LECTURES 10-11

Micro and Nano Materials Manufacturing Techniques (1)

7.1 Introduction

The term nanometer (nm) is one billionth of a meter. For comparison, a single human hair is about 80,000 nm wide, a red blood cell is approximately 7,000 nm wide and a water molecule is almost 0.3 nm across. **Nanoscience** as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale; and **nanotechnologies** as the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometer scale.

Technologies associated with this field aim towards the manufacture of improved quality products that are suitable for devices that are lighter, faster, more reliable, efficient and safer and more economical.

7.2 Reasons for Miniaturization

In general, the use of micro and nano-scale detection technologies is justified by:

(i) reducing the sensor element to the scale of the target species and hence providing a higher sensitivity,

(ii) reduced reagent volumes and associated costs,

(iii) reduced time to result due to small volumes resulting in higher effective concentrations,

(iv) amenability of portability and miniaturization of the entire system

(v) point-of-care diagnostic,

(vi) Multi-agent detection capability

(vii) Potential for use *in vitro* as well as *in vivo*

7.3 Classification of Nano Materials

Nano materials can be classified dimension wise into following categories:

- Nano rods, nano wires have dimension less than 100 nm.
- Tubes, fibers, platelets have dimensions less than 100 nm.
- Particles, quantum dots, hollow spheres have 0 or 3 Dimensions < 100 nm.

Nanostructure	Size	Example Material or Application
Clusters, nanocrystals, quantum dots	Radius: 1-10 nm	Insulators, semiconductors, metals, magnetic materials
Other nanoparticles	Radius: 1-100 nm	Ceramic oxides, Buckyballs
Nanowires	Diameter: 1-100 nm	Metals, semiconductors, oxides, sulfides, nitrides
Nanotubes	Diameter: 1-100 nm	Carbon, including fullerenes, layered chalcogenides

On the basis of phase composition, nano materials in different phases can be classified as,

- The nano material is called single phase solids. Crystalline, amorphous particles and layers are included in this class.
- Matrix composites, coated particles are included in multi-phase solids.
- Multi-phase systems of nano material include colloids, aero gels, Ferro fluids, etc.

7.4 Challenges in developing and designing Nano-based manufacturing

Some key challenges in the nano manufacture of materials include:

1) Nanostructured Material by Design

2) Manufacturing at the Nanoscale
3) Chemical-Biological-Radiological-Explosive Detection and Protection
4) Nanoscale Instrumentation and Metrology
5) Nano-Electronics, -Photonics and –Magnetics
6) Healthcare, Therapeutics, and Diagnostics
7) Efficient Energy Conversion and Storage
8) Micro craft and Robotics
9) Nanoscale Processes for Environmental Improvement

7.5 Applications of Nanotechnology

Automotive industry	**Chemical industry**	**Engineering**
• lightweight construction • painting (fillers, base coat, clear coat) • catalysts • tires (fillers) • sensors • Coatings for wind-screen and car bodies	• fillers for paint systems • coating systems based on nanocomposites • impregnation of papers • switchable adhesives • magnetic fluids	• wear protection for tools and machines (anti blocking coatings, scratch resistant coatings on plastic parts, etc.) • lubricant-free bearings
Electronic industry	**Construction**	**Medicine**
• data memory (MRAM, GMR-HD) • displays (OLED, FED) • laser diodes • glass fibres • optical switches • filters (IR-blocking) • conductive, antistatic coatings	• construction materials • thermal insulation • flame retardants • surface-functionalised building materials for wood, floors, stone, facades, tiles, roof tiles, etc. • facade coatings • groove mortar	• drug delivery systems • active agents • contrast medium • medical rapid tests • prostheses and implants • antimicrobial agents and coatings • agents in cancer therapy

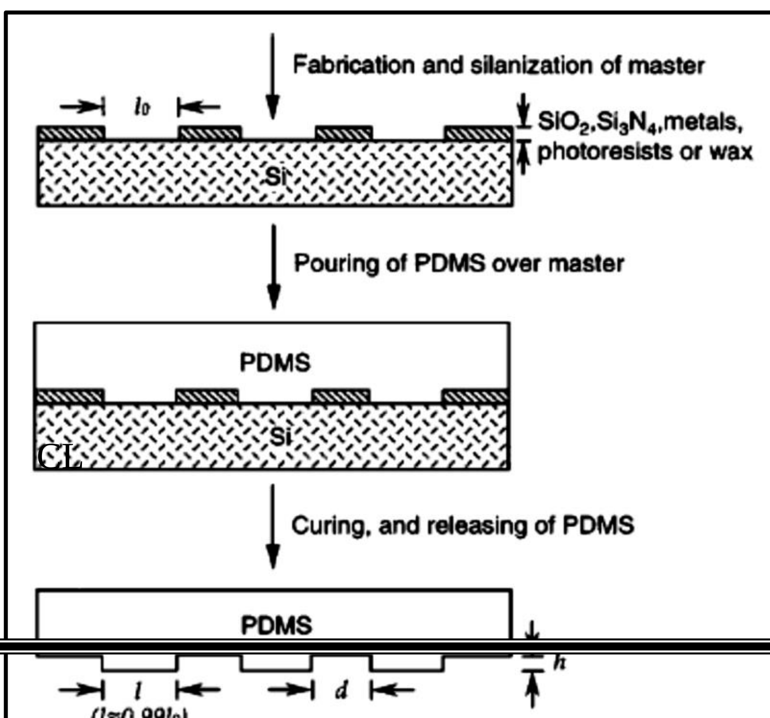
Textile/fabrics/non-wovens • surface-processed textiles • smart clothes	**Energy** • fuel cells • solar cells • batteries • capacitors	**Cosmetics** • sun protection • lipsticks • skin creams • tooth paste
Food and drinks • package materials • storage life sensors • additives • clarification of fruit juices	**Household** • ceramic coatings for irons • odors catalyst • cleaner for glass, ceramic, floor, windows	**Sports /outdoor** • ski wax • antifogging of glasses/goggles • antifouling coatings for ships/boats • reinforced tennis rackets and balls

7.6 Micro and Nano Devices Fabrication

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

7.6.1 Lithography

Lithography is a the most widely used form of which is photolithography, used in the IC industry for the production of chips. 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, strip resist and do process again and again.



Replication and Molding

• Master mold made from silicon, glass,
metal, SU-8

• Surface treatment of master

• Pour PDMS (mix, oligomer, and agent)

- Cure (~60C, 1 hr)
- Peel off PDMS structure
- Mold can be used again

Eventually, a 3-D structure is built up (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. Result: Multiple patterned layers of different materials.

7.6.1.1 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,

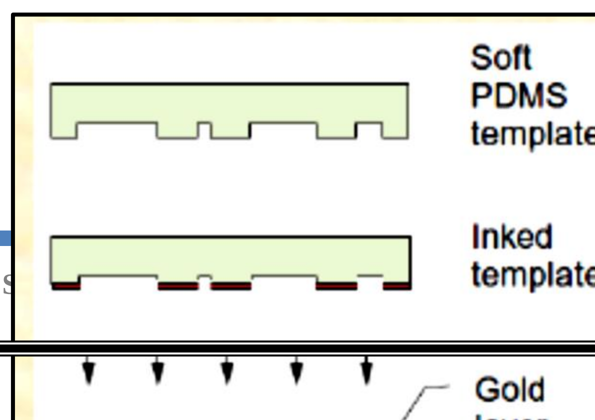
(2) masks need to be perfectly aligned with the pattern on the wafer,

(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.

7.6.2 Microcontact printing method

A chemical precursor to polydimethylsiloxane



(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.

7.6.3 Micro injection molding process

Since end of 60s' last century, with the booming of the semi-conductive materials processing technologies related to IC (Integrated Circuits) industry, parts or components in micro-scale which is hard to see with naked eyes stepped into the attention of scientists. Thereafter, the various functional micro systems were rapidly widely used in different areas, such as watch and camera industry, printer ink jet, information storage, sensors and transducers, micro-fluidic system, micro heat exchanger, micro reactor and so on. After impressive development, a new research scientific and engineering area was formed, named as Micro-Electronic-Mechanical systems (MEMs). Especially, in the last ten years, Micro optical electron system (MOEMS) and Bio- micro electron mechanical system (Bio-MEMS) played important roles in the Information Technology (IT) and Bio-Medical Engineering (BioM) fields.

Today's micro system is longing for innovative products which are small, light, more powerful, faster and cheaper to produce than present products. Micro injection molding technology is perfectly satisfied with such requests. It evaluated from conventional injection molding process and can realize large-scale production of micro parts with polymeric materials and ceramic/metal powders with polymeric bonders.

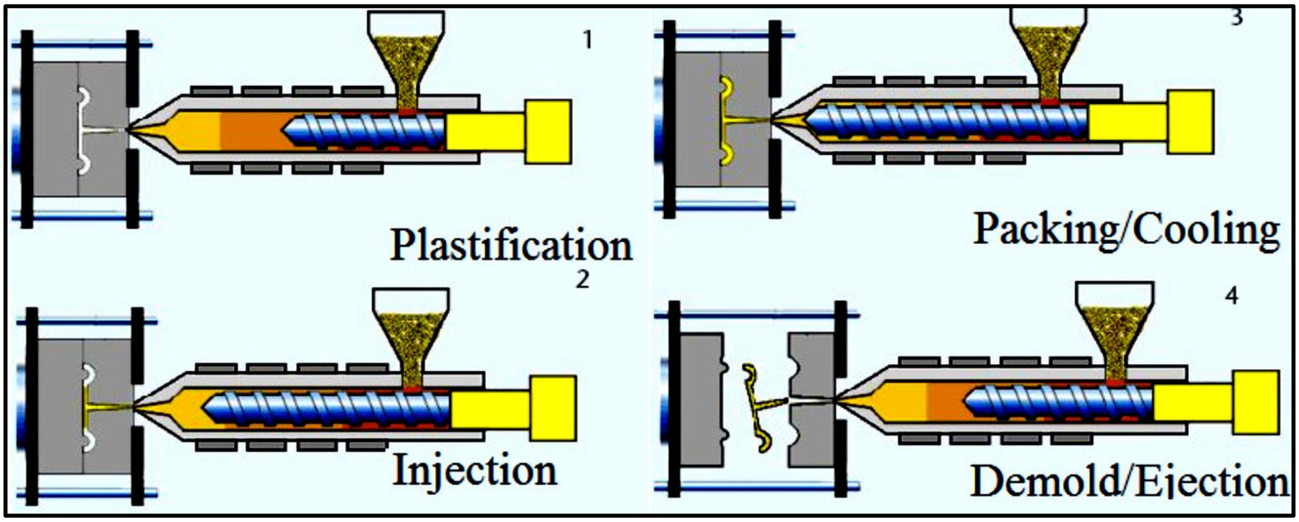


Figure 1-1. Processing cycle of conventional injection molding process

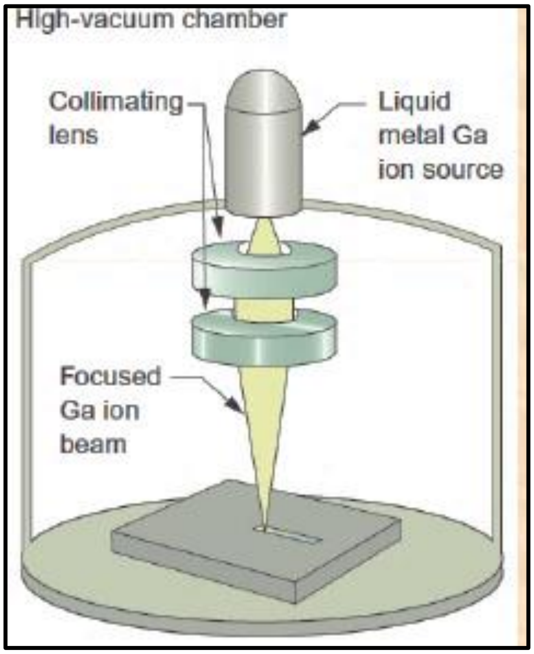
7.7. Micromachining methods

Mechanical processes are probably the most popular among the microprocesses in current use. Conventional machining operations such as turning, milling, grinding and drilling belong to this subdivision. Advances in the subsystems involved in macroscopic machining such as positioning, automation, numerical control, metrology and tools have made it possible to apply them in microfabrication.

7.7.1 Focused ion-beam (FIB) machining

FIB machining offers the greatest resolution, with the ability to make features as small as 20 nm, but it is very slow. 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 elaborate 3-D shapes. Secondary electrons are emitted when the gallium ions displace the surface atoms. These can be used to image the surface, allowing observation and control of the process as it takes place.



7.7.2 Milling processes

The mechanical production approach uses milling to crush microparticles. This approach is applied in producing metallic and ceramic nanomaterials. For metallic nanoparticles, for example, traditional source materials (such as metal oxides) are pulverized using high-energy ball mills. Such mills are equipped with grinding media composed of wolfram carbide or steel. Milling involves thermal stress and energy intensive.

7.7.3 Chemo-physical production processes

These methods are based on physicochemical principles of molecular or atomic self-organization. This approach produces selected, more complex structures from atoms or molecules, better controlling sizes, shapes and size ranges. It includes aerosol processes, precipitation reactions and sol-gel processes.

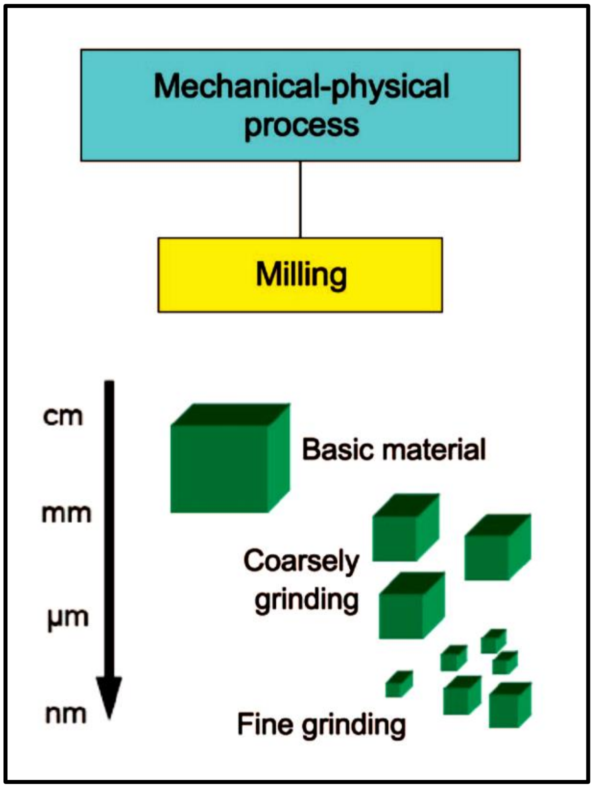


Figure 2: Overview of mechanical-Physical nanoparticle production processes

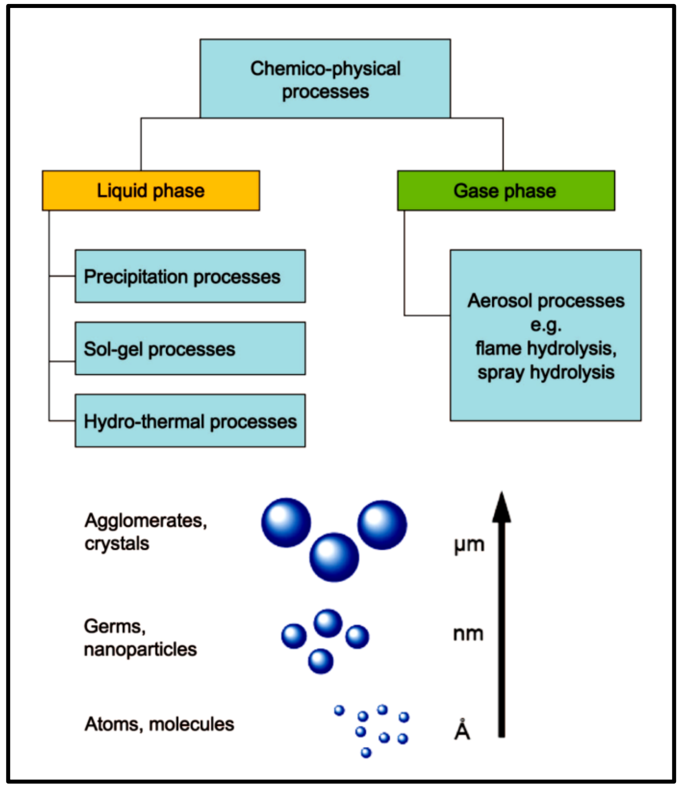


Figure 3: Chemo-physical processes in nanoparticle production

7.7.4 Micro-ultrasonic machining

Micro-USM is another mechanical microprocess having its origins in a traditional macroscopic process. It employs a tool and a mixture of a fluid (water or oil) with abrasive particles. The tool is vibrated at ultrasonic frequency and drives the abrasive to create accurately shaped cavities on the surface of the workpiece. The shape and size of the cavities depend on those of the tool. In micro-USM, microtools and fine abrasives are used, with which ±10 nm tolerance can be achieved.

7.7.5 Abrasive Jet Machining (AJM)

Abrasive Jet Machining is an operation where grains, with sizes less than 100 nm, impinge with high velocity on the workpiece surface whose material is removed by the impacts. This method is used for making accurate shallow holes in electronic components, and, with the use of masks, patterns on semiconductors. The process is fast and the equipment inexpensive.

7.5.7 Gas phase processes (aerosol processes)

Gas phase processes are among the most common industrial-scale technologies for producing nanomaterials in powder or film form. Nanoparticles are created from the gas phase by producing a vapor of the product material using chemical or physical means. The production of the initial nanoparticles, which can be in a liquid or solid state, takes place via homogeneous nucleation. Depending on the process, further particle growth involves condensation, chemical reaction(s) on the particle surface and/or coagulation processes (adhesion of two or more particles), as well as coalescence processes (particle fusion). Examples include processes in flame-, plasma-, laser- and hot wall reactors, yielding products such as fullerenes and carbon nanotubes. In flame reactors, nanoparticles are formed by the decomposition of source molecules in the flame at relatively high temperatures (about 1200–2200°C).