NANOTECHNOLOGY

5.1 Understanding Nanotechnology

"Nano" means very small. The nanometer scale is defined as 1 to 100mm. One nanometer is one billionth of metre (10^{-9}m). The size range is set normally to be minimum 1mm to avoid single atoms or very small groups of atoms being designated as nano objects. Therefore, nanoscience and nanotechnologies deal with at least clusters of atoms of 1mm size. The upper limit is normally 100mm but it is fluid limit. Often objects with greater dimensions (even 200mm) are defined nanomaterials. In fact, nanoscience is the study of materials that exhibit remarkable properties, functionality and phenomena due to the influence of small dimensions. According to the Royal Society and the Royal Academy of Engineering, "nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale". On the other hand, nanotechnologies are the design, characterization, production and application of structures, devices and systems which may help to control shape and size at nanometer scale.

Nanoscopic scale

Prefix	**Symbol**	**19^n**
Yotta	Y	10^{24}
Zetta	Z	10^{21}
exa	E	10^{18}
peta	P	10^{15}
tera	T	10^{12}
giga	G	10^{9}
mega	M	10^{6}
Kilo	k	10^{3}
lecto	h	10^{2}
deca	da	10^{1}
		10^{0}
deci	d	10^{-1}
centi	c	10^{-2}
milli	m	10^{-3}
micro	μ	10^{-6}
nano	n	10^{-9}
pico	p	10^{-12}
femto	f	10^{-15}
Atto	a	10^{-18}
Zepto	z	10^{-21}
Yocto	y	10^{-24}

There are various reasons why nanocience and nanotechnologies are so important and promising in materials, engineering and related sciences.

1. At nanoscale, properties of matter change, such as energy content. Properties like electrical conductivity, colour, strength and weight change. The metal can become a semiconductor or an insulator at nanoscale. This is possible due to quantum effects.

2. At nanoscale, nanomaterials can be fabricated atom by atom, with a process called bottom-up.

3. Nano materials have an increased surface-to-volume ratio compared to bulk materials. This has important consequences for all those processes that occur at a material surface, such as catalysis and detection.

Exceptional Properties of matter at nanoscale

- The mass of nanomaterials is extremely small and gravitational forces become negligible. Instead, electro-magnetic forces are dominant in determining the behaviour of atoms and molecules.

- For objects of very small mass, such as electrons, wavelike nature has a more pronounced effects. Thus, electrons exhibit wave behaviour and their position is represented by a wave functions.

- Nanomaterials exhibit quantum confinement, i.e. electrons are confined in space rather than move freely in bulk material.

- Molecules move due to their kinetic energy. This is called random molecular motion and is always present. At the macroscale this motion is very small compared to the sizes of the objects and thus it is not influential on how the objects move. At the nanoscale, however, these motions can be of the same scale as the size of the particles and thus have an important influence on how they behave, for example-Brownian Motion.

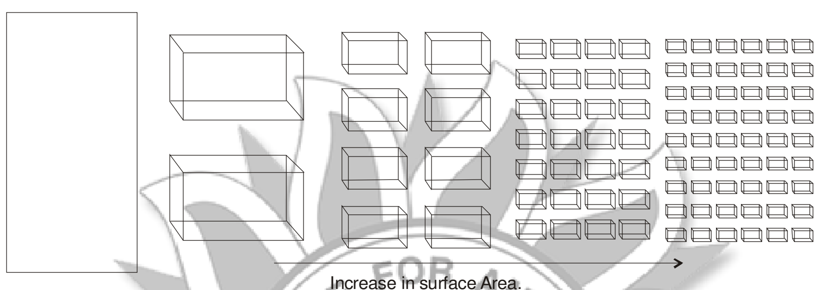


Figure: 5.1: Schematic drawing showing surface–to– volume ratio of nanomaterial

- One of the consequences is tunneling. Tunneling is the penetration of an electron into an energy region that is classically forbidden. It is a fundamental quantum effect and is used in a instrument called Scanning Tunnelling Microscope.

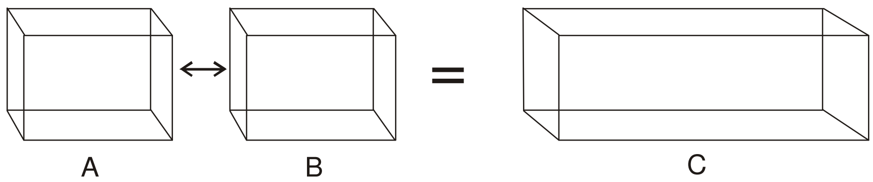
- Nanomaterials have an increased surface area. Surface-to-volume ratio determines reactivity. If a bulk material is subdivided into an ensemble of individual nanomaterials, the total volume remains the same, but the collective surface area is greatly increased (see figure 5.1) Nanomaterials have a significant proportion of atoms existing at the surface. This has a profound effect on reactions that occur at the surface such as catalysis and detection reactions and reactions that to be initiated require the physical adsorption of certain species at the materials surface.

- Nanomaterials show various types of bindings that are, intra molecular and inter molecular bonding because such materials form cluster of atoms. Intra molecular bonding that include ionic bonds, covalent bonds and metallic bonds. involve changes in the chemical structure of the molecules. On the other hand, inter molecular bonding do not involve changes in the chemical structure of the molecules. They include ion-ion and ion-dipole interactions, Vaan der Waals interactions, hydrogen bonds, hydrophobic interaction etc.

- Nanomaterials are inherently unstable therefore, there are various methods that nanomaterials adopt to minimize their inherent surface energy. One such method is agglomeration (See figure 5.2). Surface energy is an additive quantity. Nanoparticles have a strong intrinsic tendency to agglomerate. To avoid that surfactants can be used.

- Some nonmaterials exhibit exceptional electrical properties due to their unique structure, such as fullerenes and carbon nanotubes.

Figure: 5.2 Agglomeration



Surface energy of two separate cubes is higher than the surface energy of the two cubes agglomerated.

Fullerene

Fullerene is a molecule composed entirely of carbon. It is in the form of a hollow sphere, ellipsoid, tube and many other shapes. The first fullerene molecule was discovered in 1985 by Richard Smalley, Robert Curl, James Heath, Sean O' Brien and Harold Kroto at Rice University. This was named "Buckminster Fullerene (C_{60}) as a homage to Buckminster Fuller. It expounded the number of known carbon allotropes. Spherical fullerenes are also called buckyballs while cylindrical ones are known as buckytubes or, carbon nanotubes.

5.1 Development of Nanotechnology

Nanotechnology is the engineering of functional systems at the molecular scale. The concept is attributed to Nobel Prize winner Richard Feynman who envisioned the idea of building things from bottom-up with atomic precision. In 1959, Feynman wrote, "I want to build a billion tiny factories, models of each other, which are manufacturing simultaneously…… The principles of Physics, as far as I can see, do not speak against the possibility of maneuvering things atoms by atom. It is not on attempt to isolate any laws, it is something, in principle, that can be done, but in practice, it has not been done because we are two big."

Based on Feynman's vision of miniature factories using nanomachines to build complex products, advanced nanotechnology will make use of positionally-controlled mechanochemistry guided by molecular machine systems. Eric Drexler popularized the word 'nanotechnology' in the 1980s, however, it was first used by Nario Taniguchi in 1974. Drexler was talking about building machines on the scale of molecules, a few nanometers wide-motors, robot arms and even whole computers, far smaller than a cell. Drexler spent the next ten years describing and analyzing these devices. The development of nanotechnologies has been enabled by the invention of two analytic tools that have revolutionized the imaging of surfaces at nanoscale. These are Scanning Tunnelling Microscope (STM) and Atomic Force Microscope (AFM). Both are capable of imaging surface with atomic resolution (see details later in the chapter). In fact, STM is the first step in realizing Feynman's vision of atom by atom fabrication. In 2000s, the field of nanotechnology garnered scientific, political and commercial attention and commercialization of product has emerged.

Molecular Recognition

The term molecular recognition refers to the specific interaction between two or more molecules through non-covalent bonding. Such bonding includes hydrogen bonds Vander Waals interaction etc. The recognition event initiates behaviour such as replication in nucleic acids, immune response in antibodies and regulation in enzymes. Most studies of recognition in organic chemistry have been inspired by these biological phenomena. The molecules show complementarily with each other.

Over the period, two approaches to nanotechnology have been developed. In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. On the other hand, in the "top down" approach, nano objects are constructed from larger entities without atomic level control.

5.2 Characterization Methods

Characterization of nanomaterials refers to the use of external techniques to probe into the internal structure and properties of such materials. In general, two fundamental types of characterization methods exits-

1. Imaging by microscopy
2. Analysis by spectroscopy

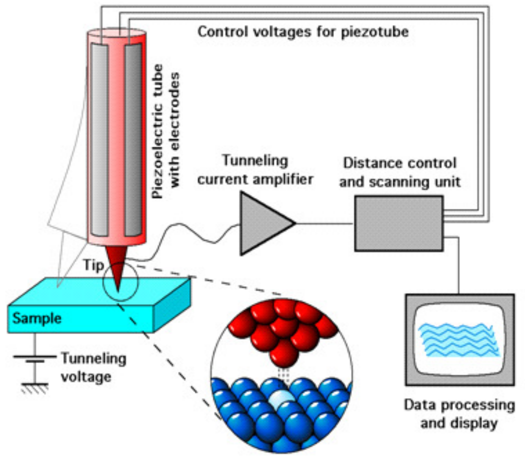
Microscopy

It is the technique of examining minute objects by an instrument called microscope which provides an enlarged image of an object. The oldest and the simplest microscope has been the optical microscope which uses visible light (an electromagnetic radiation) and a system of leases to magnify images of small samples. The resolution limit of an optical microscope is imposed by the wavelength of visible light (400-700nm). For a better resolution, electron microscopes are used which use electron beams to illuminate instead of light. These have higher magnifications of up to two million times. There are different types of electron microscopes, such as the Scanning Electron Microscope (SEM) or, Transmission Electron Microscope (TEM). Conceptually, these microscopes are similar to an optical microscope as they use a radiation to visualize a sample. However, the invention of Scanning Tunnelling Microscope (STM) by Binning and Heinrich Rohner in 1986 revolutionised the characterization of nanomaterials.

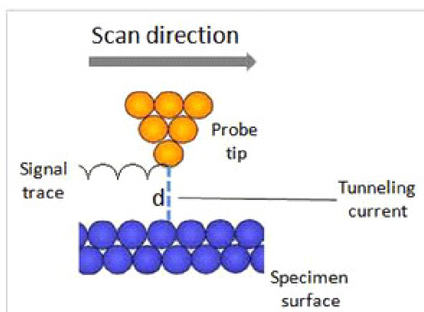
Scanning Tunnelling Microscope (STM)

According to Binning, when a small metal tip is placed very close to a conducting surface, but not actually touching, a bias between the two can allow electrons to tunnel through the vacuum between them. This creates a "tunneling current". It can be measured as it is a function of electron density on the surface. Electron density is the probability of finding an electron in a particular place. There is high electron density around the atoms and bonds in molecules. Variations in tunneling current as the probe passes over the surface are translated into an image. Thus STM can create detailed 3D images of a sampl-e with atomic resolution.

Operationally, STM is a scanning probe microscopy SPM) technique. It provides images of surface by scanning the surface line by line with a probe. ***(Fig.5.3 Schematic representation of STM scanning over a surface)***



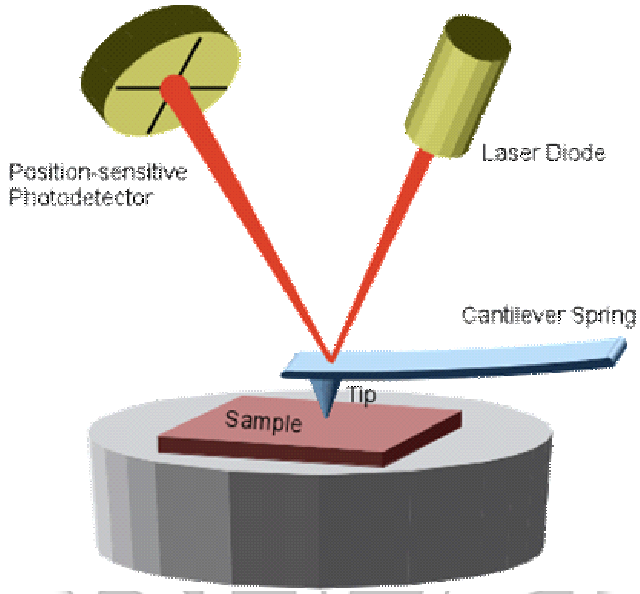
The probe is a thin needle called 'tip' made of conducting material, i.e. metal, generally tungsten. The precise movement of the tip is controlled by piezometer. When the conducting tip is brought very close to the surface, at a distance of about 0.1 nm, it can induce the tunneling current. By applying a constant tunnel current, the tip of the probe is kept at a specific distance above the surface. The movement of the tip can be transformed into a coloured height map of the surface. This provides very accurate representation of the surface.



Schematic representation of the signal trace as a tip of an STM probe scans a surface.

Atomic Force Microscope (AFM)

Atomic Force Microscope was developed specifically to overcome the intrinsic limitations of the STM, which is not suitable for imaging surface coated with biological entities such as DNA or proteins. AFM is also a kind of scanning probe microscope which measures the interaction force (attractive or repulsive) between the probe and the surface. The solid probe is located at the end of a very flexible cantilever; an optical system detects the deflection of a laser beam that bounces off the reflective back of the cantilever, thus reporting on cantilever fluctuations, which are proportional to the applied force. The probe is continuously moved on the surface and the cantilever deflection is constantly monitored. A feedback loop continuously changes the height of the probe on the surface in order to keep the applied force constant. The vertical movement of the probe is recorded to create a topographic map of the surface under study.



Operation principle of an AFM

Piezoelectric elements that facilitate tiny but accurate and precise movements on command enable the very precise scanning. In more advanced versions, currents can be passed through the tip to probe the electrical conductivity or transport of the underlying surface.

According to the nature of the motion of the tip, three modes of AFM operation have been identified.

In contact mode, the tip is dragged across the surface of the sample and the contours of the surface are measured either using the deflection of the cantilever directly or, more commonly, using the feedback signal required to keep the cantilever at a constant position.

In tapping mode, the cantilever is driven to oscillate up and down as its resonance frequency by a small piezoelectric elements is mounted in the AFM tip holder. The image is produced by imaging the force of the intermittent contacts of the tip with the surface of the sample.

In the non-contact mode, the tip of the cantilever does not come into contact with the sample surface, instead it is oscillated at either its resonant frequency or just above. The Vander Waals force tends to decrease the resonant frequency which, combined with the feedback loop system, maintains a constant oscillation amplitude or frequency by adjusting the average tip-to-sample distance. Measuring this distance allows the scanning software to construct a topographic image of the sample surface.

Spectroscopy

Spectroscopy is the branch of science that is concerned with the investigation and measurement of spectra produced when matter interacts with or emits electromagnetic radiation. The following spectroscopy methods may be used in the characterization of nanomaterials.

1. **X-ray method**

Small-angle X-ray scattering analysis (SAXS) is used in the characterization of nanomaterials. Like X-ray diffraction (XRD) it is also based on the principle of X-ray scattering. However, while XRD is useful to study bulk materials, SAXS is used to analyze particle size of the order of 1-100 nm. This can be precisely analyzed.

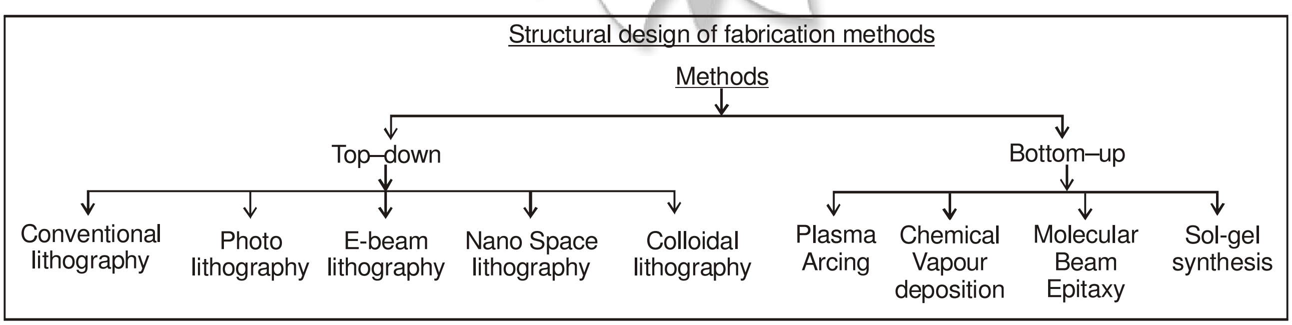
2. **UV visible Plasmon Absorption & Emission**

One of the distinguishing properties of metal nanoparticles is their optical properties. This is due to an effect called Localized Surface Plasmon Resonance (LSPR). In simpler words, when light hits a metal surface of any size some of the light wave propagates along the metal surface giving rise to surface plasmons - a group of surface conduction electrons that propagate in a direction parallel to the metal-vacuum interface. One of the consequences of the LSPR effect in metal nanoparticles is that they have very strong visible absorption due to the resonant coherent, colloids of metal nanoparticles such as gold or silver can display colours like red, purple or orange depending on the shape, size and the surrounding medium of nanoparticles.

The absorption bond is due to electron confined at the particle surface that collectively oscillate at a specific frequency. This is commonly called surface Plasmon resonance frequency. Absorption can be in the visible and UV area of the spectrum.

5.4 Fabrication Methods

Either top-down or bottom-up methods may be used for fabricating nano materials. In the top-down method, nanomaterials are derived from a bulk substrate and obtained by progressive removal of material, until the desired nanomaterial is obtained. On the other hand, in the bottom-up method gradual assembling of atomic or molecular precursors is done until the desired structure is formed.



Top-down method

1. **Conventional Lithography**

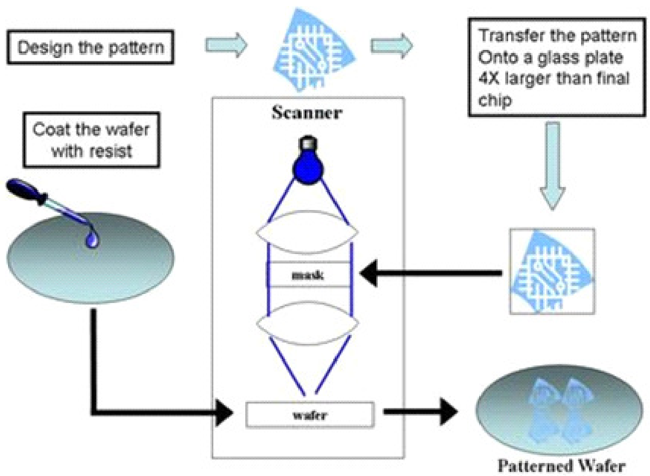
As a technique of a nano fabrication, lithography includes all such techniques that share the principles of transferring an image from a mask to a receiving substrate. The process is completed in three steps:

1. Coating the substrate (silicon wafer or glass) with a sensitive polymer layer called "resist".

2. Exposing the resist to light, electrons or ion beams.

3. Developing the resist to light image with a suitable chemical (developer).

In conventional microfabrication used in semiconductor industry, the next step after lithography is the pattern transfer from the resist to the underlying substrate. A few transfer techniques like chemical etching and dry plasma etching may be used. Conventional lithography may be of two types.



Etching

It is a process of using strong acid or mordant to cut into the unprotected parts of a metal surface to create a design in the metal.***Chemical etching*** is a process in which the cutting areas are bathed with a corrosive chemical called etchant, which reacts with the material in the area to be cut and causes the solid material to be dissolved, e.g. Potassium hydroxide (KOH) is used as an etchant.On the other hand, ***dry Plasma etching*** is an absolute chemical etch process (chemical dry etching, CDE). In this process the substrate (water surface) is not damaged by accelerated ions.In one of the types of CDE reactor (Fig. 5.6) plasma is ignited at high frequency of 2.45GHz. In the region of gas discharge there are various particles which are radicals. These radicals are natural atoms or molecules with an unsaturated electron, hence they are very reactive.

Films that can be etched by this process include

Silicon : $Si + 4F \rightarrow SiF_4$

Silicon dioxide : $SiO_2 + 4F$ $SiF_4 + O_2$

Silicon nitride : $Si3N_4 + 12F$ $3SiF_4 + 2N_2$