ChE 430
Colloidal synthesis of nanoparticles and their energy applications

MODULE 1: Techniques for the synthesis of nanomaterials

1.0. What are nanomaterials?
1.1. Possible approaches to nanomaterials
1.2. Top-down approaches
1.3. Bottom-up approaches
1.4. Summary of the methods

1.0. What are “Nanomaterials”?

What are nanoparticles and nanomaterials?

What do 0D, 1D, 2D and 3D indicate?

What application and products are they use in?

1.0. What are “Nanomaterials”?

What are nanoparticles and nanomaterials?

What applications and products are they used in?

1.1. Possible approaches to nanomaterials

Bottom-up approach

These approaches include the miniaturization of materials components (up to atomic level) with further self-assembly process leading to the formation of nanostructures.
During self-assembly the physical forces operating at nanoscale are used to combine basic units into larger stable structures.
Typical examples are quantum dot formation during epitaxial growth and formation of nanoparticles from colloidal dispersion.

Top-down approach

These approaches use larger (macroscopic) initial structures, which can be externally-controlled in the processing of nanostructures.
Typical examples are etching through the mask, ball milling, and application of severe plastic deformation.

1.1. Possible approaches to nanomaterials

- **Top-down methods**

begin with a pattern generated on a larger scale, then reduced to nanoscale.

-By nature, aren't cheap and quick to manufacture

- Slow and not suitable for large scale production.

- **Bottom-up methods**

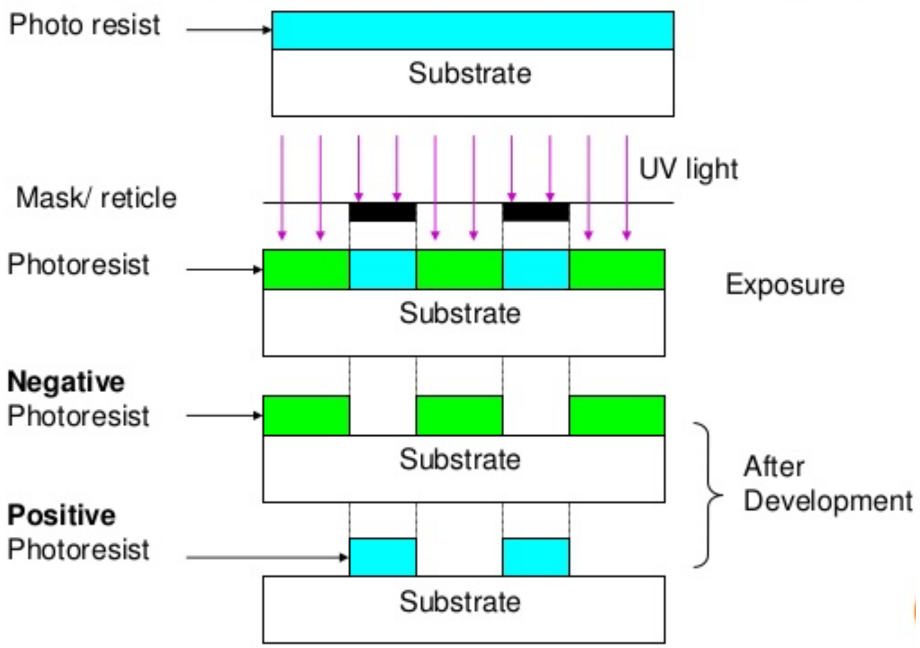
start with atoms or molecules and build up to nanostructures

-Fabrication is much less expensive

1.2. Top-down approaches

Photolitography:

At the moment, the most used top-down approach is photolitography. It has been used for a while to manufacture computer chips and to produce structures smaller than 100nm.

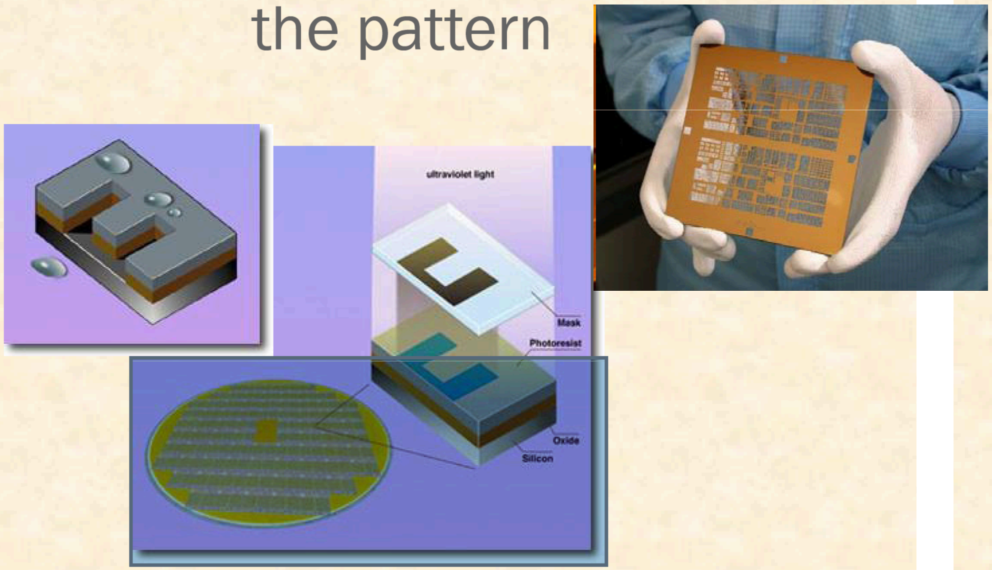


Typically, an oxidized silicon (Si) wafer is coated with a 1micron thick photoresist layer. After exposure to UV light, a positive photoresist undergoes a photochemical reaction, which breaks down the polymer chains. Subsequently, when the wafer is rinsed in a properly chosen developing solution, the exposed areas are removed. On the contrary, uv light strengthen the structure of negative photoresists making it more stable in the developing solution

1.2. Top-down approaches

Photolitography:

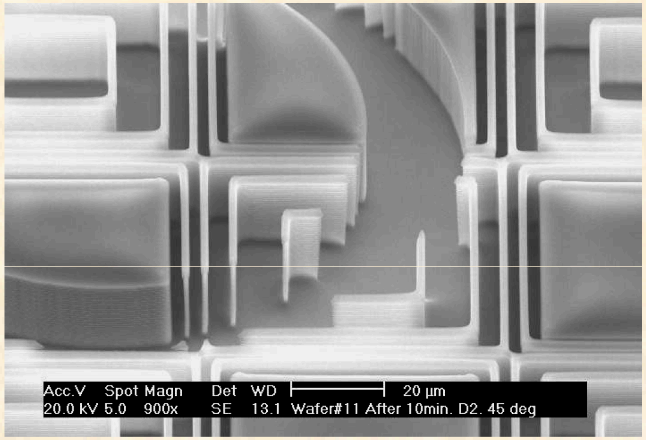
Lithographic processing: Developing the pattern



Resist is removed from exposed areas

Remaining resist faithfully reproduces mask pattern

Lithographic processing: Etch the material

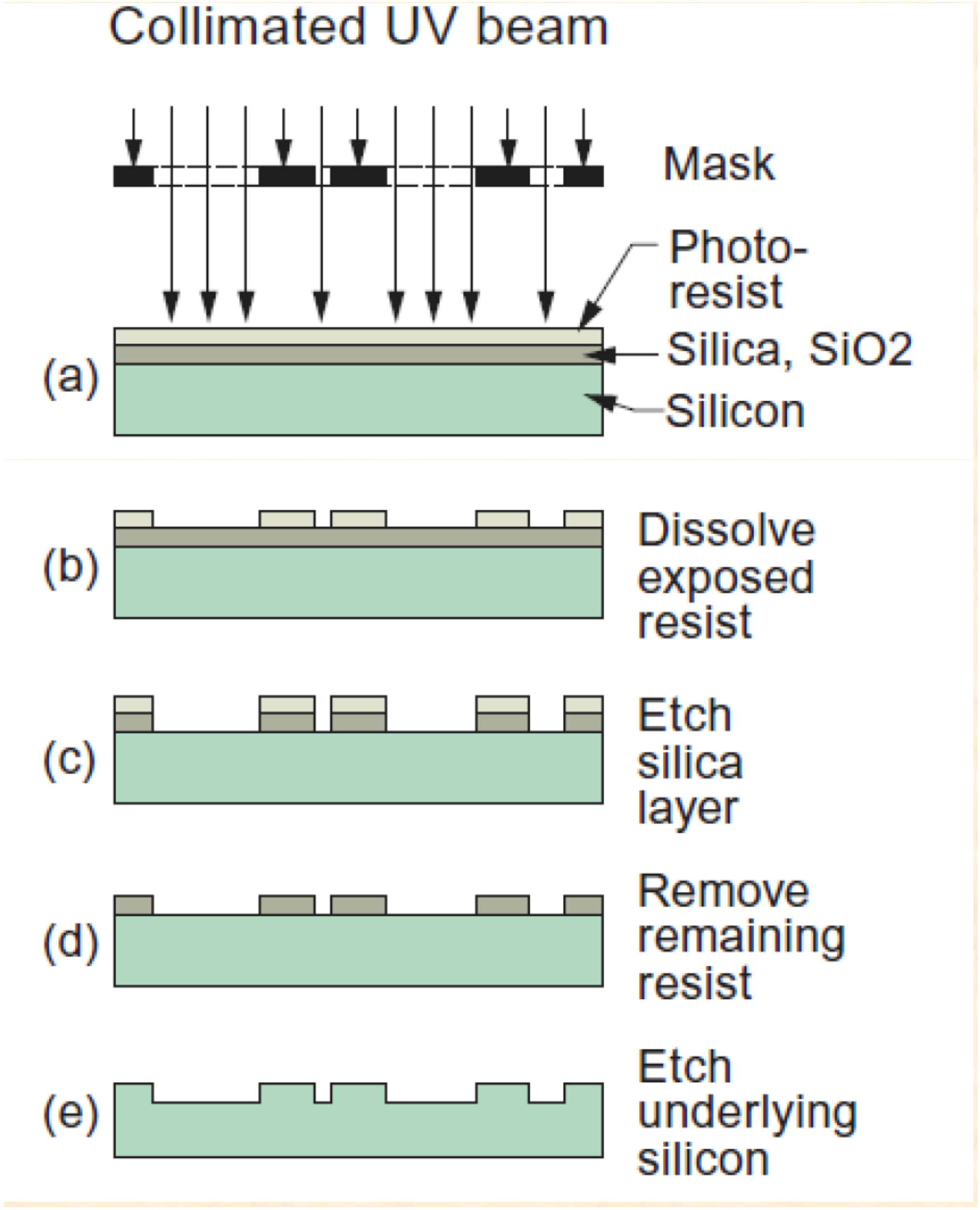


Resist protects selected regions during etch.

Pattern is transferred to substrate material.

1.2. Top-down approaches

Photolitography:

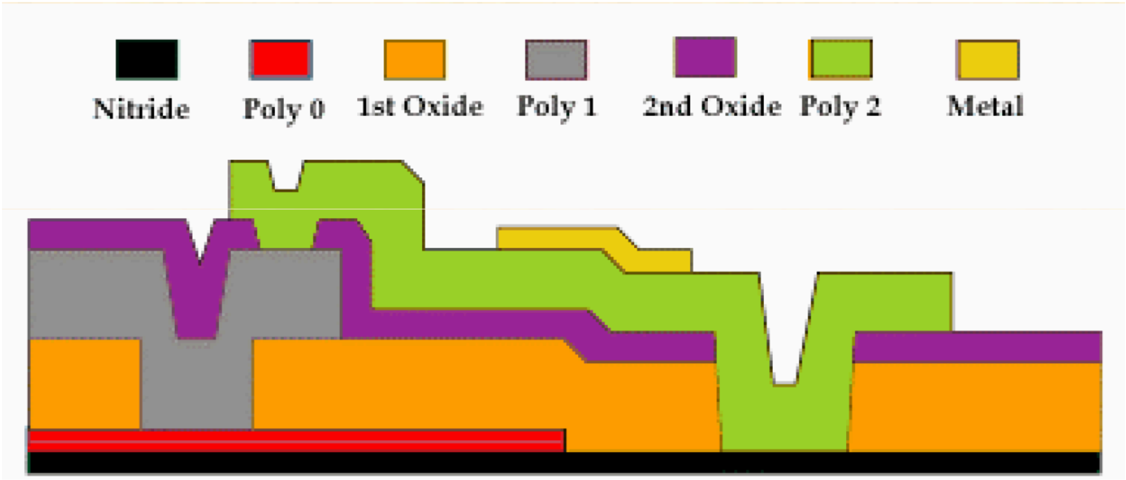


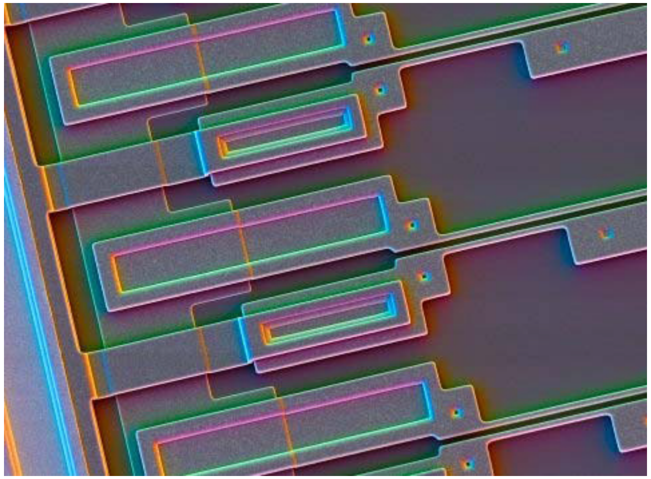
1.2. Top-down approaches

Photolitography:

The basic idea behind the photolitographic processing is:
COAT, PROTECT, EXPOSE, ETCH, REPEAT…

The Result:
Multiple patterned layers of different materials





1.2. Top-down approaches

Photolitography:

Problems in lithography

Though the concept of photolithography is simple, the actual implementation is very **complex and expensive**.

This is because

(1) nanostructures significantly smaller than 100 nm are difficult to produce due to diffraction effects,

(2) masks need to be perfectly aligned with the pattern on the wafer,

(3) the density of defects needs to be carefully controlled, and

(4) photolithographic tools are very costly, ranging in price from tens to hundreds of millions of dollars.

1.2. Top-down approaches

Electron-beam litography and X-Ray litography

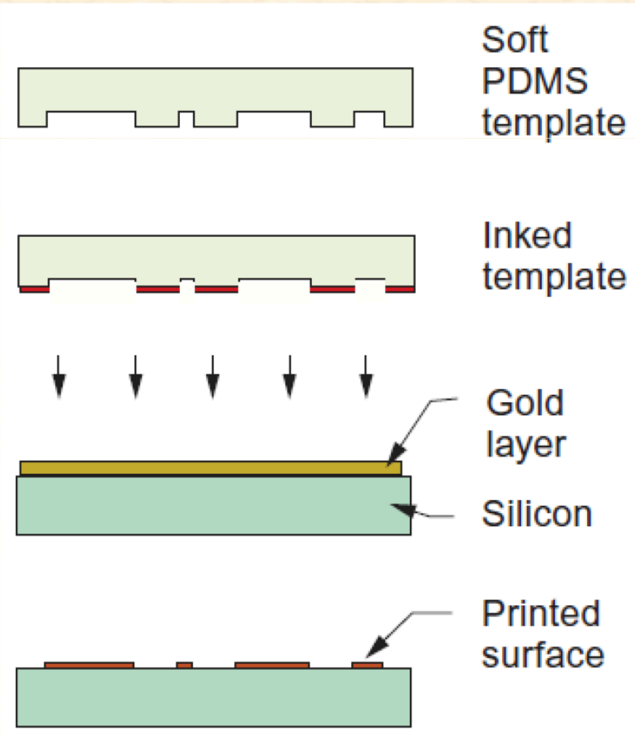
In the case of **electron beam lithography**, the pattern is written in a polymer film with a beam of electrons.
Since diffraction effects are largely reduced due to the wavelength of electrons, there is no blurring of features, and thus the resolution is greatly improved.
However, the electron beam technique is very **expensive** and very **slow**.

In the case of **X-ray lithography**, diffraction effects are also minimized due to the short wavelength of X-rays, but conventional lenses are not capable of focusing X-rays and the radiation damages most of the materials used for masks and lenses.

1.2. Top-down approaches

Microcontact printing method

Printing, **stamping**, and **molding** use mechanical processes instead of photons or electrons.
These methods are normally called **soft lithography** methods because they involve the use of polymers.

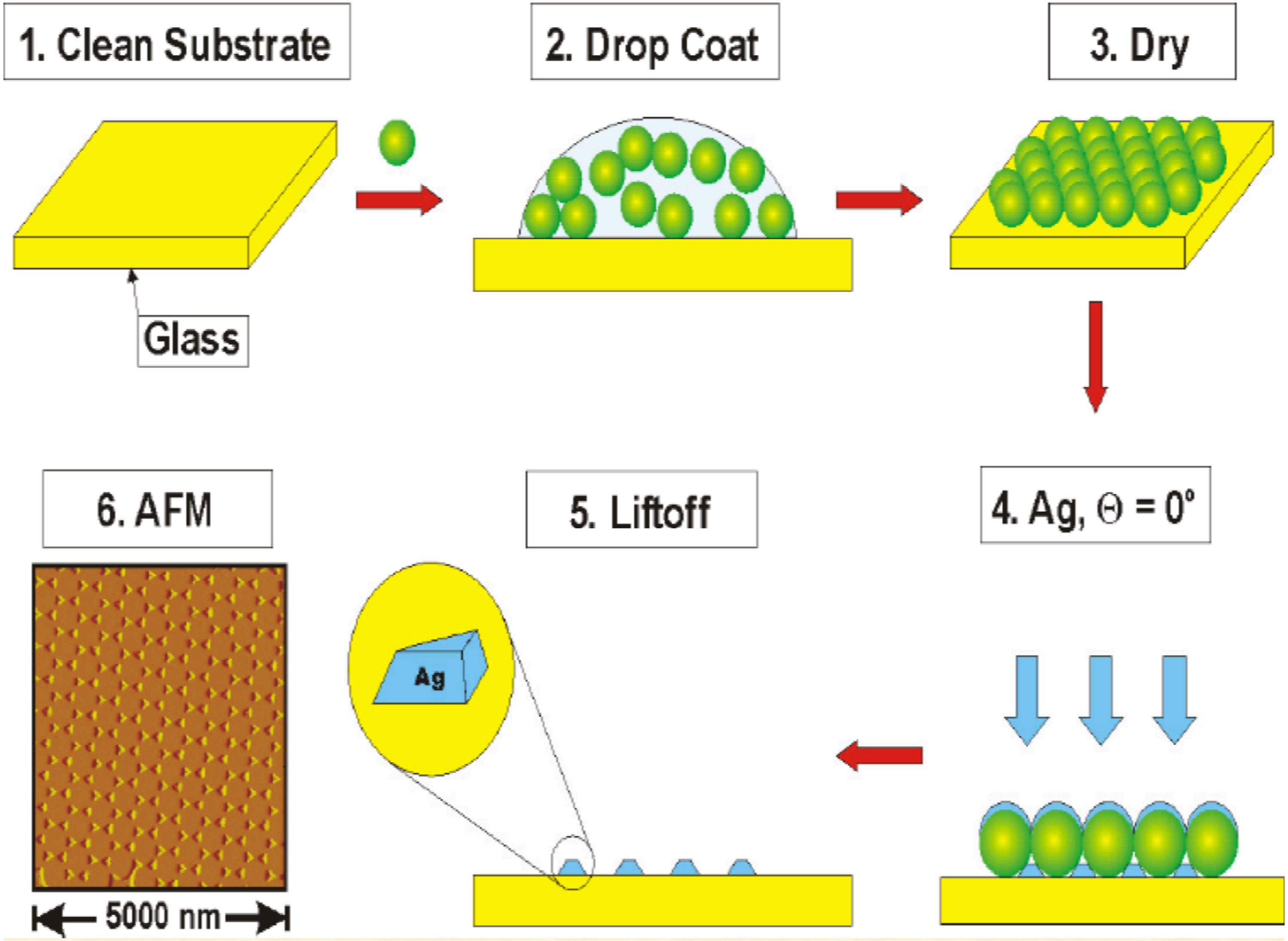


microcontact printing method

A chemical precursor to polydimethylfiloxane (PDMS) is poured over and cured into the rubbery solid PDMS stamp that reproduces the original pattern.
The stamp can then be used in various inexpensive ways to make nanostructures.
The stamp is inked with a solution consisting of organic molecules and then pressed into a thin film of gold on a silicon plate.
The organic molecules form a self-assembled monolayer on the solid surface that reproduces the pattern with a precision of approximately 50 nm.

1.2. Top-down approaches

Nanosphere lithography



1.2. Top-down approaches

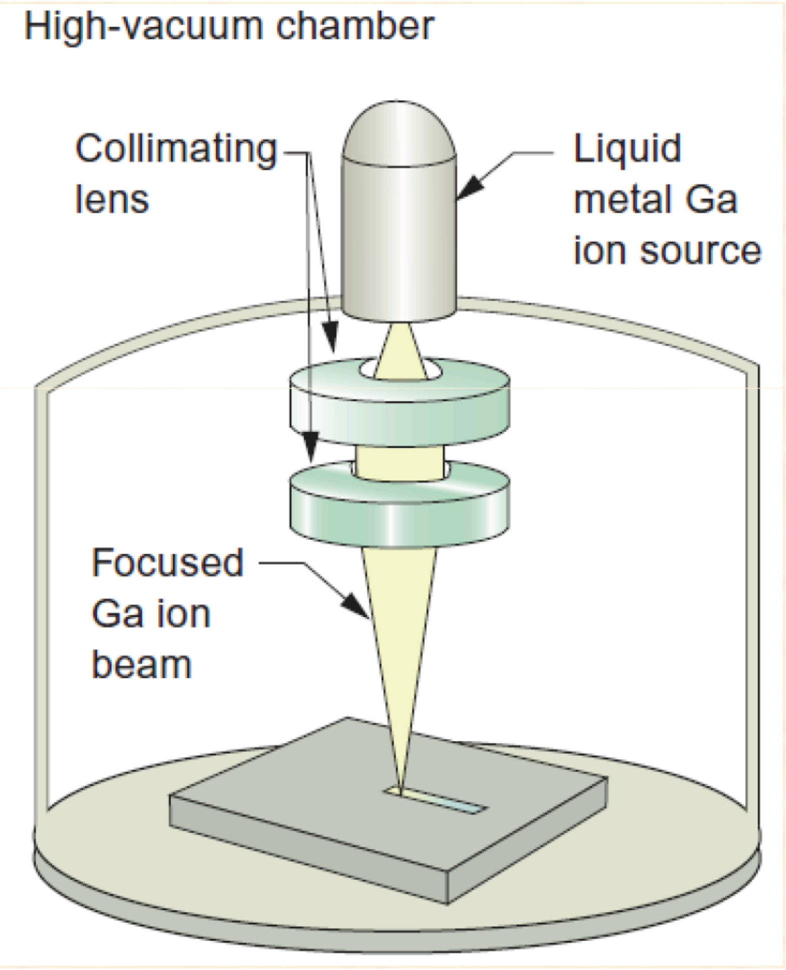
Micromachining methods

Machining Method	Materials That Can Be Machined	Feature Size (and Tolerance)	Positional Tolerance	Material Removal Rate, Microns^3/ sec
Micromachining	Metals, polymers	10 microns (2 microns)	3 microns	10,000
Micro electrodischarge machining (EDM)	Any conducting material	10 microns (3 microns)	3 microns	2,500,000
Electron beam machining (EBM)	Any conducting material	5 microns (submicron)	1 micron	100,000
Femto-second laser machining (LBM)	Any material	1 micron (submicron)	Submicron	13,000
Focused ion-beam machining (FIB)	Any material	0.2 microns (0.02 microns)	0.1 microns	0.5

1.2. Top-down approaches

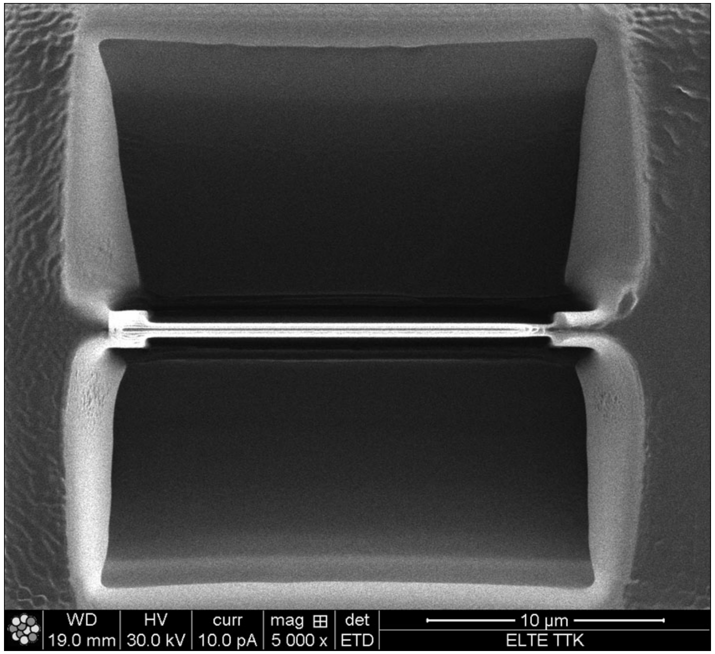
Focused ion-beam (FIB)

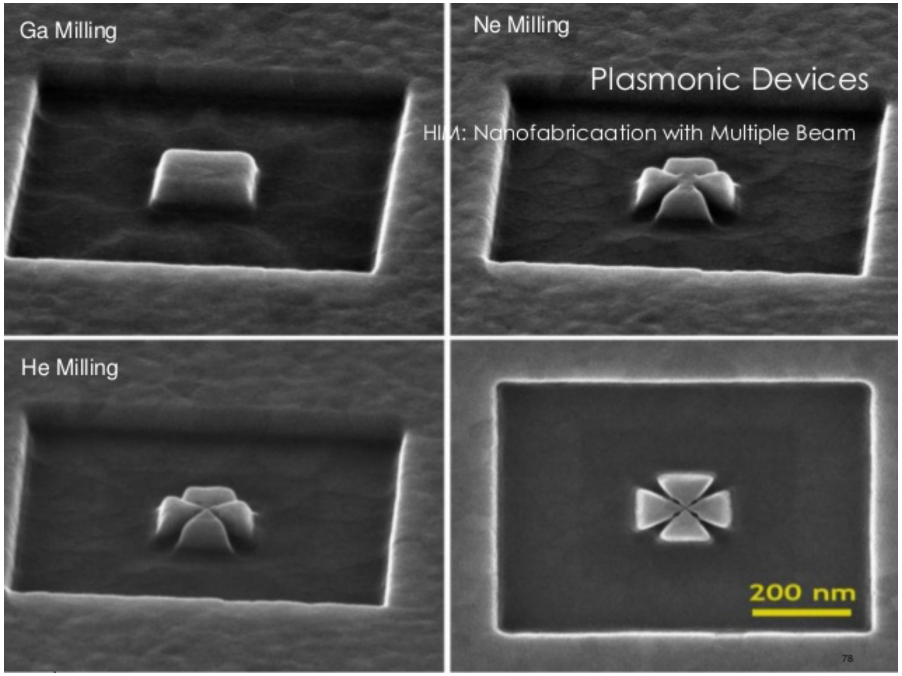
FIB machining offers the greatest resolution, with the ability to make features as small as 20 nm. In FIB a beam of gallium ions from a liquid metal ion source is accelerated, filtered, and focused with electromagnetic lenses to give a spot size of 5-8 nm. The beam is tracked across the surface contained in a chamber under high vacuum. The high energy ions blast atoms from the surface, allowing simple cutting of slots and channels or the creation of more elaborated 3D shapes.



1.2. Top-down approaches

Focused ion-beam (FIB)

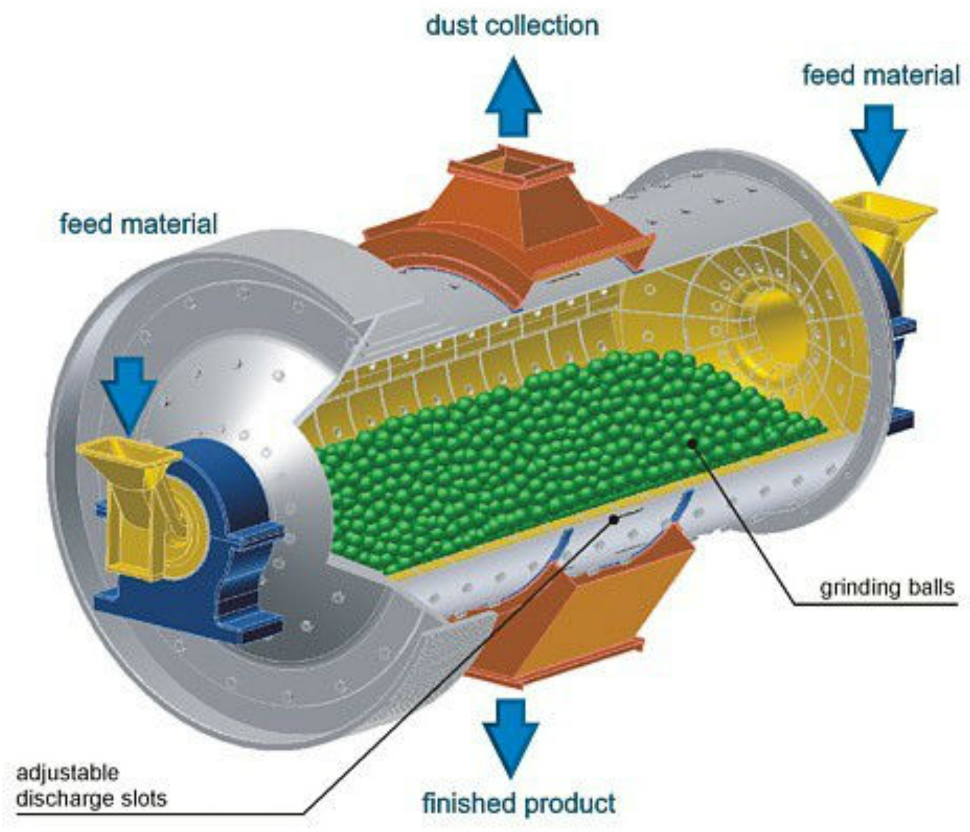


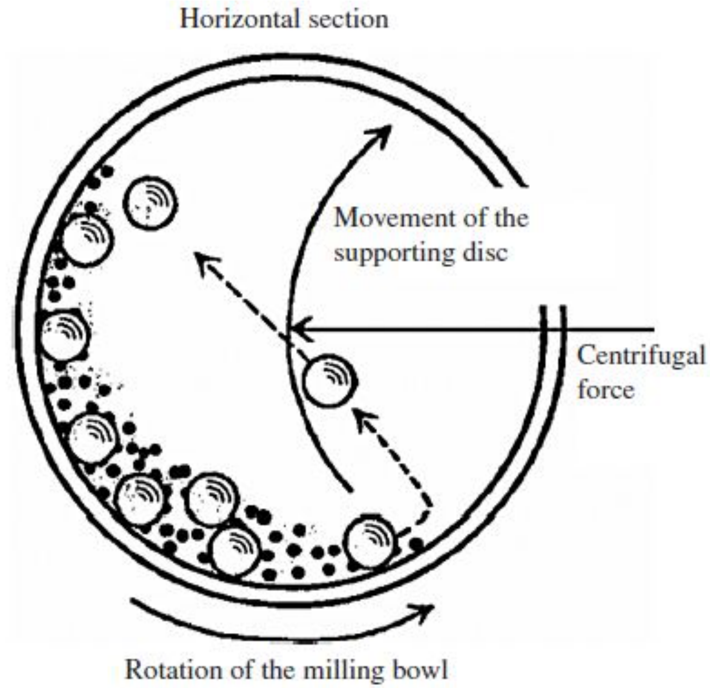


1.2. Top-down approaches

Ball milling

A **ball mill**, a type of grinder, is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw materials and paints. **Ball** mills rotate around a horizontal axis, partially filled with the material to be ground plus the grinding medium.

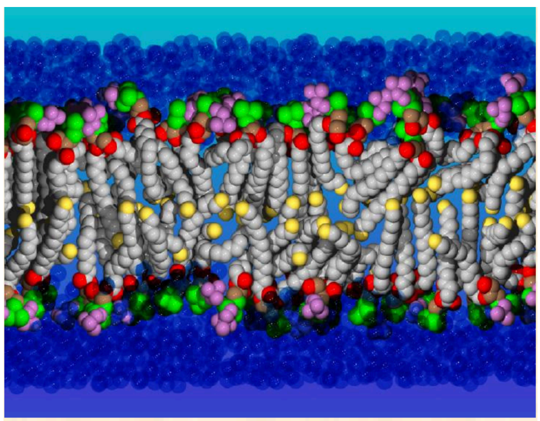




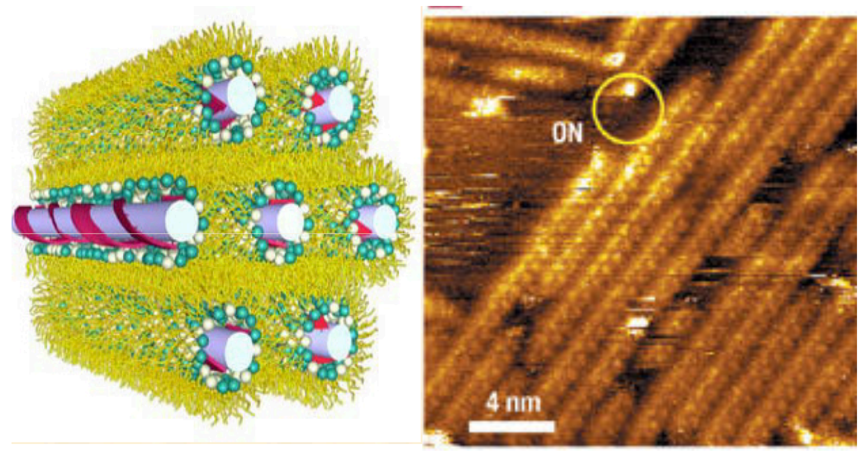
1.3. Bottom-up approaches

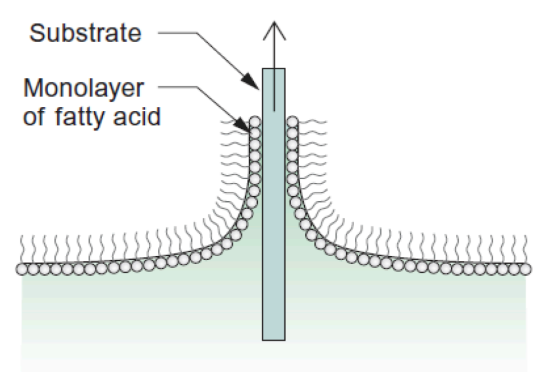
Self-assembly

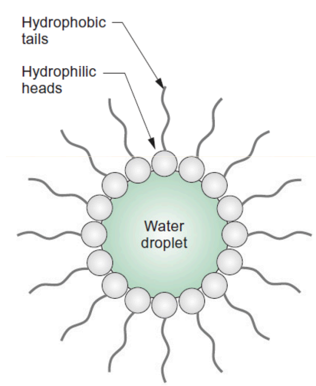
Self-assembly is the spontaneous organization of molecules into stable, structurally well defined aggregates which are at the nanometer scale.
These self-assembled structures are often being used to template the growth of different materials



Polythiophene wires

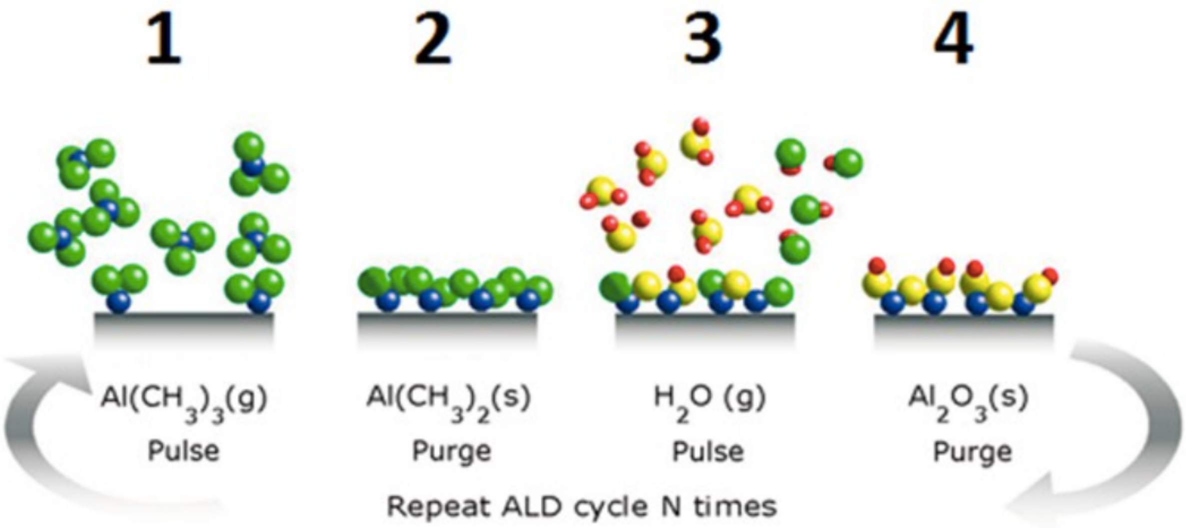






1.3. Bottom-up approaches

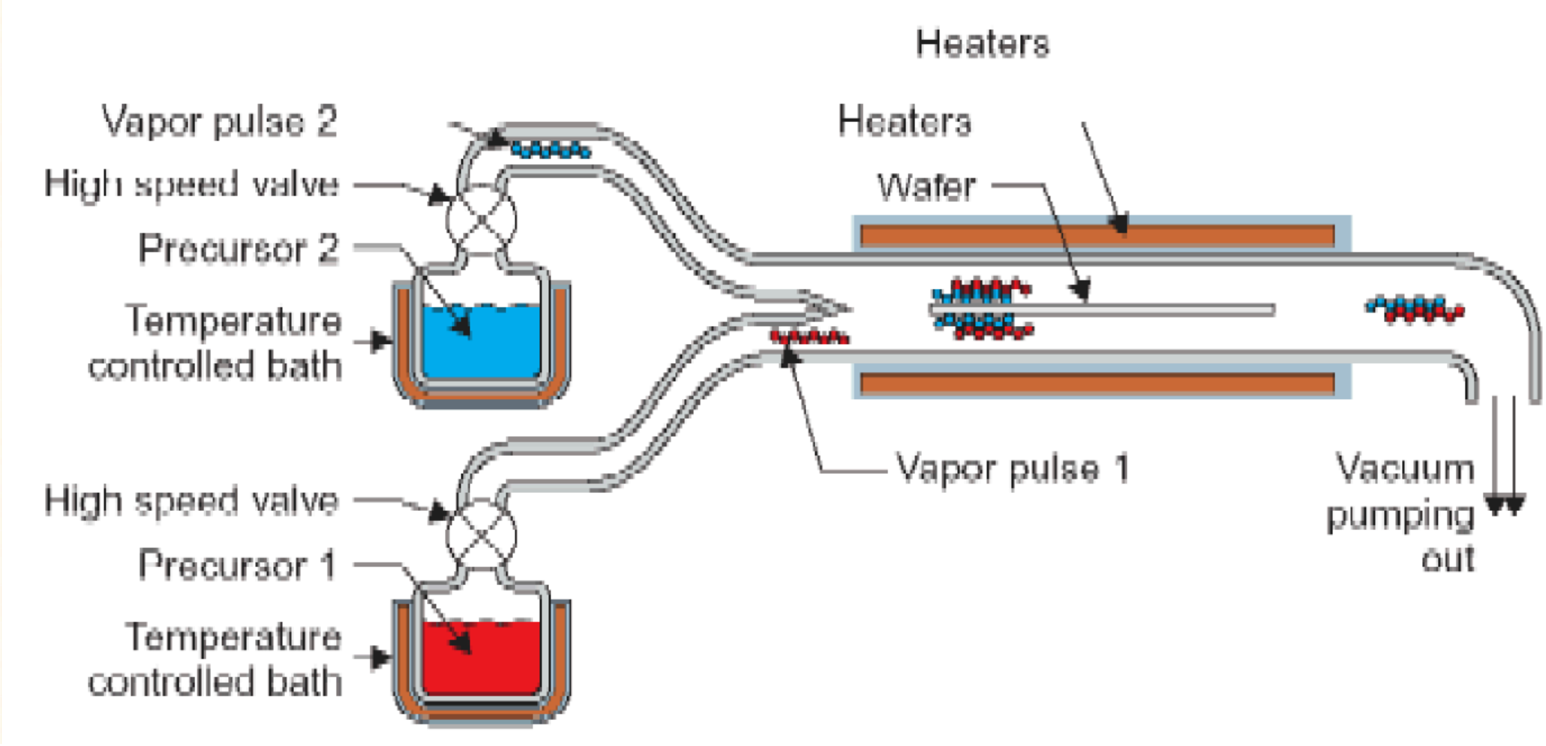
Atomic Layer Deposition



$$2 * Al(CH_3)_3 + 3 * H_2O \rightarrow Al_2O_3 + 6 * CH_4$$

1.3. Bottom-up approaches

Atomic Layer Deposition



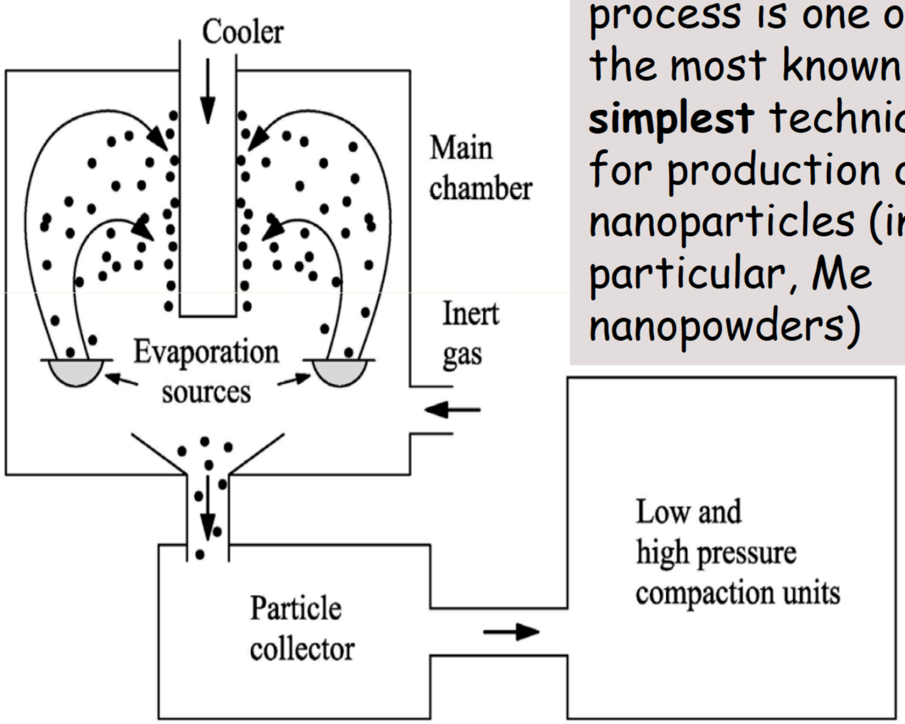
1.3. Bottom-up approaches

Methods for making 0-D Nanomaterials (Nanoclusters)

- Nanoclusters are made by either gas-phase or liquid phase processes.
- The most common of the gas-phase ones are the inert-gas condensation and flame pyrolysis
- Liquid phase processes use surface forces to create nanoscale particles and structures. There are broad types of these processes: ultrasonic dispersion, sol-gel methods, and methods relying on self-assembly.

1.3. Bottom-up approaches

Inert Gas Condensation

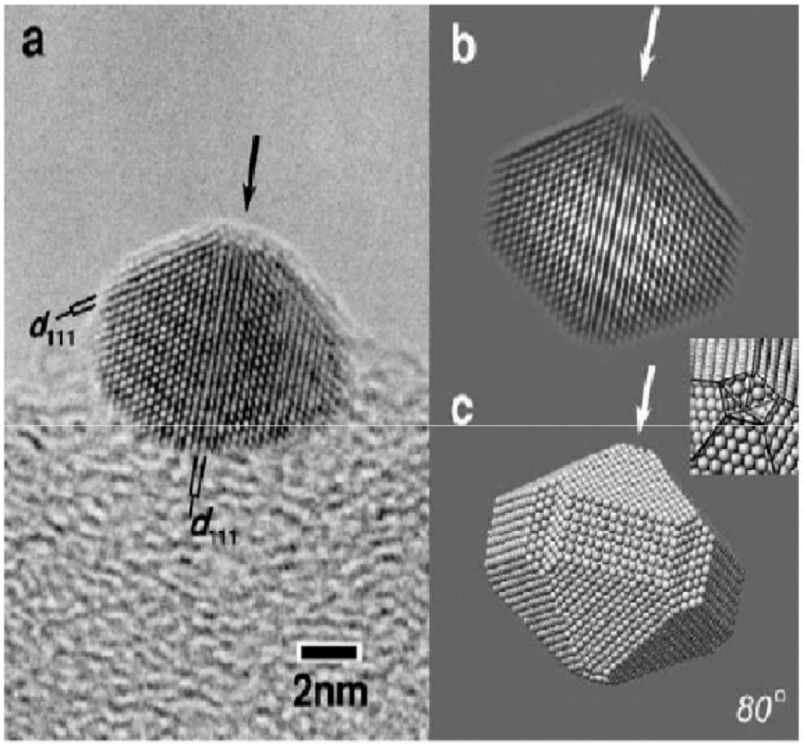


The inert gas condensation (IGC) process is one of the most known and **simplest** technique for production of nanoparticles (in particular, Me nanopowders)

An inorganic material is **vaporized** inside a **vacuum** chamber into which an **inert** gas (typically argon or helium) is periodically admitted.
Once the atoms boil off, they quickly lose their energy by colliding with the inert gas.
The vapor cools rapidly and **supersaturates** to form nanoparticles with sizes in the range 2-100 nm that collect on a finger cooled by liquid nitrogen.

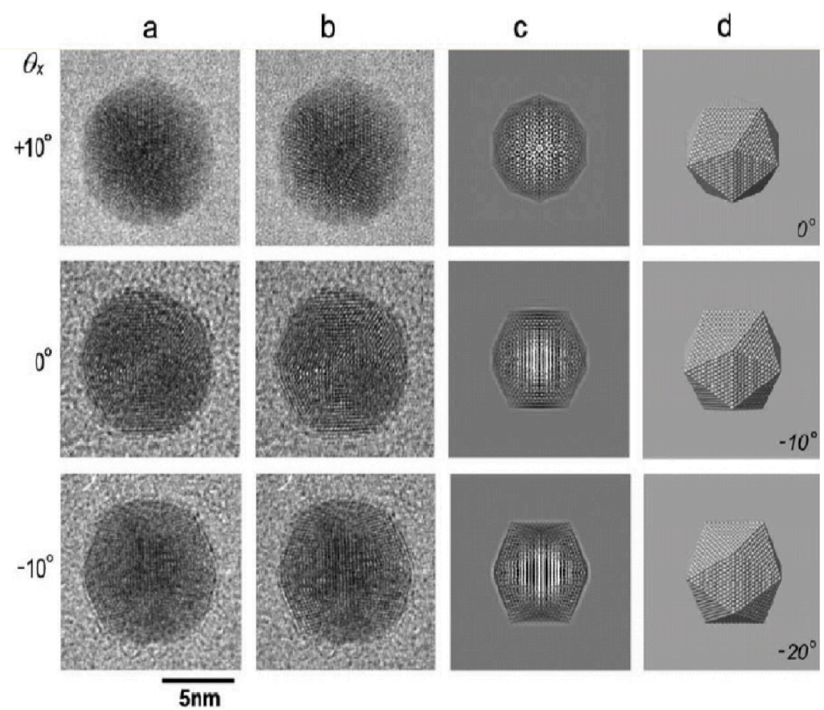
1.3. Bottom-up approaches

Inert Gas Condensation



Dodecahedral gold nanoparticle generated from an inert gas aggregation source using helium and deposited on amorphous carbon film.

Icosahedral gold nanoparticle generated from an inert gas aggregation source using helium and deposited on amorphous carbon film.



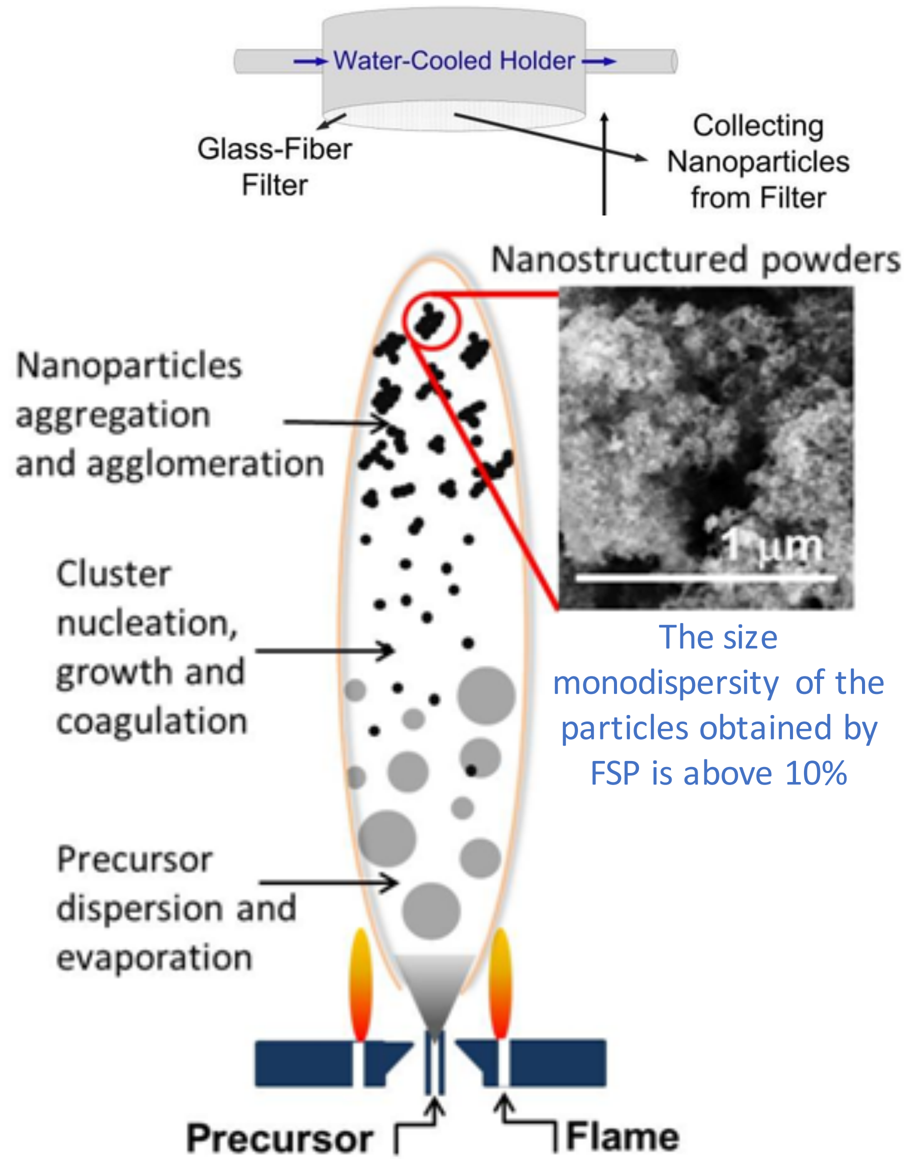
(Koga, Sugarawa, Surf. Sci. 2003, 529, 23)

1.3. Bottom-up approaches

Flame spray pyrolysis

Flame pyrolysis is already used for industrial manufacturing (i.e. TiO_2 P25 from Sigma Aldrich). The reaction in the aereosol containing the metal precursors form clusters. As these clusters leave the hot zone, nucleation and then growth occur. The nanoparticles are then collected from a water cooled filter.

Products made from FSP's vapor-phase process are limited to Al-, Ti-, Zr-, and Si-based oxides from their metal chlorides.



The size monodispersity of the particles obtained by FSP is above 10%

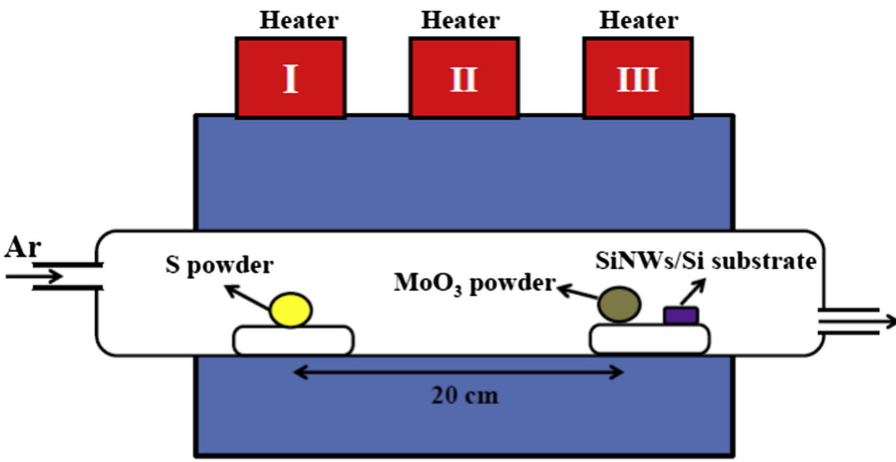
1.3. Bottom-up approaches

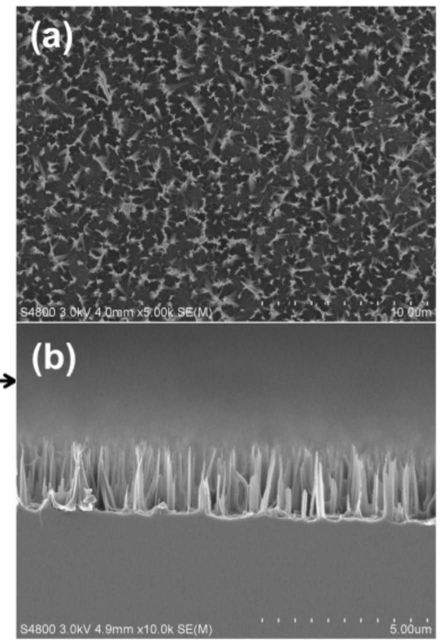
Methods for making 1D nanomaterials (rod-like, wires)

- The production route for 1D rod-like nanomaterials by liquid phase methods is similar to that of the production of nanoparticles
- Chemical Vapor Deposition (CVD) methods have been adapted to make 1D structures. Catalyst nanoparticles are used to promote nucleation.
- Molecular Beam Epitaxy (MBE) is also a quite common method to grow 1D nanowires

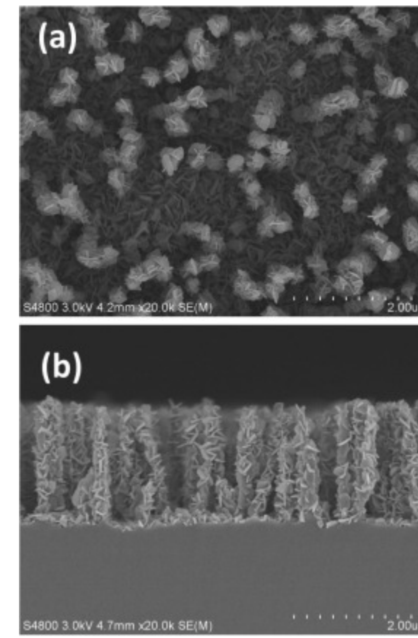
1.3. Bottom-up approaches

Chemical Vapour Deposition





(a) Plane and (b) cross-sectional FESEM images of the SiNWs/n-Si sample.



(a) Plane and (b) cross-sectional FESEM images of the MoS_2/SiNWs/n-Si sample

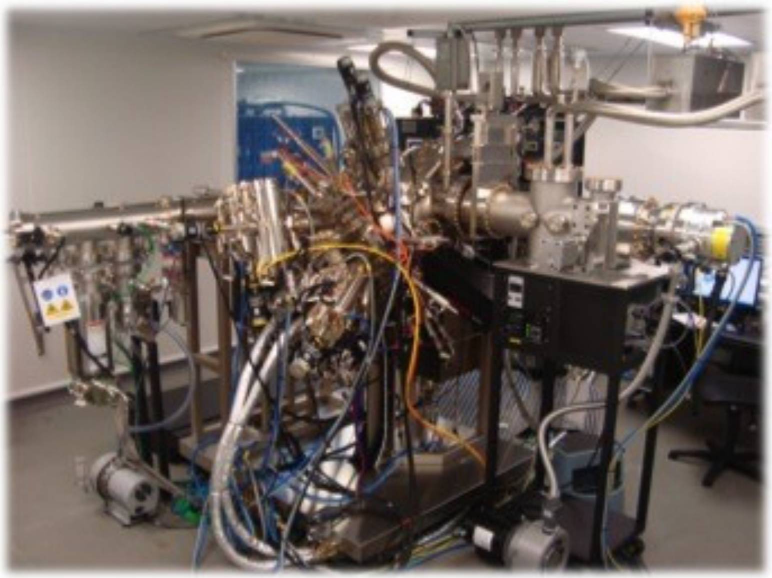
How does CVD works?

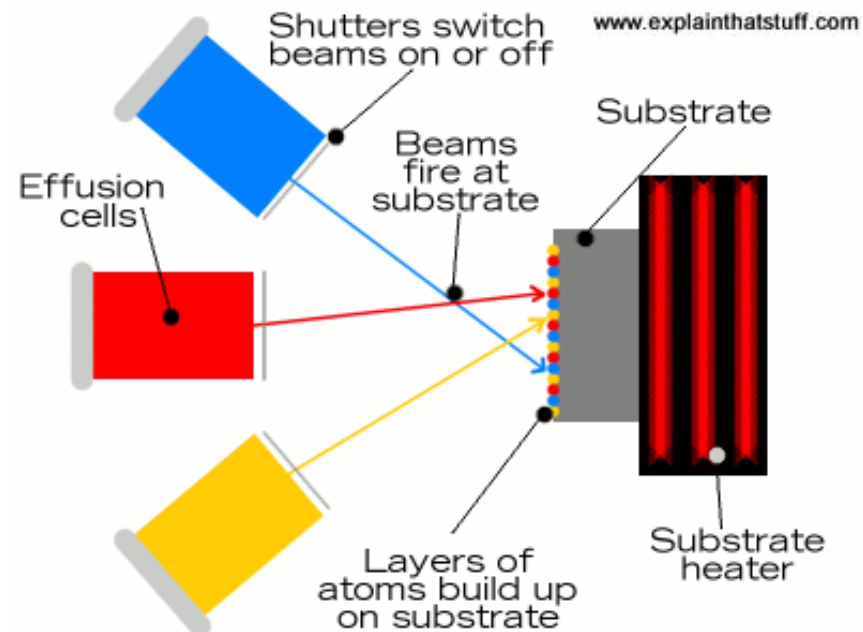
(Chen, Lin, J. Cryst. Growth 2018, 481, 18)

1.3. Bottom-up approaches

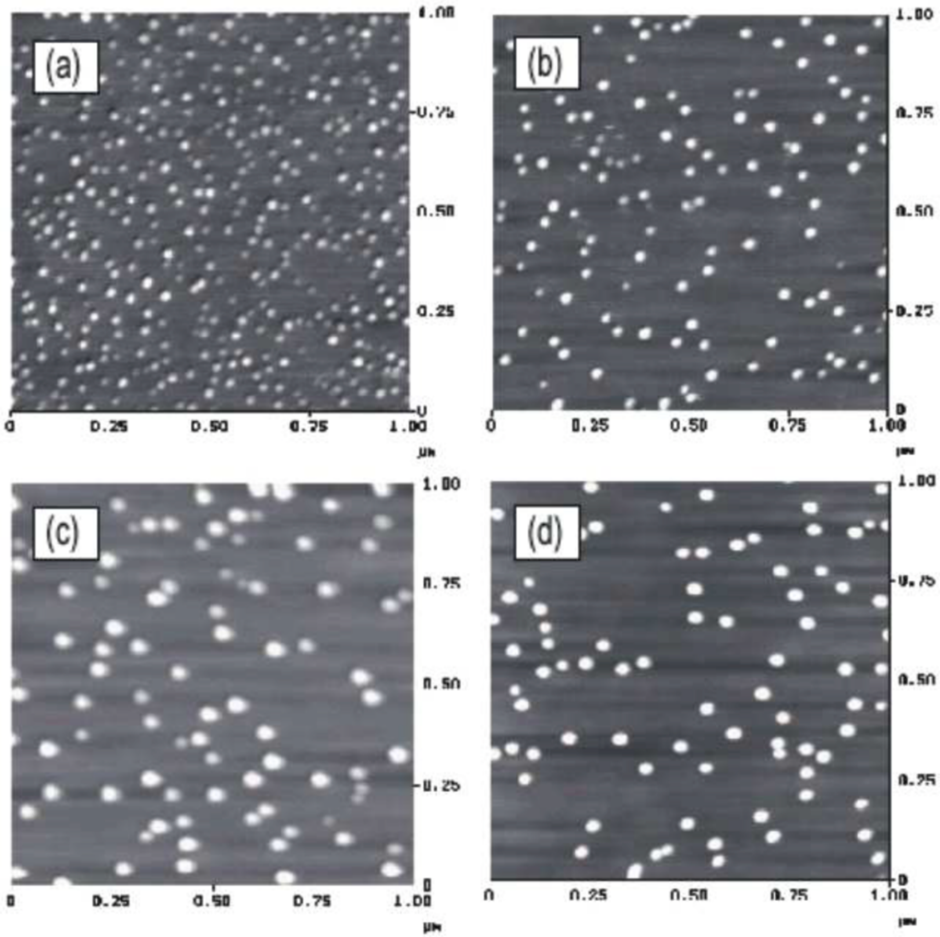
Molecular beam epitaxy (MBE)

MBE is an ultra-high vacuum technique (10^{-11}) torr. Ultrapure elements are sublimated within the chamber. The substrate (monocrystalline wafer with carefully cleaned surfaces) are heated between 300C and 600C depending on the material.





Molecular beam epitaxy (MBE)



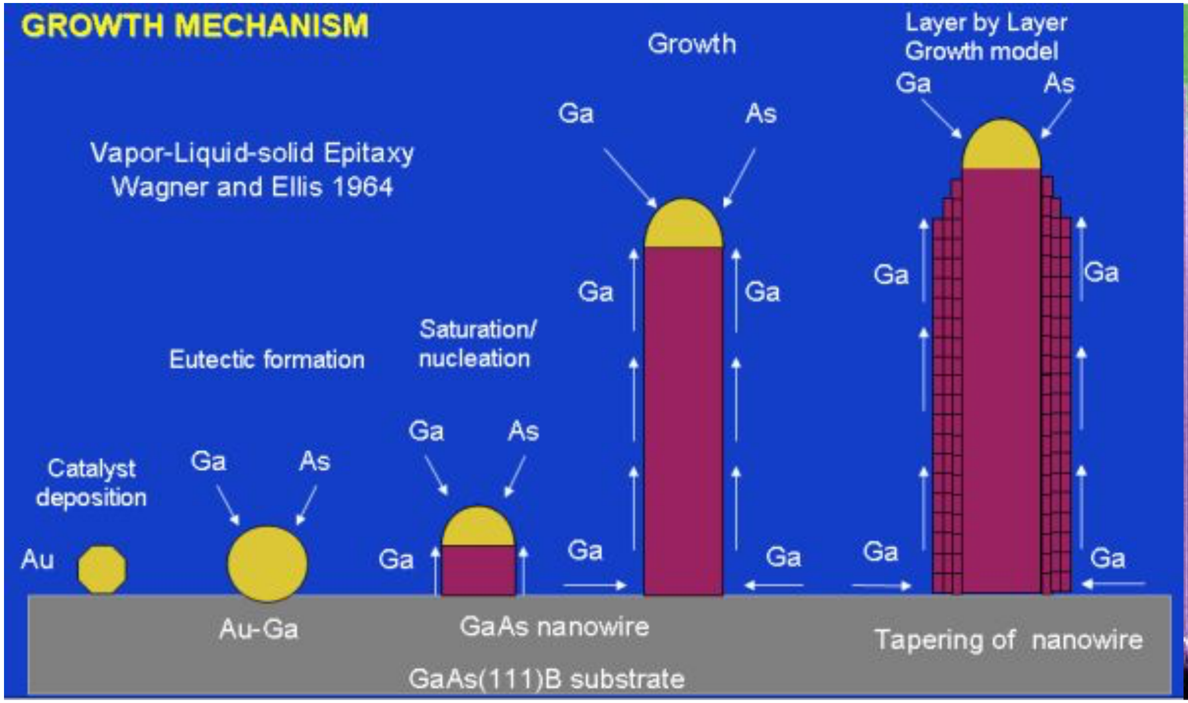
Control of dot density and size:
AFM image of samples grown at 480° (a), 487° (b), 498° (c), and 520° (d)

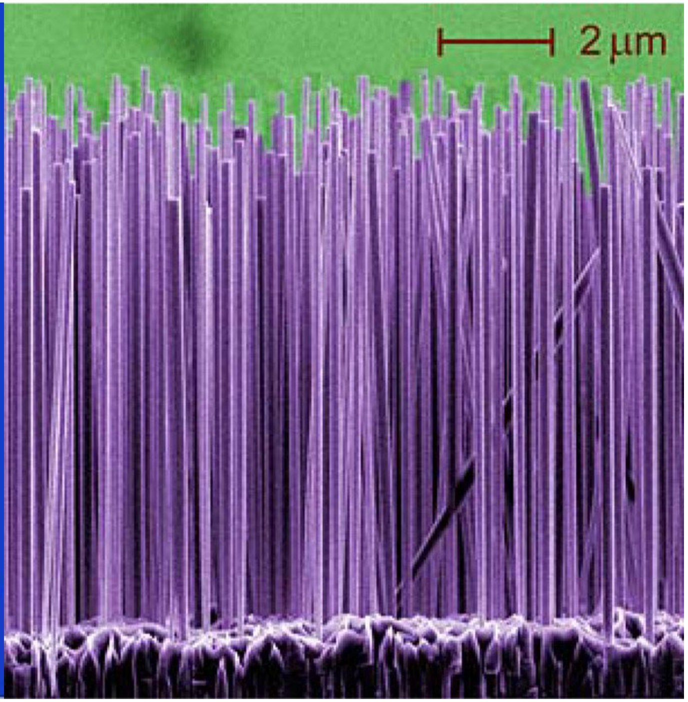
Adjustable growth parameters:

- substrate temperature
- molecular fluxes
- Substrate orientation

1.3. Bottom-up approaches

Molecular beam epitaxy (MBE)

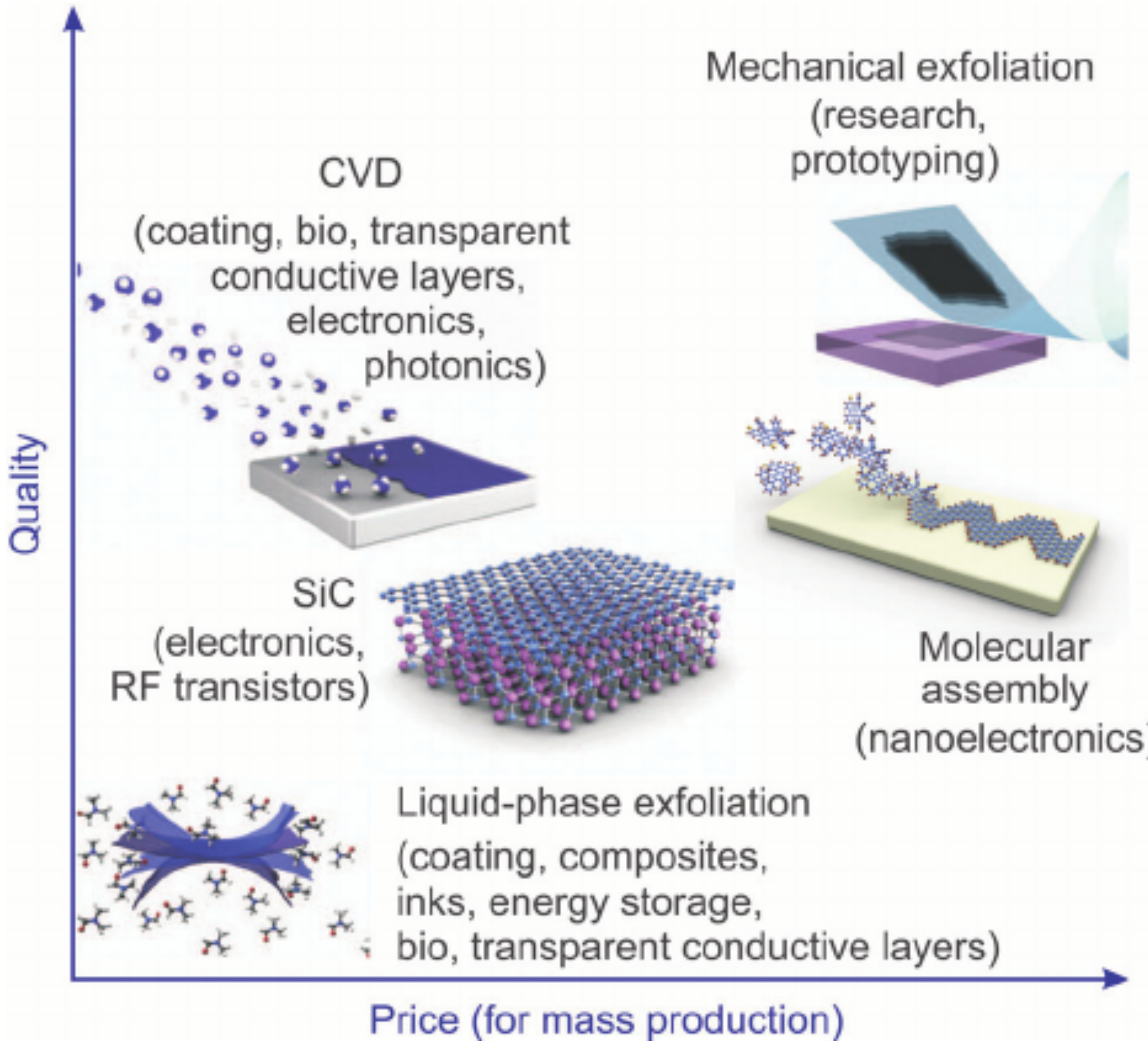




Gallium nitride (GaN) nanowires grown by molecular beam epitaxy (Photo by Lorelle Mansfield, National Institute of Standards and Technology.)

1.3. Bottom-up approaches

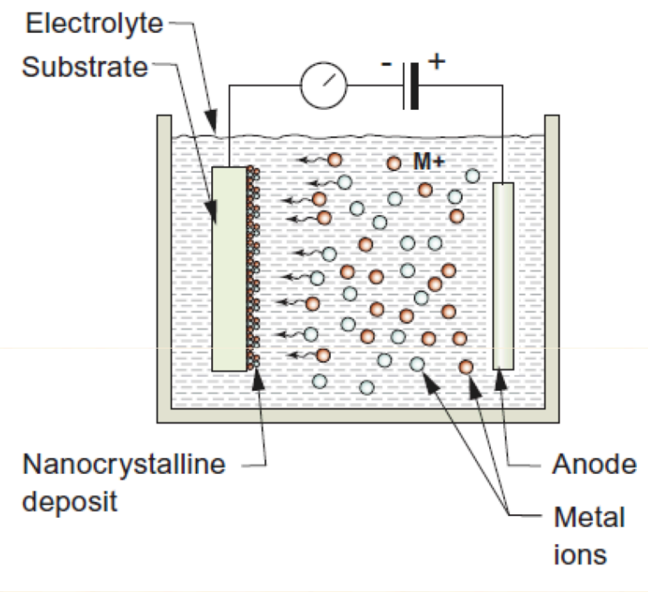
Methods for making 2D nanomaterials (graphene, nano-sheets)



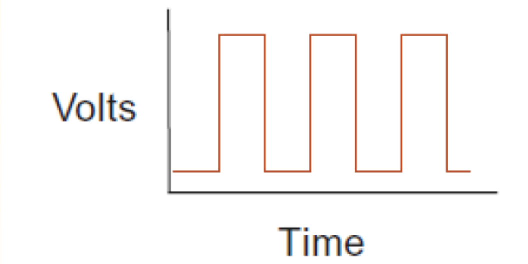
1.3. Bottom-up approaches

Electrodeposition

- **Electrodeposition** is a long-established way to deposit metal layers on a conducting substrate.
- Ions in solution are deposited onto the negatively charged cathode, carrying charge at a rate that is measured as a current in the external circuit.

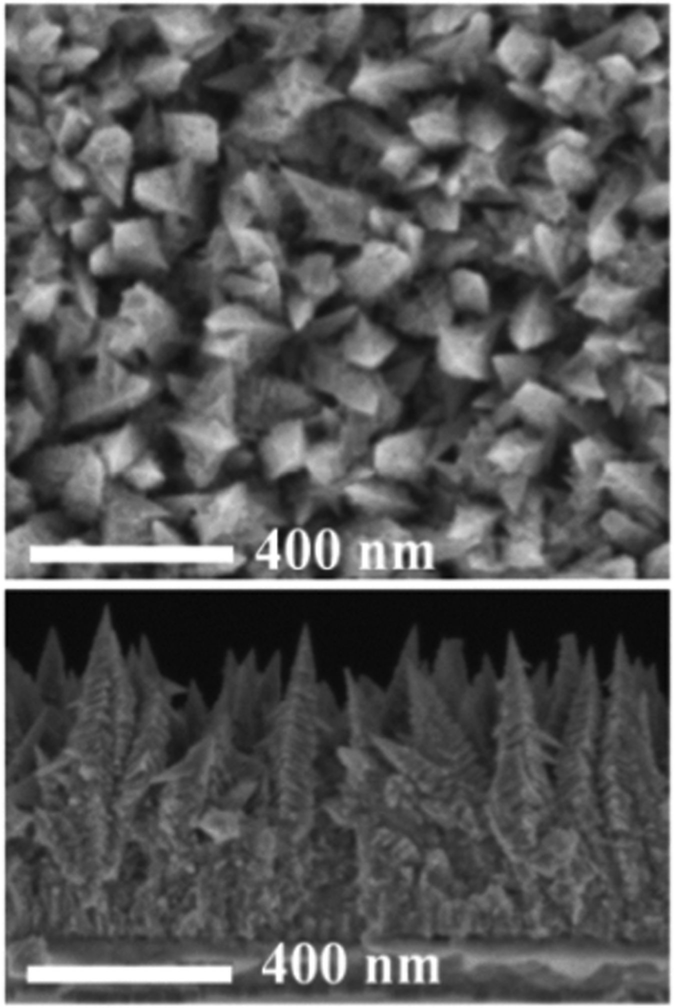


- The process is relatively **cheap** and **fast** and allows **complex** shapes.
- The layer thickness simply depends on the current density and the time for which the current flows.
- The deposit can be detached if the substrate is chosen to be soluble by dissolving it away.



1.2. Bottom-up approaches

Electrodeposition



Top and cross-sectional SEM images of Pt tree nanostructures electrodeposited from a solution containing 15 mM K_2PtCl_4 and 0.1 M H_2SO_4 at −0.2 V with a total deposition charge of 0.04 C.

Adjustable growth parameters:

- concentration
- magnitude of the potential
- amount of charge delivered
- deposition time
- pulsing or cycling the applied current of potential in a solution containing a mixture of precursors allow the production of a multilayered material.

(Choi, Kweon, Kim, Phys. Chem. Chem. Phys. 2015, 17, 23547)

1.3. Bottom-up approaches

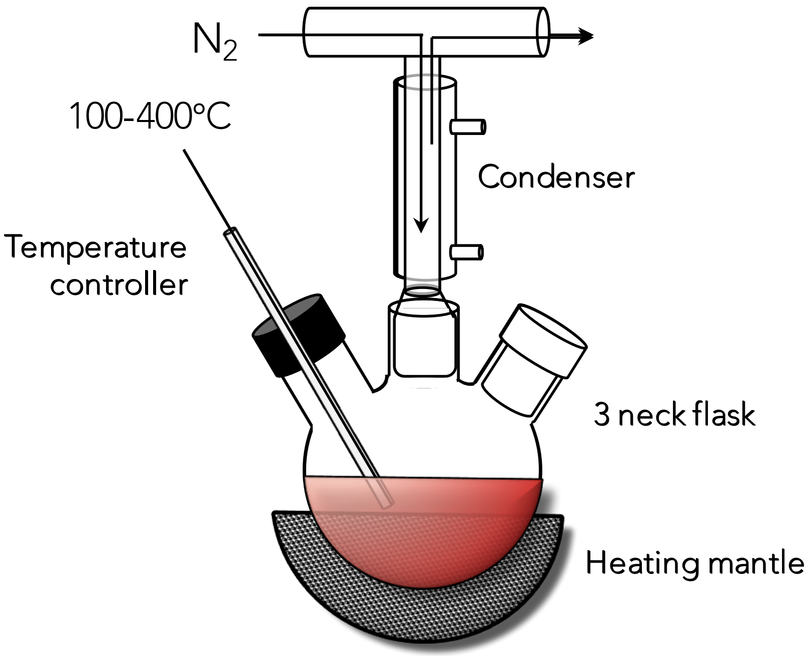
Liquid phase synthesis

Precipitating nanoparticles from a solution of chemical compounds can be classified into five major categories:

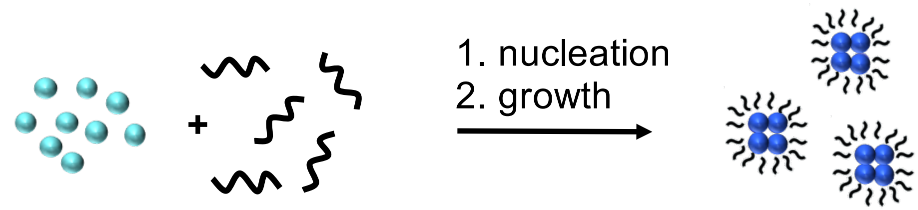
(1) colloidal methods;
(2) sol – gel processing;
(3) water – oil microemulsions method;
(4) hydrothermal synthesis; and

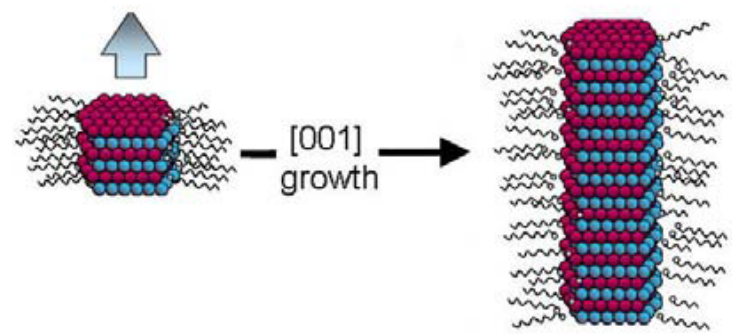
1.3. Bottom-up approaches

Colloidal synthesis



Surfactants play a key role in controlling nanocystal size and shape:

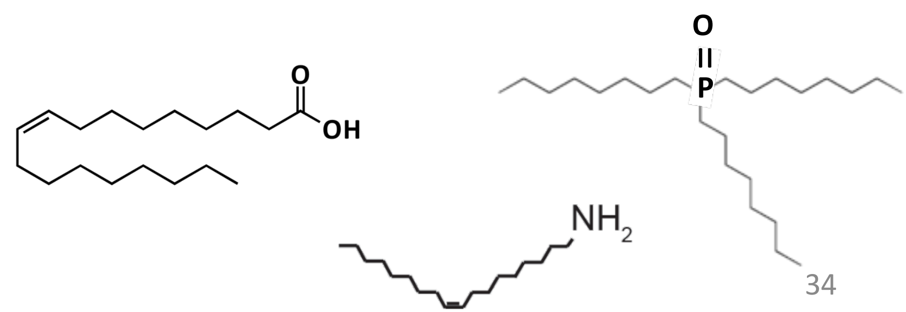




Reaction parameters:

- Ligands/Precursors reactivity
- Reaction temperature
- Reaction time
- Concentration

some typical surfactants:



1.3. Bottom-up approaches

Sol-gel technique

The sol-gel process consists in the chemical transformation of a liquid (the sol) into a gel state and, with subsequent post-treatment, into a solid **oxide** material.

tetraethylorthosilicate

This process occurs in liquid solution of organometallic precursors (TMOS, TEOS, Zr(IV)-Propoxide, Ti(IV)-Butoxide, etc.), which, by means of hydrolysis and condensation reactions, lead to the formation of a new phase (SOL).

M-O-R + H_2O → M-OH + R-OH (hydrolysis)

M-OH + HO-M → M-O-M + H_2O (water condensation)

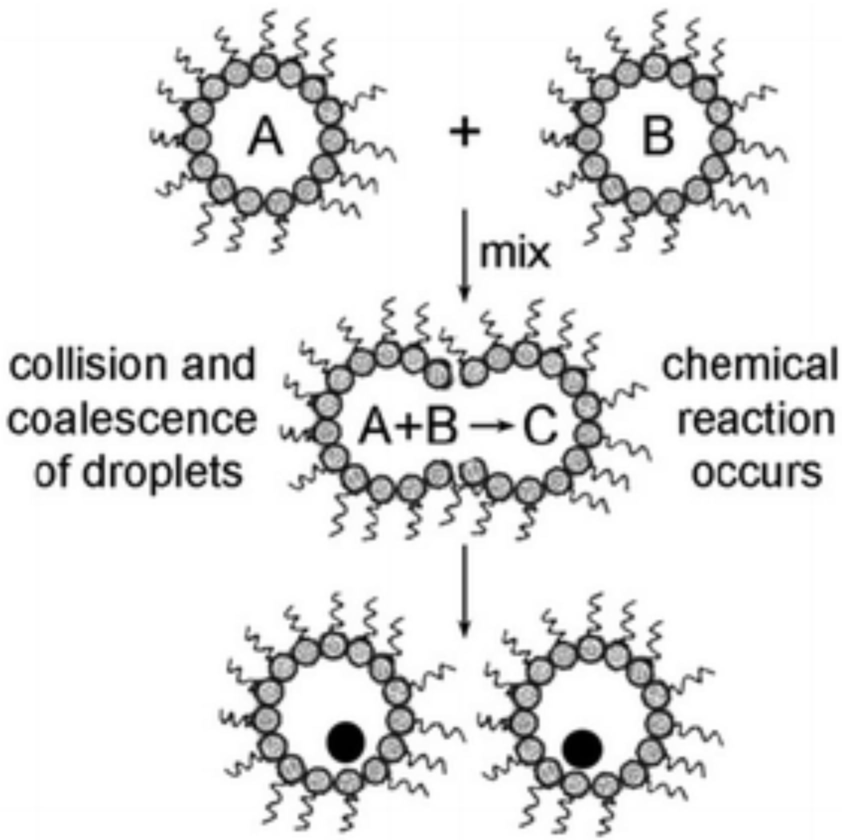
M-O-R + HO-M → M-O-M + R-OH (alcohol condensation)

(M = Si, Zr, Ti)

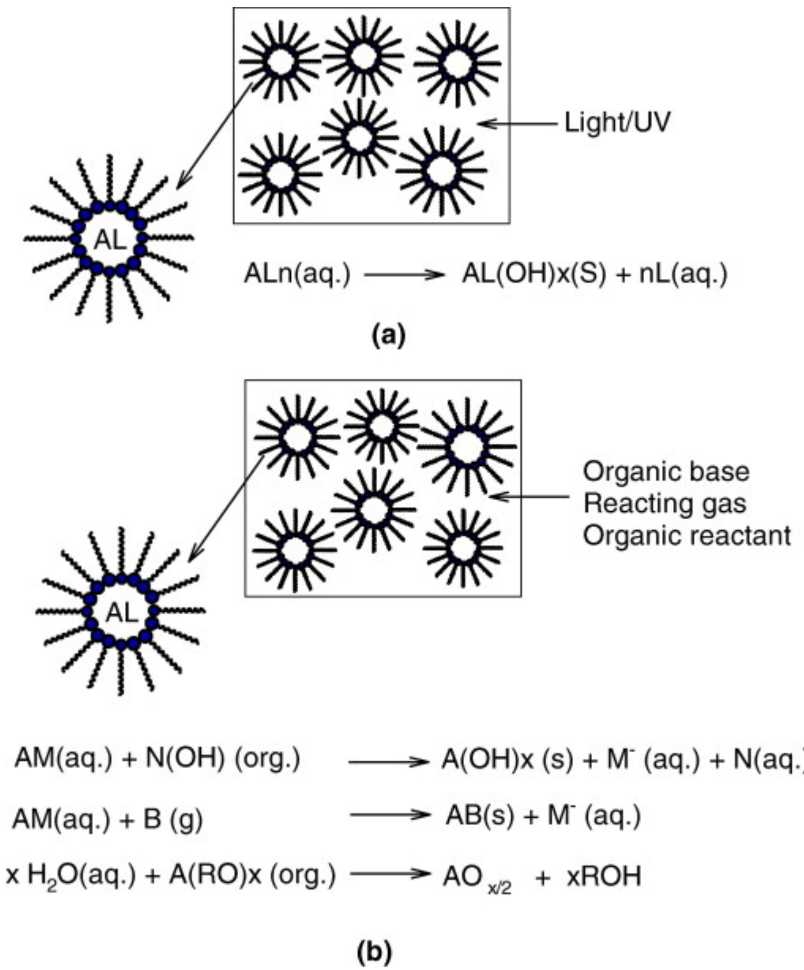
1.3. Bottom-up approaches

Microemulsion techniques

Dynamic Templates



Static Templates



1.3. Bottom-up approaches

Hydrothermal synthesis

The hydrothermal synthesis is a sol-gel process taking place in a supercritical solvent. It is often used to enhance solubility of precursors.

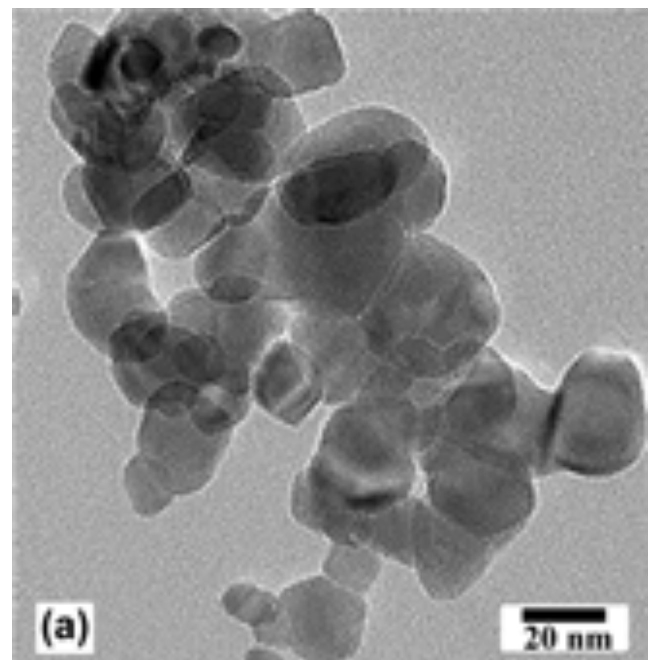
1.3. Bottom-up approaches

Hydrothermal synthesis

THE HYDROTHERMAL BOMB IS HEATED IN A CONVENTIONAL OVEN OR IN A MICROWAVE REACTOR

The size monodispersity of the particles obtained by hydrothermal synthesis is above 10%

Tungsten Oxide Nanoparticles



1.4. Summary of the methods