

## LECTURES 12-13

# MICRO AND NANO MATERIALS MANUFACTURING TECHNIQUES (2)

### 9.6 Electrothermal and thermal processes

In electrothermal and thermal processes thermal energy is provided by a heat source that is used to melt or vaporize the material to be removed. Furthermore, heat affected zones (HAZ) may appear in the workpiece. Heat effects include solidifying debris on the surface, and metallurgical transformations undergone by the layers just below the surface, which alter the properties of the material as a whole and may cause problems.

**9.6.1 Electrical Discharge Machining (EDM)** is the oldest and most-used operation of this kind. Micro-EDM is already widely used for micromachining. The workpiece (anode) and the tool (cathode) are submerged in a dielectric fluid and subjected to a high voltage. When the electrodes are separated by a small gap (whose dimensions can be precisely calculated) a pulsed discharge occurs. Sparks are generated and material is removed through local melting and evaporation. Both electrodes are worn away but the tool wear ratio varies depending on the tool material,

**9.6.2 Electron Beam Machining (EBM).** In this process, instead of electrical sparks high velocity electrons, travelling at about three quarters the speed of light, are used. The electrons are focused on an area on the surface of the workpiece and on impact their kinetic energy is converted into thermal, causing the workpiece material to melt and vaporize. The diameter of the beam is 10–200 nm, producing holes below 0.1 mm in diameter.



**9.6.3 Laser Beam Machining (LBM)** was introduced in industry for macroscopic cutting and welding of metals but lately is being used in micromachining as well. The importance of lasers in photolithography as uv sources was already discussed; here their application in ultraprecision material removal will be analysed. A thin laser beam is focused to a small spot on the surface of the workpiece and material is removed by ablation. The process is controlled by several parameters, including the light wavelength, others being spot size, beam intensity and depth of focus of the beam.

## **9.7 Electrochemical processes**

In this subsection electrochemical energy is involved in the material removal or forming operations. Additive techniques and the main processes for the production of porous Si are also included here. The most popular processes are electrochemical machining (ECM) and electrochemical grinding (ECG). ECM involves a cathodic electrode and an anodic workpiece which are separated by a highly conductive electrolyte.

Machining with ECM results in very smooth surfaces. ECM has the advantage that no HAZ are created, and there is almost no tool wear.

## **9.8 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.

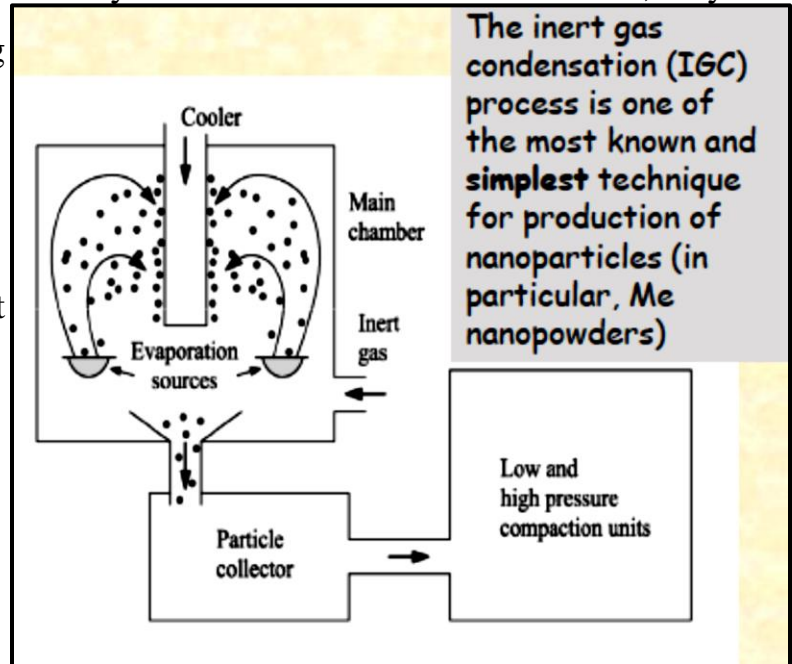
There are broad types of these processes: ultrasonic dispersion, sol-gel methods, and methods relying on self-assembly.



### 9.8.1 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.

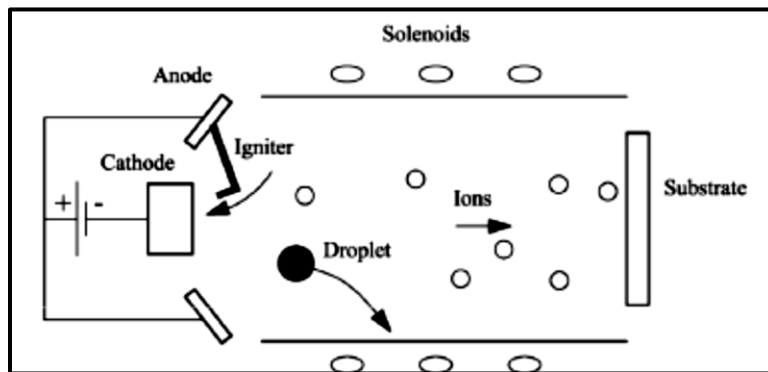


### 9.8.2 Plasma – based synthesis

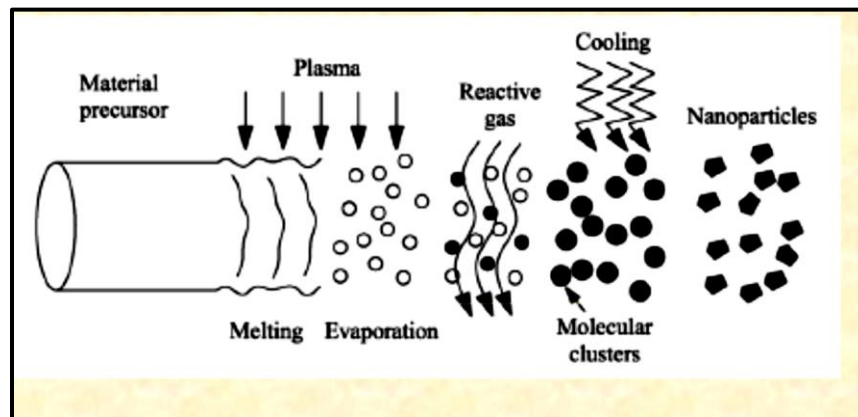
Vacuum arc deposition is well-established process for producing of thin films and nanoparticles. This technique involves the initiation of an arc by contacting a cathode made of a target material. An igniter is attached to an anode in order to generate a low-voltage, high-current self-sustaining arc.

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 .





### 9.8.3 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.

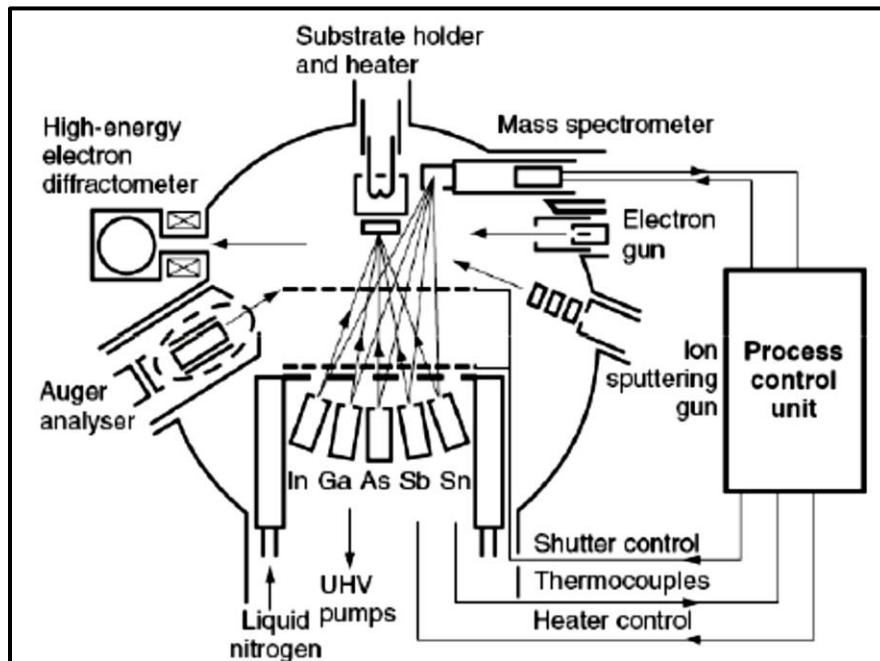
### 9.9 Methods for making 1-D and 2-D nanomaterials

- The production route for 1-D rod-like nanomaterials by liquidphase 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.



### 9.9.1 Molecular Beam Epitaxy (MBE)

A molecular beam epitaxy (MBE) machine is essentially an ultrahigh-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.



Schematic diagram of a molecular beam epitaxy thin film deposition System

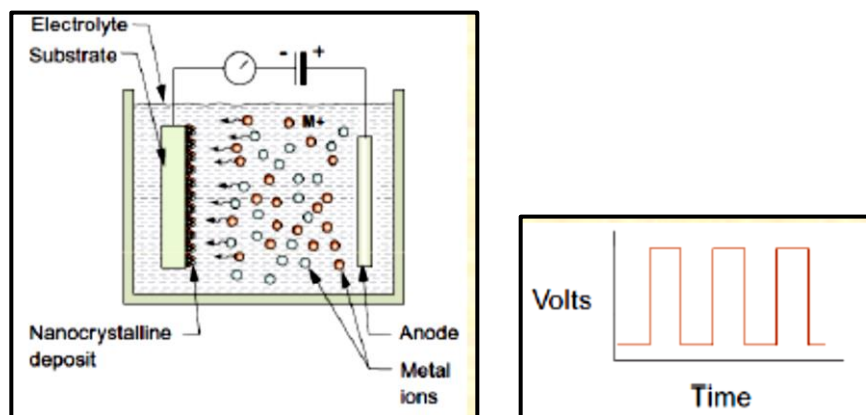
In solid-source MBE, ultra-pure elements such as gallium and arsenic are heated in separate quasi-Knudsen effusion cells until they begin to slowly evaporate. The evaporated elements then condense on the wafer, where they may react with each other. In the example of gallium and arsenic, singlecrystal gallium arsenide crystal is formed.

The term “beam” simply means that evaporated atoms do not interact with each other or any other vacuum chamber gases until they reach the wafer, due to the long mean free paths of the beams. The substrate is rotated to ensure even growth over its surface. By operating mechanical shutters in front of the cells, it is possible to control which semiconductor or metal is deposited.



## 9.10 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.



### 9.10.1 Electrodeposition and microelectronics

Electrodeposition (ED) is being exploited now to make complex 3D electrical interconnects in computer chips. The key concept is that Electrochemically fabricated flip-chip interconnects electrodeposited materials grow from the conductive substrate outward, and the geometry of the growth can be controlled using an insulating mask (so-called through mask electrodeposition).

### 9.10.2 Electrodeposition in microelectronics



The insulating mask need not have a straight line-of-sight path between the substrate and the electrolyte; even tortuous masks can be filled with materials, so long as the whole path through A ten level copper on-chip interconnect scheme of 90 nm CMOS node fabricated in low dielectric constant material. the mask is wetted with the ED electrolyte.

The resulting deposit is a high fidelity negative replica of the mask itself. Through-mask ED has been used extensively to pattern metals, semiconductors, and polymers on conductive substrates.

### **9.10.3 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).

### **9.11 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 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 nanometerscale pores in the protein. 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 twodimensional (2D) space groups built from chiral molecules. Moreover, they are



readily engineered through molecular biology, providing an attractive foundation for nanotechnology

## **9.12 Methods of nanomaterials production**

The following methods are used for the production of nanomaterials:

### **9.12.1 Electrospinning technology for Nano fiber production**

Nano fibres production has been achieved by use of the electrospinning technology to produce three dimensional, ultra-fine fibres with diameters in the range of a few nanometers (more typically 100 nm to 1 micron) and lengths up to kilometers. These nano fibres present unique properties such as extraordinarily high surface area per unit mass, very high porosity, tunable pore size, tunable surface properties, layer thinness, high permeability, low basic weight, ability to retain electrostatic charges and cost effectiveness among of others.

### **9.12.2 Nano particles by spraying**

Spraying drying has been found to be a suitable method that offers the advantage of drying and particle formation in a single step continuous and scalable process with general engineering possibilities [20]. Typically various particle properties such as particle size, bulk density and flow properties can be easily tuned through simple manipulation of process parameters or spray drier configuration [21]. Spray drying comprises atomization of feed into spray, spray-air contact, drying of spray and separation of dried product from the drying air.

### **9.12.3 Template synthesis- membrane based technology for generation of nano/micro materials**



The basic principles of templates synthesis is similar to that of producing components through the use of replication for example like making ice candies out of molds. This technique involves the deposition of materials within the pores of the membranes by either electrochemical or chemical (electroless) reduction of the appropriate metal ion.

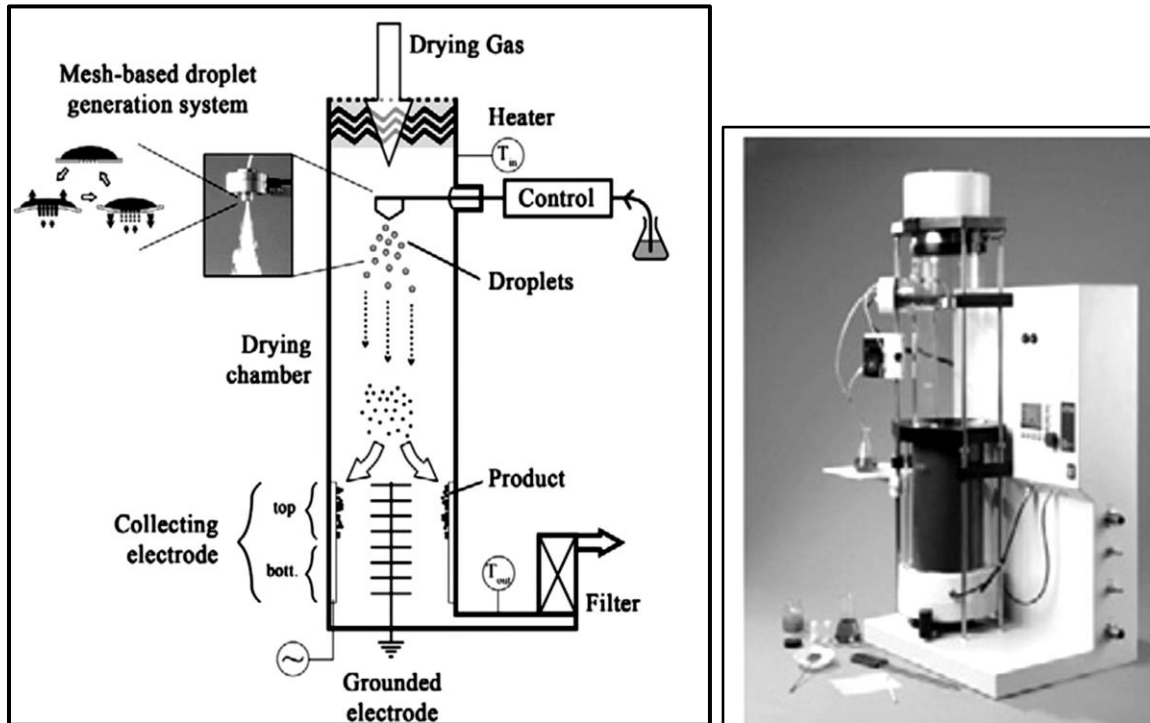


Figure.1: Nano Spray Dryer utilizes a vibrating mesh technology for fine droplets generation.



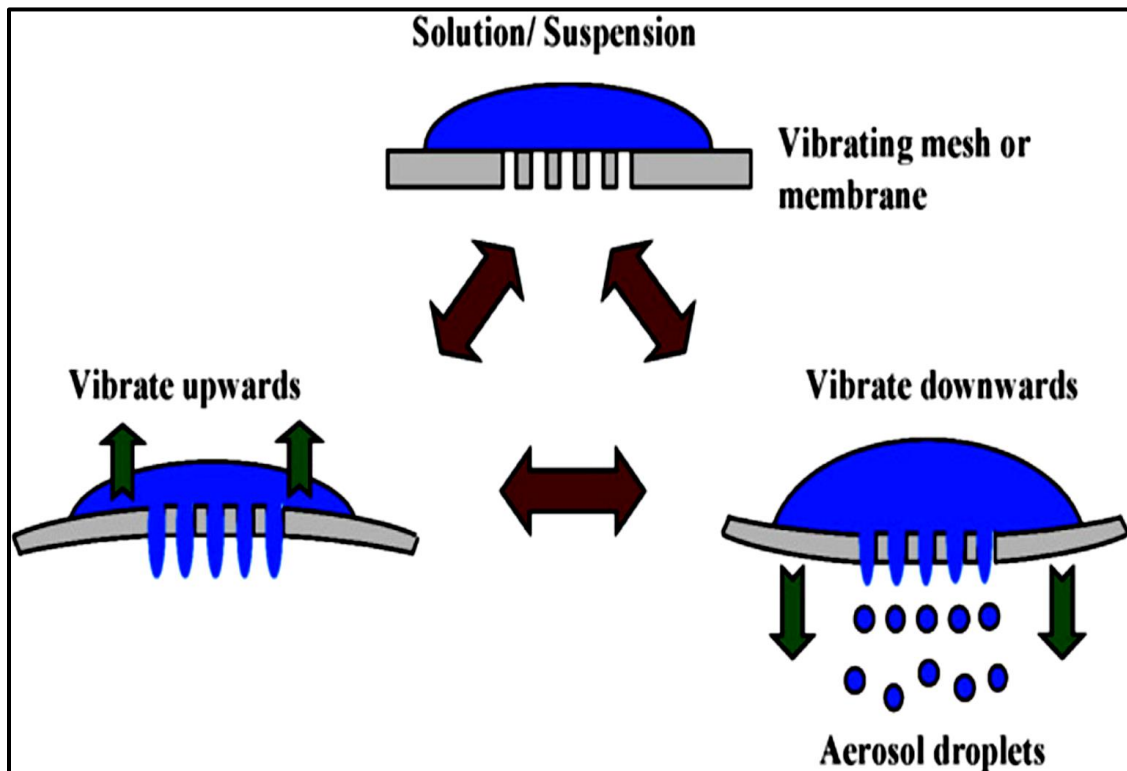


Figure.2: The functional principle of mesh vibration occurring at the piezo-electric driven spray head of the Nano Spray

#### 7.12.4 Laser nano manufacturing

Laser materials processing finds applications in cutting, welding, drilling, cleaning, additive manufacturing, surface modification and micromachining. It is known that in most cases, the feature size and the resolution of machining are above 1  $\mu\text{m}$ . One of the reasons for the limited resolution is the diffraction limit of the laser beams in the far field