Nanotıp

Nanomalzemelerin Sentezinde Kullanılan Teknikler

İçerik

- Nanomalzeme üretimi için mümkün olan yaklaşımlar nelerdir?
  - Top-Down (Bütünden küçüğe)
  - Bottom-Up (Küçükten bütüne)
  - Sıvı faz üretim teknikleri
  - Mekanik yollar ile nanoparçacık sentezi
- Metotlara genel bir bakış

Nanoboyuta nasıl ulaşılır?

- Nanomalzeme ve nanoyapıların üretimi için iki genel yaklaşım izlenmektedir.

Bottom-Up Yaklaşımı

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 Yaklaşımı

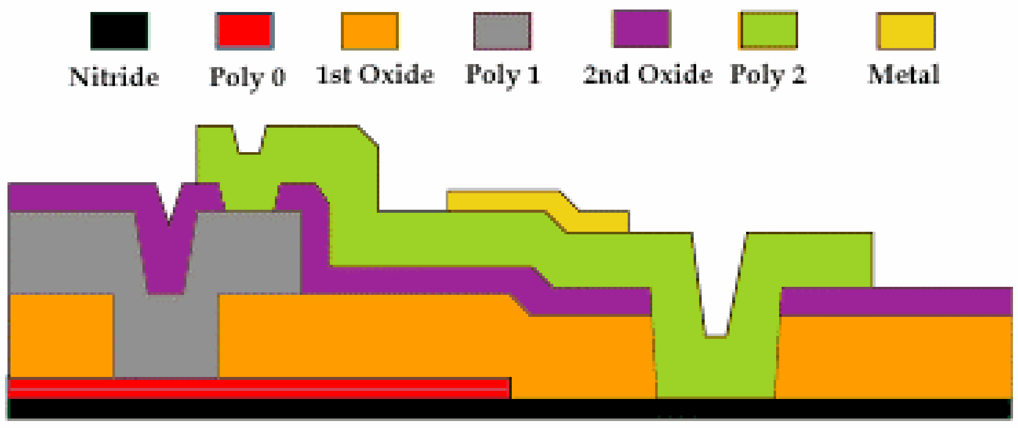
These approaches use larger (macroscopic) initial structures,
which can be externally-controlled in the processing of nanostructures.
Typical examples are etching through the mask, ball milling, and
application of severe plastic deformation

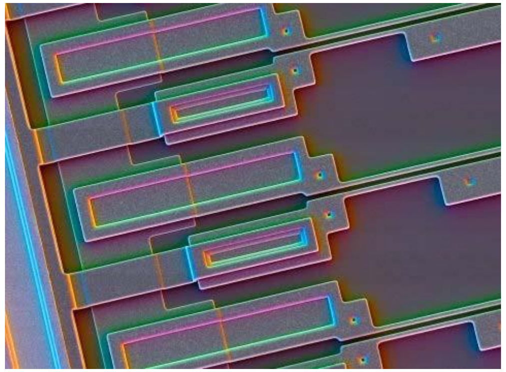
Top-Down, Bottom-up kıyaslaması

- 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

Top-Down: lithography

- At the moment, the most used top-down approach is photolithography. It has been used for a while to manufacture computer chips and produce structures smaller than 100 nm.
- Typically, an oxidized silicon (Si) wafer is coated with a 1μm thick photoresist layer. After exposure to ultraviolet (UV) light, the photoresist undergoes a photochemical reaction, which breaks down the polymer by rupturing the polymer chains.

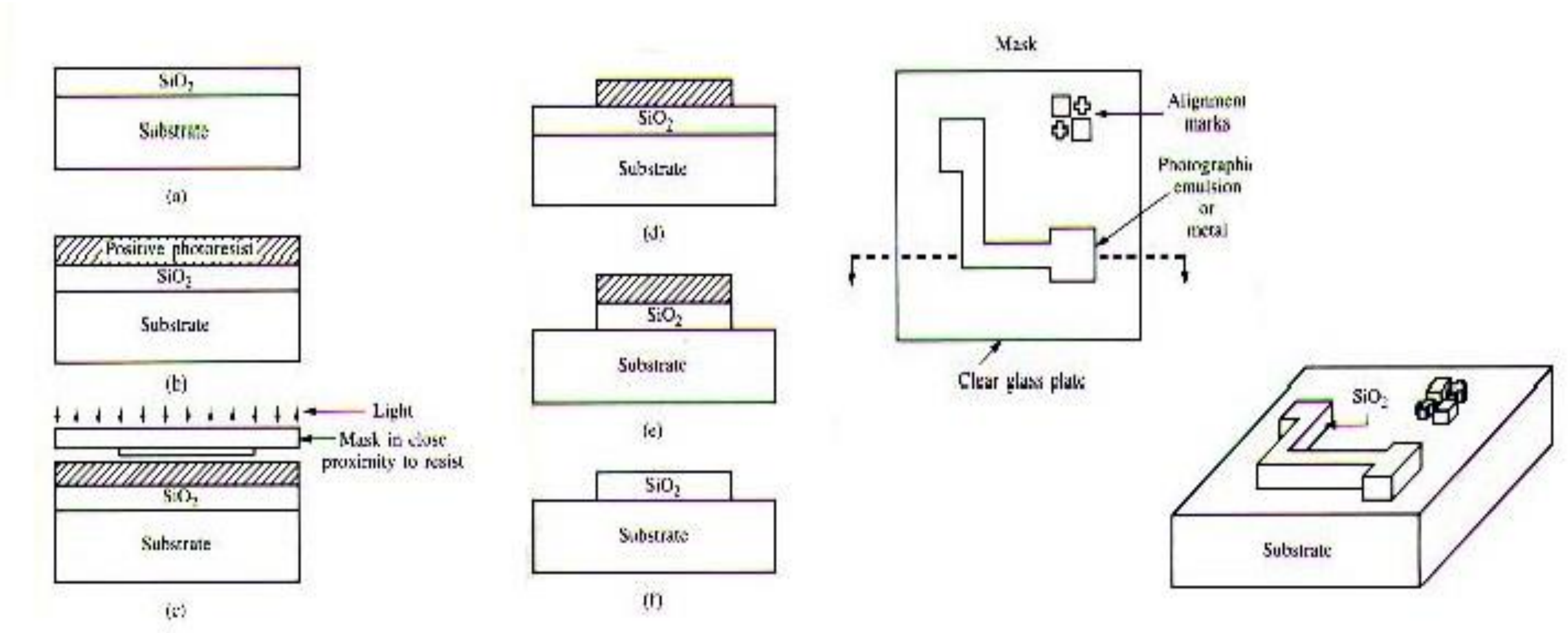




Strip resist and do process again and again.

Eventually, a 3-D structure is built up

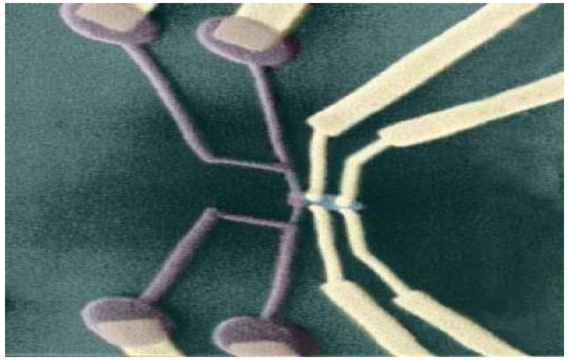
Litografik işlemlerin arkasındaki basit fikir



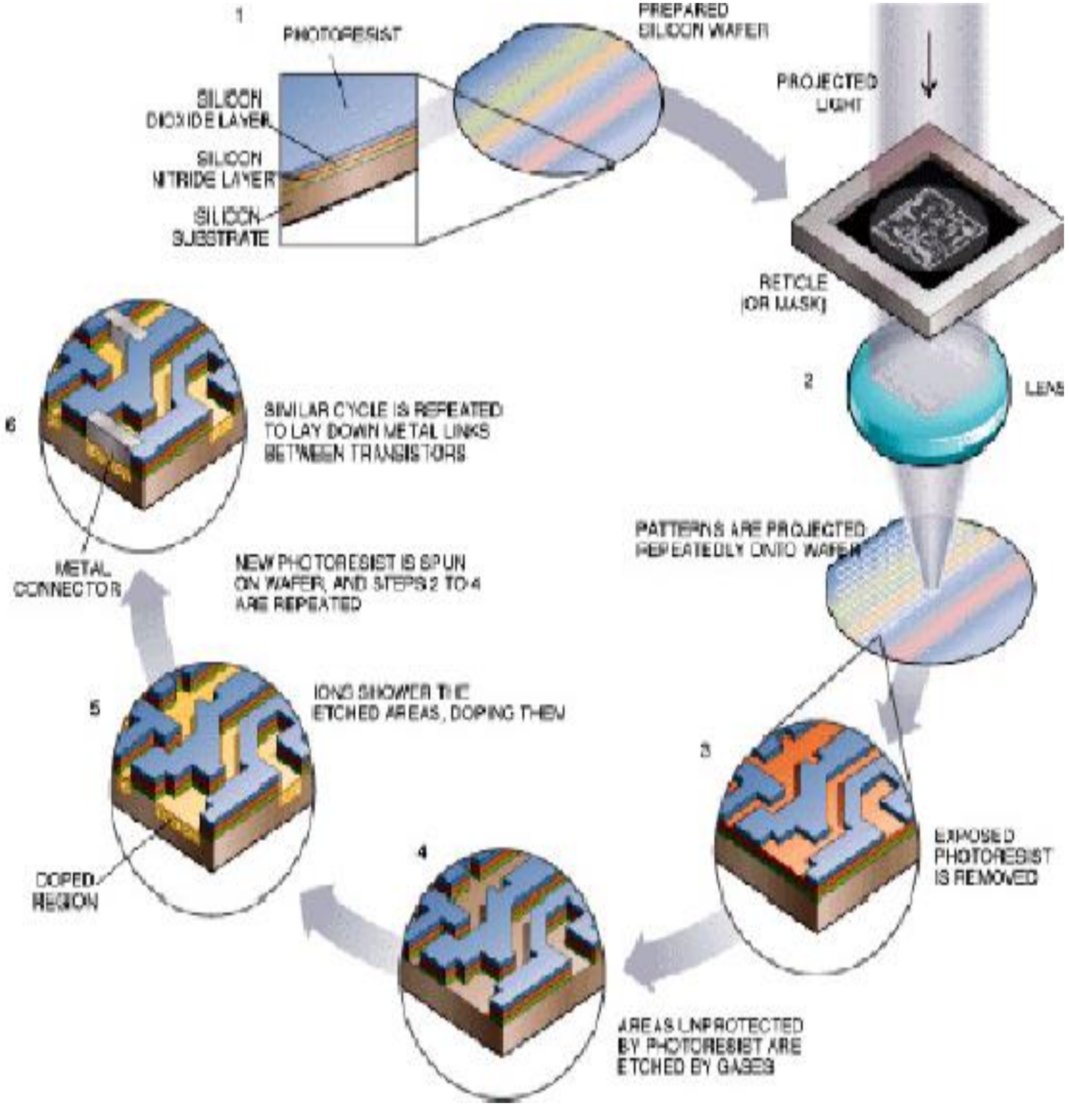
Kapla, Koru, Işığa maruz bırak,
Dağla, Tekrar et

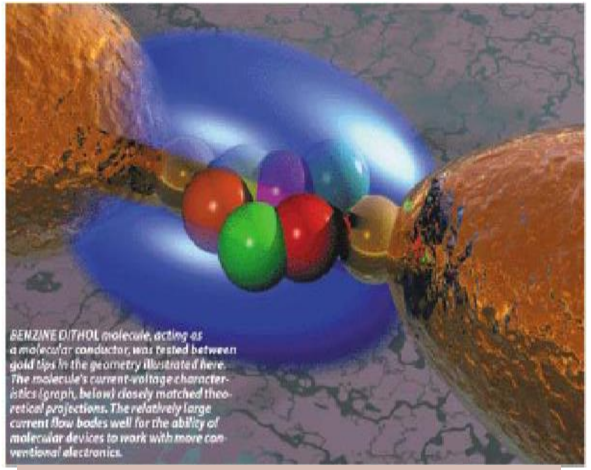
Sonuç:
Farklı mazlemelerin, çoklu desenli katmanlar.

Bu yöntemle yapılabilecekler



Ferromagnetic/superconducting devices (e-beam lithography)

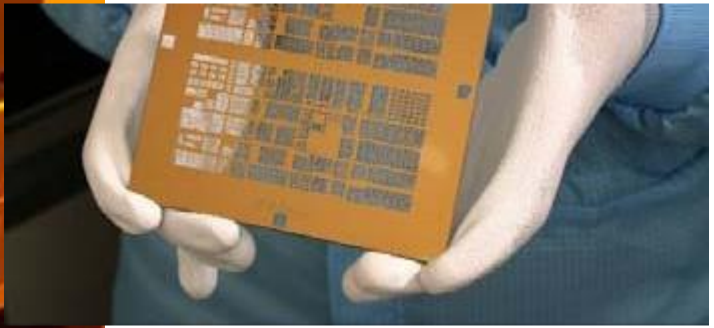




Molecular electronics (e-beam lithography)

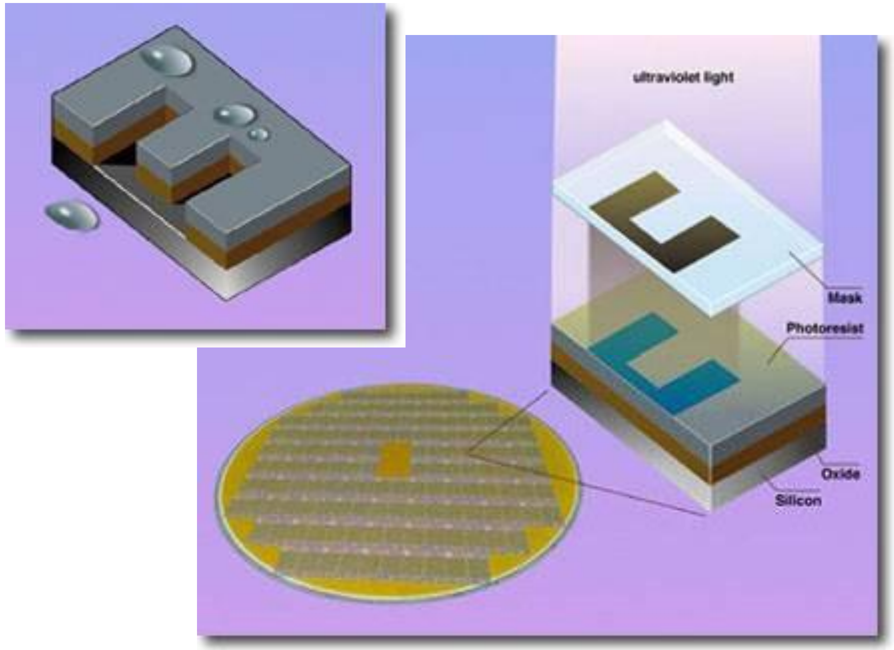
Litografik işleme: Maskeleme ve Maruz Bırakma

Expose resist to UV light through a mask



Mask is aligned to wafer before exposure.

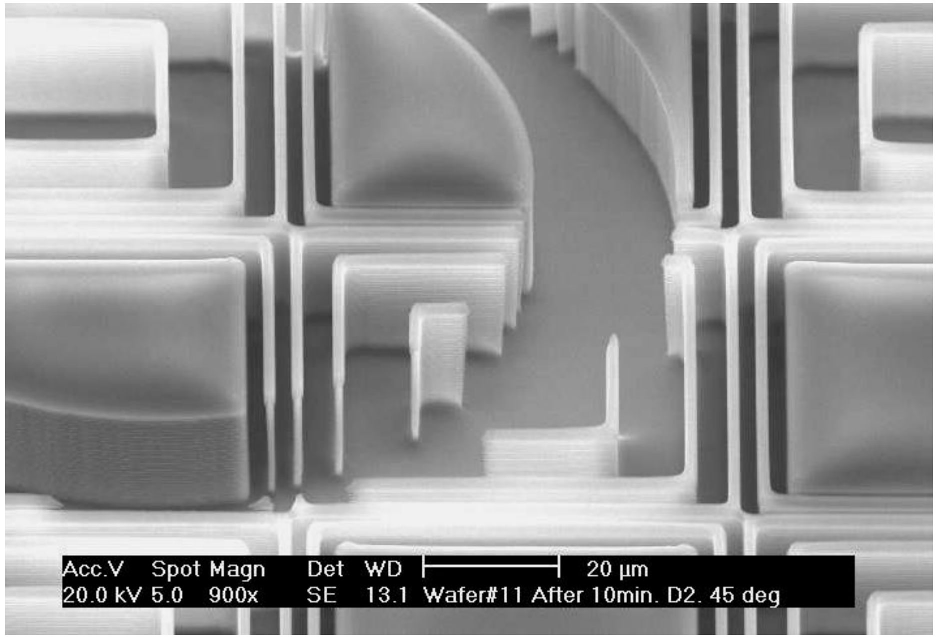
Lithographic processing: Developing the pattern



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.

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

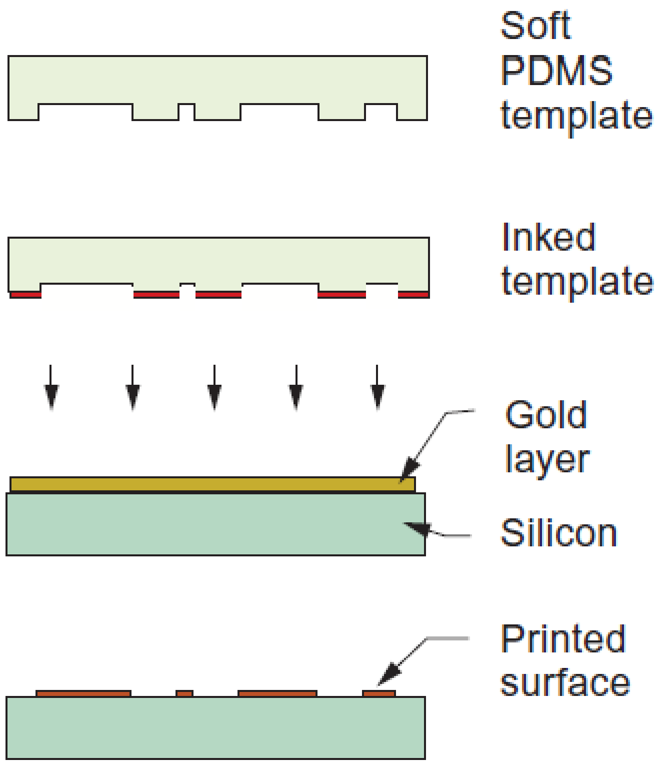
4) photolithographic tools are very costly, ranging in price from tens to hundreds of millions of dollars.

Electron-beam lithography

- Electron-beam lithography and X-ray lithography techniques have been developed as alternatives to photolithography.
- 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.

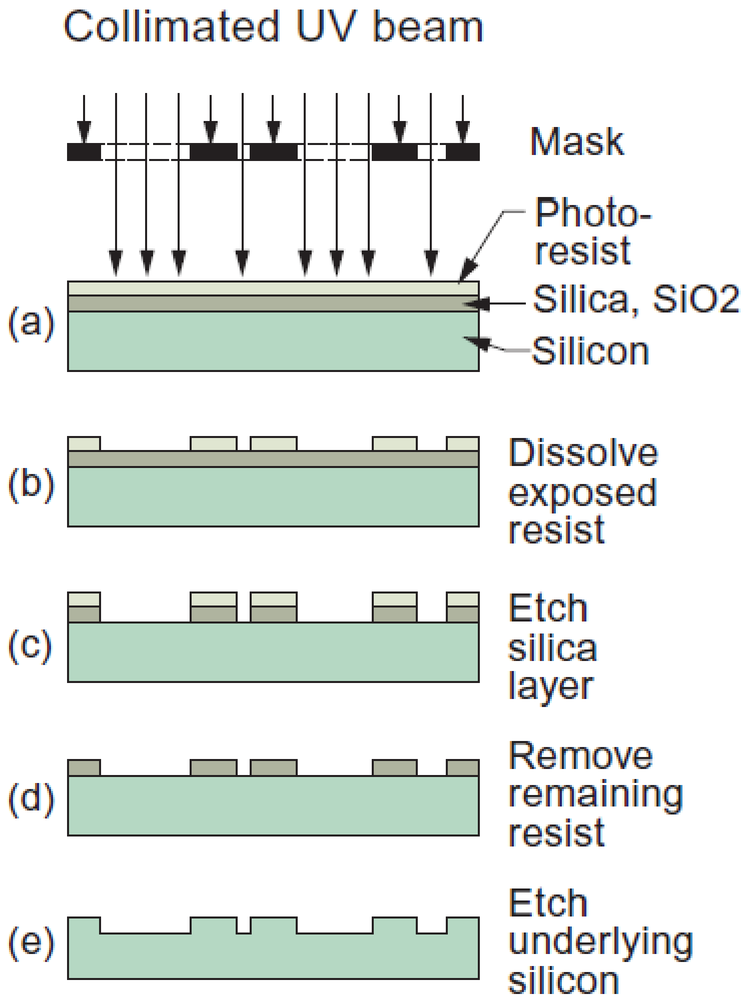
The most recent lithography methods

- 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.

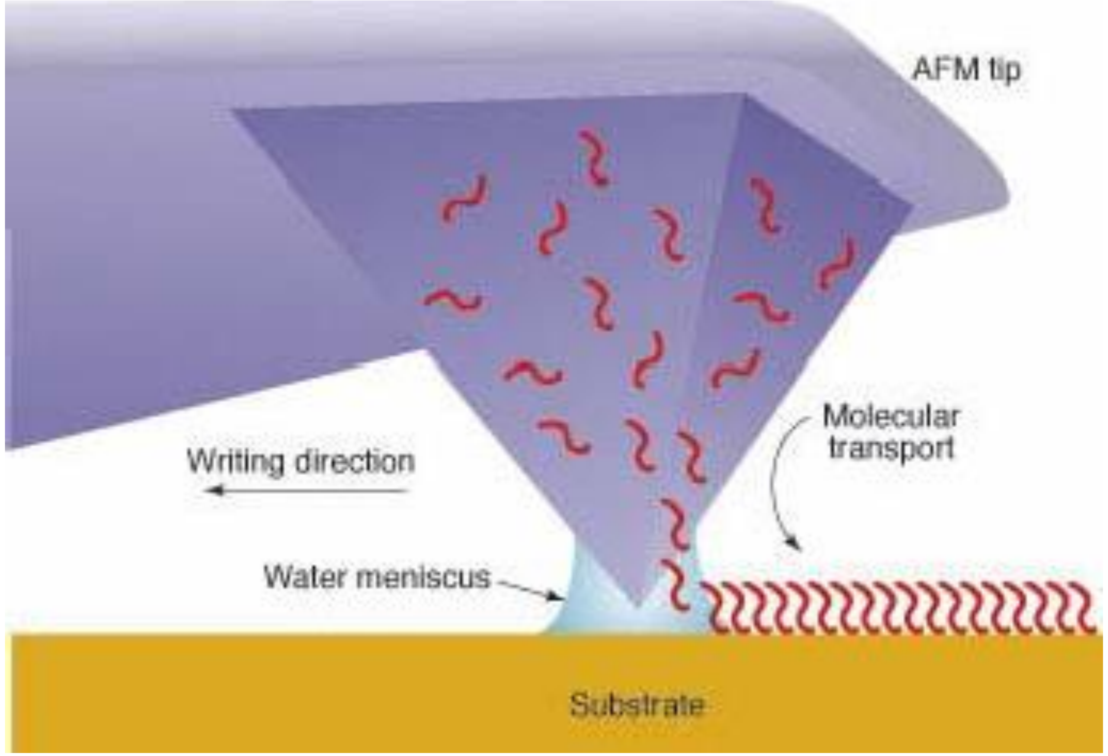


Advantages of lithography

- Once the master template has been made, no special equipment is required.
- Soft lithographic methods are capable of producing nanostructures in a wide range of materials and can print or mold on curved as well as planar surfaces
- Photolithography. A beam of UV light activates the photoresist, transferring the pattern from the mask to the sample.



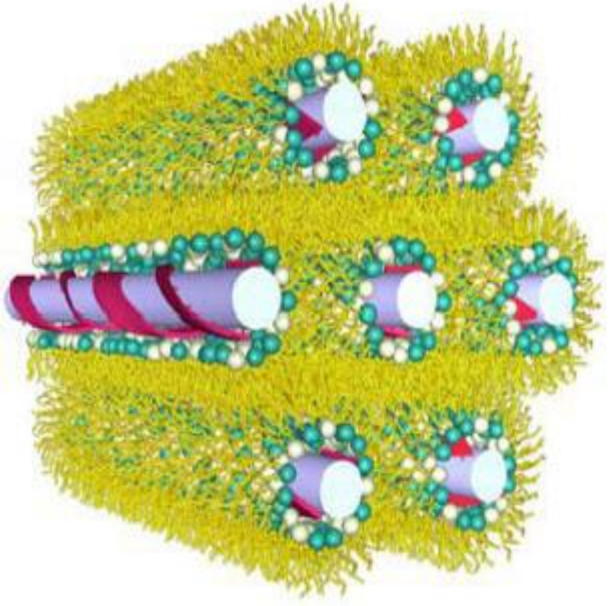
Bottom-up methods



1.High precision actuators move atoms from place to place
2.Micro tips emboss or imprint materials
3.Electron (or ion) beams are directly moved over a surface

1. Chemical reactors create conditions for special growth
2. Biological agents sometimes used to help process
3. Materials are harvested for integration

Bottom-Up: Molecular self-assembly



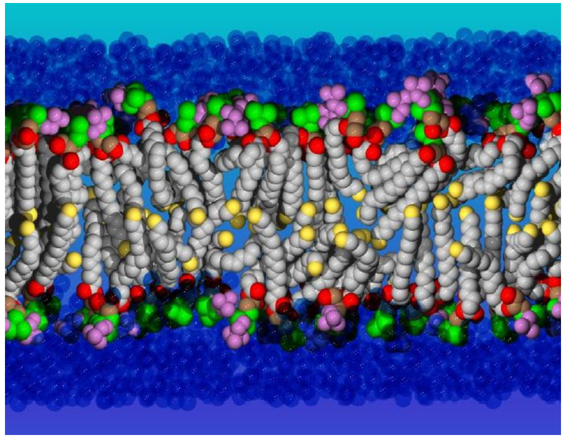
Polythiophene wires

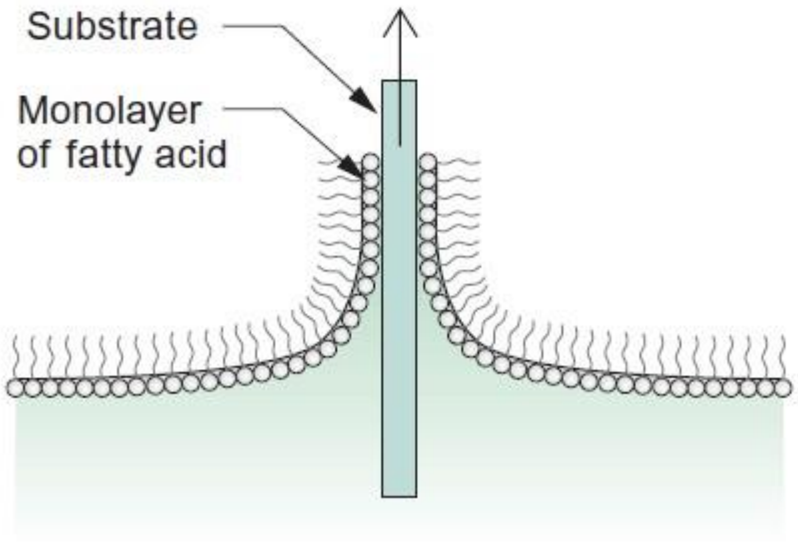
- Nature uses self-assembly in infinitely subtler ways; indeed, the whole of the natural world is self-assembled.

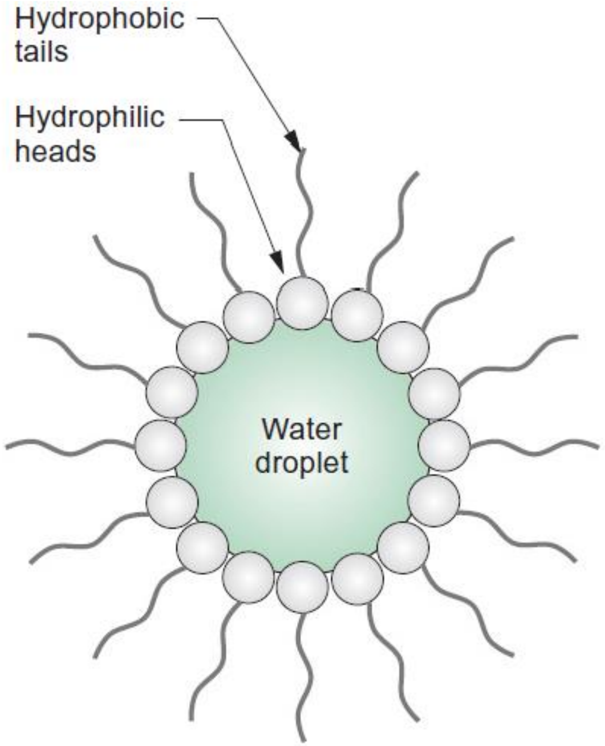
- Spontaneous organization of molecules into stable, structurally well-defined aggregates (nanometer length scale).

- Molecules can be transported to surfaces through liquids to form self-assembled monolayers (SAMs).

Self-assembly örnekleri







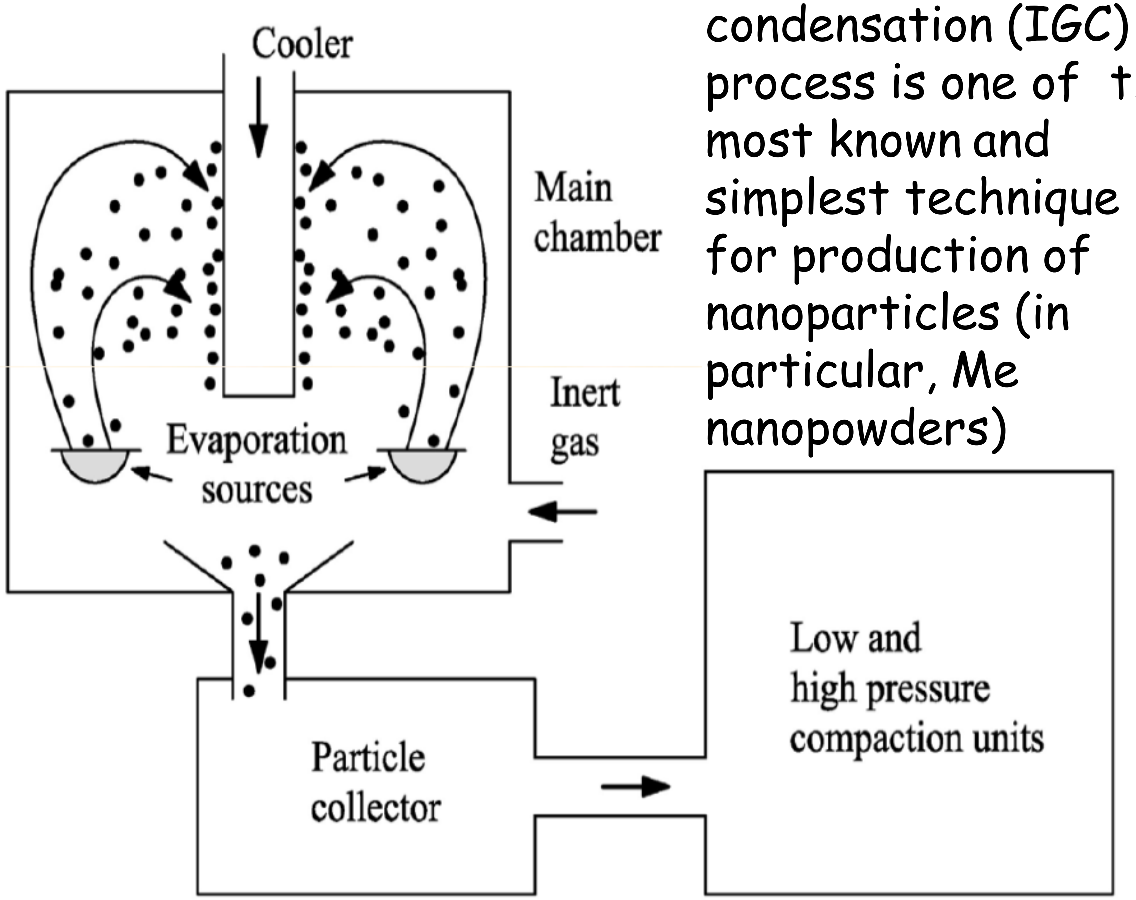
Methods for making 0-D Nanomaterials

- Nanoclusters are made by either gas-phase or liquid-phase processes.
- The commonest of which are inert-gas condensation and inert-gas expansion.
- 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.

Nanoparticle condensation in inert gas

- 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.

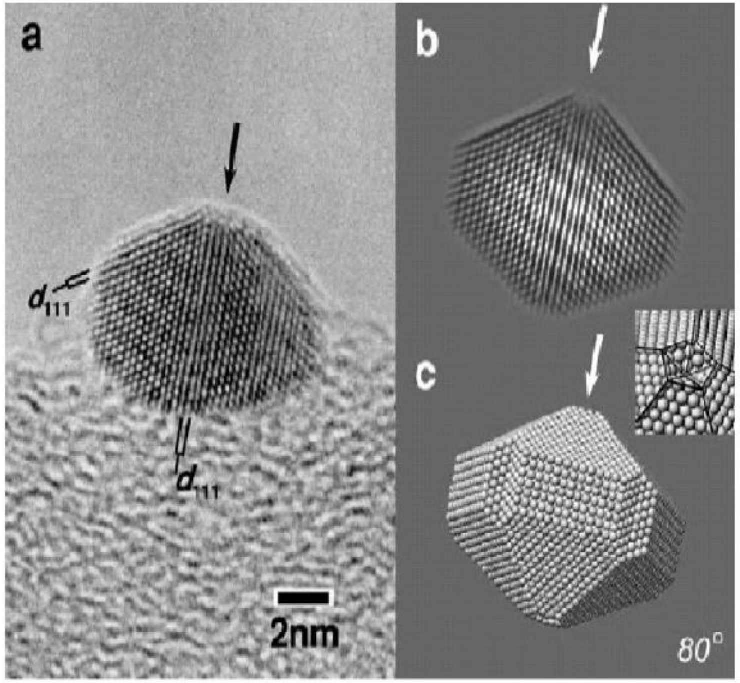
The inert gas condensation (IGC) process is one of the most known and simplest technique for production of nanoparticles (in particular, Me nanopowders)



Nanoparticle condensation in inert gas

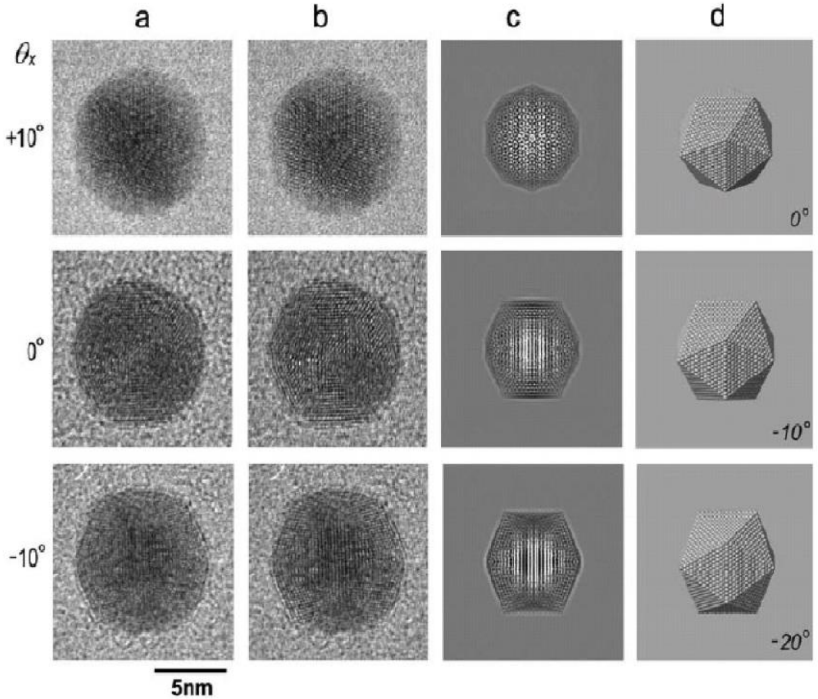
- A material, often a metal, is evaporated from a heated metallic source into a chamber which has been previously evacuated to about 10–7 torr and backfilled with inert gas to a low-pressure.
- The metal vapor cools througchto sluchilos'? h collisions with the inert gas atoms, becomes supersaturated and then nucleates
- homogeneously; the particle size is usually in the range 1–100 nm and can be controlled by varying the inert gas pressure.
- Ultimately, the particles are collected and may be compacted to produce a dense nanomaterial.

Example of nanoparticles obtained by IGC



Icosahedral gold nanoparticles generated from an inert gas aggregation source using helium and deposited on amorphous carbon film
[K. Koga, K. Sugawara, Surf. Sci. 529 (2003) 23]

Decahedral gold nanoparticle generated from an inert gas aggregation source using helium and deposited on amorphous carbon film
[K. Koga, K. Sugawara, Surf. Sci. 529 (2003) 23]



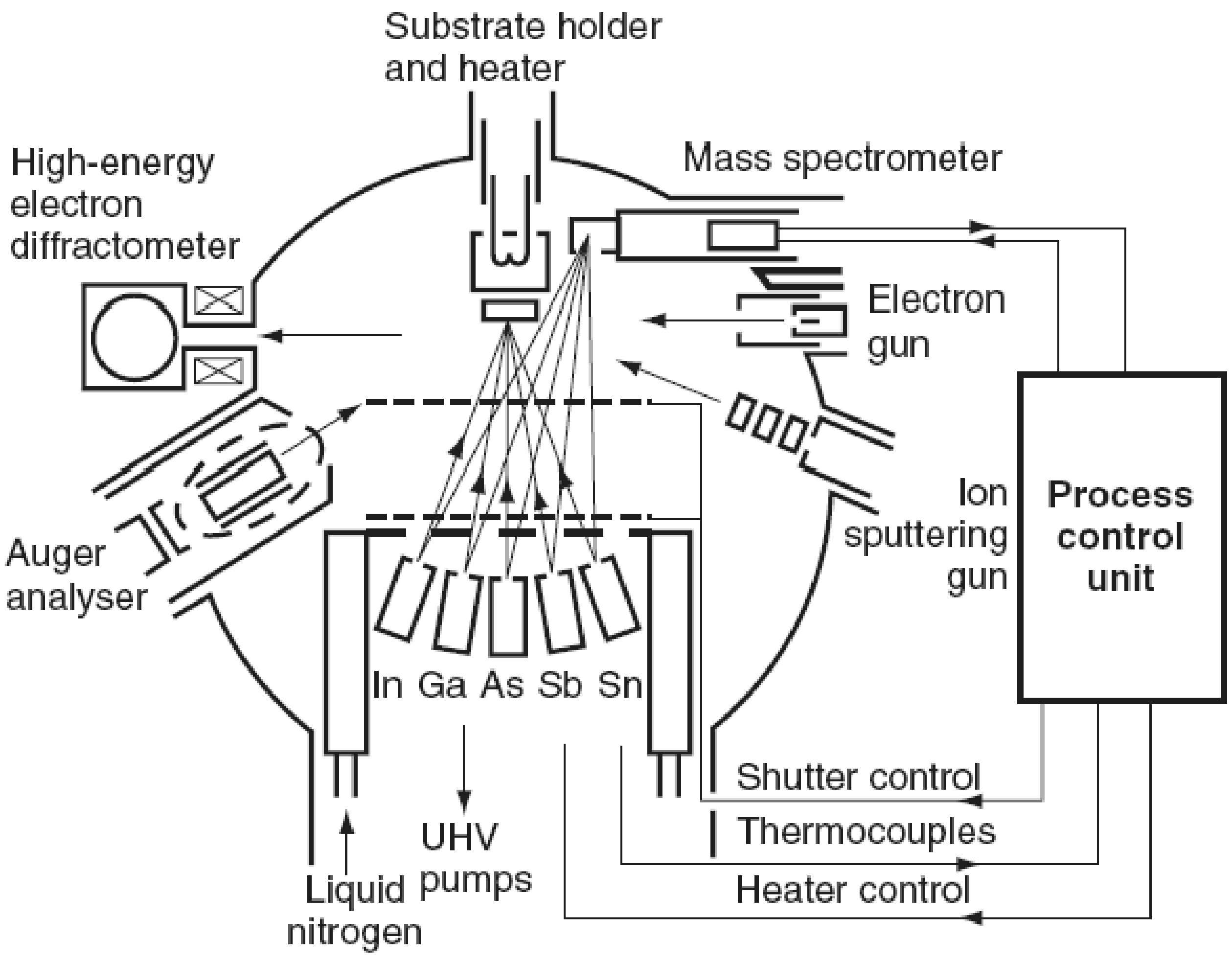
Methods for making 1-D and 2-D nanomaterials

- The production route for 1-D rod-like nanomaterials by liquid- phase methods is similar to that for the production of nanoparticles.
- CVD methods have been adapted to make 1-D nanotubes and nanowires. Catalyst nanoparticles are used to promote nucleation.
- Nanowires of other materials such as silicon (Si) or germanium (Ge) are grown by vapor-liquid-solid (VLS) methods.

Molecular Beam Epitaxy (MBE)

- A molecular beam epitaxy (MBE) machine is essentially an ultra-high-precision, ultra clean evaporator, combined with a set of in-situ tools, such as Auger electron spectroscopy (AES) and/or reflection high- energy electron diffraction (RHEED), for characterization of the deposited layers during growth.

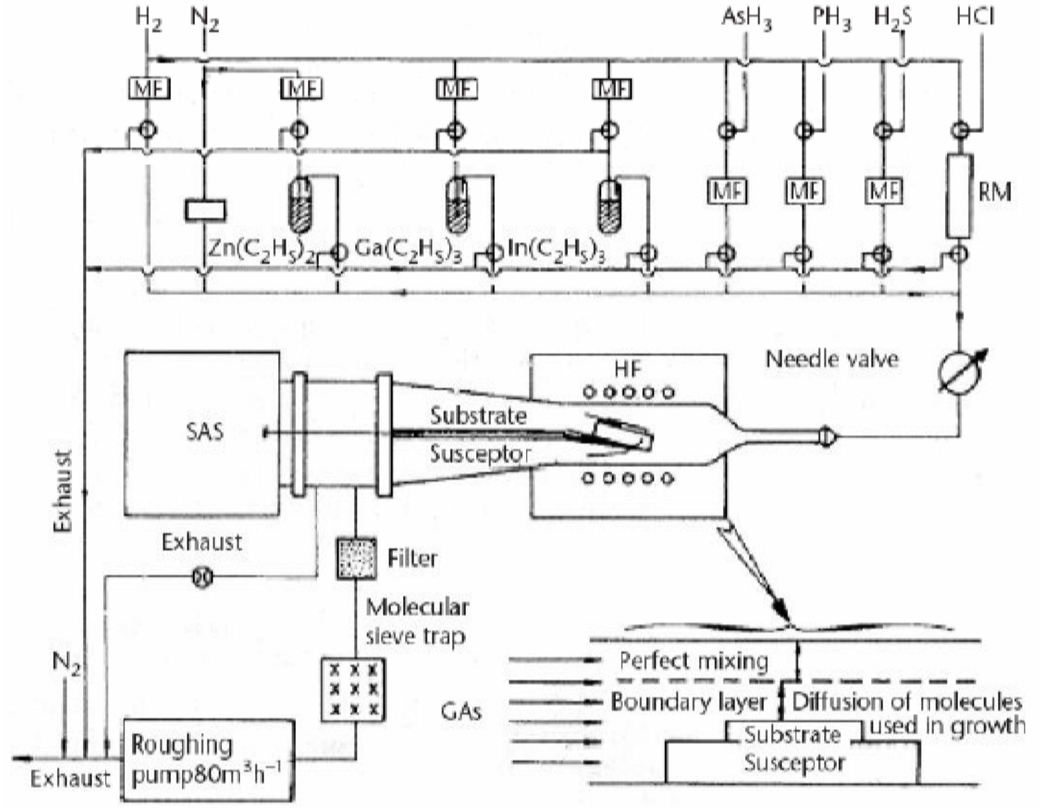
Molecular Beam Epitaxy (MBE)



Schematic diagram of a molecular beam epitaxy thin film deposition system (adapted from *Nanoscale Science and Technology*, Eds. R.W. Kelsall, I.W. Hamley, M. Geoghegan, John Wiley&Sons Ltd, 2005).

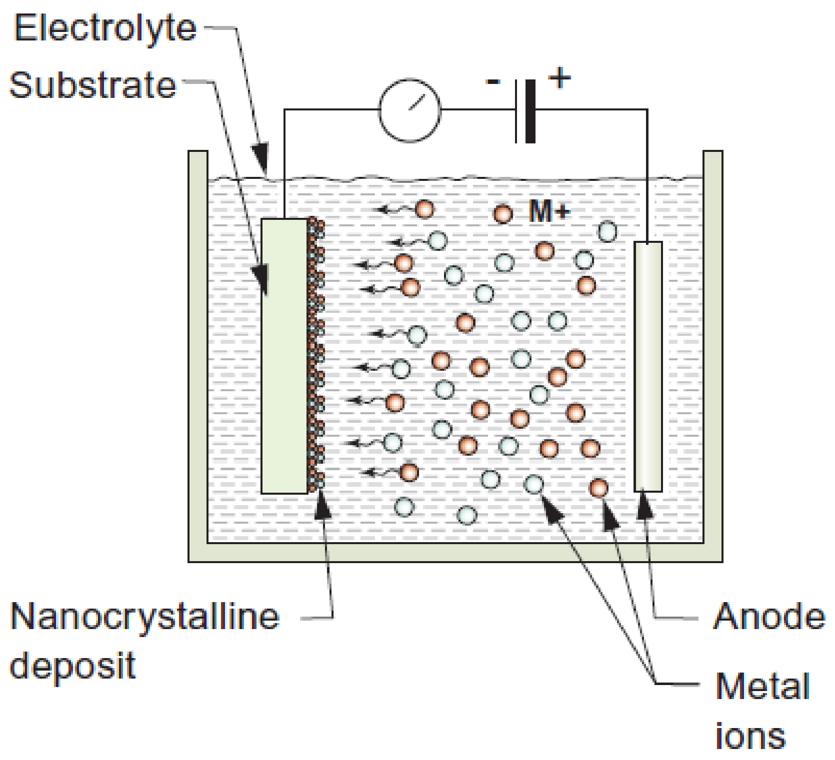
Metal-organic Chemical Vapor Deposition (MOCVD)

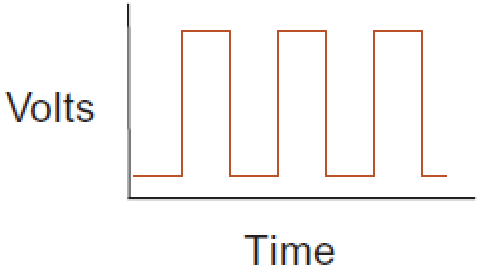
Schematics of the commercial MOCVD system



Electrodeposition

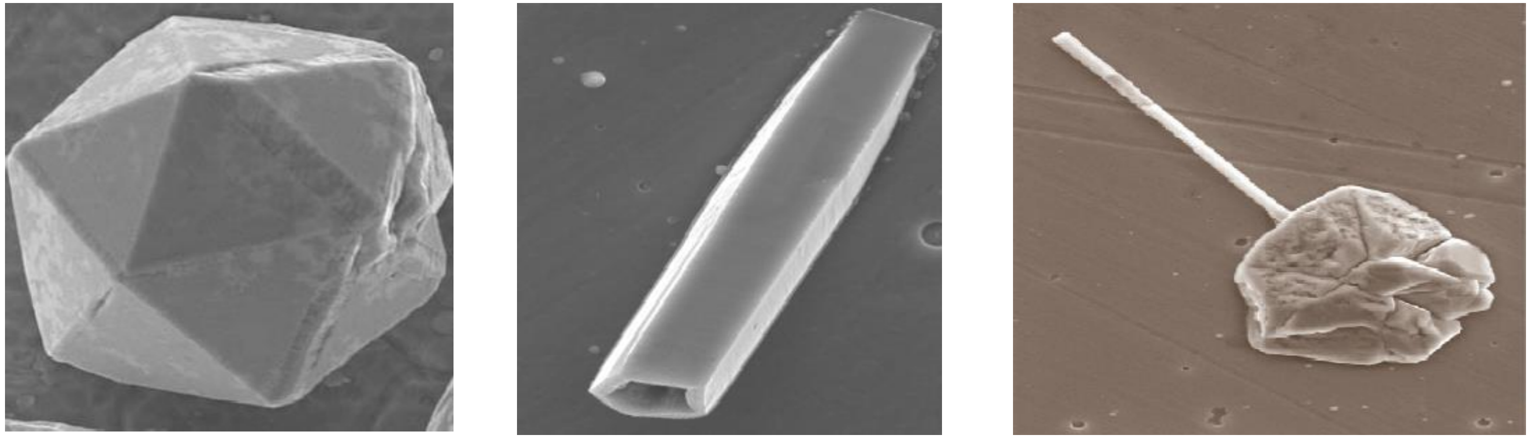
- Electrodeposition is a long-established way to deposit metal layers on a conducting substrate.
- Ions in solution are deposited onto the negatively charged cathode, carrying charge at a rate that is measured as a current in the external circuit.
- The process is relatively cheap and fast and allows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





Electrodeposition - basics

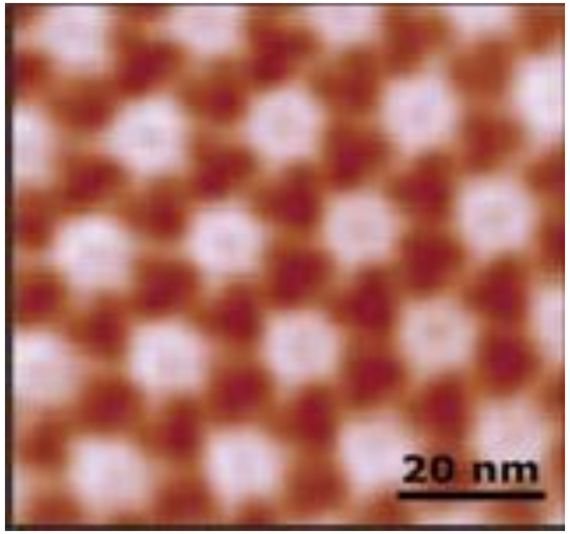
- The principle of electrodeposition is inducing chemical reactions in an aqueous electrolyte solution with the help of applied voltage, e.g. this is the process of using electrical current to coat an electrically conductive object with a relatively thin layer of metal.
- This method is relevant to deposition of nanostructured materials include metal oxides and chalcogenides.



Icosahedral microparticles, pentagonal microtubes and whiskers obtained in the process of copper electrodeposition [after A.A. Vikarchuk]

Electrodeposition and nanobiosystems

As a water-based process, it is often more *environmentally friendly* than deposition methods that require hazardous solvents and reactive precursor chemicals (like organometallic compounds, for instance).



Nanometer-scale cuprous oxide (colorized red) can be electrodeposited through the openings in the hexagonally packed intermediate layer protein (white regions) from the bacterium Deinococcus radiodurans. Purified crystalline protein sheets are first adsorbed to a conductive substrate, and then electrodeposition is carried out to fill the nanometer-scale pores in the protein.

Biological fabrication.
Proteins are responsible for the nucleation, growth, composition, and shape of functional biological structures like bones, teeth, and shells. Using proteins to control the growth of ED materials is truly a frontier area where biology meets nanotechnology. One way that proteins are being used in electrochemical nanotechnology is as masks for through mask electrodeposition. Proteins can self-organize into complex structures representing all possible two- dimensional (2D) space groups built from chiral molecules. Moreover, they are readily engineered through molecular biology, providing an attractive foundation for nanotechnology.

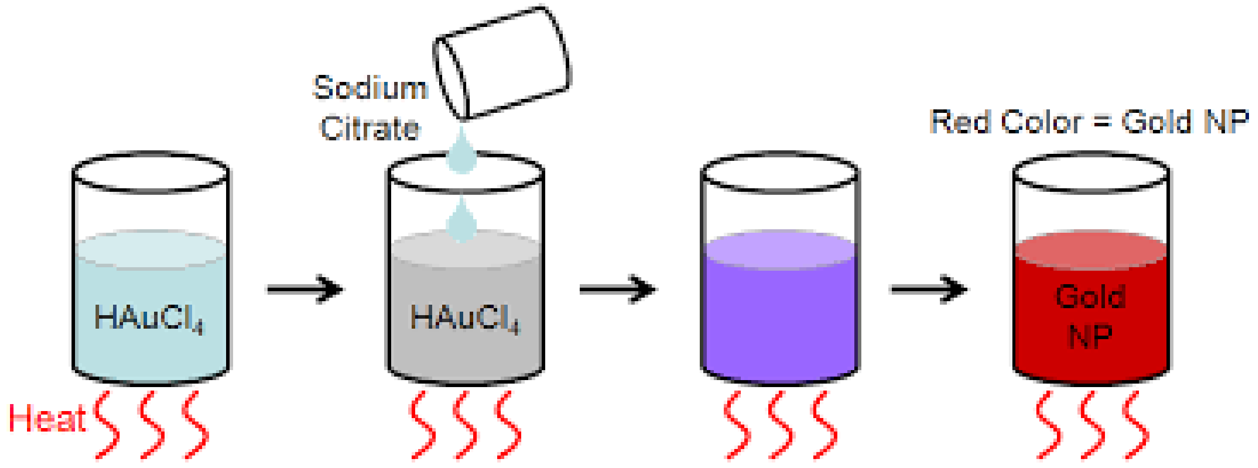
Liquid phase synthesis

- Precipitating nanoparticles from a solution of chemical compounds can be classified into five major categories:
  - colloidal methods;
  - sol – gel processing;
  - water – oil microemulsions method;
  - hydrothermal synthesis; and
  - polyol method.
- Solution precipitation relies on the precipitation of nanometer-sized particles within a continuous fluid solvent. An inorganic metal salt, such as chloride, nitride and so on, is dissolved in water. Metal cations exist in the form of metal hydrate species, for example, Al(H2O)3+ or Fe(H2O6)3+.
- These hydrates are added with basic solutions, such as NaOH or Na4OH. The hydrolyzed species condense and then washed, filtered, dried and calcined in order to obtain the final product.

Colloidal methods

- Colloidal methods are simple and well established wet chemistry precipitation processes in which solutions of the different ions are mixed under controlled temperature and pressure to form insoluble precipitates.
- For metal nanoparticles the basic principles of colloidal preparation were known since antiquity. E.g. gold colloids used for high quality red and purple stained glass from medieval times to date.
- However, proper scientific investigations of colloidal preparation methods started only in 1857 when Faraday has published results of his experiments with gold. He prepared gold colloids by reduction of $HAuCl_4$ with phosphorus.
- Today, colloidal processes are widely used to produce such nanomaterials like metals, metal oxides, organics, and pharmaceuticals.

Colloidal methods



Sol-gel technique

- Sol-gel technology is a well- established colloidal chemistry technology, which offers possibility to produce various materials with novel, predefined properties in a simple process and at relatively low process cost.

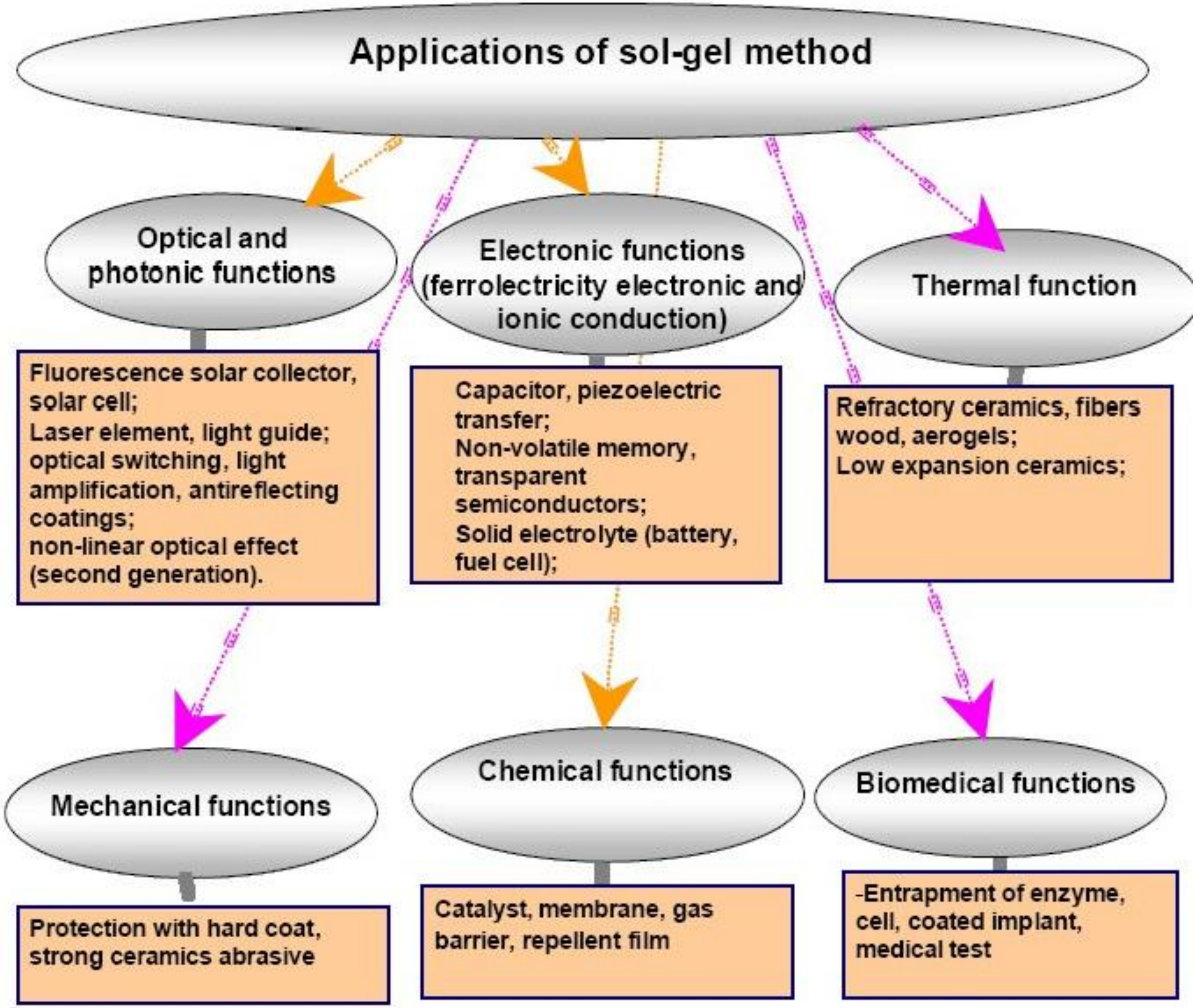
The sol is a name of a *colloidal solution* made of solid particles few hundred nm in diameter, suspended in a liquid phase.

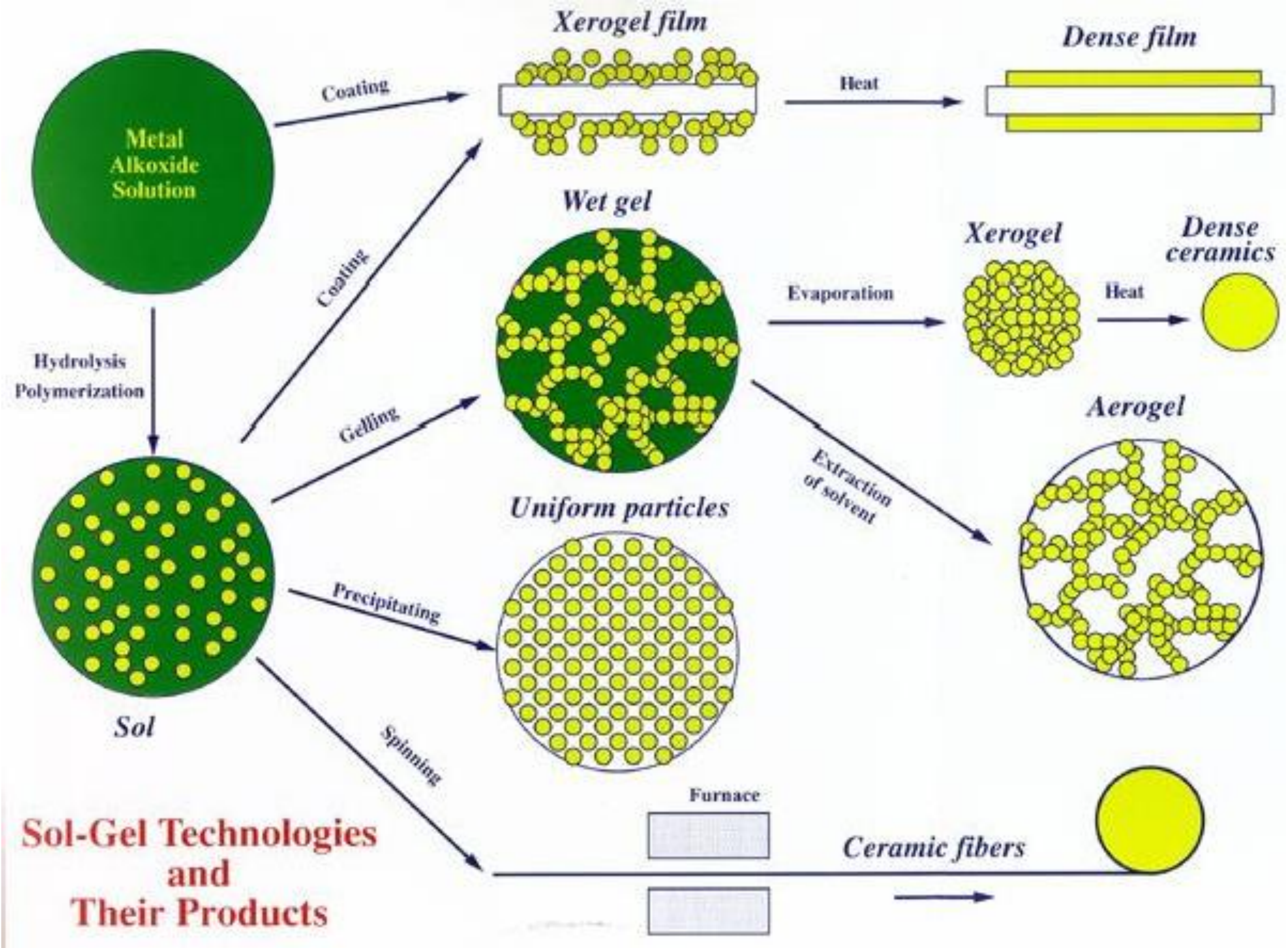
+

The gel can be considered as a solid macromolecule immersed in a solvent.

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

The main benefits of sol–gel processing are the high purity and uniform nanostructure achievable at low temperatures.


Applications of sol-gel method
Optical and photonic functions
Fluorescence solar collector, solar cell; Laser element, light guide; optical switching, light amplification, antireflecting coatings; non-linear optical effect (second generation).
Electronic functions (ferrolectricity electronic and ionic conduction)
Capacitor, piezoelectric transfer; Non-volatile memory, transparent semiconductors; Solid electrolyte (battery, fuel cell);
Thermal function
Refractory ceramics, fibers wood, aerogels; Low expansion ceramics;
Mechanical functions
Protection with hard coat, strong ceramics abrasive
Chemical functions
Catalyst, membrane, gas barrier, repellent film
Biomedical functions
-Entrapment of enzyme, cell, coated implant, medical test



Start with precursor

Form Solution (e.g., hydrolysis)

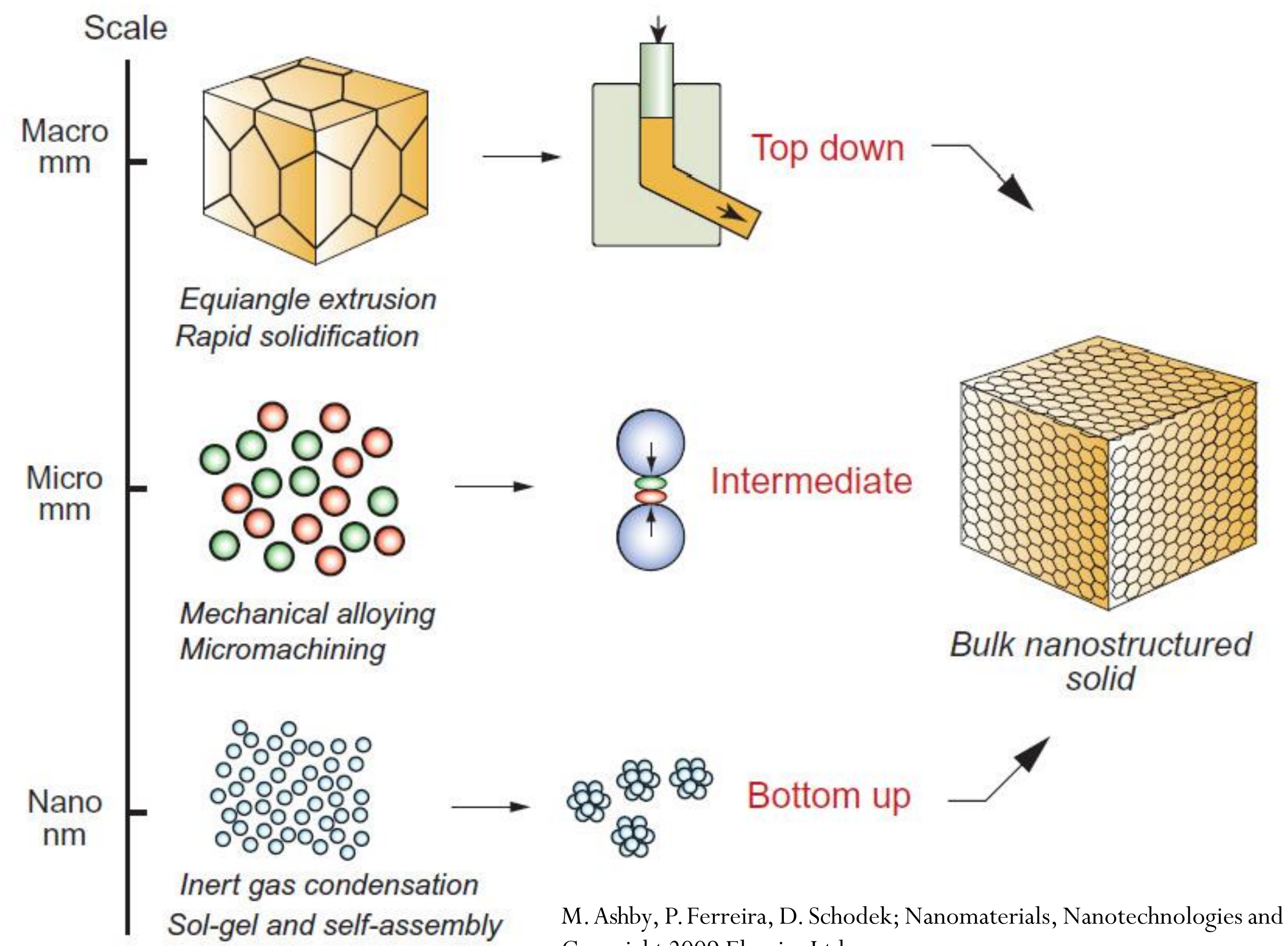
Form Gel (e.g., dehydration)

Then form final product

Aerogel (rapid drying)

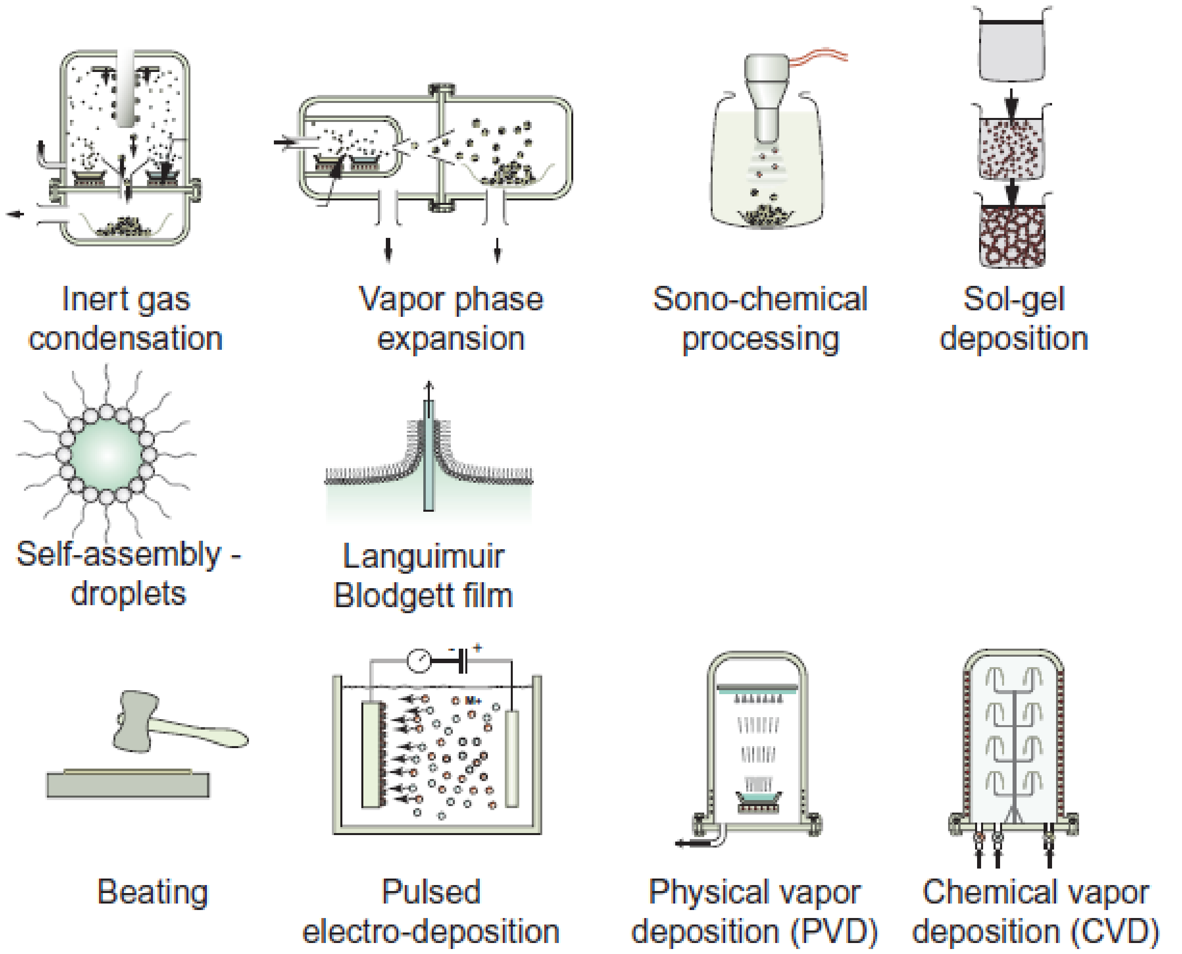
Thin-films (spin/dip)

The top-down, intermediate, and bottom-up approaches to making bulk nanostructured solids



M. Ashby, P. Ferreira, D. Schodek; Nanomaterials, Nanotechnologies and Design;

Summary - Methods for making nanoparticles, nanoclusters and nanolayers



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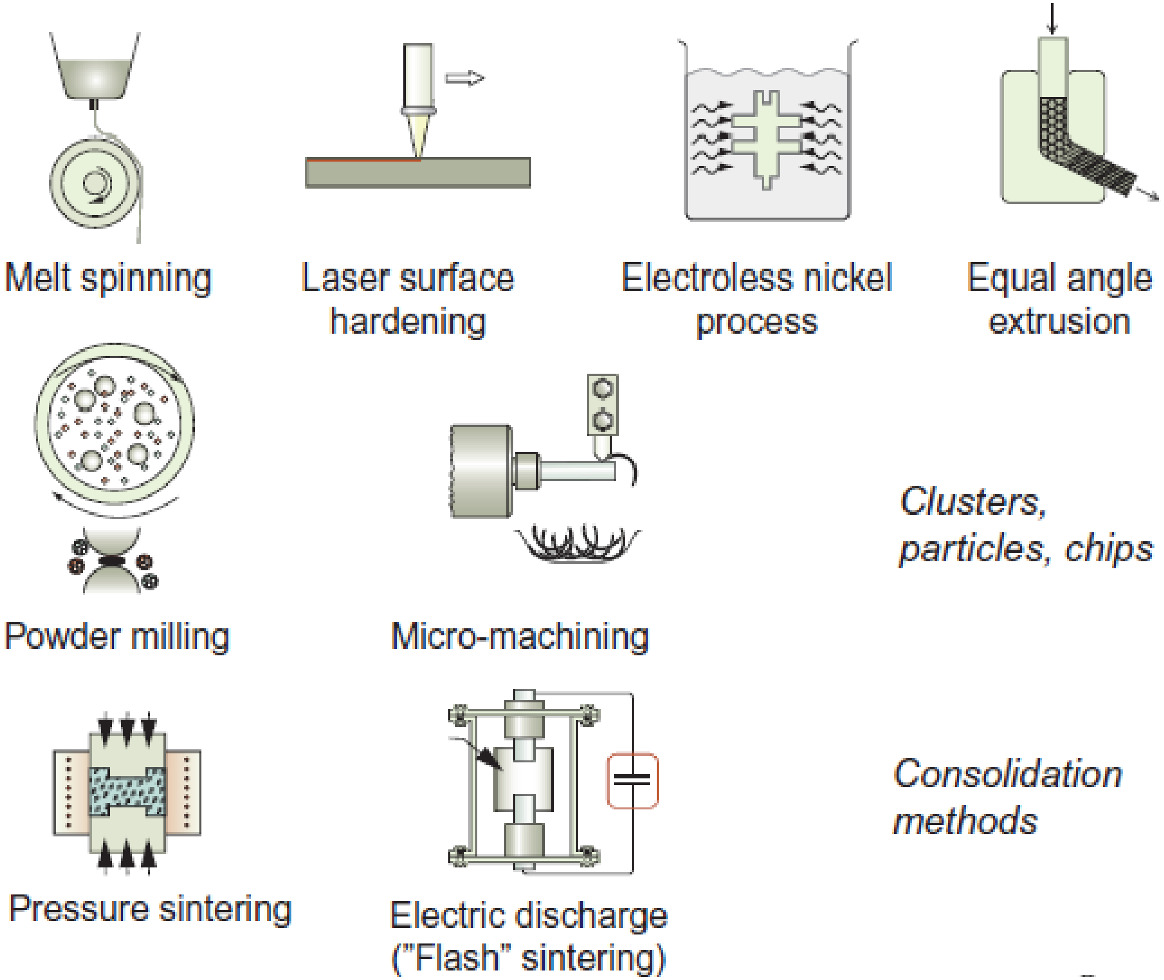
Summary - Methods for making bulk nanostructures



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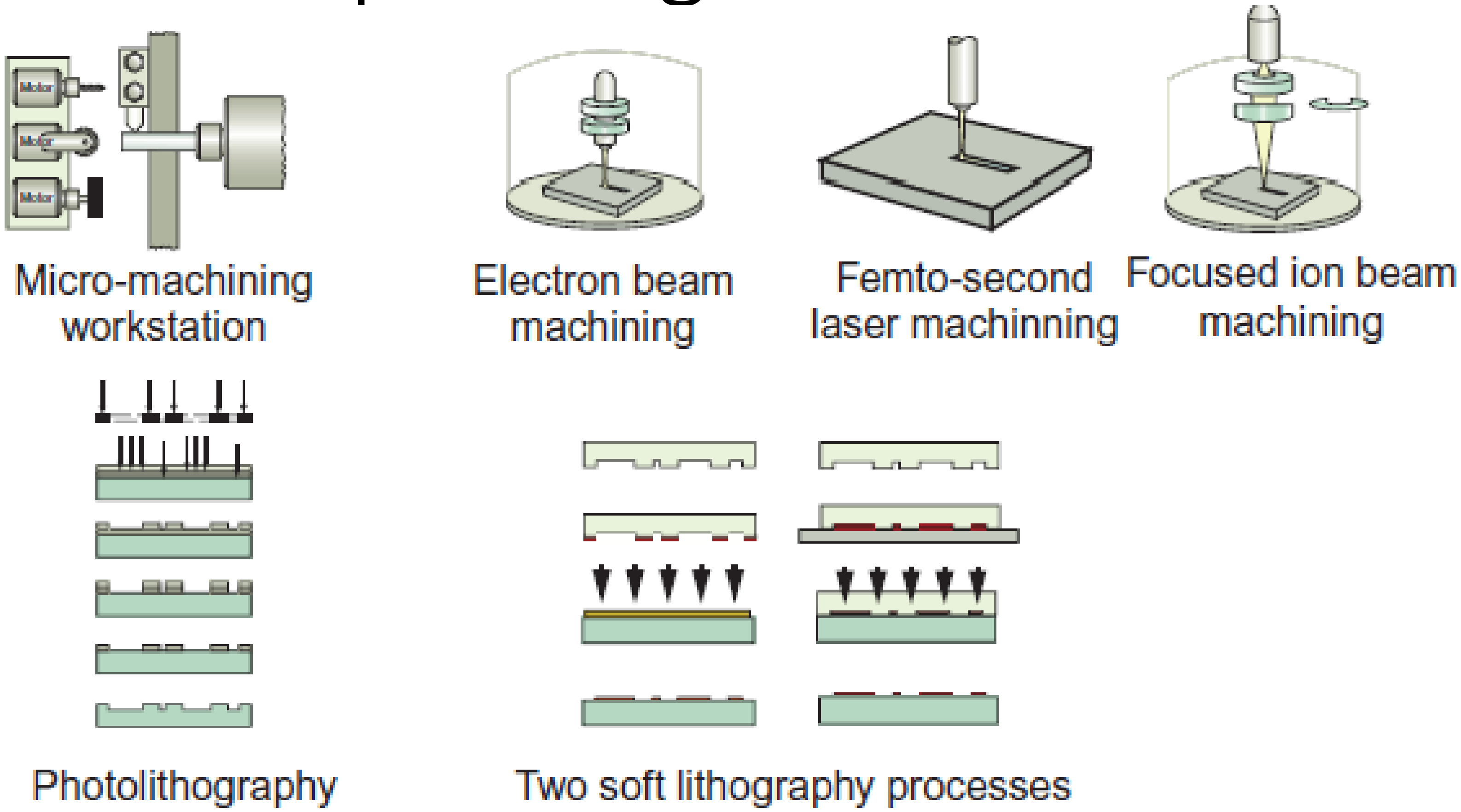
Summary - Methods for nanoprofiling



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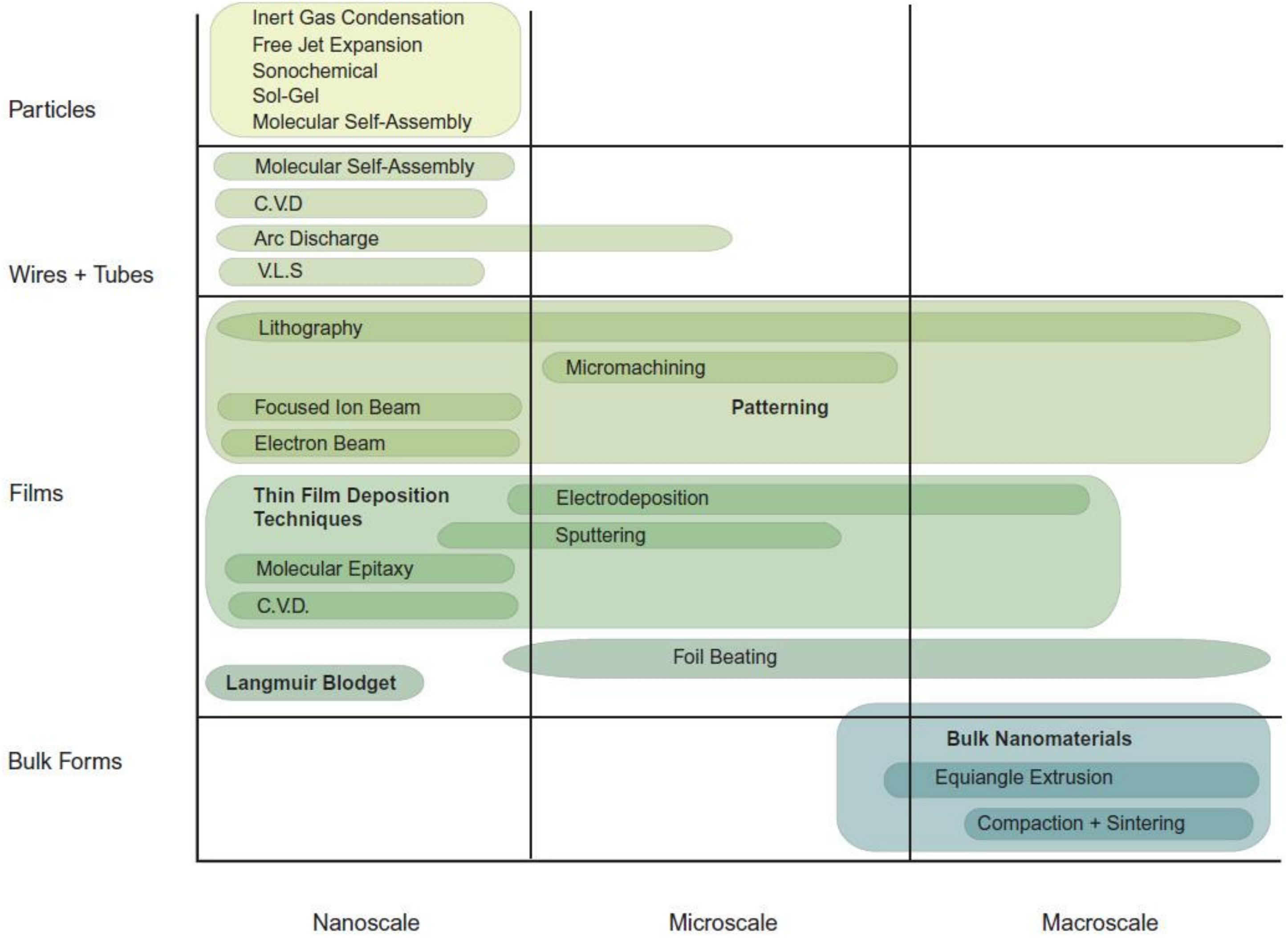
Summary of processes used to make nanomaterials



NANOMATERYALLERİN SENTEZ TEKNOLOJİSİ

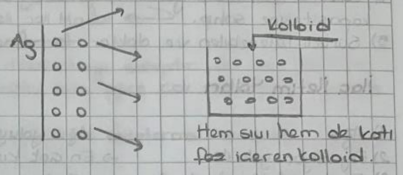
1) Kolloidal metodlar
2) Sol-Jel Teknikleri
3) Yağ-Su Emülsiyonları
4) Hidrotermal Sentez
5) Polyol Metodu

} Nanoparçacık üretiminde kullanılan yöntemlerdir. En sık kullanılan ilk üç yöntemdir. Sadece sıvı halde gerçekleştirilir.

Kolloidal Metodlar

$AgNO_3$ tuzu —indirgeme→ Ag

$NaBH_4$



∝ Parçacıkların indirgenmesi ile olur.

Sol-Gel Teknikleri

∝ Kullanılacak çözelti türü oldukça önemlidir.

∝ Öz. düşük sıcaklıklarda çalışıyorsa saflaştırmak oldukça önemlidir. Jel ortamda bulunduğu için saflaştırma işlemi zorlaşmaktadır.

∝ Parçacık elde etmede çok iyi bir yöntem olmasına rağmen saflaştırmada kötüdür.

Enzim (E) + Substrat (S) ⟶ E + Ürün (P)

↑ ↑

∝ Jelatin ile kaplama yapıp; bunu iletken yüzey haline getirebiliriz.

❗ Litografi = Yüzeye nano boyutta yazma işlemi. Özel bir işlemdir. Günümüzde sıkça kullanılmaya başlanmıştır. Elektrokimyasal biyosensörlerde kullanılır.

İLAÇ İLETİMİ

İstenilen bir ilacın bir araç vasıtası ile hasta bölgeye iletilmesi işlemine denir.

İlaç → Kişisel Terapi → Kontrollü Salım

- İlaç → Absorbsiyon, dağılım ve metabolizması kişiden kişiye değişir.
- Kontrollü Salım → Doz miktarı ayarlanmış olarak ilacın uygun bölgede salınımı.
  - ⇒ Klasik ilaçlarda: Ağız yoluyla jelatin kapsüller kullanılır.
  - ⇒ Nanoteknoloji var.