Basic Techniques for synthesis of nanomaterials

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How to get at nano scale?

There are two general approaches to the synthesis of nanomaterials and the fabrication of nanostructures

Bottom-up approach

Top-down approach

Top-down vs. bottom-up

1)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.

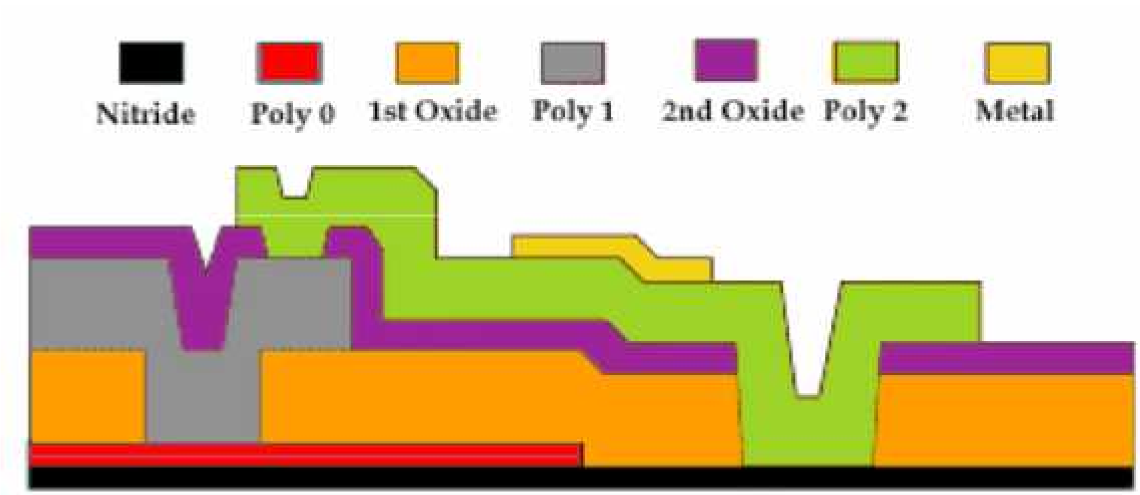
2)Bottom-up methods

- Start with atoms or molecules and build up nanostructures.

- Fabrication is much less expensive.

Top-Down: lithography

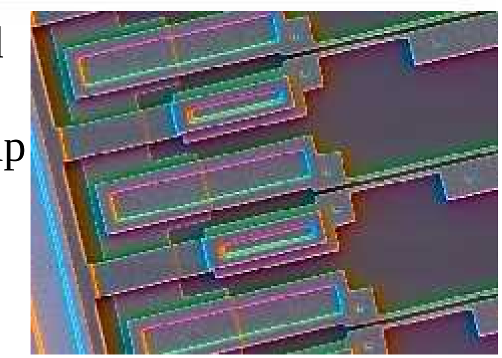
At the moment, the most used top-down approach is photolithography. It has been used for a while to manufacture computer chips and produce structures smaller than 100 nm.



- 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.
- Subsequently, when the wafer is rinsed in a developing solution, the exposed areas are removed.

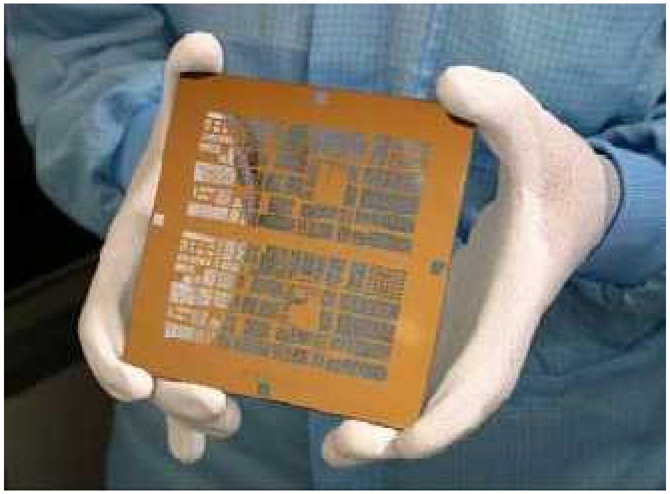
Strip resist and do process again and again.

Eventually, a 3-D structure is built up



Lithographic processing: Masking and exposure

Expose resist to UV light through a mask



Mask is aligned to wafer before exposure.

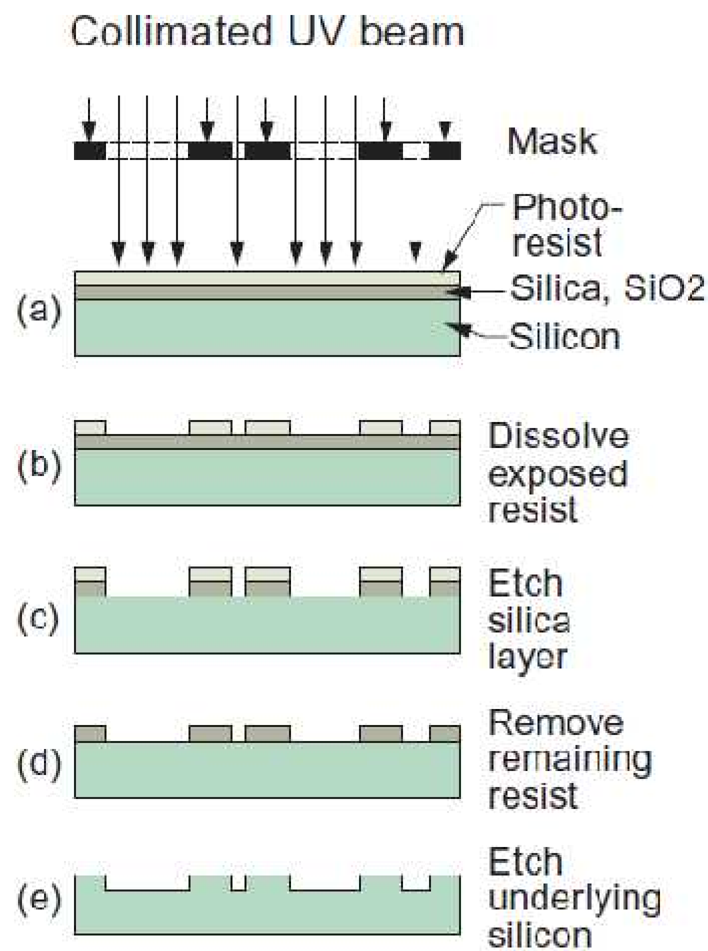
Advantages of Lithography

1) Once the master template has been made, no special equipment is required.

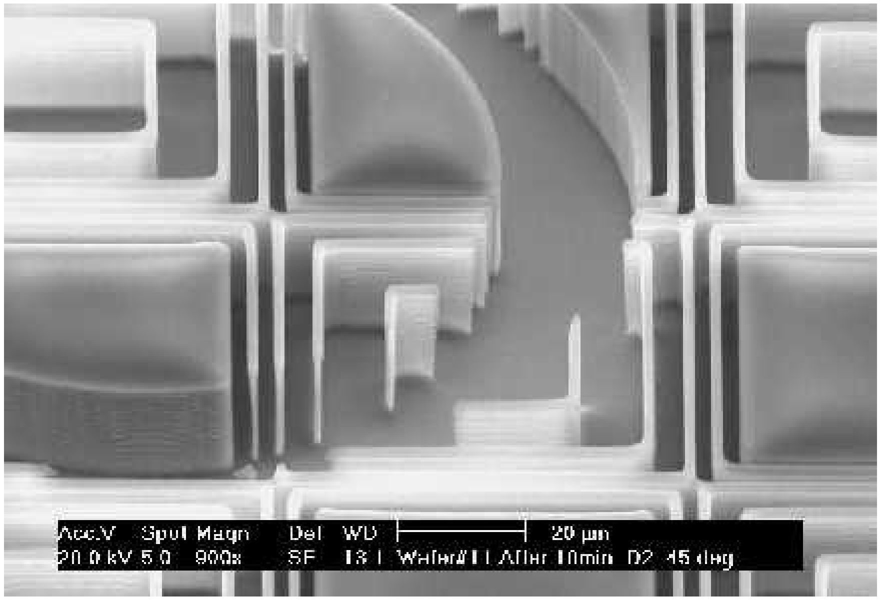
2)Soft lithographic methods are capable of producing nanostructures in a wide range.

3) Photolithography of materials and can print or mold on curved as well as planar surfaces.

4) A beam of UV light activates the photoresist, transferring the pattern from the mask to the sample.



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.

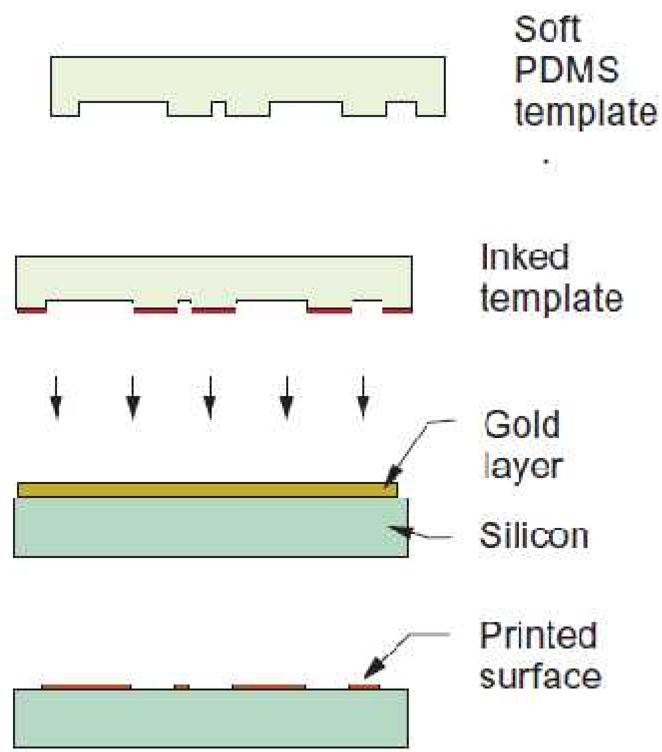
- The resolution is greatly improved.

- However, the electron beam technique is very expensive and very slow.

- Conventional lenses are not capable of focusing X-rays and the radiation damages most of the materials used for masks and lenses.

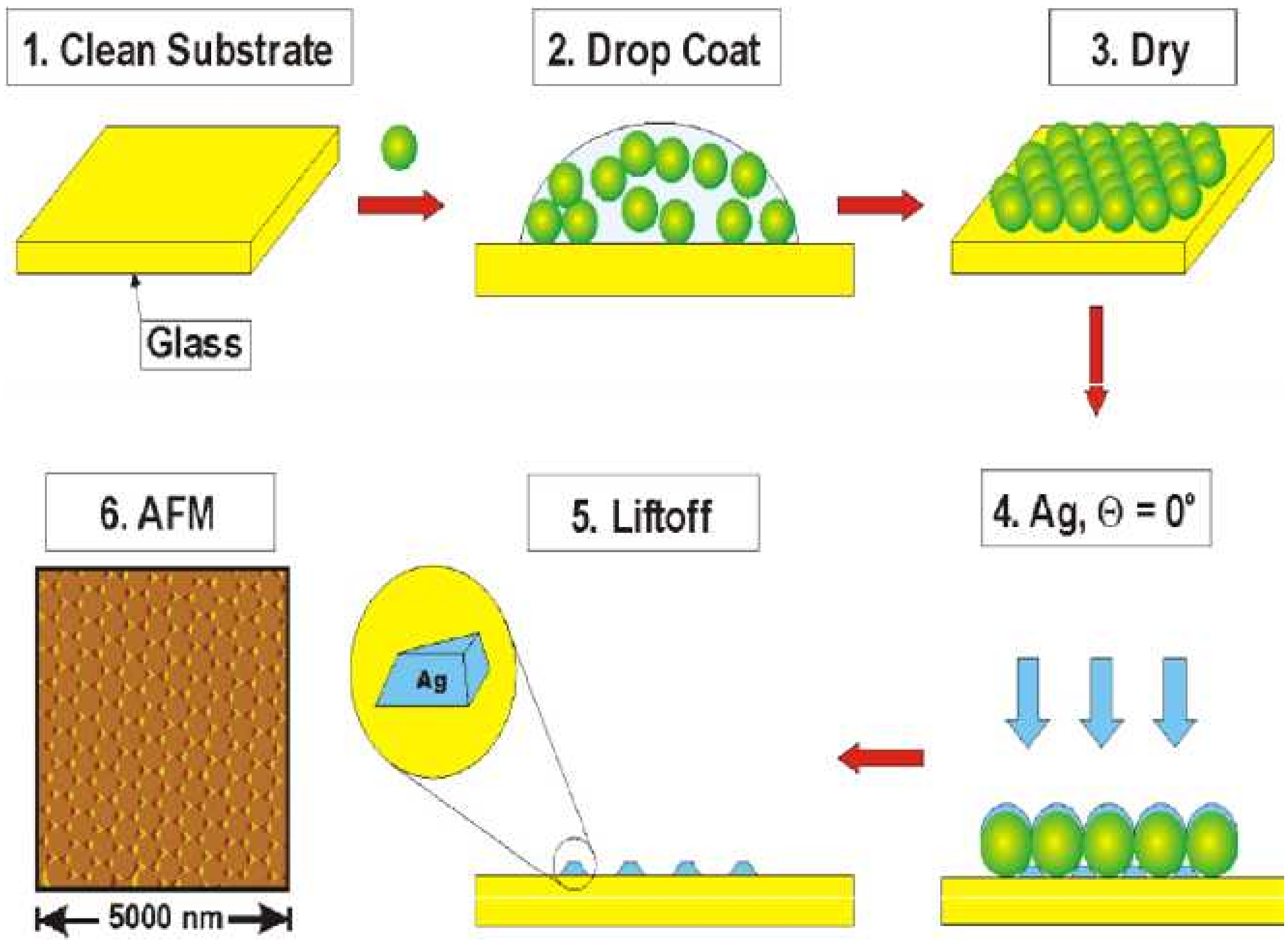
The most recent lithography methods

Printing, stamping, and molding use mechanical processes instead of photons or electrons.

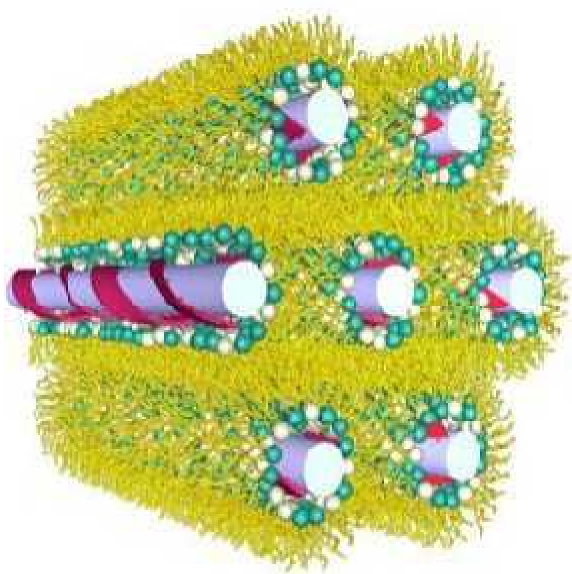


The organic molecules form a self-assembled monolayer on the solid surface that reproduces the pattern with a precision of approximately 50 nm.

Nanosphere Lithography



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).

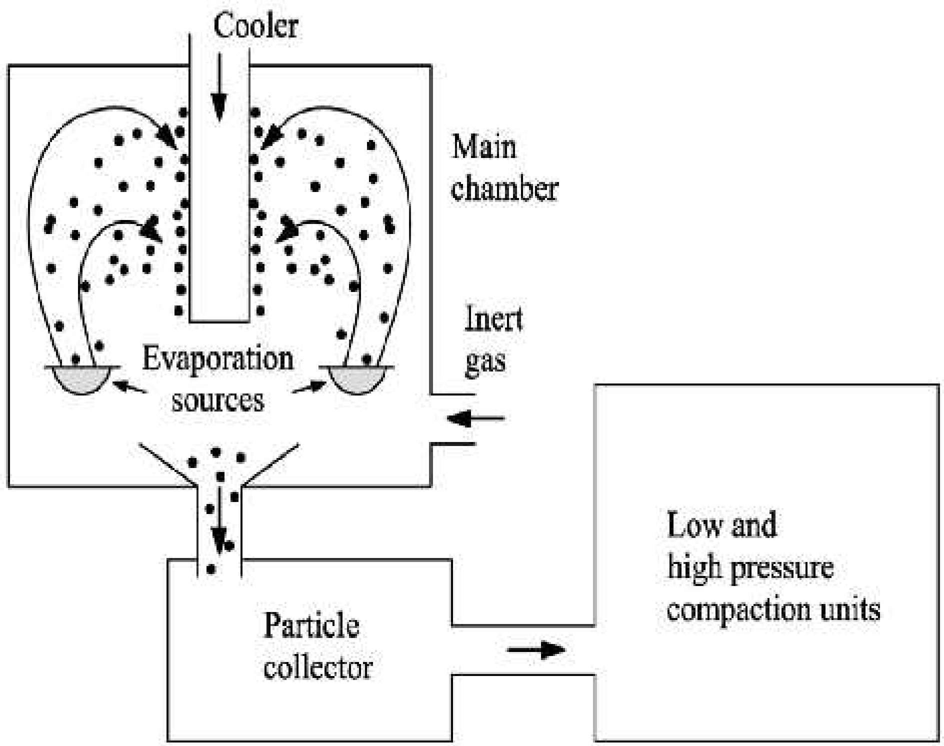
Methods for making 0-D Nanomaterials

- 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.

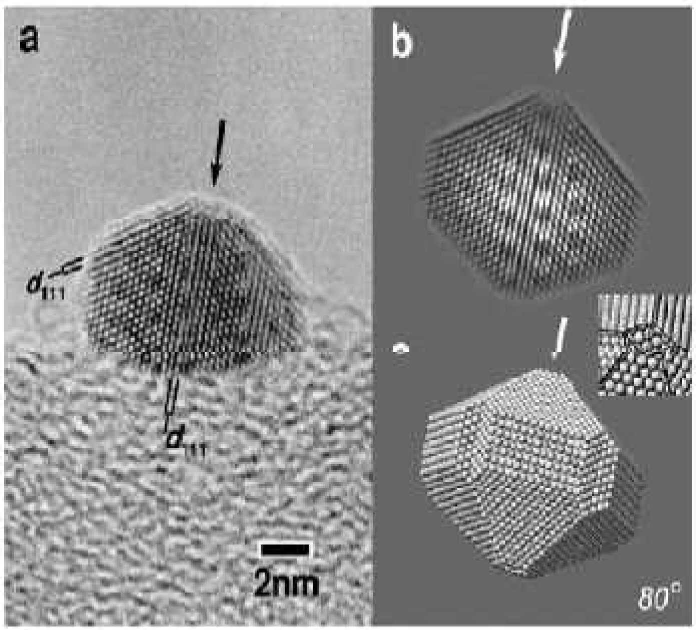
- There are broad types of these processes: ultrasonic dispersion, sol-gel methods, and methods relying on self-assembly.

Nanoparticle condensation in inert gas

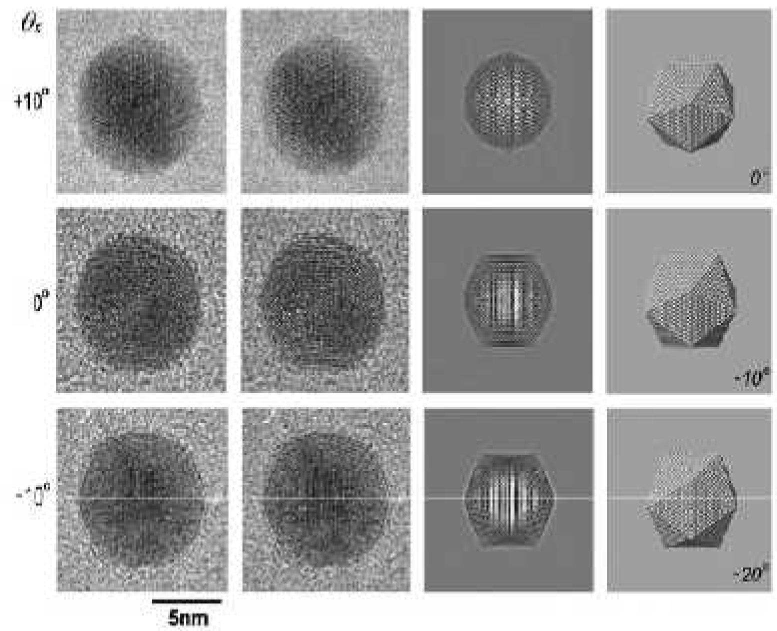


- An inorganic material is vaporized inside a vacuum chamber into which an inert gas (typically argon or helium) is periodically admitted.
- Once the atoms boil off, they quickly lose their energy by colliding with the inert gas.
- The vapor cools rapidly and supersaturates to form nanoparticles with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

Example of nanoparticles obtained by IGC

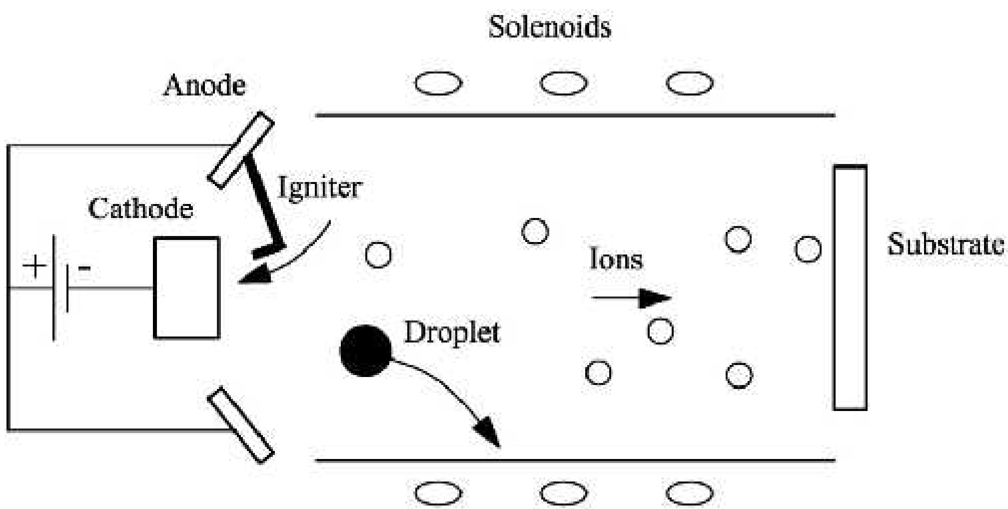


Decahedral gold nanoparticle generated from an inert gas aggregation source using helium and deposited on amorphous carbon film
[K. Koga, K. Sugawara, Surf. Sci. 529 (2003) 23]



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

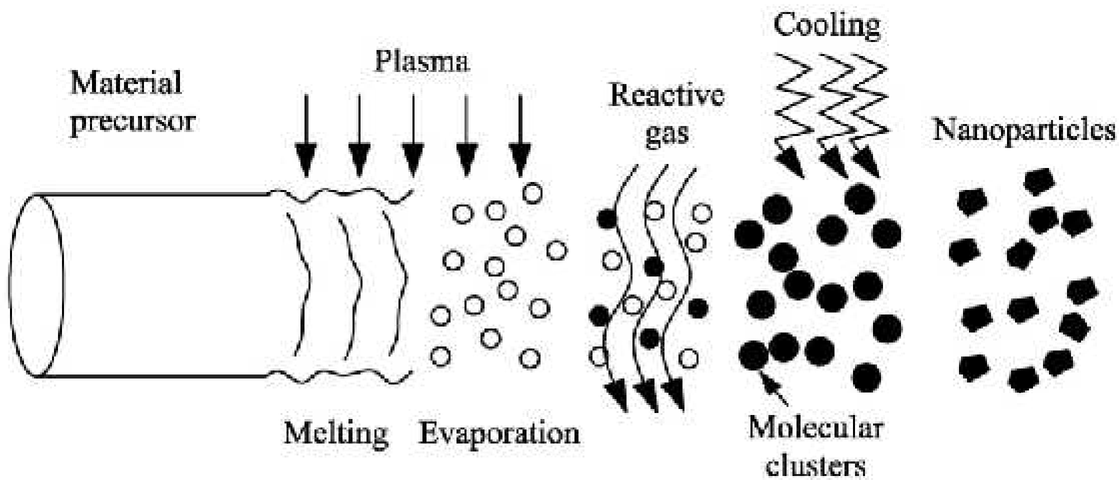
Plasma-Based Synthesis



- Vacuum arc deposition is well-established process for producing of thin films and nanoparticles. This technique involves the initiation of an arc by contacting a cathode made of a target material. An igniter is attached to an anode in order to generate a low-voltage, high-current self-sustaining arc.

- The arc ejects ions and material droplets from a small area on the cathode. Further, the ions are accelerated towards a substrate while any large droplets are filtered out before deposition .

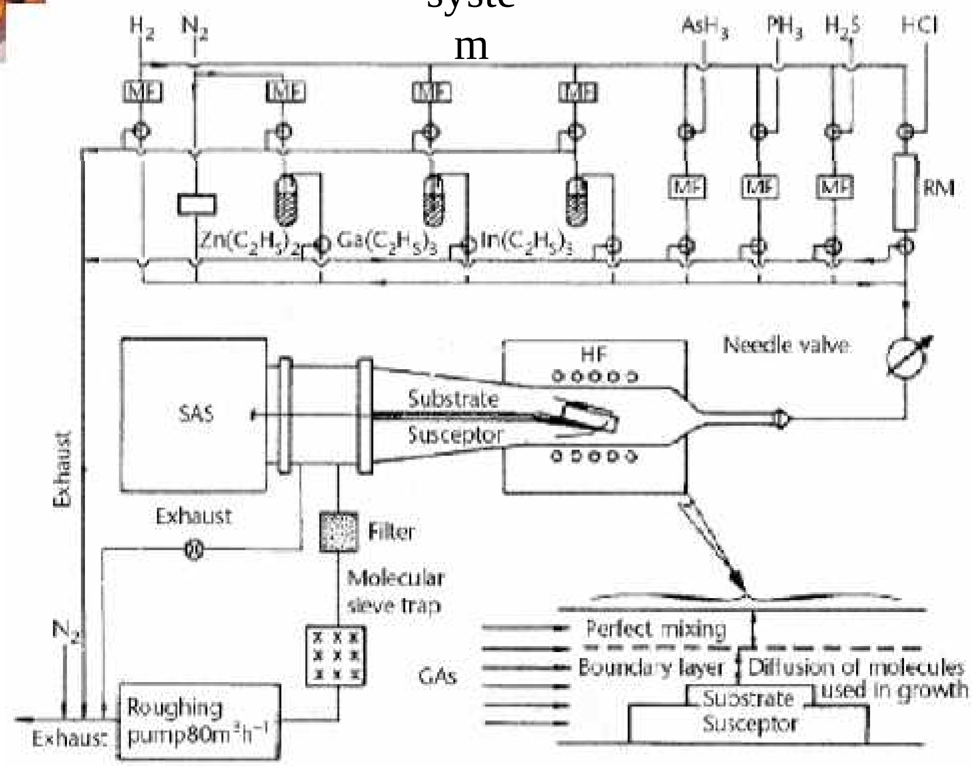
Vapor condensation



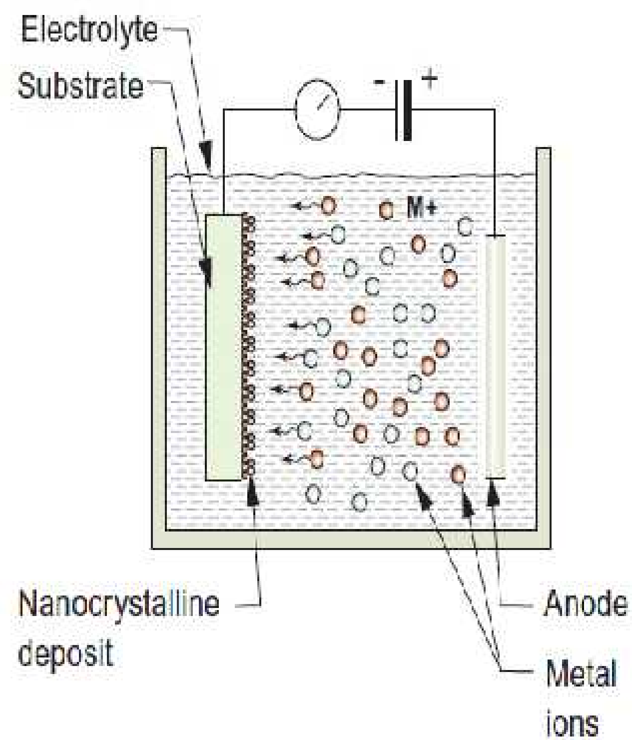
- One of the outstanding strides in plasma processing for nanoparticles synthesis is the developed process of the vapor condensation.
- The precursor material is put into the working chamber with a stable arc.
- The chamber is filled by reactive gas that becomes ionized; then molecular clusters are formed and cooled to produce nanoparticles.

Metal-organic Chemical Vapor Deposition

Schematics of the commercial MOCVD syste m

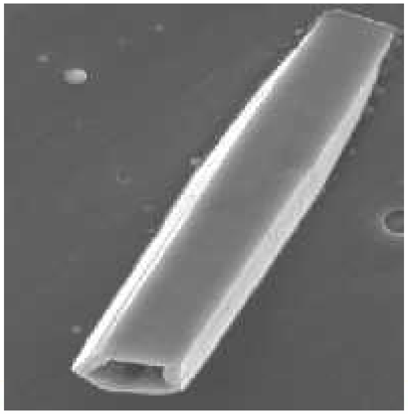
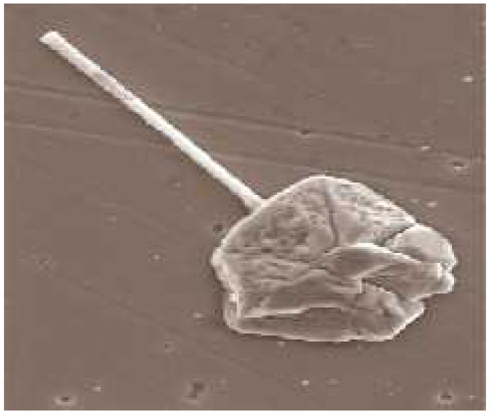


Electrodeposition



- 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

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

- 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.

Electrodeposition - features

1) Electrodeposition is relatively cheap and can be performed at low temperatures which will minimize interdiffusion of materials in the case of a multilayered thin film preparation.
2) The film thickness can be controlled by monitoring the amount of charge delivered, whereas the deposition rate can be followed by the variation of the current with time.
3) The composition and defect chemistry can be controlled by the magnitude of the applied potential.

4) The potential during the pulse will determine the species deposited whilst the thickness of individual layers is determined by the charge passed.

5) Alternatively, the substrate can be transferred periodically from one electrolytic cell to another.

6)The final films can range in thickness from a few nanometers to tens of microns and can be deposited onto large specimen areas of complex shape, making the process highly suitable for industrial use.

Why electrodeposition?

Miniature copper mask from the site of Loma Negra on the far north coast of Peru, ca. 200 C.E. Removal of the green copper corrosion products reveals a bright gold surface. The extremely thin layer of gold was applied to the sheet copper by electrochemical replacement plating.
[Heather Lechtman, Sci. Amer., 250(6), 56 (1984).]

Electrodeposition has three main attributes that make it so well suited for nano-, bio- and microtechnologies.

1) It can be used to grow functional material through complex 3D masks.

2) It can be performed near room temperature from water-based electrolytes.

3) It can be scaled down to the deposition of a few atoms or up to large dimensions.