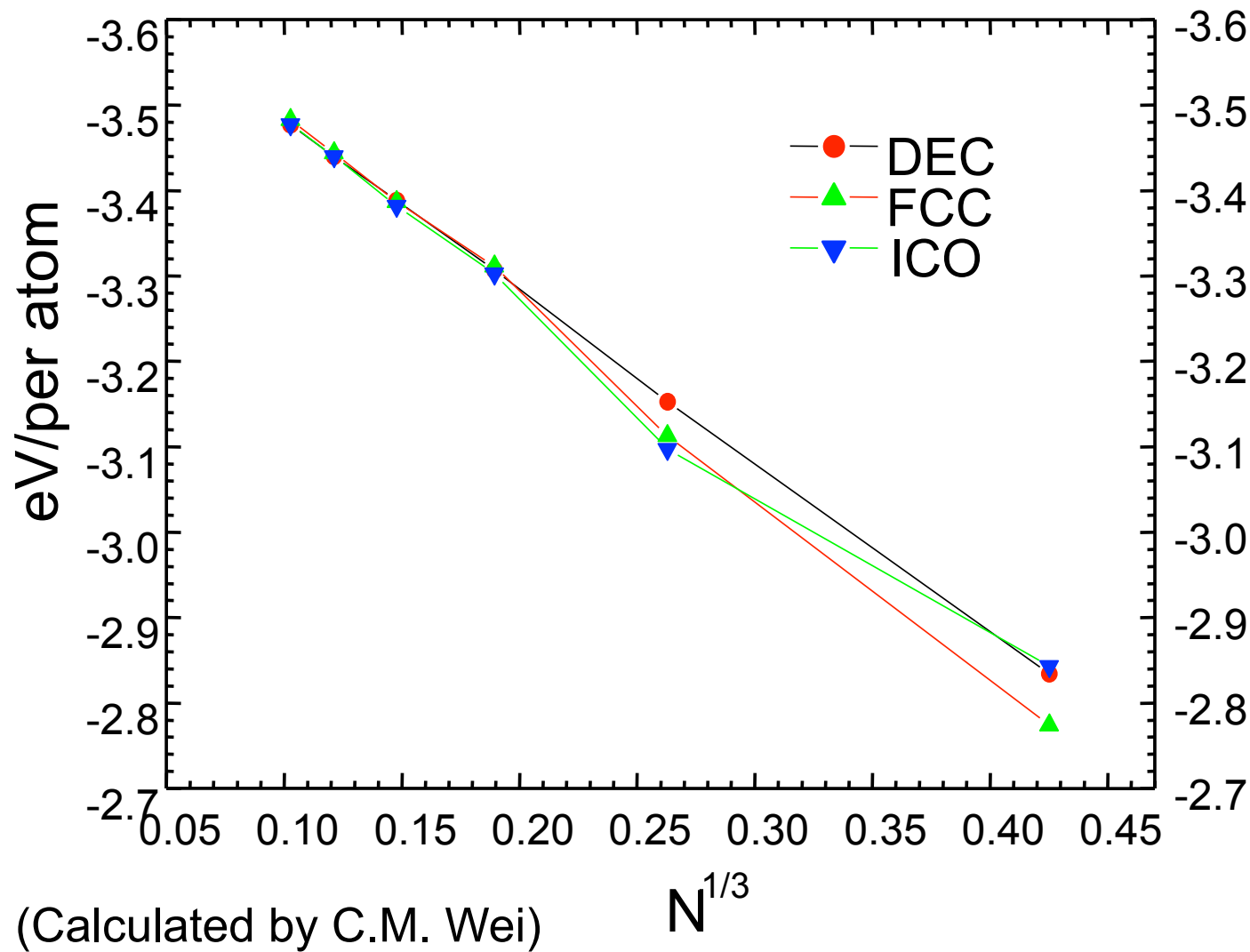


Icosahedral $\Leftrightarrow$ Decahedral



(Courtesy of C.M. Wei)

Binding energy for Al nano particles



Definition of a composite

A material having two or more distinct constituents or phases, and have to satisfy the following criteria:

1. Both constituents have to present in reasonable proportions, say greater than 5%;
2. The constituents phases have different properties, and hence the composite properties are noticeably different from the properties of the constituents;
3. A man-made composite is usually produced by intimately mixing and combining the constituents by various means.

Nanocomposites: Composites contain two or more nano-sized fillers.
(Nano-structural composites)

Hierarchical nanocomposites

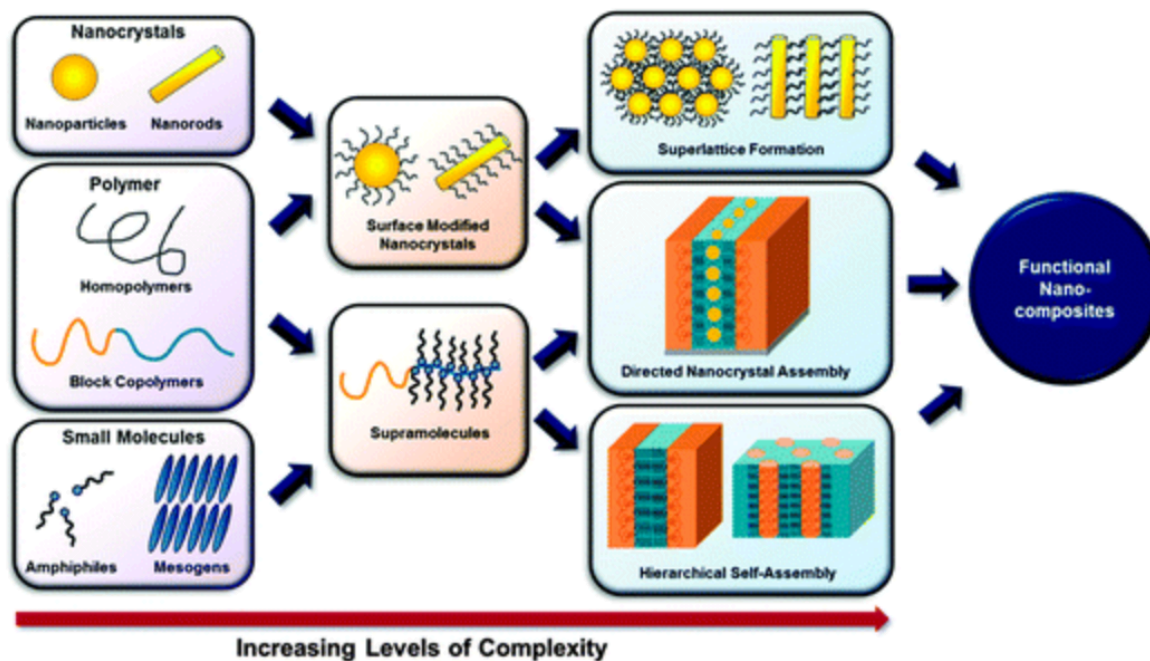
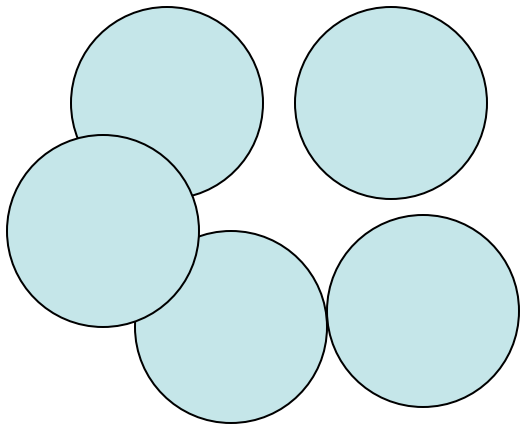
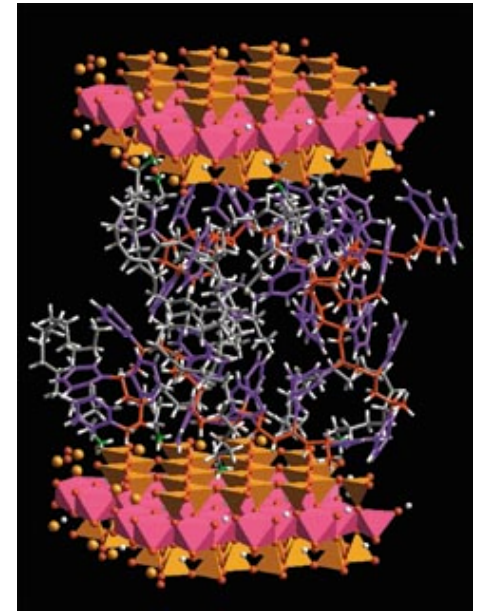


Fig. 1 Hierarchical co-assemblies of nanocrystals, polymers, and small molecules toward functional nanocomposites.

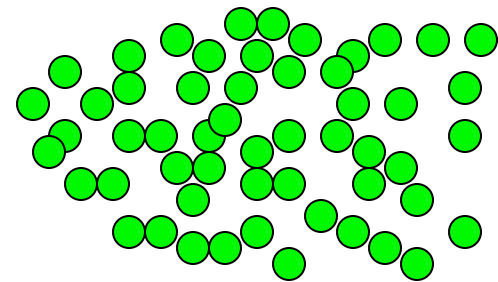
Why Nanocomposites?

Size does matter

Increased surface area on nanoparticles



Microparticles

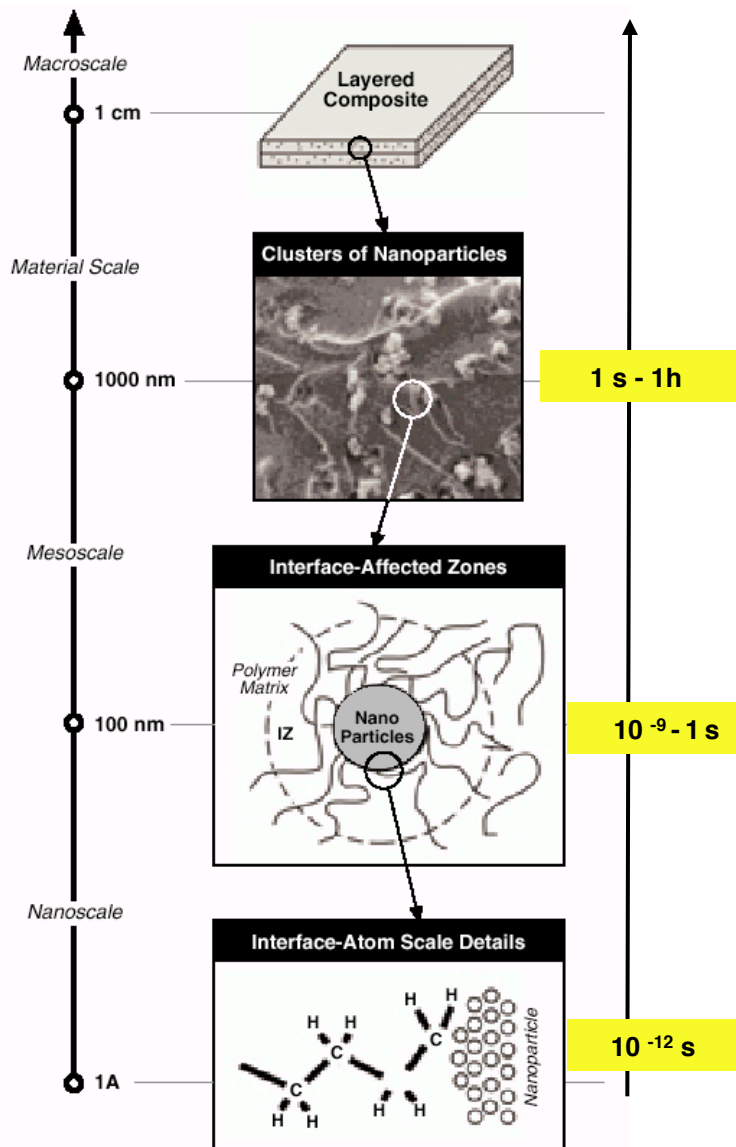


Nanoparticles

Why nanocomposites? → Multi-functionality

- Small filler size:
 - High surface to volume ratio
 - Small distance between fillers → bulk interfacial material
 - Mechanical Properties
 - Increased ductility with no decrease of strength,
 - Scratching resistance
 - Optical properties
 - Light transmission characteristics particle size dependent

Nanocomposite as a Multiscale System



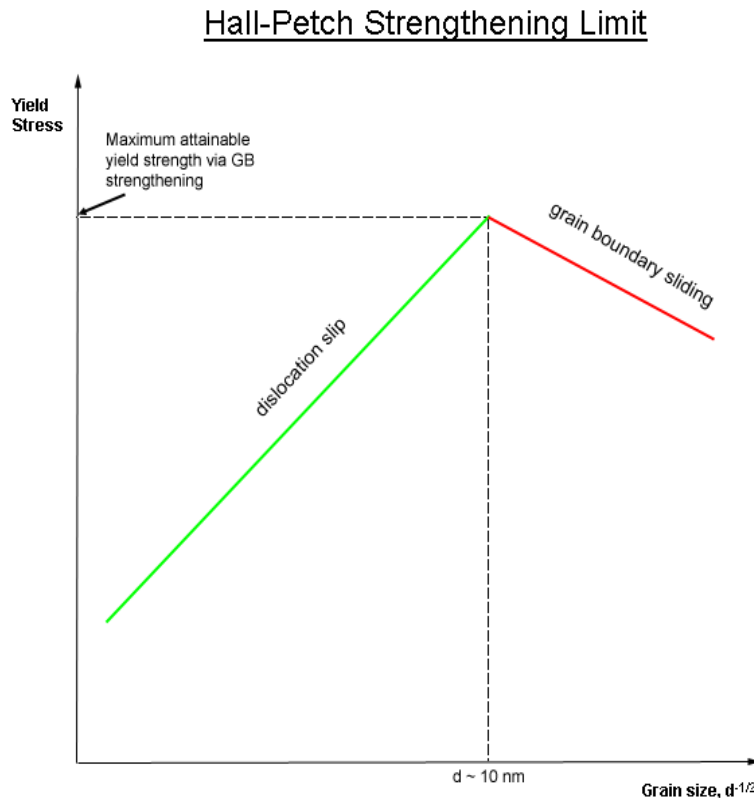
– Macroscale composite structures

– Clustering of nanoparticles - micron scale

– Interface - affected zones - several to tens of nanometers - **gradient of properties**

– Polymer chain immobilization at particle surface is controlled by electronic and atomic level structure

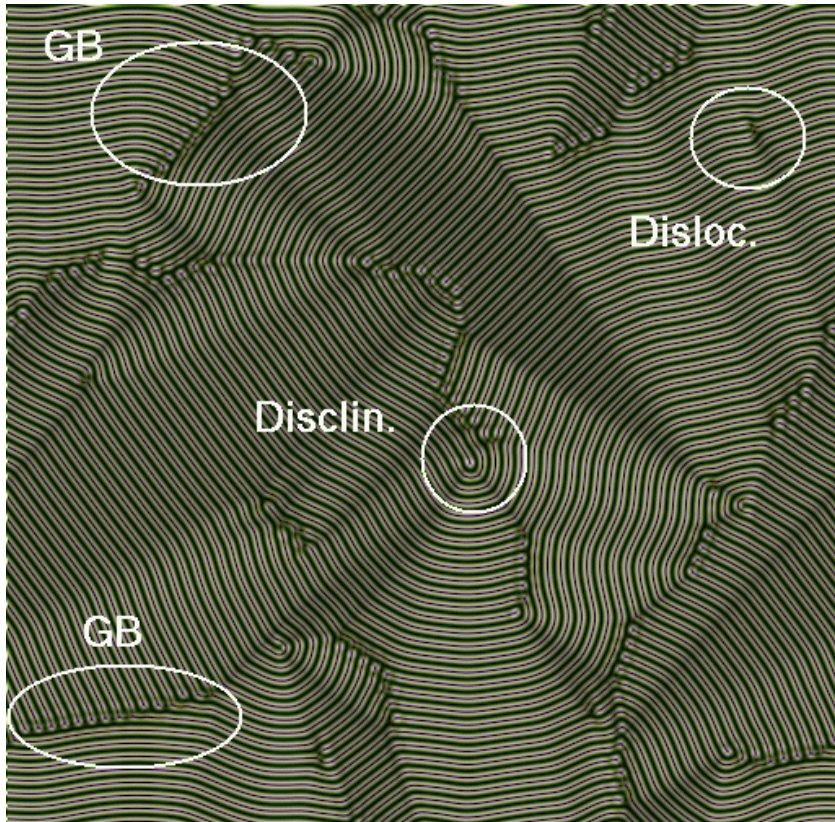
Hall–Petch equation



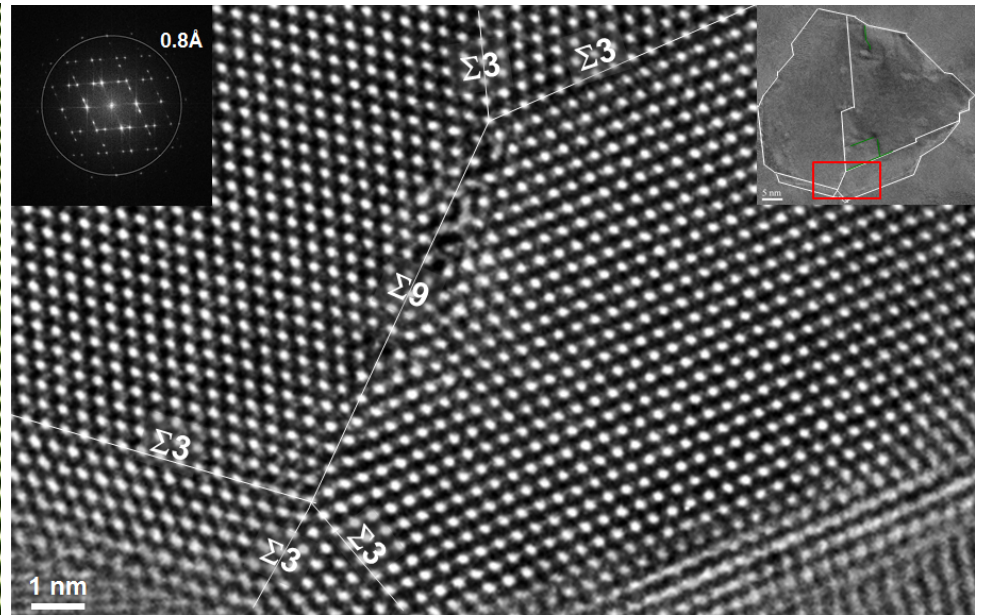
The relation between yield stress and grain size is described mathematically by the :

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

In grain-boundary strengthening, the grain boundaries act as pinning points impeding further dislocation propagation. Since the lattice structure of adjacent grains differs in orientation, it requires more energy for a dislocation to change directions and move into the adjacent grain.



Grain boundary



Triple line boundary