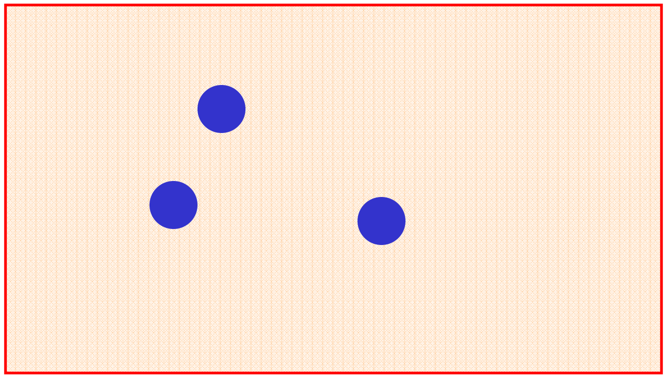
Growth of nanoparticles

Top down approach

Patterning (LITHOGRAPHY0, milling and separation from substrate –

Chemical reaction at surface – no separation from substrate (porous Si)

Bottom up approach



Homogeneous nucleation from liquid or vapor

(vapor phase reaction, solid phase segregation)

MBE growth

Fundamentals of homogeneous nucleation

If the concentration of a solute in a solvent exceeds its equilibrium solubility or the temperature decreases below the phase transformation point, a new phase appears.

A supersaturated solution decreases its Gibbs energy by forming a solid phase and maintaining an equilibrium concentration in the rest of the solution. The change of the Gibbs free energy depends on the concentration of the solute:

$$\Delta G_v = -\frac{kT}{\Omega}\ln\left(\frac{C}{C_0}\right) = -\frac{kT}{\Omega}\ln\left(1+\sigma\right)$$

C: concentration of solute; C_o equilibrium concentration or solubility, k: Boltzman constant, T: temperature; ΔG is the change in Gibbs free energy per unit volume, Ω: atomic volume, σ is the supersaturation equal to $(C-C_o)/C_o$

Assuming an spherical nucleus with a radius r, the change of the volume energy is

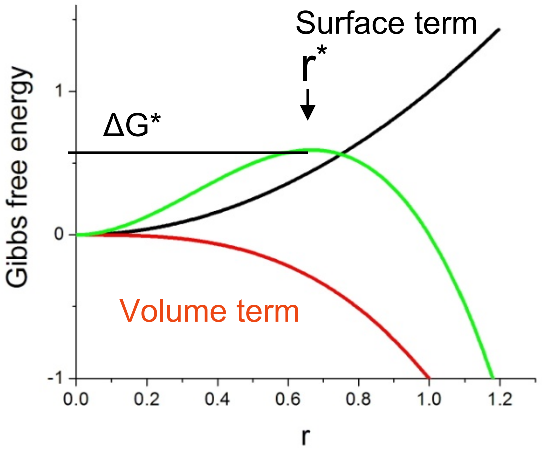
$$\Delta\mu_v = \frac{4}{3}\pi r^3\ \Delta G_v$$

This energy reduction is counterbalanced by the surface energy. The increase in the surface energy is

$$\Delta\mu_s = 4\pi r^2\ \gamma$$

The total change in the Gibbs free energy is $\Delta G = \Delta\mu_v + \Delta\mu_s = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$

Fundamentals of homogeneous nucleation



The newly formed nucleus is stable only if the radius exceeds a critical size r^* . If $r < r^*$ it will dissolve into the solution to reduce the overall Gibbs free energy.

If $r > r^*$ the nanoparticle is stable and continuous to grow bigger. At the critical size $r = r^*$

$$\frac{d}{dr}(\Delta G) = 0$$

and the critical size r^* and critical energy ΔG^* are defined by:

$$r^* = -2\frac{\gamma}{\Delta G_v} \qquad \Delta G^* = \frac{16\pi\,\gamma}{3(\Delta G_v)^2}$$

This is valid for a supersaturated solution, but all the concepts can be generalized for a supersaturated vapor and a supercooled gas or liquid.

In synthesis of nanoparticles by nucleation this critical size represents a limit. To reduce this limit one needs to increase the change of the Gibbs free energy ΔG_v and reduce the surface energy of the new phase γ. The value of ΔG_v can be increased by increasing the super-saturation σ, which increases with decreasing the temperature.

Fundamentals of homogeneous nucleation

The rate of nucleation per unit volume and per unit time R_N is proportional to:

* the probability of a thermodynamical fluctuation of the critical free energy ΔG*

$$P = \exp\left(-\Delta G^* / kT\right)$$

* the number of growth species per unit volume that can be used as nucleation centers (in homogeneous nucleation this is proportional to the concentration).

* the successful jump frequency of growth species which is given by , $\Gamma = kT / 3\pi\lambda^3\eta$

where λ is the diameter of the growth species and η is the viscosity of the solution.

So the rate of nucleation can be described by

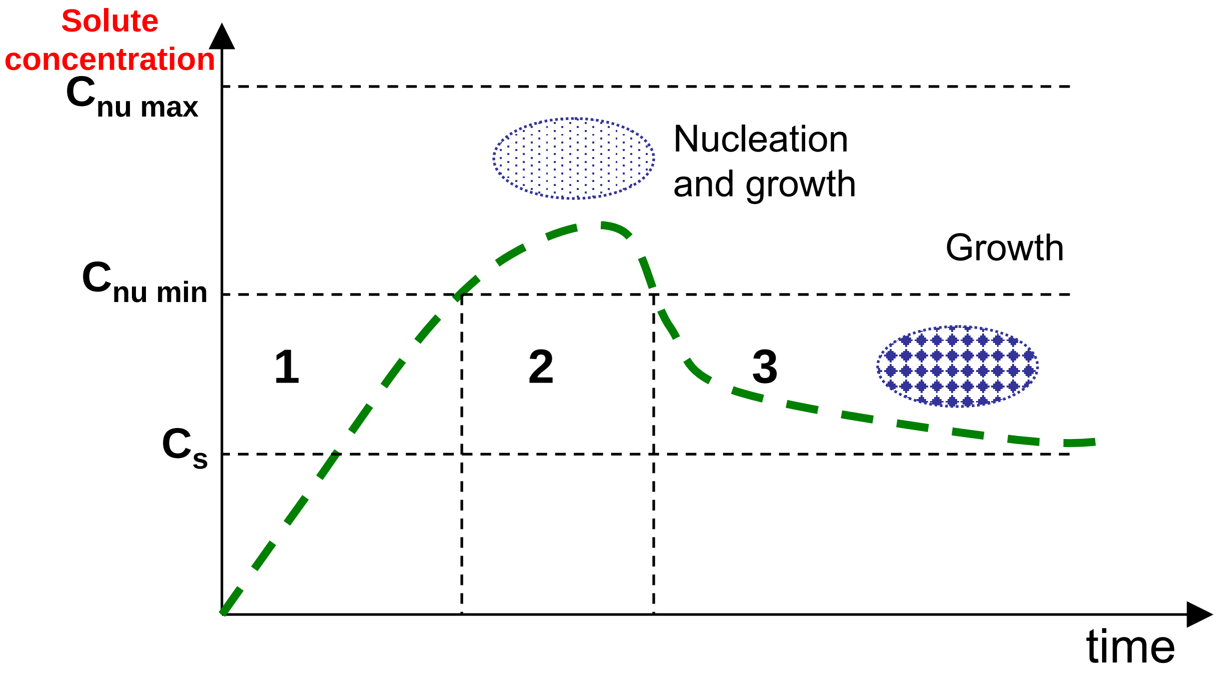
$$R_N = nP\Gamma = \left\{\frac{C_0 kT}{3\pi\lambda^3\eta}\right\}\exp\left(-\frac{\Delta G^*}{kT}\right)$$

Fundamentals of homogeneous nucleation

$$R_N = nP\Gamma = \left\{\frac{C_0 kT}{3\pi\lambda^3\eta}\right\}\exp\left(-\frac{\Delta G^*}{kT}\right)$$

Large number of nuclei if: high initial concentration, low viscosity and low critical energy barrier

For a given concentration solute a large number of nuclei means smaller sized nuclei



1: when C increases with time no nucleation occurs even above the equilibrium solubility

2: when supersaturation reaches a value corresponding to the energy barrier nucleation starts

3: after nucleation the concentration decreases. When concentration decreases below the critical energy, nucleation stops and only growth proceeds until the equilibrium concentration is reached.

Growth of metal nanoparticles

Process: reduction of metal complexes in dilute solutions

Colloidal gold: first publication Faraday 1857

Most common method: Chlorauric acid dissolves into water to make 20 ml very dilute solution of ~2.5×10^{-4} M. Then 1 ml is added into the boiling solution. The mixture is kept at 100 ˚C till color changes, while maintaining the overall volume of the solution constant by adding water.

Colloidal sol is very stable and uniform particle size of ~20 nm is obtained.

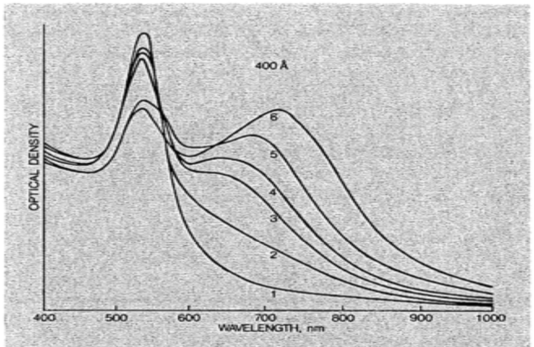


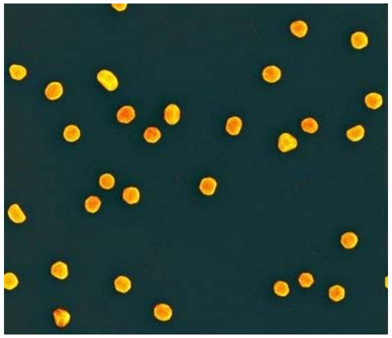
Fig. 12 Optical absorbance spectra of standard citrate sols containing 400 nm colloidal gold in varying states of coagulation by addition of aluminium nitrate solution viz:

1. Zero Al^{3+}
2. 0.001% Al^{3+}
3. 0.0017% Al^{3+}
4. 0.0025% Al^{3+}
5. 0.0033% Al^{3+}
6. 0.005% Al^{3+}

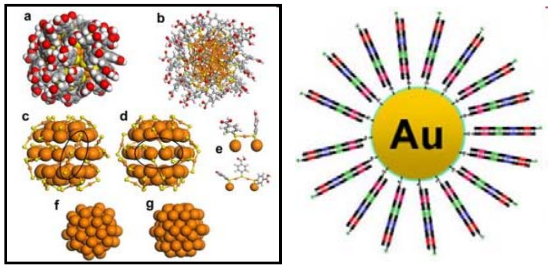
The gold concentration in each case was 42 mg/l

J. Turkevich, Gold Bull. **18**, 86 (1985)

False color scanning electron micrograph (250,000 times magnification) showing the gold nanoparticles created by NIST and the National Cancer Institute's Nanotechnology Characterization Laboratory for use as reference standards in biomedical research laboratories. Credit: Andras Vladar, NIST



Gold nanoparticles can be functionalized



By attaching DNA strands to gold nanoparticles, Berkeley Lab and UC Berkeley scientists have developed a ruler capable of measuring protein-DNA interactions. (Image courtesy of DOE/Lawrence Berkeley National Laboratory)

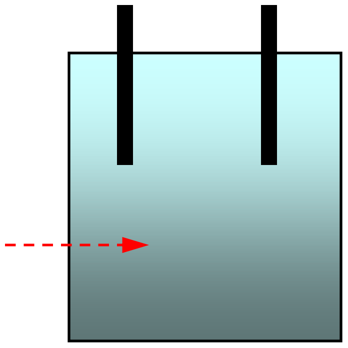
Growth of metal nanoparticles

Comparison of average sizes of Au nanoparticles synthesized using various reduction agents

Reducton reagents	436 nm emission	546 nm emission	XRD	SEM
Sodium Citrate	29.1 nm	28.6 nm	17.5 nm	17.6 nm
Hydrogen Peroxide	25.3	23.1	15.1	15.7
Carbon Monoxide	9.1	7.4	9.0	5.0

Metallic nanoparticles can also be prepared by an electro-chemical deposition

Organic solution of tetra-alkylammonium halogenides used as stabilizer. When the field is applied, the anode undergoes oxidative dissolution forming metal ions that migrate towards the cathode. The reduction of metal ions by ammonium ions leads to nucleation and growth of metallic nanoparticles in solution. Pd, Ni and Co nanoparticles have been grown with sizes ranging from 1.4 to 2.8 nm. *M,T, Reetz and W. Helbig, J. Am.Ch. Society vol. 116, 7401 (1994)*



Anode (+)

Metal of interest

Cathode (-)

Metal or glassy carbon

Growth of semiconductor nanoparticles

Synthesis of CdE (E=S, Se, Te) used Dimethylcadmium(Me_2Cd) as the Cadmium source, and bis(trimethylsilyl)sulfide ($(TMS)_2S$), trioctylphosphine selenide (TOPSe) and trioctylphosphine telluride (TOPTe) were used for S, Se, Te precursors. Mixed tri-n-octylphosphine (TOP) and tri-n-octylphosphine oxide (TOPO) solutions were used as solvents and capping layers.

Reaction takes place at 300˚C under a ~1 atm of argon. Temperature and concentration are key to control final size of nano-dots.

X-ray diffraction and transmission electron microscopy have been used to determine that the crystal structure of the nanoparticles is wurtzite as the 'bulk'.

8710 *J. Am. Chem. Soc., Vol. 115, No. 19, 1993*

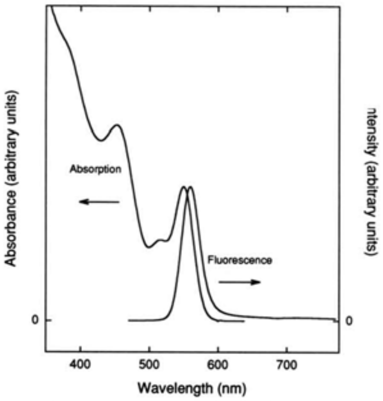
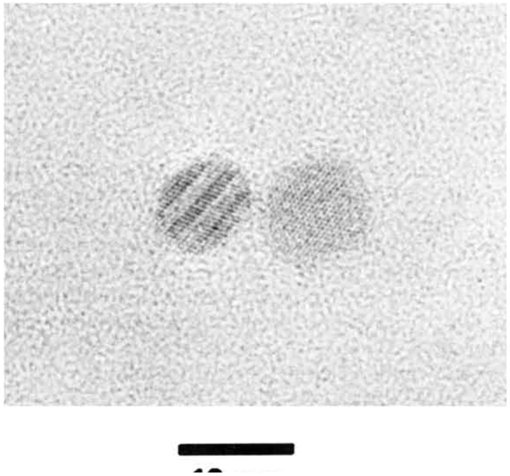


Figure 5. Typical room temperature band edge luminescence and absorption spectra for 35 Å diameter CdSe crystallites. No deep trap luminescence is detected.

Synthesis of CdE Semiconductor Nanocrystallites



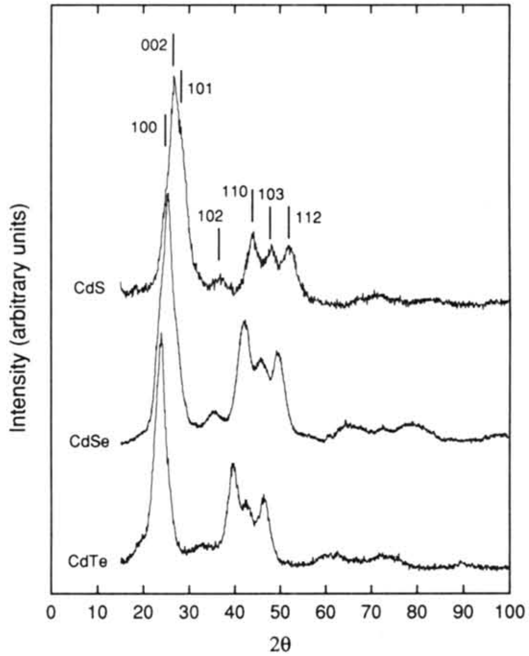


Figure 10. Powder X-ray diffraction spectra of ~35 Å CdS, CdSe, and CdTe crystallites. The positions of bulk reflections for wurtzite CdS are indicated.

J. Am. Chem. Soc., Vol. 115, No. 19, 1993 8711

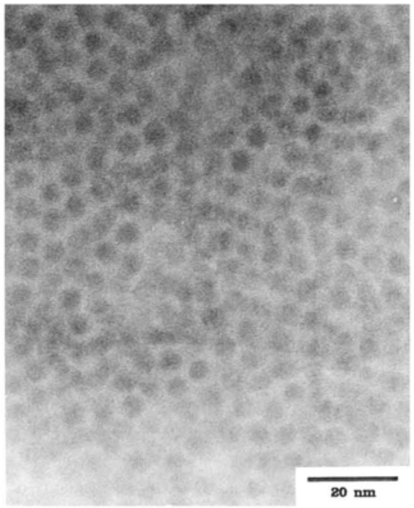


Figure 9. A near monolayer of 51 Å diameter CdSe crystallites showing short-range hexagonal close packing.

Murray et al.

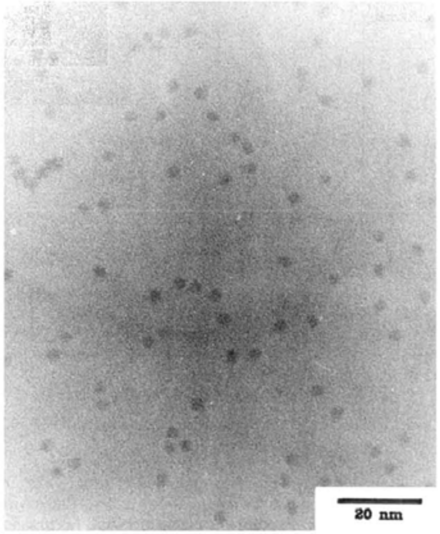


Figure 6. TEM image taken in bright field with lattice contrast shows a collection of slightly prolate particles. The elongated (002) axis measures 35.0 Å ± 5% while the perpendicular axis measures 30 Å ± 6%. The particles are well dispersed and not aggregated.

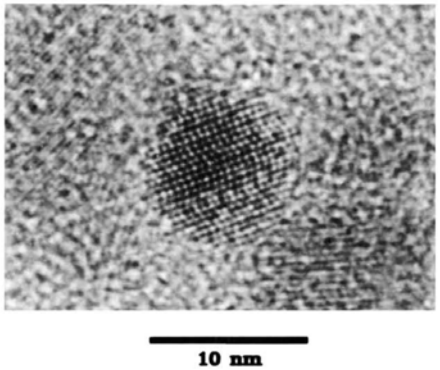


Figure 7. An 80 Å diameter CdSe crystallite imaged in bright field with atom contrast shows the presence of stacking faults in the (002) direction.

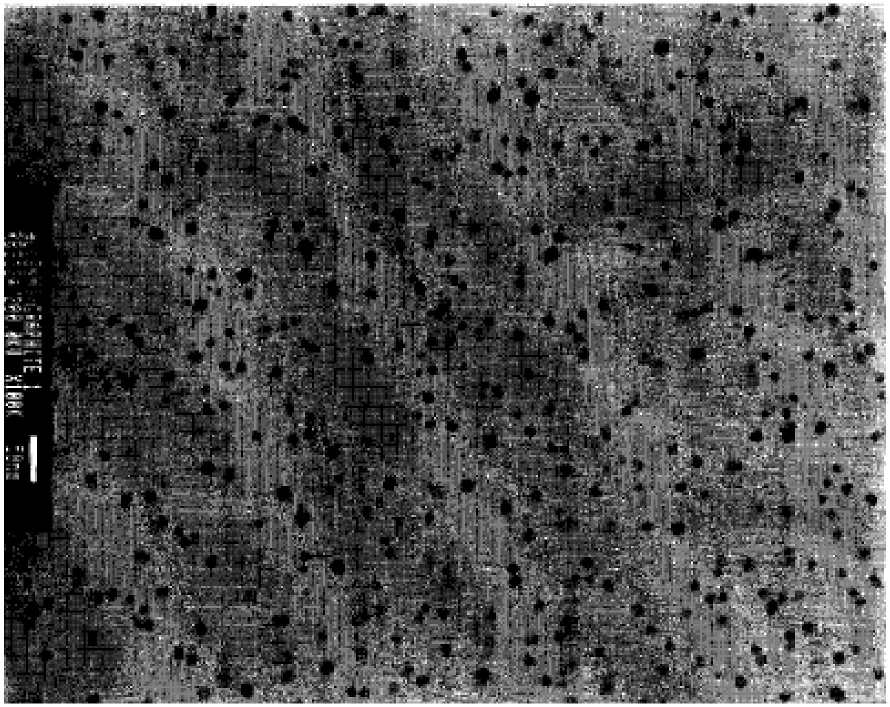
J.B. Murray et al, J. Am. Chem Soc. 1993, **115**, 8706.

Synthesis of nanoparticles

For synthesis of nanoparticles we need nucleation centers. Evaporated metals as Ag and Au tend to form small metal nanoparticles associated with surface defects:

- When edges are the only defects the particles are concentrated only around the edges.
- Nanoparticles grow in other defects as pit holes over the substrate surface.

For example gold clusters were produced by condensing evaporated gold in nanometer-sized preformed pits on the surface of highly oriented pyrolytic graphite (HOPG). The height of the clusters was 6.7 -0.7 nm, the lateral width was 10.1 - 1.9 nm



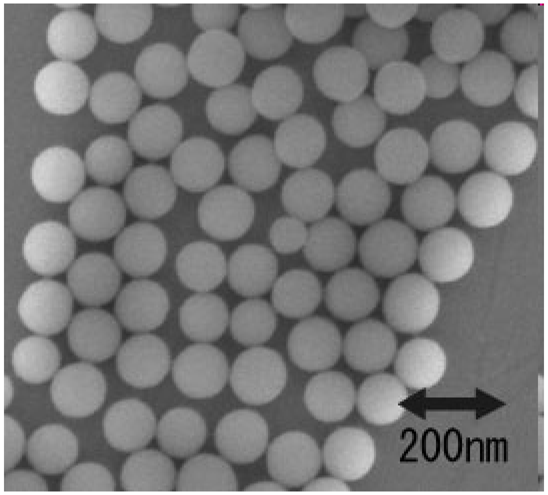
Growth of oxide nanoparticles

Example: SiO_2, TiO_2, ZrO_2

Techniques to grow oxide nanoparticles are less elaborated than those of metal and semiconducting nanoparticles. Process is similar: burst of homogeneous nucleation followed by diffusion controlled growth. Reaction and growth are more difficult to control because oxides are generally more thermally and chemically stable than metals and semiconductors. Conditions vary from system to system.

Most oxide nanoparticles are grown by the sol-gel process. The sol-gel process consists of hydrolysis and condensation of precursors, with both processes occurring in parallel. Precursors are generally metal alkoxides or inorganic or organic salts. Organic or aqueous solvants are used to dissolve precursors.

Condensation gives rise to the formation of nanoscale clusters of metal oxides or hydroxides, often with organiz groups embedded or attached to them. The organic ligands help control the reactivity of the precursors.



Fluorescent Silica Nanoparticle Has Been Developed Utilizing Nanotechnology - Enabling Detection of Biomolecule Samples by Means of High-Intensity Fluorescent Labeling Reagents for Biomolecule Detection - http://www.furukawa.co.jp/english/what/2007/070618_nano.htm

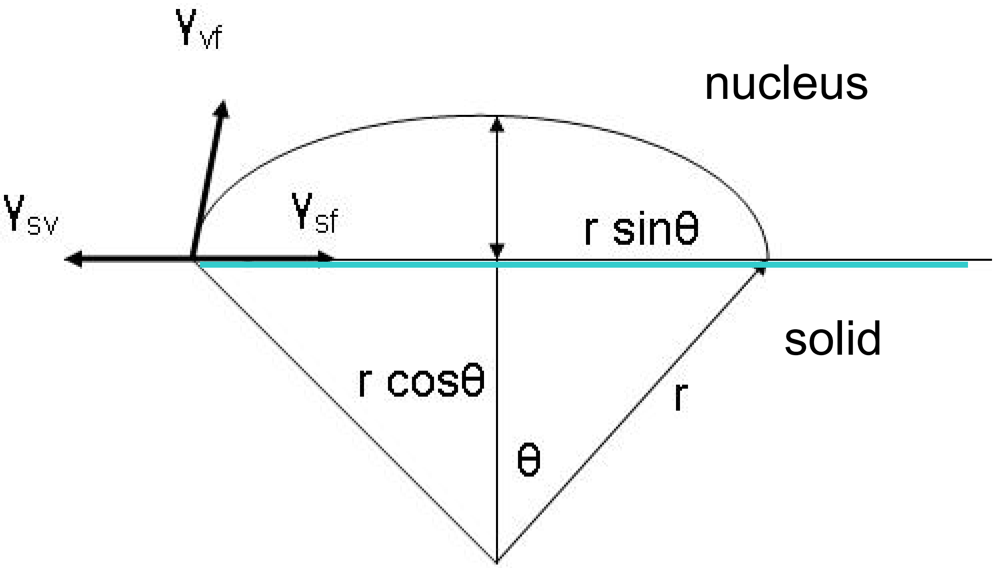
Heterogeneous nucleation

When a new phase is formed on the surface of another material, the process is called heterogeneous nucleation.

Assuming that the growth species in the vapor phase impinge at the surface, the growth species diffuse and aggregate to form a nucleus.

The total change in the free energy ΔG associated with the formation of this nucleus is given by

$$\Delta G = a_3\, r^3\, \Delta\mu_v + a_1\, r^2\, \gamma_{vf} + a_2\, r^2\, \gamma_{fs} - a_2\, r^2\, \gamma_{sv}$$



r is the mean dimension of the nucleus , $\Delta\mu_v$ is the change in the free Gibbs energy per unit of volume, γ_{vf} , γ_{fs} , γ_{sv} are surface energies and the geometrical constants are

$$a_1 = 2\pi(1 - \cos\theta)$$

$$a_2 = \pi \sin^2\theta$$

$$a_3 = 3\pi\left(2 - 3\cos\theta + \cos^2\theta\right)$$

The relation between these coefficients is defined by the Young's equation $\gamma_{sv} = \gamma_{fs} + \gamma_{vf}\cos\theta$

Heterogeneous nucleation

The formation of a new phase results in a reduction of the Gibbs free energy and an increase in the total surface energy. The nucleus will be stable only when its size is larger than the critical size r* :

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

and the critical energy barrier ΔG* is given by $\Delta G^* = \frac{4\left(a_1\gamma_{vf} + a_2\gamma_{fs} - a_2\gamma_{sv}\right)^3}{27\,a_3^3\,\Delta G_v}$

Substituting the constants

$$r^* = -\frac{2\,\gamma_{vf}}{\Delta G_v}\left\{\frac{\sin^2\theta\cos\theta + 2\cos\theta - 2}{2 - 3\cos\theta + \cos^3\theta}\right\}$$

$$r^* = -2\frac{\gamma}{\Delta G_v}$$

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

$$\Delta G^* = \frac{16\pi\,\gamma}{3\left(\Delta G_v\right)^2}$$

The first term represents the critical energy barrier while the second term is the wetting factor. When the contact angle θ is 180° the wetting factor equals 1 and the critical energy barrier equals the one obtained in homogeneous nucleation.

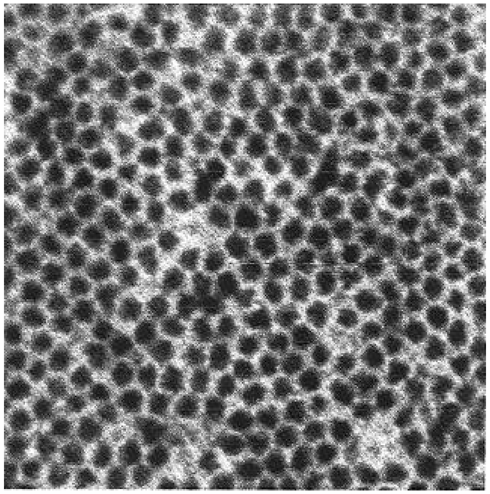
For angles smaller than 180° the energy barrier for heterogeneous nucleation is always smaller than the energy barrier for homogeneous nucleation.

Heterogeneous nucleation is easier than homogeneous nucleation in most cases. When the contact angle is zero, the wetting factor is zero and there is no barrier for the formation of the new phase. This occurs for example when the deposit is the same as the substrate.

Examples of hetero-nanostructures

CdSe nanocrystals capped with ZnS

M.A. Hines, and P. Guyot-Sionnest, J.Phys.Chem. **100**, 468 (1996)



TEM picture of CdSe/ZnS nanocrystals. Picture size is 95x95 nm

Blue shift of CdSe/ZnS nanocrystal-labels upon DNA-hybridization
Jürgen Riegler, **Franck Ditengou**, **Klaus Palme** _ and **Thomas Nann**
Journal of Nanobiotechnology 2008, **6:**7doi:10.1186/1477-3155-6-7

Luminescence color multiplexing is one of the most intriguing benefits, which might occur by using semiconductor Quantum Dots (QDs) as labels for biomolecules. It was found, that the luminescence of QDs can be quenched, and replaced by a luminescence peak at approximately 460 nm on hybridization with certain regions of Arabidopsis thaliana tissue. This effect is site selective, and it is unclear whether it occurs due to an energy transfer process, or due to quenching and scattering of the excitation light. The article describes methods for phase-transfer of differently coloured, hydrophobically ligated QDs, coupling of DNA strands to the QD's surface, and hybridization of the labelled DNA to different cell types of Arabidopsis thaliana. The reason for the luminescence blue-shift was studied systematically, and narrowed down to the above mentioned causes.

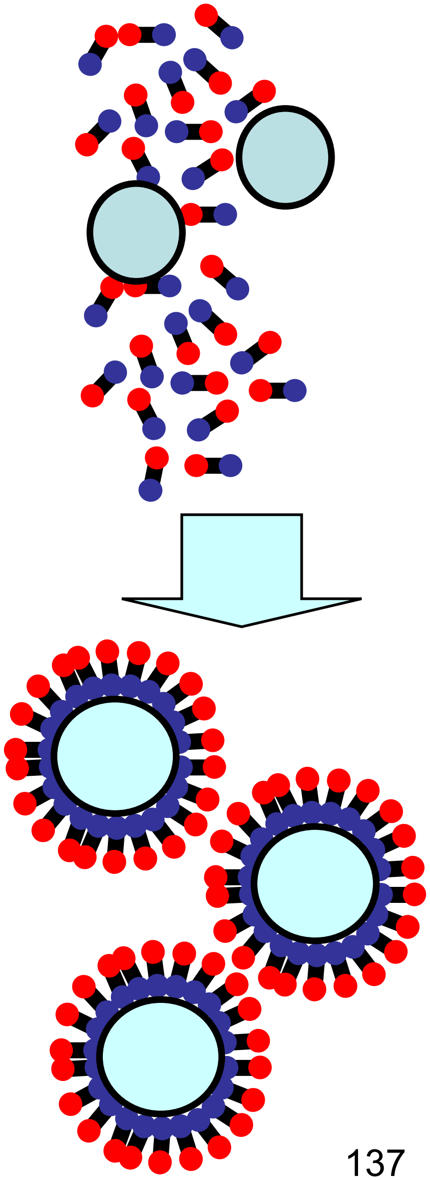
Synthesis of nanoparticles: kinetically confined

Kinetically controlled growth is to spatially confine the growth so that it stops when a given amount of material is consumed or the available space is filled up. Spatial confinement is divided into

i) liquid droplets in gas phase

ii) liquid droplets in liquids such as micelles

iii) template based synthesis and iv) self terminating synthesis.



Synthesis inside micelles

Synthesis is achieved by confining the reaction in a restricted space: micelles or microemulsions.

The reaction proceeds only with the reactants available inside the micelle volume.

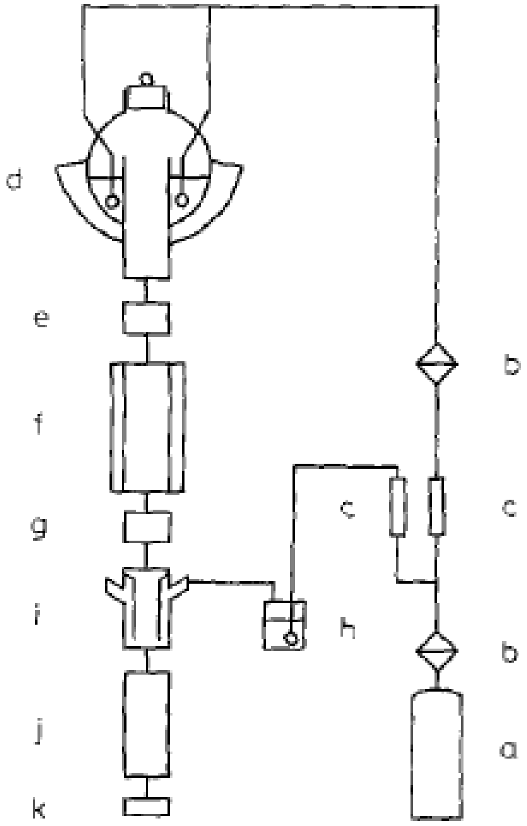
When surfactants or polymers typically consisting of two parts, one hydrophilic and another hydrophobic are dissolved in a solvent they preferentially self assemble at air/aqueous solution or hydrocarbon/aqueous solution interfaces. The hydrophilic part is turned towards the aqueous solution. When the concentration of the surfactants or polymers exceeds a critical level they self assemble in such a way to form micelles.

A microemulsion is a dispersion of droplets of an organic solution in an aqueous media. The chemical reactions in these systems takes place either at the interfaces between the organic droplets and the aqueous media or inside the droplets.

Synthesis of nanoparticles: kinetically confined

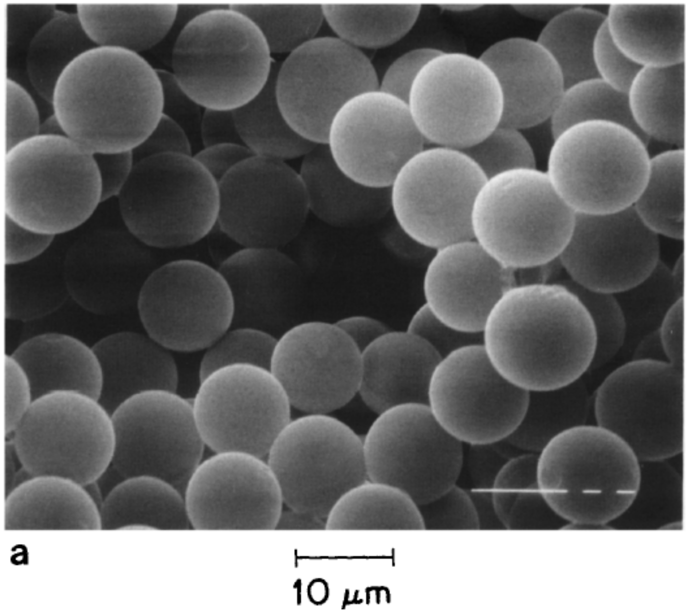
Aerosol synthesis

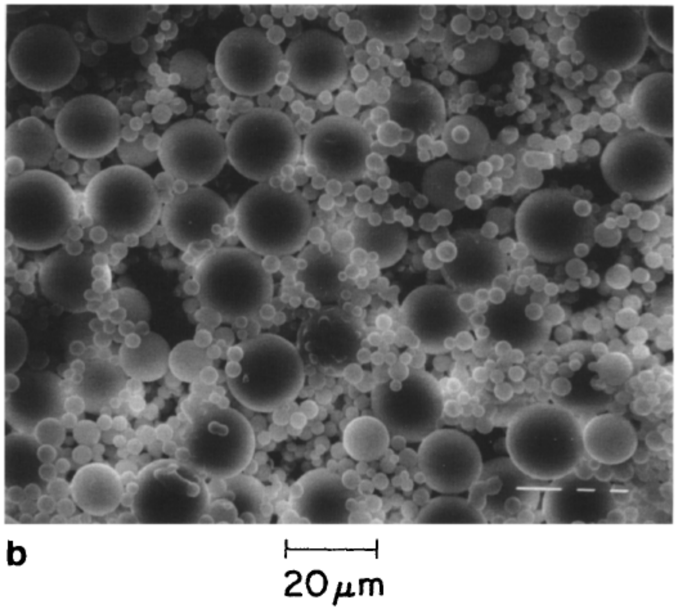
In this method a liquid precursor is prepared. The precursor can be a simple mixture solution of desired constituents elements or a colloidal dispersion. Then it is mystified to produce an aerosol. The liquid droplets in gas may simply solidify by evaporation or further reach with some reactant in the gas phase. The resulting particles are spheres and their size is determined by the size of the initial liquid droplets. Depending on the especial procedure the size distribution, morphology, and homogeneity of the nanoparticles can vary.

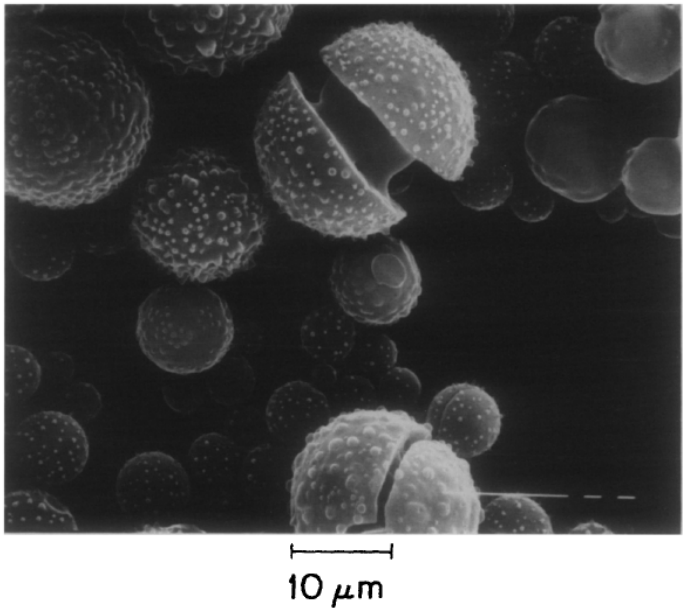


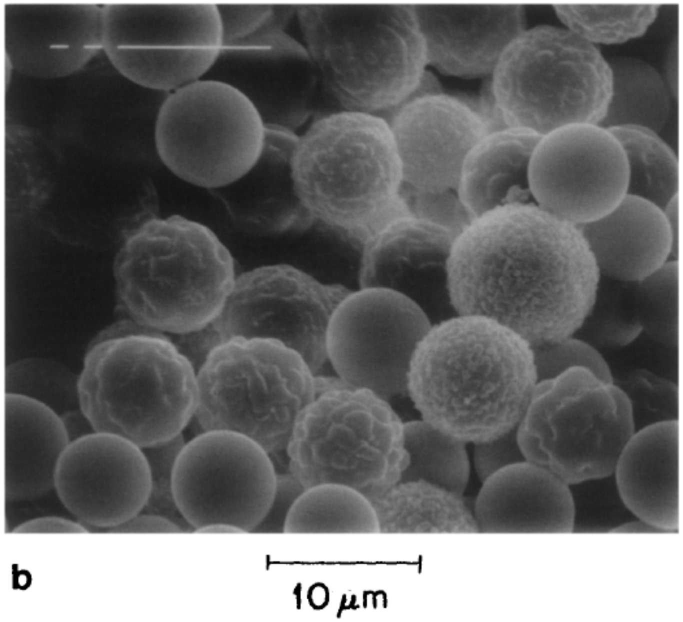
Schematic diagram of the apparatus used to produce polymer colloids: (a) helium gas tank; (b) Millipore membranes of 0.1 μm pore size; (c) flow meters; (d) boiler; (e) chamber for forming droplets; (f) reheater; (g) chamber for reforming droplets; (h) initiator reservoir; (i) initiator injection chamber; (j) reaction chamber; (k) therrnopositor.

Synthesis of nanoparticles: kinetically confined





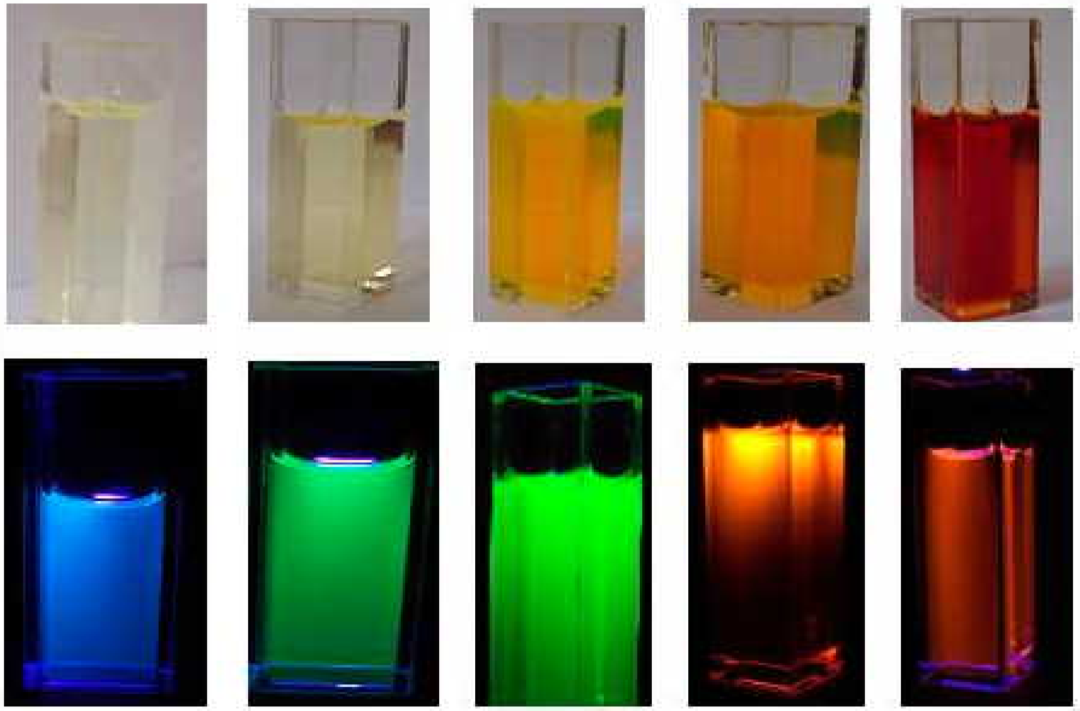




Synthesis of nanoparticles: kinetically confined

Growth termination

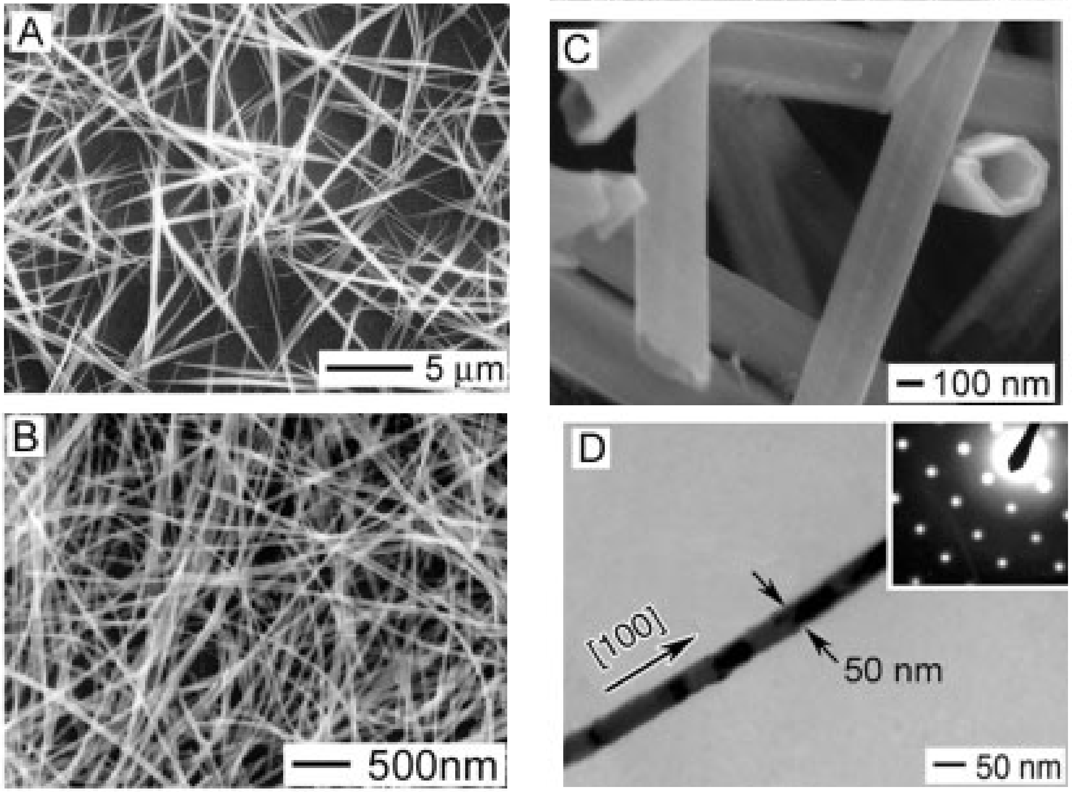
This method uses a suitable element to stop or control the growth in size of the nanoparticels. For example particles of CdS can be controlled in size by terminating the growth by capping the surface of the crystallites with thiophenol. The thyophenol attaches to the surface of the growing CdS crystal covering the surface, quenching the chemical reaction and canceling the crystal growth. With this method and a control of the reactants concentrations it is possible to accurately control the size of the nanoparticles that can be as small a 3.5 nm. The characterization of these nanoparticels can be done studying the spectral composition of the photoluminescence.



Nanowires and nanorods

One-dimensional structures have been called in different ways: nanowires, nanorod, fibers of fibrils, whiskers, etc. These structures have a nanometer size in one of the dimensions, which produces quantum confinement in the material and changes its properties.

Many techniques have been developed to synthesize these structures and can be grouped into four categories: Spontaneous growth, Template synthesis, Electrospinning, Lithography



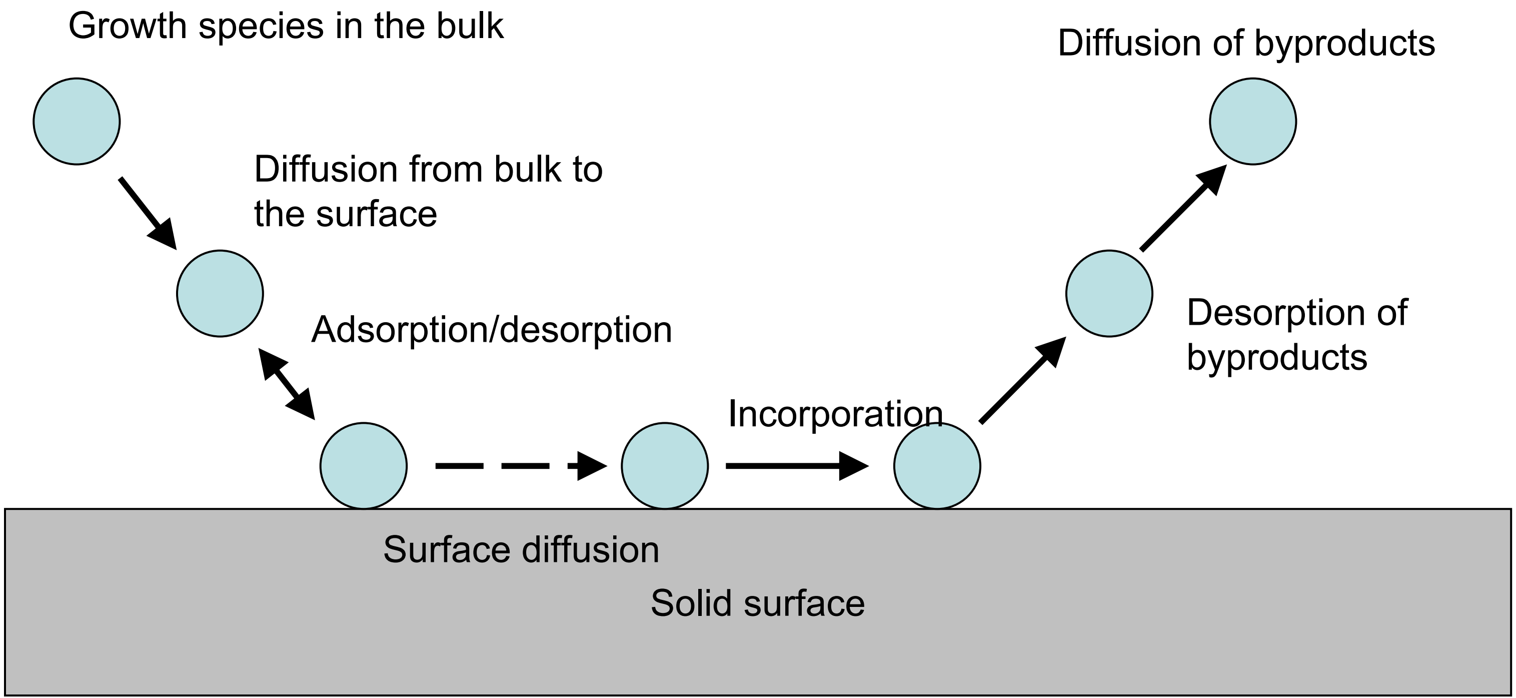
Nanowires and nanorods: Spontaneous Growth

The spontaneous growth is driven by the reduction of the Gibbs free energy of the system. This reduction commonly means a phase transformation, a chemical reaction or a release of stress. Also needed is an anisotropic growth:

In the case of uniformly sized nanowires, they can be produced when the crystal grows in one direction whereas no growth is experimented in the other direction.

Impurities on the growth surface can determine the morphology of the nanowire.

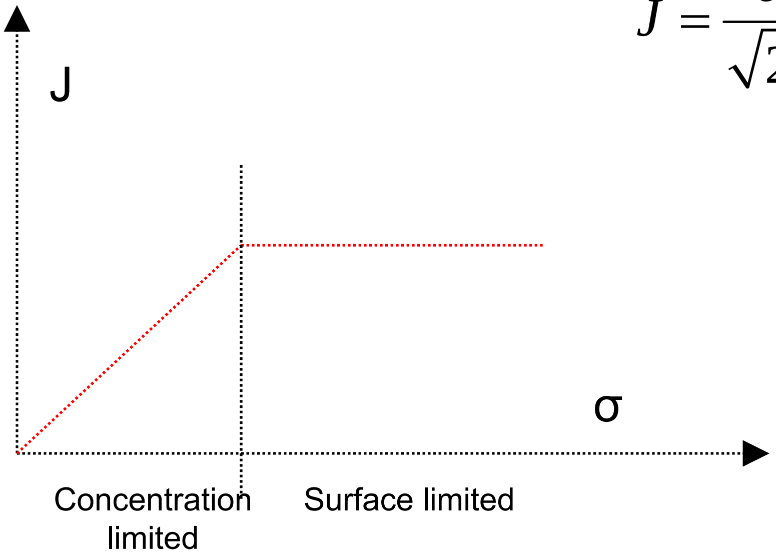
<u>Evaporation-condensation growth</u>   Typical growth process



Nanowires and nanorods: Spontaneous Growth

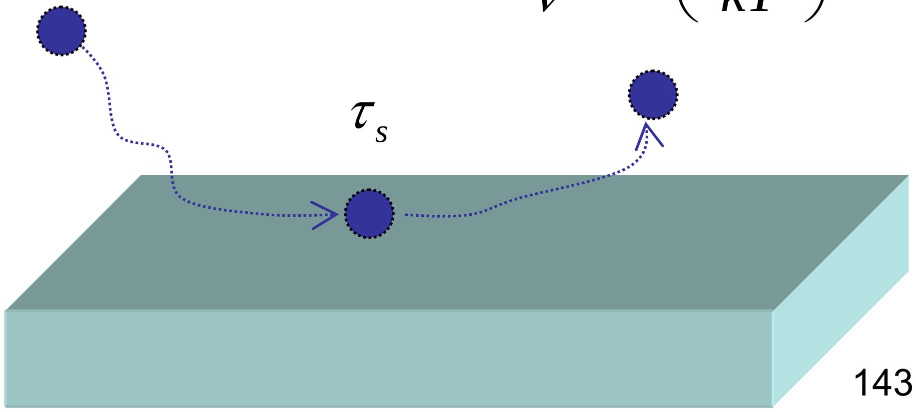
For most crystal growth, the rate limiting step is either adsorption/desorption or surface growth. When step adsorption/desorption is the rate limiting process, the growth rate is determined by the condensation rate given by the factor J (atoms cm^{-2} s^{-1})

$$J = \frac{\alpha\, \sigma\, P_0}{\sqrt{2\pi mkT}}$$

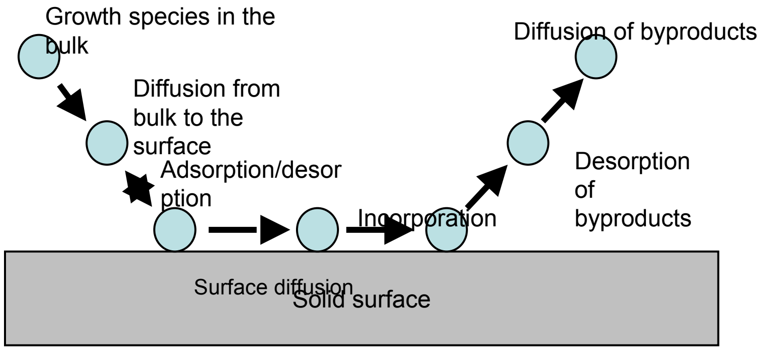


The growth of a specie onto the growth surface can be described in terms of the residence time and/or the diffusion distance before escaping back to the vapor phase. The residence time on the surface is described by

$$\tau_s = \frac{1}{\nu}\exp\left(\frac{E_{des}}{kT}\right)$$



Nanowires and nanorods: Spontaneous Growth



While residing at the surface, the growth species will diffuse in the surface with coefficient D_s given by

$$D_s = \frac{1}{2} a_0 \, \nu \, \exp\left(- \frac{E_s}{kT} \right)$$

So the mean diffusion distance X for a growth specie from the site of incidence is

$$X = 2\sqrt{D_s \, \tau_s} = a_0 \exp\left(\frac{E_{des} - E_s}{kT} \right)$$

If the mean diffusion distance is much larger than the distance between growth centers, all adsorbed growth species will be incorporated in the crystal structure: the accommodation coefficient will be 1.

If the diffusion distance X is much smaller than the distance between growth sites, the growth species will return to the vapor and the accommodation coefficient will be zero.

The accommodation coefficient is dependent on the desorption energy, the activation energy of surface diffusion and on the density of growth sites.

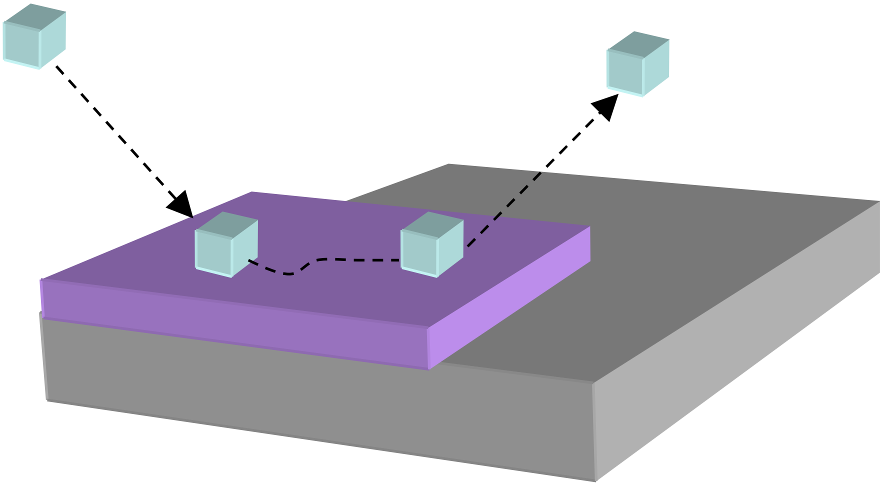
$$J = \frac{\alpha \, \sigma \, P_0}{\sqrt{2\pi mkT}}$$

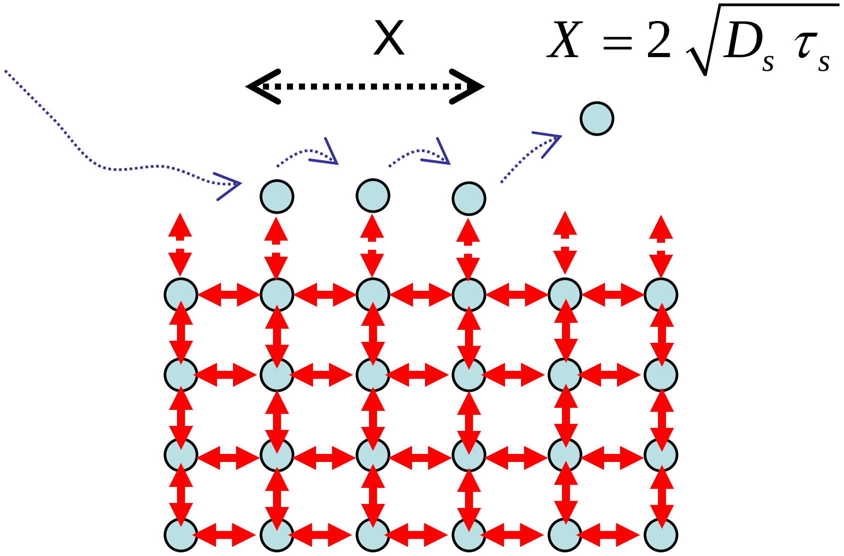
Nanowires and nanorods: Spontaneous Growth

Crystal facets can be characterized in three categories depending on the number of dangling periodic bond chains in a facet: flat surface, stepped surface and kinked surface.

The number of periodic broken bond chains can be understood as the number of broken bonds per atom on a given facet.

Example: cubic crystal. Each atom have a coordination number of 6



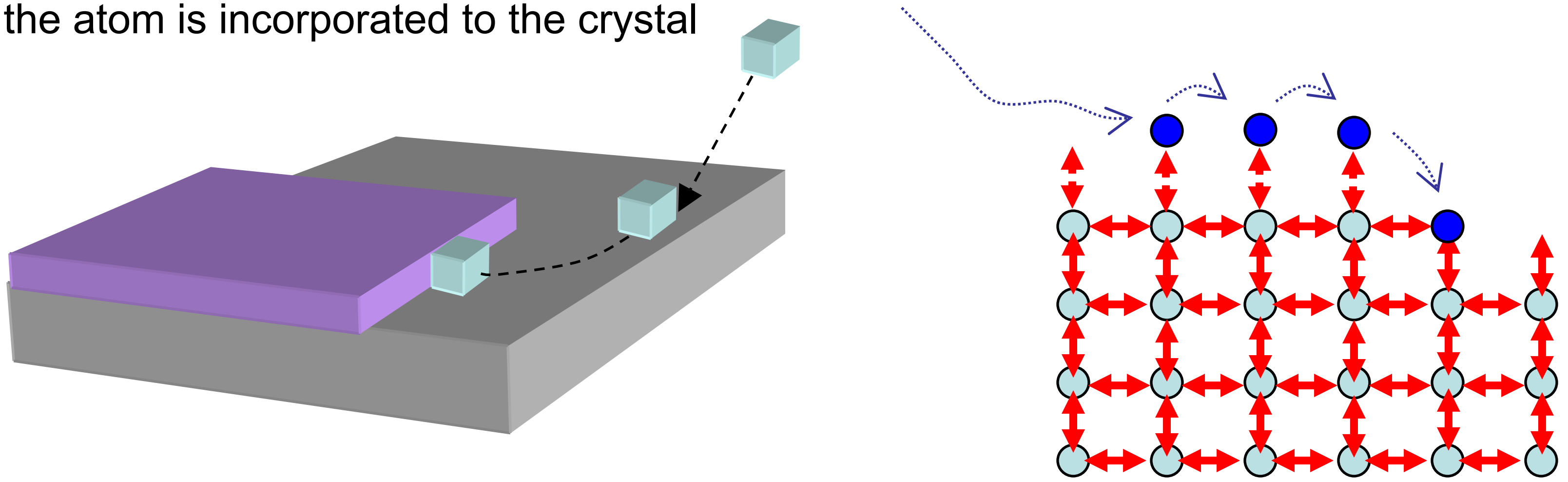


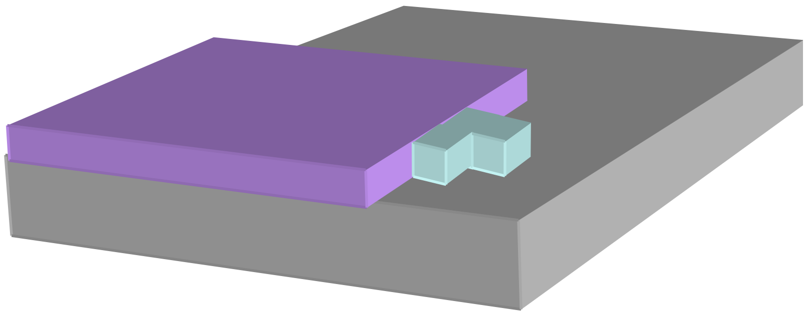
$$X = 2\sqrt{D_s \tau_s}$$

If it is adsorbed in a flat surface, it would form <u>one</u> chemical bond. This atom is considered a unfavorable energy state. It will diffuse in the surface. If the adatom does not find a growth site it will return to the bulk solution/vapor phase

Nanowires and nanorods: Spontaneous Growth

If in its diffusion the adatom finds a ledge or a ledge-kink in the surface it can form a double (ledge) of a triple (ledge-kink) chemical bond. In this situation the energy configuration is more favorable and the atom is incorporated to the crystal





The surface growths by the continuos advancement of the edge due to the incorporation of the atoms in the ledge

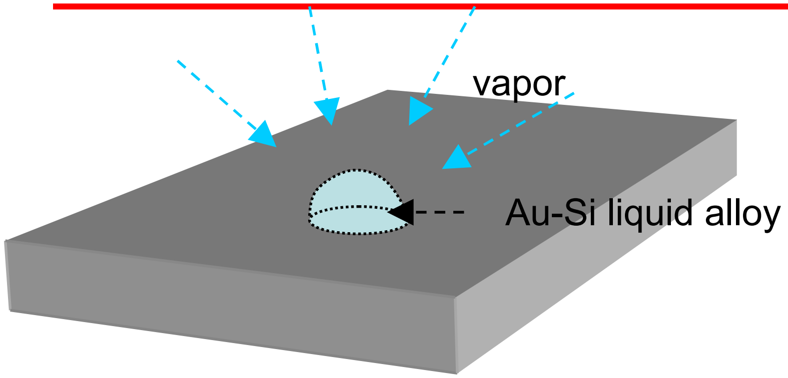
Nanowires and nanorods: Spontaneous Growth

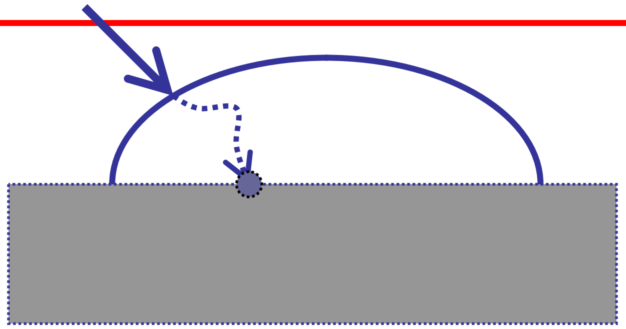
Vapor-Liquid-Solid and Solution-Liquid-Solid growth (VLS and SLS)

In the VLS growth a second phase material, commonly referred as either impurity or catalyst is purposely introduced to direct and confine the crystal growth.
A catalyst forms a liquid droplet by itself or by alloying with growth material during the growth, which acts as a trap of growth species.
Enriched growth species in the catalyst droplets subsequently precipitates at the growth surface resulting in one-directional growth.
The requirements for VLS growth are:

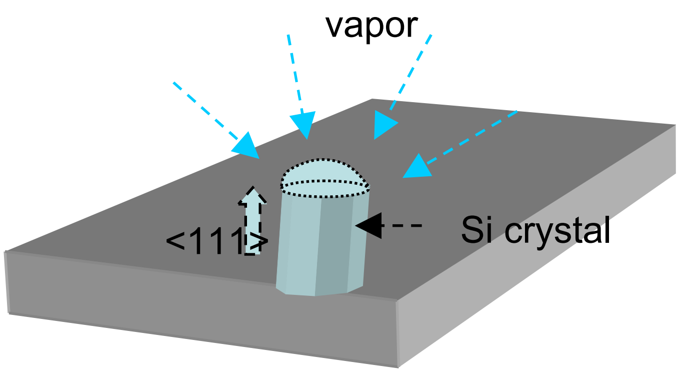
- The catalyst must form a liquid solution with the crystalline material to be grown at the deposition temperature.
- The distribution coefficient of the catalyst must be less than unity at the deposition temperature
- The equilibrium vapor pressure of the catalyst over the liquid droplet must be very small
- The catalyst must be chemically inert
- The wetting characteristics influence the diameter of the nanowire. For a given volume of the droplet , a small wetting angle results in a large growth area and a large diameter nanowire
- For a compound nanowire growth, one of the constituents can serve as the catalyst.
- For a controlled unidirectional growth the solid-liquid interface must be well defined crystallographically.

Nanowires and nanorods: Spontaneous Growth

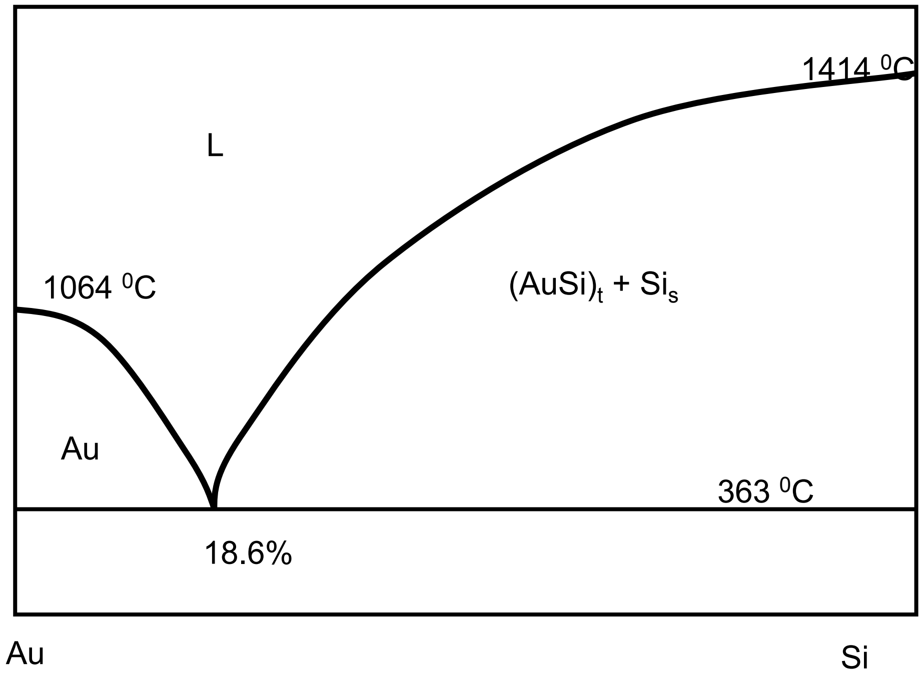




The growth species (Si) is adsorbed in the vapor-liquid interface, incorporated in the liquid, diffuse to the liquid-solid surface and finally incorporated in the solid phase. The material transport is diffusion controlled and occurs essentially under isothermal conditions.



Growth occurs in a preferential crystal orientation



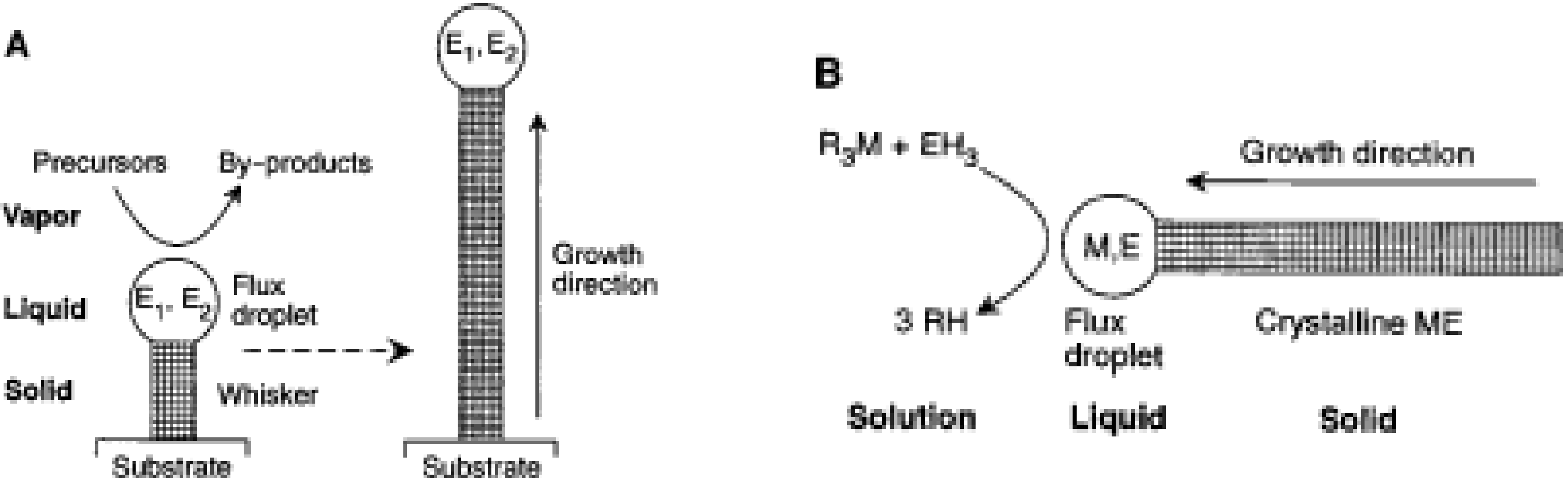
Nanowires and nanorods: Spontaneous Growth

Solution-Liquid-Solid Growth (SLS)

It is necessary a high temperature to produce the VLS growth. An alternative is the SLS method. Example: growth of InP nanowires. The precursor is an organometallic compounds as In(t-Bu)$_3$ and PH$_3$ dissolved into a hydrocarbon solvent. In the solution the precursors reacts to form In and P compounds for the growth with the following reaction:

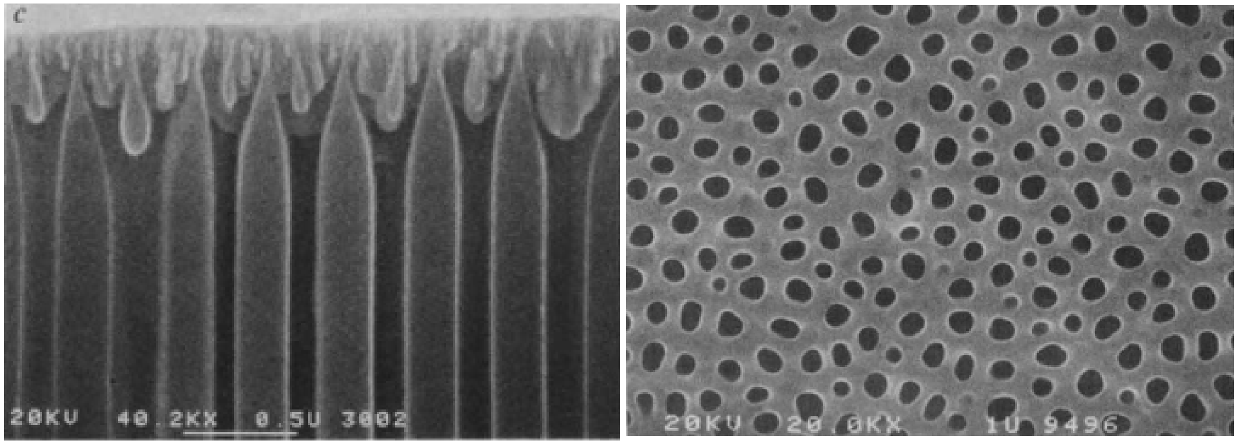
$$In\left(t-Bu\right)_3 + PH_3 \rightarrow InP + 3\left(t-Bu\right)H$$

Indium metal functions as the catalyst for the growth of InP nanowires. It was found that the nanowires are predominantly <111> similar to VLS method.

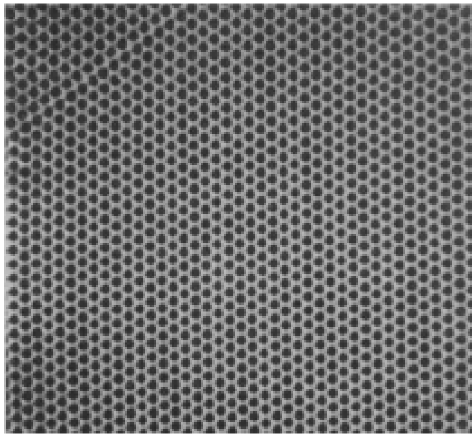


Nanowires and nanorods: Template based synthesis

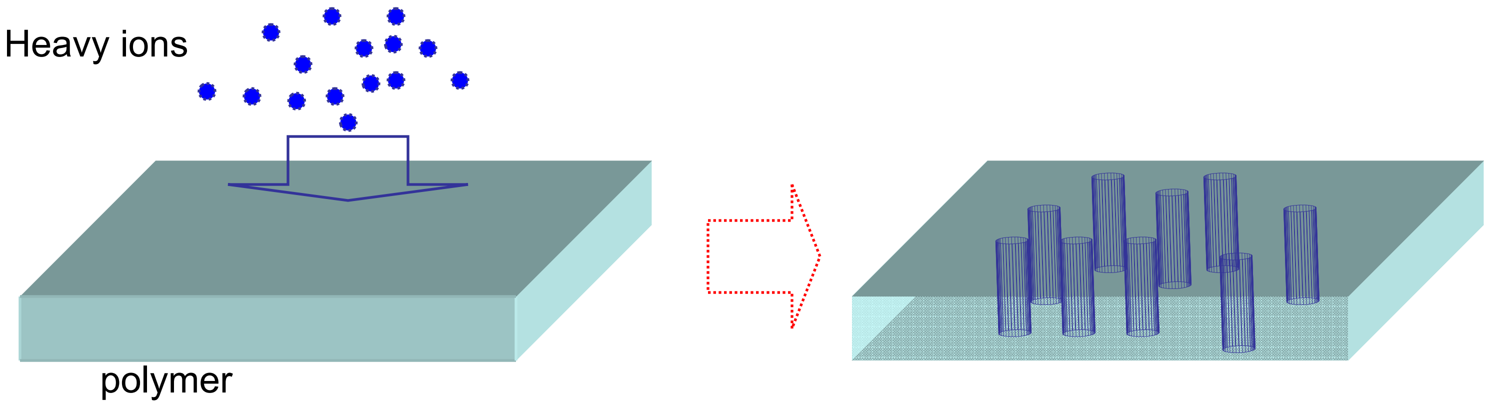
This method can be used to grow nanorods and nanowires. Various templates with nanometer size channels have been explored for the template growth. The most commonly used are anodized alumina membranes, radiation track etched polymer membranes, nanochannel array glass, radiation track etched mica and mosoporous materials.



Anodized Al



Glass



Nanowires and nanorods

Electrochemical deposition, electrodeposition or electroplating

Involves an electrolysis process that results in the deposition of solid material in an electrode. The process involves:

* oriented diffusion of charged growth species through a solution with an external electric field.

* reduction of the charged growth species at the growth surface that also is one of the electrodes of the electrolysis process.

When electrodeposition (also knows as electroplating) is confined inside the pores of template membranes, nanocomposites are produced. If the template is removed, nanorods or nanowires are prepared.

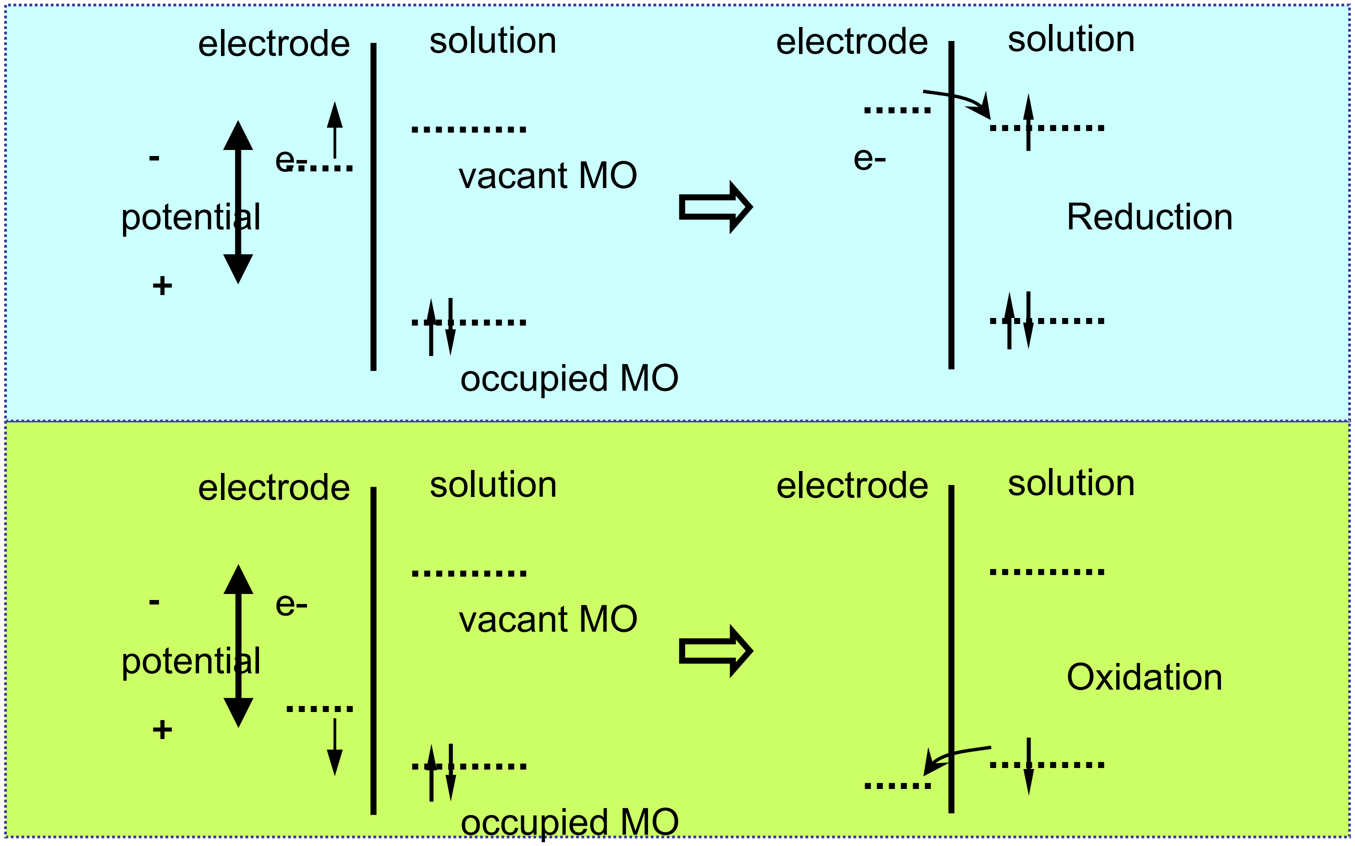
When a solid is immersed in a polar solvent or an electrolyte solution, surface charge will be developed. At an interface between an electrode and an electrolyte solution, an oxidation or reduction reaction occurs accompanied by a charge transfer through the interface until the equilibrium is achieved. For a given system, the electrode potential or surface charge density is described by the Nernst equation

$$E = E_0 + \frac{R_g T}{n_i F} \ln\left(a_i\right)$$

Nanowires and nanorods

When the electrode potential is more negative (higher) than the energy level of vacant molecular orbital in the electrolyte solution, electrons will transfer from the electrode to the solution accompanied with dissolution or reduction of the electrode. The reaction stops when the equilibrium is achieved.

When two electrodes of different materials immerse into one electrolyte solution, each electrode will establish equilibrium with the solution. This equilibrium is broken when the electrodes are connected to an external circuit. Since different electrodes have different electrode potentials, this difference will drive electrons from the electrode with higher electrode potential to the lower one.



Nanowires and nanorods

Example Cu and Zn electrodes immersed in an aqueous solution.
The Cu electrode has a more positive electrode potential (0.34 eV) than that of the Zn (-0.76 eV).
In the external circuit electrons flow from the negative electrode (Zn) to the more positive (Cu). At the Zn/solution interface the following reaction takes place

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$

These electrons flow through the external circuit to another electrode (Cu). At the same time Zn continues to dissolve from the electrode into the solution. At the Cu/solution interface a reduction reaction takes place resulting in the deposition of Cu

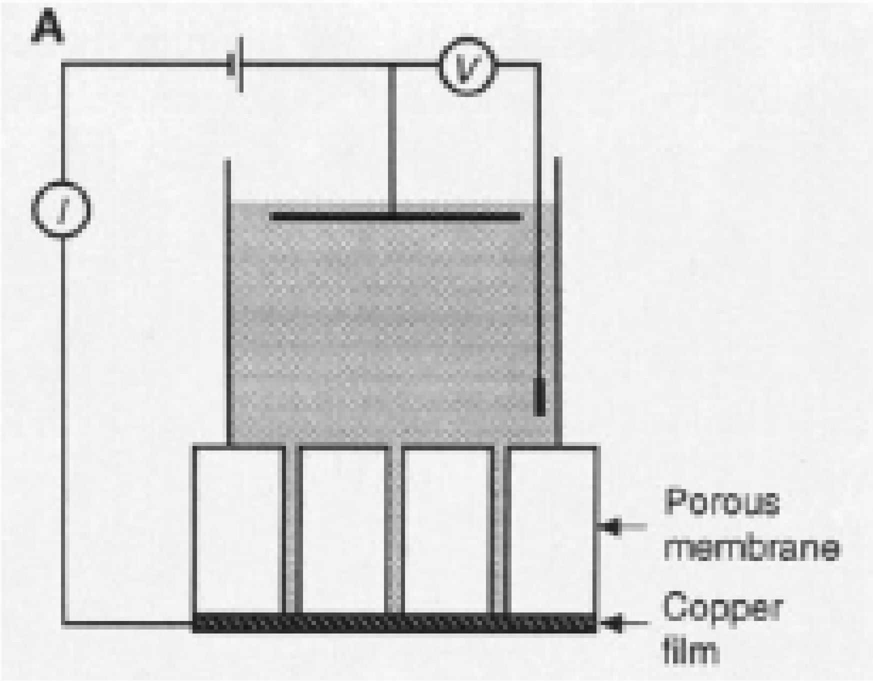
$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

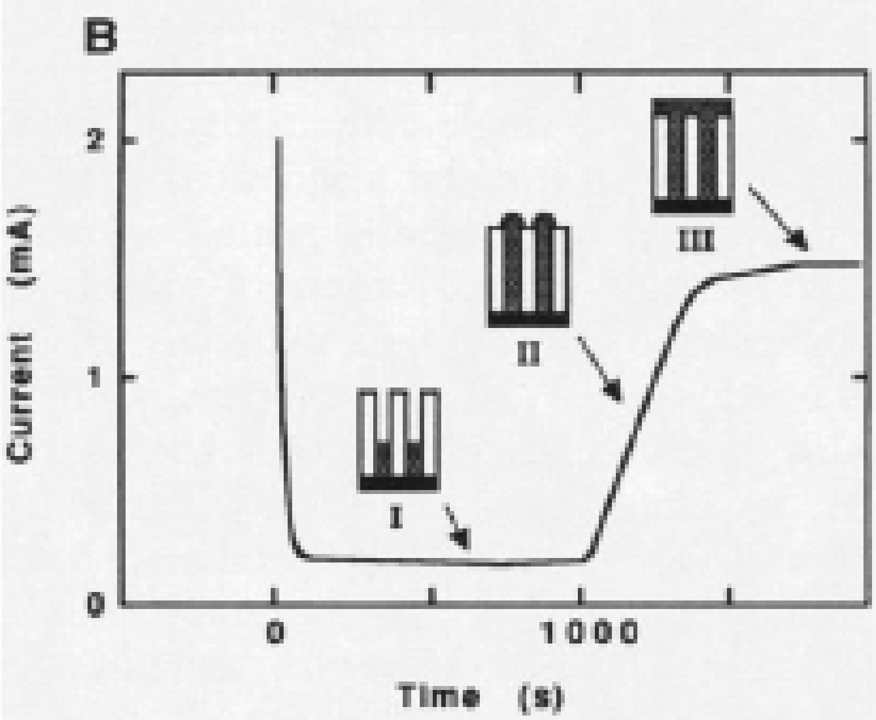
This process ends when an equilibrium is reached.
The Cu electrode potential decreases due to a decrease in copper ion activity in the solution whereas the Zn electrode potential increases due to an increased activity of Zn ions in the solution as both electrochemical reactions takes place.

In the electrolytic deposition the electrode connected to the positive side of the power supply acts as the anode where the oxidation takes place. The electrode connected to the negative side of the poser supply acts as the cathode where the reduction reaction takes place accompanied by deposition. Sometimes electrolytic deposition is also called cathode deposition.

Nanowires and nanorods

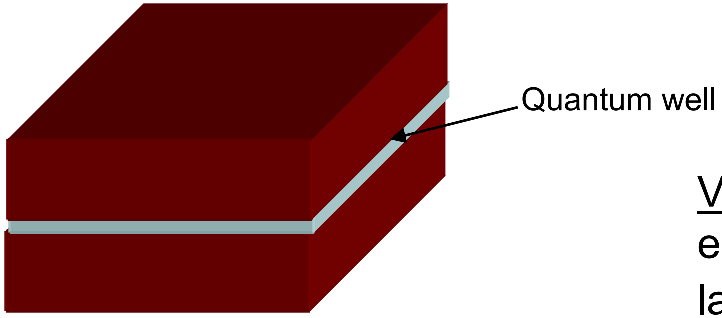
A typical electrolytic process composes of a series of steps:
a- Mass transfer through the solution from one electrode to another
b- Chemical reactions at the interfaces between electrode-solution
c- Electrons transfer at the electrode surfaces and through the external circuit
d- Other surface reactions such as adsorption, desorption or recrystallization.





Quantum confined materials: quantum wells

A quantum well is fabricated by depositing very thin layers of different materials. The carriers (electrons or holes) located in the thin crystal will experience a potential well that will keep them confined in a plane allowing only free movement in two dimensions and forcing them to occupy a planar region. Quantum confinement take place when the quantum well thickness becomes comparable at the de Broglie wavelength of the carriers ($\lambda = h/p$)

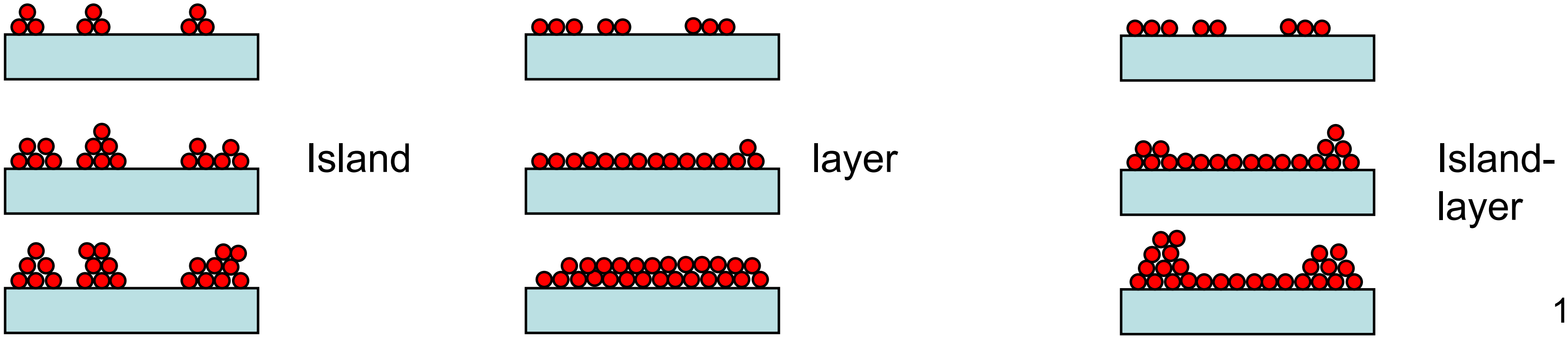


Thin film growth methods can be divided in two main groups:

Vapor-phase deposition: evaporation, molecular beam epitaxy, sputtering, chemical vapor deposition and atomic layer deposition.

Liquid-phase deposition: electrochemical deposition, chemical solution deposition, Langmiur-Blodgett films and self-assembled monolayers

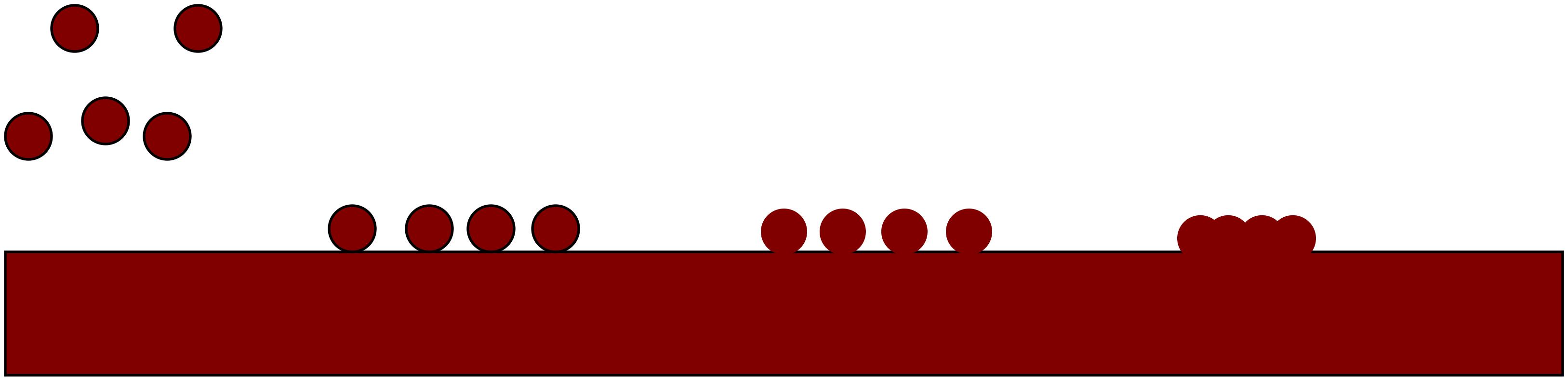
Nucleation modes: Island, layer, island-layer.



Nuclei growth

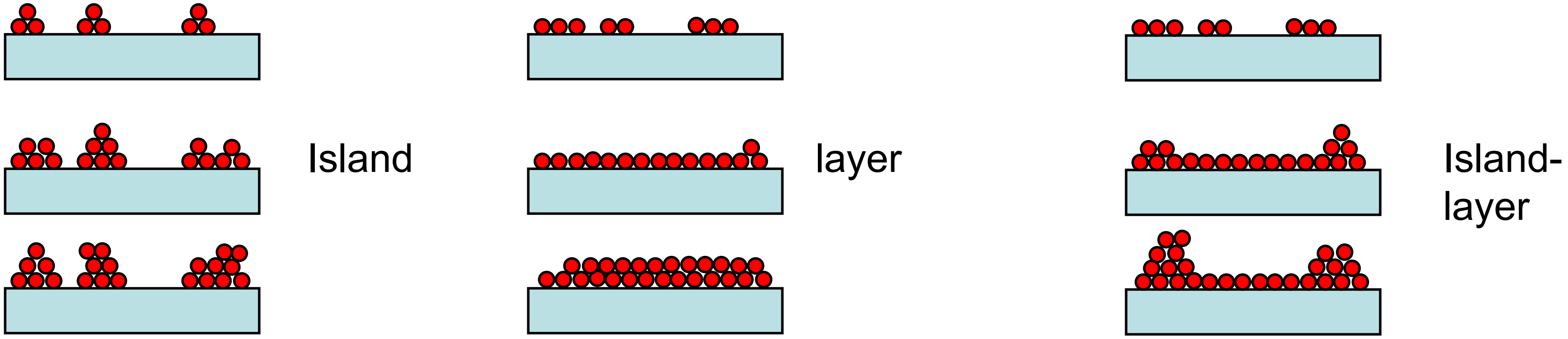
The growth process of the nuclei involves several steps:

- generation of growth species
- diffusion of the growth species from the bulk solution to the surface of the growth nuclei
- adsorption of the growth species onto the growth surface
- surface growth due to irreversible incorporation of the growth species onto the solid surface.



Two dimensional structures: thin films

Nucleation modes: Island, layer, island-layer.



Island growth occurs when the growth species are more bounded to each other than to the substrate. Many metals on insulator substrates, alkali halides, graphite and mica substrates display this type of nucleation during the initial film deposition stages. Subsequent growth generates islands that coalescence to form a continuous film.

Layer growth is the opposite. The growth species are more likely to bound to the substrate than to each other. In this case a first monolayer is formed before the deposition of a second layer. The most important examples of this type of nucleation is the epitaxial growth of single crystal layers.

The island-layer growth is an intermediate situation. Such type of growth usually involves the stress which is developed during the formation of the nuclei or films

$$r^* = \frac{2\pi\gamma_{vf}}{\Delta G_v}\left\{\frac{\sin^2\theta\cos\theta + 2\cos\theta - 2}{2 - 3\cos\theta + \cos^3\theta}\right\}$$

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

Two dimensional structures: thin films

For island growth the contact angle must be greater than zero. If we look at the Young's equation,

$$\gamma_{sv} = \gamma_{fs} + \gamma_{vf} \cos\theta$$

That means $\gamma_{sv} < \gamma_{fs} + \gamma_{vf}$

If the deposit does not wet the substrate at all or θ = 180°, the nucleation is a homogeneous. For layer growth, the deposit wets the substrate completely and the contact angle equals zero; the corresponding Young's equation becomes:

$$\gamma_{sv} = \gamma_{fs} + \gamma_{vf}$$

Single crystal films are growth either *homoepitaxy* or *heteroepitaxy*
Homoepitaxy is like a simple extension of the substrate. The crystal structure in the deposit and the substrate has no difference and virtually there is no interface. This occurs when the lattice constants of the substrate and deposit are equal or very similar.
If the lattice constants are different, that commonly leads to stress in the deposit that originates the island-layer growth.
When the deposit is elastically strained due to for example lattice mismatch, strain energy is developed. In this case the Gibbs function includes the strain energy

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

Two dimensional structures: thin films

The sign of ΔG_v is negative and the sign of ω is positive, the overall barrier to nucleation increases. When the stress exceeds a critical point, and cannot be released the strain energy per unit area of deposit is large with respect to γ_{vf} permitting nuclei to form above the initial layer deposit. In this case the surface energy of the substrate exceeds the combination of both the surface energy of the deposit and the interfacial energy between the substrate and the deposit.

$$\gamma_{sv} > \gamma_{fs} + \gamma_{vf}$$

Whether the deposit is single crystalline, polycrystalline of amorphous depends on the growth conditions and the substrate. The deposition temperature and the impinging rate of growth species are the two most important factors:

- Growth of single crystal layers requires i) a single crystal substrate, ii) a clean substrate to avoid secondary nucleations iii) a high growth temperature to assure sufficient mobility of the growth species and iv) low impinging rate to assure a sufficient time for the surface diffusion and incorporation of growth species into the crystal structure and for the structural relaxation before arrival of next growth species.
- Deposition of amorphous films occurs when i) low growth temperature is applied and there is insufficient surface mobility and/or ii) when the influx of growing species is very high and the growth species does not have time to find growth sites.
- Polycrystalline films falls in between these two situations. In general the temperature is high to assure a good mobility and the influx of deposit is large.

Two dimensional structures: thin films

Epitaxy is a process that refers to the formation or growth of single crystals on top of single crystals substrates. Epitaxy growth can be divided into homoepitaxy and heteroepitaxy.

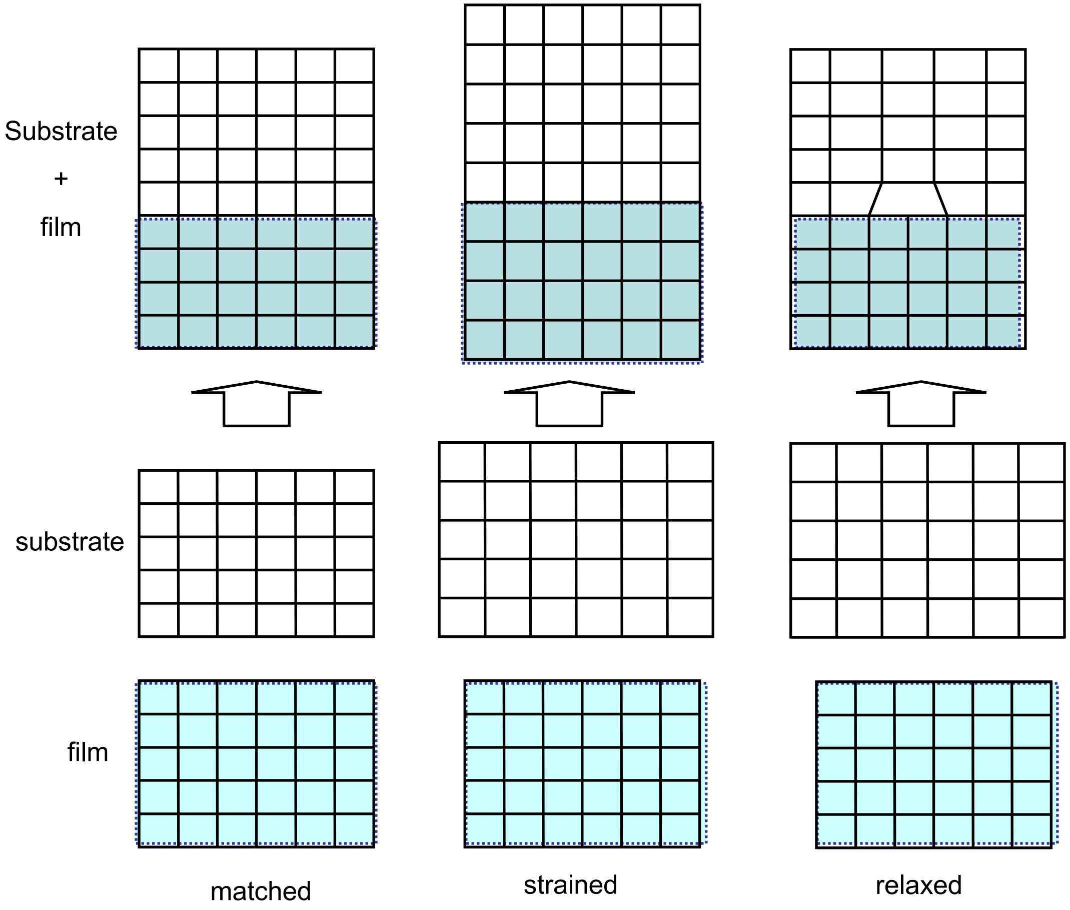
The lattice mismatch is also called misfit and it is given by

$$f = \frac{a_s - a_f}{a_f}$$

If f > 0 the film is strained in tension whereas if f < 0 the film is strained in compression.

Strain energy develops in strained films

$$E_s = 2\,\mu_f \left(\frac{1+\nu}{1-\nu}\right) \varepsilon^2\, h\, A$$



Two dimensional structures: Physical vapor deposition

Evaporation

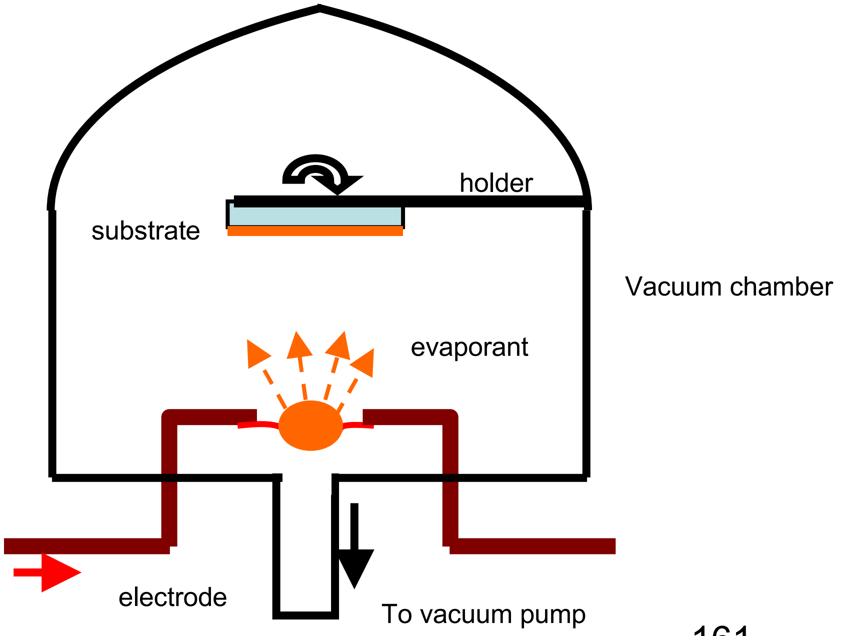
Consists of an evaporation source that vaporizes the desired material and a substrate located at an appropriate distance. The concentration of the growth species can be controlled changing the source temperature and the flux of the carrier gas. The equilibrium vapor pressure can be estimated as:

$$\ln P_e = -\frac{\Delta H_e}{R_g\, T} + C$$

Evaporation of compounds is more complicated as they can undergo chemical reactions, such as pyrolysis, decomposition and association, and frequently the vapor composition differs from the composition of the source material. The rate of evaporation depends on the material in question

$$\Phi_e = \alpha_e\, N_A \left(P_e - P_h\right) / \sqrt{2\pi\, m\, R_g\, T}$$

Different elements can evaporate differently and that will deplete the abundance of this element in the source. As a consequence that can change the vapor composition and change the composition of the film for different thickness.

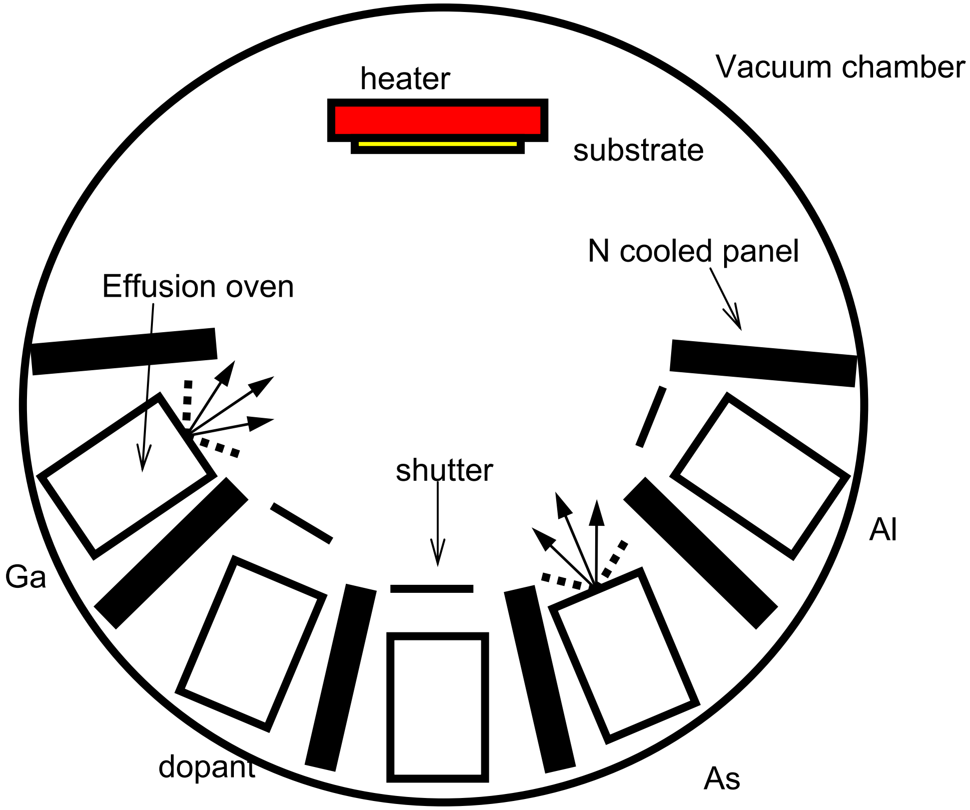


Two dimensional structures: Molecular beam epitaxy (MBE)

MBE can be considered as a special case of evaporation for single crystal film growth with highly controlled evaporation rates in ultra high 10^{-10} to 10^{-11} torr.

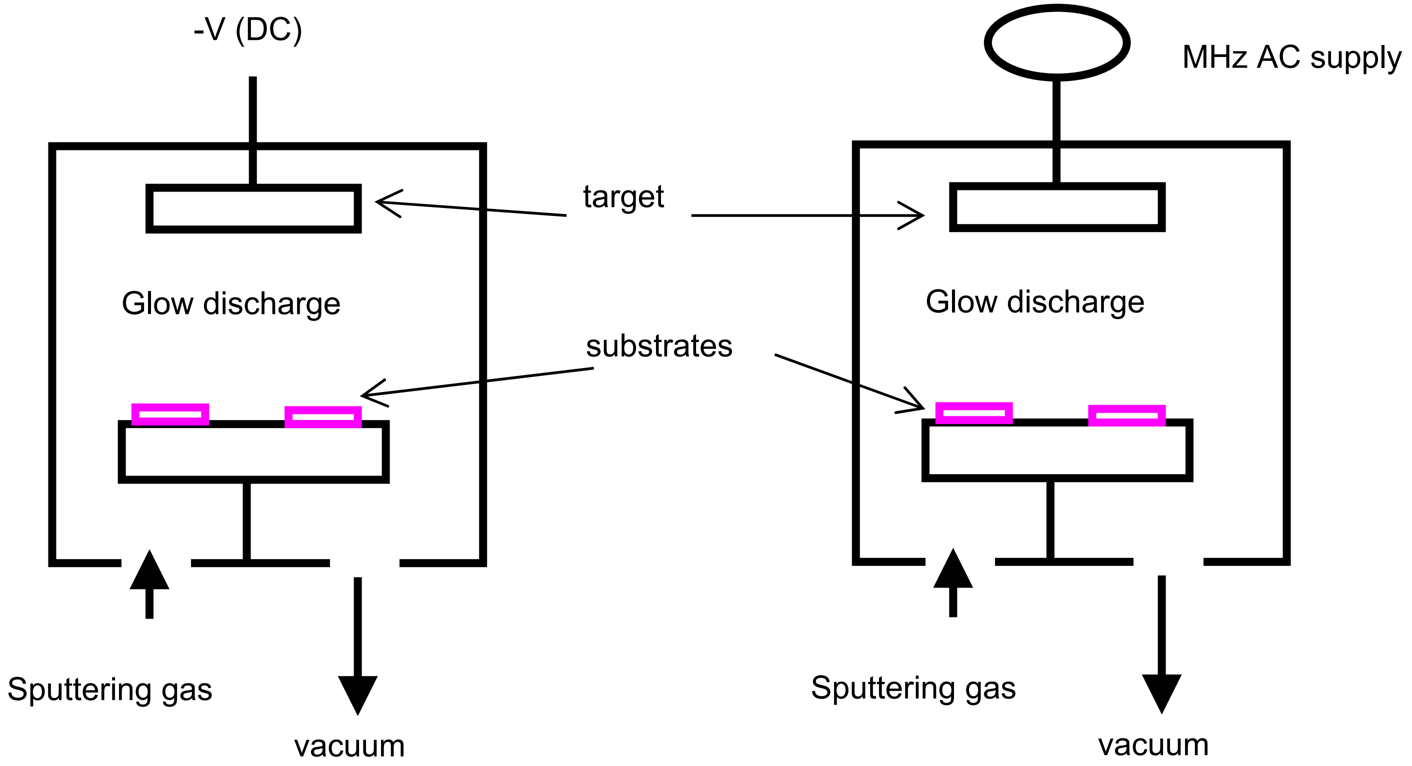
The individual evaporation source allows a good control of the chemical composition of the film. The slow deposition rate allows a long diffusion time and minimize the crystal defects.

- A low growth temperature that limits the diffusion and maintain abrupt interfaces, which are important in the fabrication of quantum wells.
- A slow growth rate that ensures a well controlled two dimensional growth at a typical growth rate of 1 micron per hour
- A simple growth mechanism that ensures a better understanding of the layer, due to the individual control of the independent sources
- A variety of in situ analysis capabilities that gives valuable information of the growth process



Two dimensional structures: Sputtering

Sputtering uses energetic ions to knock atoms or molecules out from a target that acts as one electrode and consequently deposit these atoms/molecules on the other electrode. The ions impinging the surface of the target are knock out the bulk material and deposited in a substrate located nearby. The target is the cathode of the discharge.



Two dimensional structures: Chemical vapor deposition (CVD)

CVD is the process to chemically reacting a volatile compound of a material to be deposit, with other gases to produce a non-volatile solid that deposits atomistically on the surface of a substrate. There are many possible reactions and the chemistry is the most important component of this method. Gas phase and surface reactions are intrinsically mixed in this method. The wide range of possible reactions can be grouped into pyrolysis, reduction, oxidation and compound formation

- Metalorganic compounds are used as precursors: MOCVD
- Plasma is used to enhance the reaction is called PECVD
- Low pressure CVD (LPCVD)
- Laser enhanced CVD (LECVD)
- Aerosol assisted CVD (AACVD).

Pyrolysis or thermal decomposition

$$SiH_4(g) \rightarrow Si(s) + 2H_2(g) \quad at\ 650^oC$$

$$Ni(CO)_4(g) \rightarrow Ni(s) + 4CO(g) \quad at\ 180^oC$$

Reduction

$$SiCl_4(g) + 2H_2(g) \rightarrow Si(s) + 4HCl(g) \quad at\ 1200^oC$$

$$WF_6 + 3H_2(g) \rightarrow W(s) + 6HF(g) \quad at\ 300^oC$$

Oxidation

$$SiH_4(g) + O_2(g) \rightarrow SiO_2(s) + 2H_2(g) \quad at\ 450^oC$$

$$4PH_3(g) + 5O_2(g) \rightarrow 2P_2O_5(s) + 6H_2(g) \quad at\ 450^oC$$

Compound formation

$$SiCl_4(g) + CH_4(g) \rightarrow SiC(s) + 4HCl(g) \quad at\ 1400^oC$$

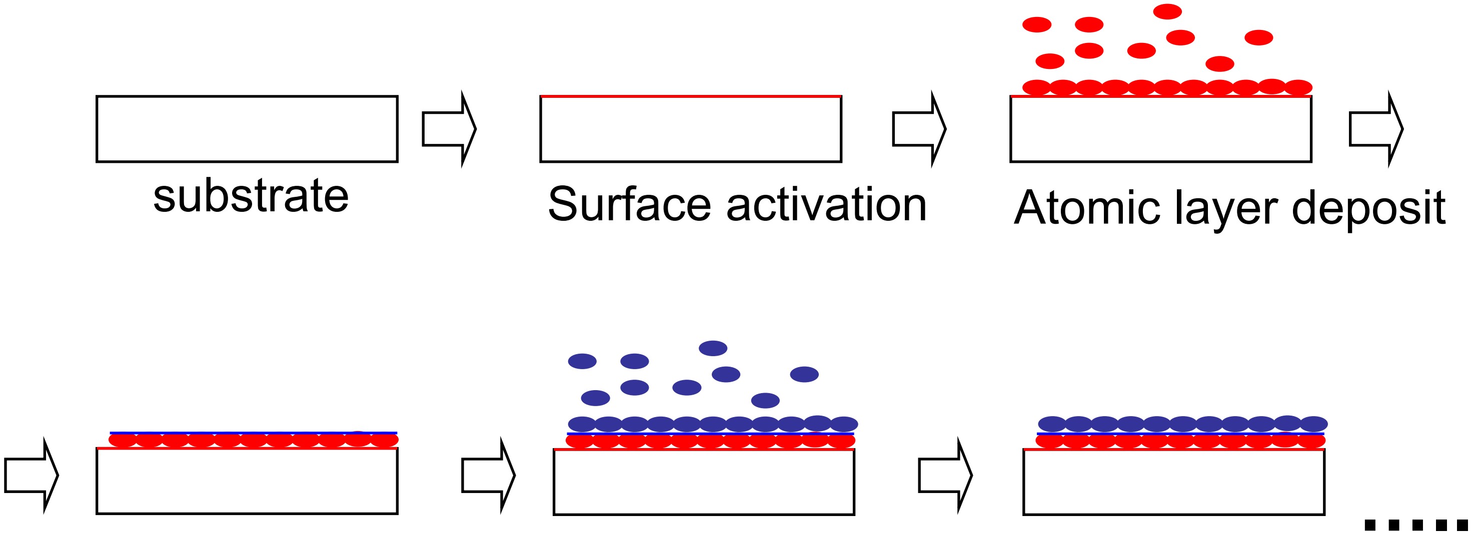
$$TiCl_4(g) + CH_4(g) \rightarrow TiC(s) + 4HCl(g) \quad at\ 1000^oC$$

Two dimensional structures: Atomic layer deposition

Atomic layer deposition is self limited growth Atomic layer deposition (ALD) is also called atomic layer epitaxy (ALE), atomic layer growth (ALG) atomic layer CVD (ALCVD) and molecular layer epitaxy (MLE).

Can be considered as a modification of the CVD.

- The surface of the substrate is first activated by a chemical reaction.
- When precursor molecules are introduced into the deposition chamber they react only with the activated surface of the substrate and form chemical bonds in the surface.
- The precursors will not react with each other.
- In a second activation reaction, the newly formed surface is activated by other surface reaction and a new layer of equal or different precursor atoms can be added.



substrate

Surface activation

Atomic layer deposit

New surface activation

2nd Atomic layer deposit

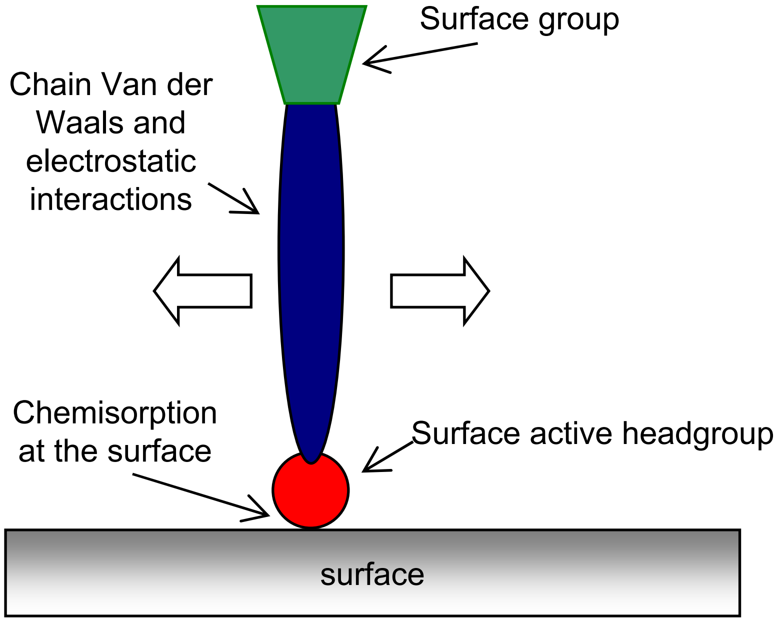
.....

Two dimensional structures: Self assembly

Molecules or small components as small particles are spontaneously organized: chemical reactions, electrostatic attraction and capillary forces.
Self assembled monolayers are molecular assemblies that are formed spontaneously by the immersion of an appropriate substrate into a solution of an active surfactant in an organic solvent.
A self assembly surfactant molecule is composed by three parts

- Head group that provides the most exothermic process by chemisorption to the surface of the substrate.
- A chain: exothermic interactions between chains in different molecules is through van der Waals interactions and typically are one order of magnitude smaller than the molecular chain that produces the attachment to the surface.
- Terminal functionality.

Self assembly monolayers consists of ordered and closely packed molecular assemblies that have a two dimensional crystalline like structure, though there exists a lot of defects.
Forces includes hydrophobicity, hydrophilicity, electrostatic forces, capillary forces and chemisorption.

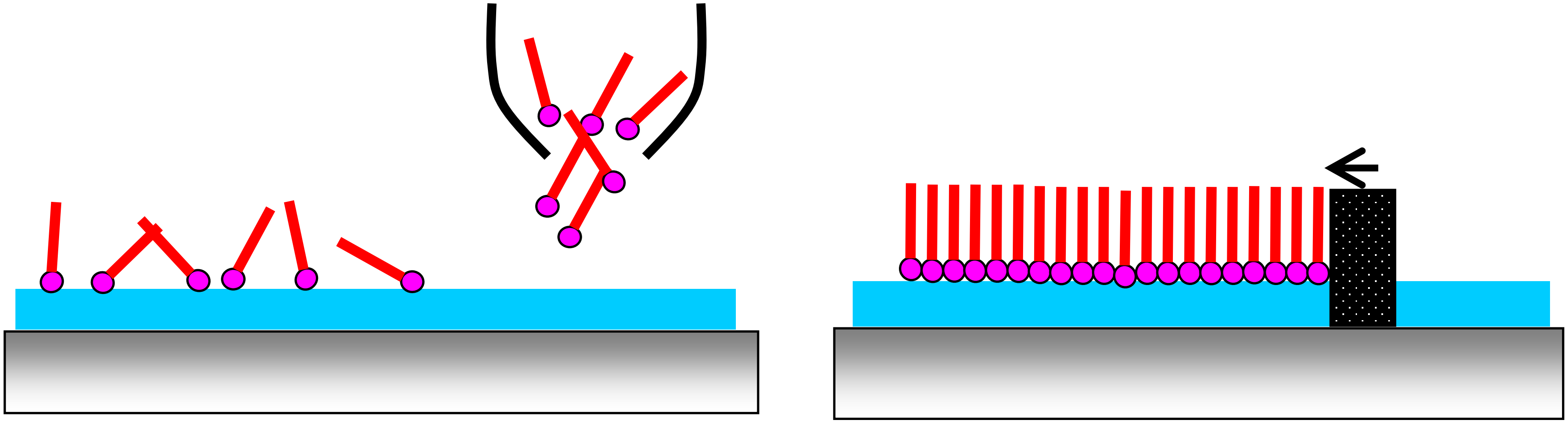


Two dimensional structures: Langmuir Blodgett films

Are monolayers and multilayers of amphiphilic molecules transferred from the liquid gas interface (commonly water/air interface) onto a solid substrate

Molecules insoluble in water with one part hydrophobic and a part hydrophilic. These molecules are located in the water/air interface, with the hydrophobic part residing in the air or in a non polar solvent.

The LB technique is unique as these monolayers established in the liquid interface can be transferred to different substrates.



Two dimensional structures: Langmuir Blodgett films

To transfer monolayers from the water/air interface to the substrate, the most common method is the vertical deposition.

Another to transfer a monolayer to a substrate is the Schaefer’s method or horizontal lifting. This method is very well suited to transfer very rigid films

Thermal stability and order-disorder transitions are two important issues for any practical application of the LB films.

LB films allow the possibility to design and construct stable organic super-lattices.