# NANOTECHNOLOGY—
# AN INTRODUCTION

**1**

## Learning Objectives

After going through this chapter, the reader will be able to

- trace the origin of nanoscience and technology
- learn about the efforts taken towards miniaturization of devices and systems, particularly in the fields of integrated circuits and computer technology that prepared the ground to embark upon research and development programmes in science and technology of the small world
- have a glimpse of Richard Feynman's 'big vision of the small world'
- learn about the advances in the field of imaging technologies such as optical, electron, and atomic force microscopy, NMR imaging (MRI), and X-ray and electron diffraction methods in determination of the physical and electronic structures of atomic clusters/nanostructures, setting the stage for the arrival of nanotechnology in the 1980s
- understand the important role played by the development of scanning probe microscopes—particularly the use of scanning tunneling microscopes—in providing atom-by-atom handling capability in the assembly of nanostructures and devices
- learn about the position of nanometre scale (nanoscale) in the scheme of different scales and form an idea about the relative size of nanosize objects
- appreciate the multidisciplinary nature of nanotechnology that embraces all the branches of science and technology
- know that the properties of nanoscale particles and structures show dependence on size and dimensions, with high surface-to-volume ratio
- realize that quantum mechanics is the key to understanding the behaviour of nanosize structures, devices, and machines
- learn about the existence of nanostructures in nature, both living and non-living
- know that nanomaterials were already in use for ages
- have a glimpse of the prospects of nanotechnology

## 1.1 INTRODUCTION

The word 'nano' is derived from the Greek word *nanos* or Latin word *nanus*, meaning 'dwarf'. It qualifies objects of matter having at least one physical dimension in the range 1–100 nanometres, as nanoscale objects. Here, one nanometre, abbreviated as nm, refers to a billionth of a metre, that is, $10^{-9}$ metre.

*Such nanoscale objects of matter with varying [sizes]*
*as nanoparticles, nanomaterials, or nanostructures.*

*Norio*
*Taniguchi*

• The branch of science *[dealing with]* *nature and behaviour of nanomaterials* *[defines experimental observations and]* *formulation of general laws* *[studying]* their properties is called nanoscience. *Norio Taniguchi* pro*[fessor of Tokyo]* University, coined the term *nanotechnology* *for the first time in 1974* *[to describe]* semiconductor processes such as thin-film *deposition* and ion-beam milling exhibiting characteristic control on the order of *a nanometre.* Nanotechnology cuts across all disciplines, borrowing liberally from physics, chemistry, material science, and biology, and is truly multidisciplinary in nature, as shown in Fig. 1.1. Based on the fundamental research and understanding of nanomaterials, nanotechnology enables development of products with possible practical applications employing nanostructures.
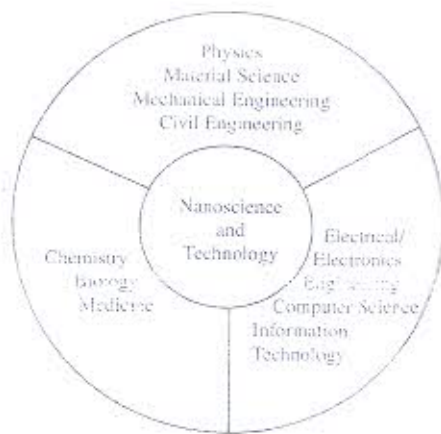


FIG. 1.1   Various disciplines engaged in research and development in nanotechnology

Scientists and technologists have always been fascinated and are working tirelessly to make novel and improved devices as a symbol of the continuous progress of mankind, in terms of their size, performance, and cost. To achieve this goal, they have laid major emphasis on the miniaturization of the devices and implements, which has been particularly useful in the field of electronics. The bulky vacuum tubes were replaced by discrete semiconductor junction transistors, which in turn, gave way to integrated circuits. The bipolar integrated circuits have been substituted by low power, economic, metal-oxide semiconductor (MOS) technology. Then, microelectromechanical systems (MEMS), with devices and machines on the micron to millimetre scale, were developed in the last three decades. In a quick succession to MEMS technology, nanotechnology has opened new avenues for fabrication of devices and systems on the nanoscale with high sensitivity and frequency response in the range of gigahertz and beyond.

## 1.2 HISTORICAL PERSPECTIVES

The emergence of nanotechnology is based on the fundamentals of quantum mechanics and other scientific and technological advances [...]

[...] and more. Even today, microwave vacuum tubes form a part of the high [frequency] communication systems such as mobile phones, Wi-Fi, radar, and satellite transmission. This era has provided sophisticated tools and techniques for investigating the atomic structure of solids such as X-ray, electron, and neutron crystallography and imaging techniques such as scanning probe electron and atomic force microscopes, making it possible to image down to the atomic level. These tools and techniques form the basic necessity for imaging and characterization of nanostructures and devices. They are discussed in the following sections.

### 1.2.1 Vacuum Electron Tube

Developments in the field of electronics beginning from the late 19th century have played the most dominant role in the rapid progress of science and technology. The invention of the vacuum tube, an active component of electronic circuits, was crucial to the initial growth of electronics and was the first major landmark in the history of electronics. The vacuum tube, consisting of two or more electrodes vacuum-sealed in a thin transparent glass or metal–ceramic container, is essentially based on thermionic emission of electrons, and is used in electronic circuits to control the flow of electrons between electrodes.

The thermionic emission, later used in making vacuum tubes, was first observed by Frederick Guthrie in 1873. He observed that the negatively charged red-hot iron sphere was getting discharged, but the same effect did not happen if the sphere was positively charged. Thomas Edison took the next step in 1883 while developing the incandescent electric bulb. He faced the problem of the glass casing of the electric bulbs becoming blackened, making their lives short. It was known to him that the particles leaving the hot element were negatively charged, which on striking the glass caused blackening. He, therefore, introduced a second element with positive polarity to attract the negative particles to get rid of the problem and observed the flow of current between the hot element and the positive electrode in the circuit. However, on reversing the potentials, he noticed that this did not happen. Though fascinated by the effect, Edison could not make any practical use of the effect and it was later termed as the *Edison effect.* Subsequent to identification of the electron by J.J. Thomson, Owen W. Richardson further studied the phenomenon of electron ejection from red-hot metals, terming it the *thermionic emission*, thus formulating the law of thermionic emission in 1901.

John A. Fleming was the first to transform the observation of the Edison effect into a practical device in 1901. By then it was known that the charged particles emitted by the hot filament were electrons, which were attracted by positive electrodes. Fleming observed that when an alternating current with frequency 80–100 Hz was passed through the bulb, only half cycle was passed, that is, it was rectified producing direct current. He called the device *oscillating valve* in analogy to the valve in a pump that allows water or gas to flow only in one direction. This was the first electronic rectifier diode and was known as *Fleming valve.* The [...]

② Nanomaterial

Engineered. — carbon black ( form of paracrystalline carbon that has a high surface-area-to-vol. ratio

carbon black is widely used as a model compound for diesel soot for ~~titanium dioxide~~ diesel oxidation experiments.

carbon black is mainly used as a reinforcing filler in tires & other rubber products. In plastics, paints and inks, carbon black is used as a color pigment

(carcinogenic - carbon)

Titanium dioxide — ultrafine ($TiO_2$) is used in sunscreens due to its ability to block UV radiation while remaining transparent on the skin.

— ultrafine $TiO_2$ is used in housing & construction as an additive to paints, plastics, cements, windows, tiles.

Incidental — vehicle engine exhausts, welding fumes combustion processes from domestic solid fuel heating & cooking.

ultrafine particles (UFP) — by product printer toner & automobile exhaust

medical & technology field
( Diagnostic imaging & novel drug delivery system

Natural — The structure of foraminifera ( mainly chalk viruses ( protein, capsid ), the wax crystals covering a lotus or nasturtium leaf, spider & spider-mite silk, some butterfly wing scales, natural colloids ( milk, blood ) horny material ( skin, claws, beaks, feathers, horns, hair ) Pape

classical mechanics deals with the motion of objects under forces or their own momentum.

Quantum mechanics deals with the behaviour of objects at the microscopic level where matter & energy start to mathematically coverage because both can be observed to have wave-like behaviour at the level of planck's constant.

$(F = ma)$
Newton second law

schrödinger eqⁿ
matrix mechanics
werner Heisenberg
- path integral formulat

$$i\hbar \frac{\partial}{\partial t} \left| \psi(r,t) \right\rangle = \hat{H} \left| \psi(r,t) \right\rangle$$

$i$ = imaginary unit
$\hbar$ = planck constant = $\frac{h}{2\pi}$
$\psi$ = Greek letter psi
$r$ & $t$ = position vector & time
$\hat{H}$ = Hamiltonian operator.

(wavefunt

scale representing them is known as 'nanoscale'. Thus, the lower part of the microscopic/mesoscopic scale below 100 nm is now distinctly designated as the 'nanoscale'. The three sizes of scales, that is, macroscopic scale (down to 10 μm), microscopic scale (10 μm down to 0.1 nm), and nanoscale (100 nm–0.1 nm) are shown in Fig. 1.4.
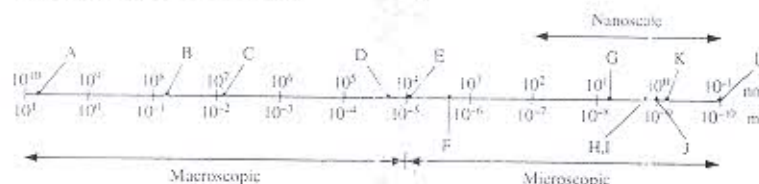


FIG. 1.4 Material objects on macroscopic, microscopic, and nanometre scales, indicated on the line in nanometres (above) and in metres (below). The nanometer scale (0.1–100 nm) is shown forming a part of microscopic scale.

In order to form an idea about the large difference in the sizes of worldly objects involved, they are represented by the dots on the scale for comparison and marked by alphabets A, B, C, D, etc. The relative sizes of these objects with respect to the hydrogen atom (diameter $1 \times 10^{-10}$ m or 0.1 nm) are given in the last column of Table 1.3. A–D and E–L belong to macroscale and microscale, respectively. Objects G–L are common to both microscale and nanoscale. Our sun is nearly a perfect sphere with a diameter of about 1,392 million km, which is $1.392 \times ten$ quintillion times larger than the hydrogen atom. The figure quintillion represents $10^{18}$.

Table 1.3 Comparison of the sizes of different objects to that of the hydrogen atom

| Serial alphabet | Object | Size | | Size relative to hydrogen atom (times) |
|---|---|---|---|---|
| | | metre (m) | m/cm/mm/μm/nm | |
| A | Height of Indian male | 1.66 | 1.66 m | $1.66 \times ten$ billion |
| B | Cricket ball | $7.2 \times 10^{-2}$ | 7.2 cm | $7.2 \times$ hundred million |
| C | House fly | $8.0 \times 10^{-3}$ | 3.0 mm | $8.0 \times ten$ million |
| D | Human hair | $2.0 \times 10^{-5}$ | 20.0 μm | $2.0 \times$ hundred thousand |
| E | Red blood cell (RBC) | $9.0 \times 10^{-6}$ | 9.0 μm | $9.0 \times ten$ thousand |
| F | Tuberculoses bacillus length | $2.0 \times 10^{-6}$ | 2.0 μm | $2.0 \times ten$ thousand |
| G | Quantum dot | $5.0 \times 10^{-9}$ | 5.0 nm | fifty |
| H | DNA helix diameter | $2.0 \times 10^{-9}$ | 2.0 nm | twenty |
| I | Nanotube diameter | $2.0 \times 10^{-9}$ | 2.0 nm | twenty |
| J | Bucky ball | $1.0 \times 10^{-9}$ | 1.0 nm | ten |
| K | Amino acid molecule | $8.0 \times 10^{-10}$ | 0.8 nm | eight |
| L | Hydrogen atom | $1.0 \times 10^{-10}$ | 0.1 nm | one |

$cm = 10^{-2}$ m, $mm = 10^{-3}$ m, $\mu m = 10^{-6}$ m, and $nm = 10^{-9}$ m

Some of these objects lying on the three different scales are shown in Fig. 1.5. Since only the objects larger than 10 μm are visible to the naked eye, it forms

the lower limit of the macroscopic scale. The conventional microscopic scale (10–0.0001 μm) has been split into microscopic scale (10–0.1 μm) and nanoscale (100–0.1 nm) scales, with transition at 0.1 μm (100 nm).



| Macro world | Man | Fly | MEMS gear | Human hair |
|---|---|---|---|---|
| (Lower limit 10 μm) | 1.66 m | 10 mm | 80 μm | Width 15–180 μm |
| Micro world (10–0.1 μm) [10–0.0001 μm as per definition] | Red blood cell 9 μm | E-coli bacteria 9 μm long | | Visible spectra 0.4–0.7 μm |
| | DNA | Nanotube | Virus | Buckyball | H-atom |
| Nano world (100–0.1 nm) | 2 nm wide | 2 nm wide | 50 nm | 1.0 nm | 0.1 nm |

FIG. 1.5 Different material objects on macroscopic, microscopic, and nanometre scales

## 1.4 BIG VISION FOR THE SMALL WORLD

The recent origin of nanoscience and technology can be traced back to the predictions made by Richard P. Feynman, one of the greatest scientific geniuses of the 20th century. He demonstrated that there is scope to decrease the size of things in a practical way (what is possible according to the laws of physics). He envisioned that small structures could be formed in the future by arranging the atoms one by one, in the way we want. He was very confident and speculated that if we can have some control on the arrangement of things at a small scale, we will get an enormously greater range of i) possible properties that substances can have, and ii) different things that we can do. He thought about building electrical circuits on a small scale (nanoscale) that work at higher frequencies due to reduced transit time of the carriers in smaller components, resulting in very low time constant of the circuit. In addition, he envisioned that as we get to a very, very, small world, for example, a circuit consisting of a few atoms, this group of atoms on a small scale (read: the nanoparticles), forms an entirely new system that obeys the laws of quantum mechanics. By working with different laws, we can do different things involving quantized energy levels, interaction of quantized spins (values in multiples of ½), etc.

Table 1.1 (contd.)

| Discovery/Invention/Contributions | Nobel Prize winner(s) | Year |
|---|---|---|
| Discovery of fullerenes | Robert F Curl Jr, Harold W. Kroto, and Richard E. Smalley | 1996 |
| Discovery of superfluidity in helium-3 | David M. Lee, Douglas D. Osheroff, and Robert C. Richardson | 1996 |
| Discovery of a new form of quantum fluid with fractionally charged excitations | R.B. Laughlin, H.L. Störmer, and D.C. Tsui | 1998 |
| Developing semiconductor heterostructures used in high-speed- and opto-electronics | Zhores I. Alferov and H. Kroemer | 2000 |
| Basic work on information and communication technology inventing of the integrated circuit | Jack S. Kilby | 2000 |
| The achievement of Bose–Einstein condensation in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates | Eric C. Cornell, Wolfgang Ketterle, and Carl E. Wieman | 2001 |
| Pioneering contributions to the theory of superconductors and superfluids | Alexei A. Abrikosov, Vitaly L. Ginzburg, and Anthony J. Leggett | 2003 |
| Contribution to the quantum theory of optical coherence | Roy J. Glaube, | 2005 |
| Discovery of giant magnetoresistance | Albert Fert and Peter Grünberg | 2007 |
| Ground-breaking experiments regarding the two-dimensional material grapheme | Andre Geim and Konstantin Novoselov | 2010 |
| Ground-breaking experimental methods that enable measuring and manipulation of individual quantum systems | Serge Haroche and David J. Wineland | 2012 |

## 1.3 PHYSICAL SIZE SCALES ■

Depending upon how many physical dimensions of nanostructures lie within the nanoscale, and consequently, degree(s) of charge carrier confinement, they are further classified into three categories—one-dimensional quantum wells, two-dimensional quantum wires, and three-dimensional quantum dots nanostructures—that will be discussed in detail in Chapter 3. Conversely, the degree(s) of free movement of charge carriers in a nanoparticle will be the same as the number of physical dimensions of size larger than 100nm. For example, a quantum well has one degree of carrier confinement, and two degrees of free carrier movement, and so on.

In order to visualize the size-scale of nanomaterials with respect to the vast size variation of objects existing in the universe, we should look at the different size-scales in use, prior to the formal arrival of nanomaterials in the late 1980s. In a broader sense, material objects can be represented on two size-scales, leaving aside the astronomical and subatomic scales on the two extremes, namely, macroscopic and microscopic. The macroscopic scale refers to the large objects visible to the

naked eye. The lower size limit of these objects, which are visible to the naked eye is around 10 μm (Symbol μ stands for factor micro = $10^{-6}$, m for metre, and μm normally called micron, being a millionth of a metre). Thus, all objects larger than ten micron fall within the macroscopic scale, such as the height of a human being, the size of a tennis ball, a house fly, and a human hair. The human hair's thickness lies in the range of 15–180 μm, with the lower side being close to the visibility limit of the unaided eye. All the macroscopic objects obey the laws of classical mechanics characterized with average or bulk properties. Different factors used in scientific notations are given in Table 1.2

Table 1.2 Factors used in scientific notation to express small and large numbers in metric system

| Prefix (symbol) | Factor | Name | Prefix (symbol) | Factor | Name |
|---|---|---|---|---|---|
| deca (da) | $10^1$ | ten | deci (d) | $10^{-1}$ | Tenth |
| hecto (h) | $10^2$ | hundred | centi (c) | $10^{-2}$ | hundredth |
| kilo (k) | $10^3$ | thousand | milli (m) | $10^{-3}$ | thousandth |
| mega (M) | $10^6$ | million | micro (μ) | $10^{-6}$ | millionth |
| giga (G) | $10^9$ | billion | nano (n) | $10^{-9}$ | billionth |
| tera (T) | $10^{12}$ | trillion | pico (p) | $10^{-12}$ | trillionth |
| peta (P) | $10^{15}$ | quadrillion | femto (f) | $10^{-15}$ | quadrillionth |
| exa (E) | $10^{18}$ | quintillion | atto (a) | $10^{-18}$ | quintillionth |
| zetta (Z) | $10^{21}$ | sextillion | zepto (z) | $10^{-21}$ | sextillionth |
| yotto (Y) | $10^{24}$ | septillion | yocto (y) | $10^{-24}$ | septillionth |

The objects that are smaller in size than the eye's visibility limit and that require a microscope to be detected or observed clearly, down to individual atoms, fall within the microscopic scale. Presently, electron microscopes are capable of imaging even the individual atoms. The scanning-probe-type electron microscopes, particularly, the atomic force microscope (AFM) and scanning tunnel microscope (STM), are used in scientific investigations to image objects as small in size as that of an atom. Thus, all objects with size variation between 10 μm and an individual hydrogen atom of 0.1 nm may be considered to lie on the microscopic scale. As the size of objects decreases, they continue to obey the laws of classical mechanics with average/bulk properties, independent of particle size. The number of atoms on the surface of such particles is quite negligible, as compared to the number of atoms lying inside the particle, the bulk properties being dominant. As the particle size approaches a sub-micron limit of about 0.1 μm (100 nm), a transition occurs in material properties, shifting their size-independent classical behaviour to size-dependent quantum-mechanical behaviour. The surface-to-volume ratio of these particles increases with decrease in size, and their surface properties start dominating the bulk properties. This amounts to increase in the number of atoms on the surface as compared to those inside the particle. Obeying quantum mechanical laws would mean that they possess discrete energy states like those of atoms or smaller molecules. These material particles are called 'nanoparticles' and the

Nano particles / Nano structures

particles, objects or devices with size in the range 0.1 - 100 nm are called nanostructures or nanoparticles.

Ex Nano structure our own body is a perfect example of a nano-structured material.

nanoparticles - Titanium dioxide metal, dielectric & semiconductor

Nanomaterial - CNT, nanoparticles metal rubber, quantum dots, nanopores

Nanoscale - scale of length that is used in measurement and characterization of nanoparticles in units of $10^{-9}$ m or nm spanning the range 0.1 - 100 nm

* __Macroscopic scale__ refers to the Large objects visible to the __unaided__ naked eye. The lower size limit of these objects visible to the naked eye is around 10 micron

*without them*

* Ex - ht. of a human being, the size of a tennis ball, a house fly and a human hair.

* All the macroscopic objects obey the laws of classical Mechanics characterized with avg. or bulk properties! (projectile motion, colors of rainbow

** objects that are smaller in size than the eye's visibility limit and that require a microscope to detect or observe them, down to individual atoms, fall on the microscopic scale which also encompasses the nanoscale.

* Today, electron microscopes are capable of imaging even individual atoms.

- obey the laws of quantum mechanics (jumping from the roof of 1 building onto another)

Nanoscale Properties

Mechanical - Increase in hardness and strength of metal & alloys, enhanced ductility, toughness and form ability of ceramics, super strength and super plasticity

Electrical - Higher electrical conductivity in ceramics & magnetic nanocomposites, higher resistivity in Metals

Optical - Increase in luminescent efficiency of semiconductors, transparency of nanoparticle

Chemical - substantial increase in catalytic properties & reaction rates

Mechanical - vibrational modes
elastic moduli
yield limits
strength
toughness
Temp. & pr. effects on mechanical properties (creep)

## Electrical

- chemical potential (for electrons, protons)
- band gaps in the bulk & at the surface
- fermi energy pinning by defects & surfaces
- Electron transfer rates (tunneling through barriers at surfaces)

<u>optical</u> · Density of electronic states
- polariability
- Dielectric / constant (frequency dependent)
- optical absorption as function of wavelength
- quantum dots & lines
- Nonlinear optical properties

optical (color, transparency)
electrical (conductivity)
physical (Hardness, boiling point)
chemical (reactivity, reaction rates)

**Nanoscale visualization techniques** — The techniques which is used for visualization the ~~the~~ visualize the internal structure of particles at a nano range.

◦ **Electron microscope** — It is used for high magnification & resolution, employing electron beams in place of light & using electron lenses.

— The electron microscope is a type of microscope that uses a beam of electrons to create an image of the specimen. It is capable of much higher magnifications and has a greater resolving power than a light microscope, allowing it to see much smaller objects in finer details.

TEM — Transmission Electron Microscope

SEM — Scanning Electron Microscope

CryoSEM — cryogenic Scanning Microscope

The general steps operating in any type of electron microscope are the following.

① Formation of a stream of electrons from the source

② Acceleration of electrons by applying a positive electrical potential towards the specimen.

③ concentration of the electron beam into a focused monochromatic beam with the help of metal apertures and magnetic lenses.

④ focusing of the beam using magnetic lens on the sample.

⑤ Interactions in the sample affecting the electron beam

⑥ Transformation of these interactions into an image

(SEM), the electron spot formed by the objective lens is scanned over the sample in a raster pattern by magnetic deflection coils. The schematic representation of an SEM is shown in Fig. 2.25. SEM resolution can approach ~1 nm. The objective lens normally has a long focal length and, therefore, SEMs have a large depth of focus in the range of 5–30 mm, vastly exceeding the depth of focus for optical microscopes. A short, working distance objective is the requirement of optical microscopes due to the constraints imposed by diffraction, and a contact is required in case of scanning probe microscopes. This feature of SEMs makes them especially suited for imaging large objects without much loss in resolution. A commercial SEM of JEOL model—JSM 7800–SEM with a field emission electron gun can be employed to observe the finest structural morphology of nanomaterials at 1,000,000 magnification with sub-1nm resolution, as shown in Fig. 2.26.
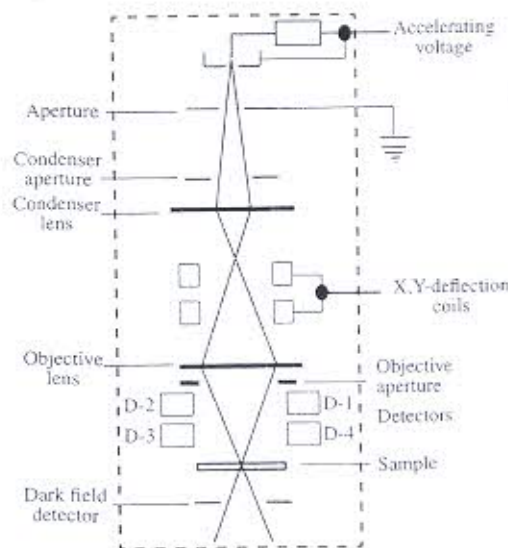


FIG. 2.25 Schematic of a scanning electron microscope, which contains the electron gun, electromagnetic lenses, electromagnetic deflection coils, apertures, sample stage, and detectors in a vacuum chamber. The condenser lens forms a bright image of the filament that is scanned by the X,Y- deflection coils and then focused into the sample by the objective lens. Backscattered electrons are collected by the detectors above the sample, while the electrons transmitted through thin samples in the STEM mode are collected below the sample. Inelastically scattered secondary electrons (SE) and X-rays generated by the incident electrons can also be detected.
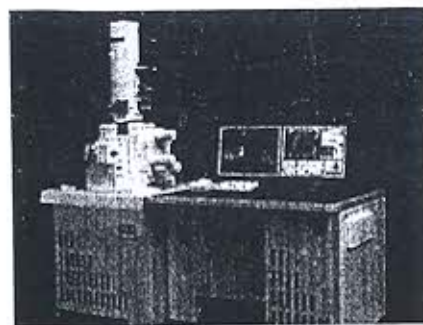


FIG. 2.26 Field emission-scanning electron microscope (FE-SEM) model JEOL JMS-7800 SEM manufactured by JEOL Ltd, Tokyo, Japan. The model can be used to observe structural morphology of nanomaterials at 1,000,000 magnification with sub-1nm resolution, collect large area electron backscattered diffraction (EBSD), and image thin, electron transparent specimens of with sub-0.8 nm resolution.

Images can be formed from several different signals from the sample. If the by a detector placed below the sample and the image will be formed from the transmitted current. Further, the image can be formed either from the central bright portion, called bright field (BF), or from the outer relatively darker portion, called dark field (DF) of the transmitted signal. This is called as scanning transmission electron microscopy (STEM). In case of thicker samples, elastically backscattered electrons can be collected by a detector placed above the sample. Yet another signal is obtained from inelastically backscattered electrons excited by the incident beam, distinguished from elastically scattered electrons by their lower energy. Lastly, if the energy of the incident beam is high enough and sufficient to excite the core electrons in an atom, then X-ray detectors can be used to map the corresponding X-rays from a chosen element in the sample. Thus, the atomic composition of the sample can be mapped at a very high resolution.

## 2.8.2 Electron Crystallography

Electron crystallography, based on the combination of electron diffraction and atomic resolution electron microscopy with image processing techniques, has emerged as a new powerful tool for crystal structure analysis. It can be used for 3D image reconstruction, which preserves both the phase and amplitude information by focusing the diffracted electron beam onto an image and allows better resolution of the reciprocal lattice points. The resolution obtained by experimental electron diffraction instruments is very much dependent on focusing the electron beam of focal lengths as short as 1 mm or less by using strong axial magnetic fields. Using such lenses in electron microscopes, the resolutions of ~1 Å have been achieved. By employing such instruments, images showing individual isolated atoms of moderately high atomic number may be obtained. The resolution is sufficient to distinguish neighbouring rows of adjacent atoms in the projected structures of thin crystals when viewed from favourable orientations [Cowley et al. 2006]. The electron diffraction technique is particularly suited for nanoscale single crystals, whereas other techniques would be limited to studying the diffraction from a multicrystalline or powder sample.

Aron Klug and D.J. DeRorier developed the 3D reconstruction method that combines data from electron diffraction and electron microscopic images. This has been the most widely employed technique in the determination of the crystal structure of numerous biological macromolecules, such as membrane proteins and viruses. Aron Klug won the Nobel Prize for Chemistry in 1982 for recognition of his work on development of crystallographic electron microscopy and determination of biologically important nucleic acid–protein complexes.

Atomic scale resolution of electron crystallography requires an understanding of the wave-like nature of an electron as given by the de Broglie equation $\lambda = h/p$, a detailed discussion given in Chapter 3. Wavelength of electrons accelerated under applied voltage in the electron microscope can be calculated from the energy equation as follows:

$$E = \frac{p^2}{2} = eV$$

# Scanning electron microscopy (SEM)

i)

A scanning electron microscope is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons.

The most commonly used configuration of electron microscope, called SEM, the electron spot formed by the objective lens is scanned over the sample in a raster pattern by magnetic deflection coils as shown schematic representation.

SEM — SEM is a method of scanning a thick conductive specimen with a fine, focused and high energy electron beam using backscattered electrons from its surface to generate a 2D electronic map.

Controlled via computer, the SEM operator can adjust the beam to control magnification as well as determine the surface area to be scanned.

The beam is focused onto the stage, where a solid sample is placed. Most samples require some preparation before being placed in the vacuum chamber.

Of the variety of different preparation processes, the two most commonly used prior to SEM analysis are sputter coating for non-conductive samples and dehydration of most biological specimens.

In addition, all samples need to be able to handle the low pressure inside the vacuum chamber.

The interaction between the incident electrons and the surface of the sample is determined by the acceleration rate of incident electrons, which carry significant amounts of kinetic energy before focused onto the sample.

When the incident electrons come in contact with the sample, energetic electrons are released from the surface of the sample. The scatter patterns made by the interaction yields information on size, shape, texture and composition of the sample.

A variety of detectors are used to attract different types of scattered electrons, including secondary and backscattered electrons as well as x-rays.

Backscatter electrons are incidental electrons reflected backwards; images provide composition data related to element and compound detection. Although topographic information can be obtained using a backscatter detector, it is not as accurate as an SED.

Diffracted backscatter electrons determine crystalline structures as well as the orientation of minerals and micro-fabrics.

X-rays, emitted from beneath the sample surface, can provide element and mineral information.

SEM produces black and white, three-dimensional images.

Image magnification can be up to 10 nanometers and, although it is not as powerful as its TEM counterpart, the intense interactions that take place on the surface of the specimen provide a greater depth of view, higher-resolution and, ultimately, a more detailed surface picture.
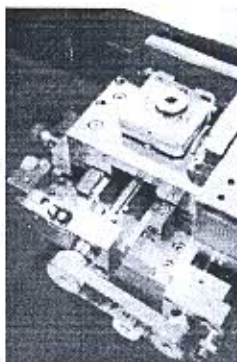
## SEM Applications

SEMs have a variety of applications in a number of scientific and industry-related fields, especially where characterizations of solid materials is beneficial.

In addition to topographical, morphological and compositional information, a Scanning Electron Microscope can detect and analyze surface fractures, provide information in microstructures, examine surface contaminations, reveal spatial variations in chemical compositions, provide qualitative chemical analyses and identify crystalline structures.

SEMs can be as essential research tool in fields such as life science, biology, gemology, medical and forensic science, metallurgy.

In addition, SEMs have practical industrial and technological applications such as semiconductor inspection, production line of miniscule products and assembly of microchips for computers.

## SEM Advantages

Advantages of a Scanning Electron Microscope include its wide-array of applications, the detailed three-dimensional and topographical imaging and the versatile information garnered from different detectors.

SEMs are also easy to operate with the proper training and advances in computer technology and associated software make operation user-friendly.

This instrument works fast, often completing SEI, BSE and EDS analyses in less than five minutes. In addition, the technological advances in modern SEMs allow for the generation of data in digital form.

Although all samples must be prepared before placed in the vacuum chamber, most SEM samples require minimal preparation actions.

Energy dispersive
X-ray spectroscopy

EDS -

BSE - Back-scattered
Electrons

SEI - Solid Electrolyte
Interphase

## SEM Disadvantages

The disadvantages of a Scanning Electron Microscope start with the size and cost.

SEMs are expensive, large and must be housed in an area free of any possible electric, magnetic or vibration interference.

Maintenance involves keeping a steady voltage, currents to electromagnetic coils and circulation of cool water.

Special training is required to operate an SEM as well as prepare samples.

The preparation of samples can result in artifacts. The negative impact can be minimized with knowledgeable experience researchers being able to identify artifacts from actual data as well as preparation skill. There is no absolute way to eliminate or identify all potential artifacts.

In addition, SEMs are limited to solid, inorganic samples small enough to fit inside the vacuum chamber that can handle moderate vacuum pressure.

Finally, SEMs carry a small risk of radiation exposure associated with the electrons that scatter from beneath the sample surface.

The sample chamber is designed to prevent any electrical and magnetic interference, which should eliminate the chance of radiation escaping the chamber. Even though the risk is minimal, SEM operators and researchers are advised to observe safety precautions.

## Hitachi's Scanning Electron Microscope

Hitachi High-Technologies, formed in 2001, manufactures a variety of science and technology related products.

Some Hitachi products include spectrophotometers, a variety of analyzers, inspection equipment, electronic devices, and semiconductor products as well as a line of microscopes.

They currently manufacture three scanning electron microscope models:

- S-3700N, an analytical style SEM ideal for studying large, heavy and tall samples
- S-3400N, a user-friendly, more compact model that utilizes new technology in electron optics
- SU1510, a compact, high performance SEM that can handle large samples and provides high-resolution imaging

A Scanning Electron Microscope provides detailed surface data of solid samples.

SEMs take incidental electrons and focus them onto a specimen; the electrons that scatter off the surface following this interaction can be analyzed with a variety of detectors that provide topographical, morphological and compositional information regarding the surface of a sample.

Although SEMs are large, expensive pieces of equipment, they remain popular among researchers due to their wide range of applications and capabilities, including the high-resolution, three-dimensional, detailed images they produce.

For information about the Transmission Electron Microscope click here.

Related articles: Cryo-electron Microscopy and Virtual Electron Microscopy.

Return from Scanning Electron Microscope to Electron Microscope

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Shop Related Products

TEM is a form of electron microscope in which an image is derived from electrons which have passed through the specimen, in particular one in which the whole image is formed at once rather than by scanning.

# Introduction (Transmission Electron Microscope)

The use of optical microscope limited the ability to resolve an object because of it's wavelength. TEM stands for Transmission Electron Microscopy was technique developed to obtain magnification and hence details of a specimen, to a much better level than the conventional optical microscopes. In TEM a beam of electrons is passed through an ultra-thin specimen interacting with the specimen as it passes through. When electrons are accelerated up to high energy levels (few hundreds keV) and focused on a material, they can scatter or backscatter elastically or inelastically, or produce many interactions, source of different signals such as X-rays, Auger electrons or light. Some of them are used in transmission electron microscopy (TEM). An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

The probable interaction between an electron and a specimen is given as below
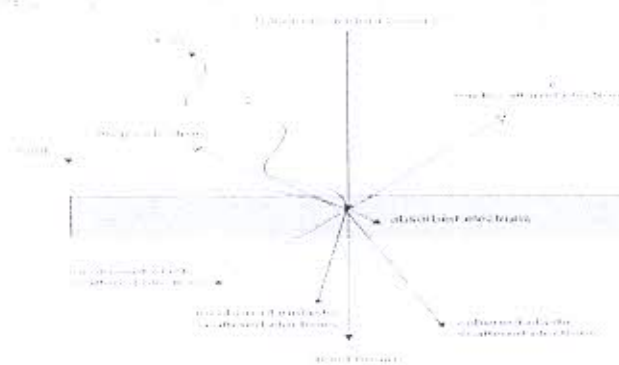


The development of TEM took into consideration the quantum mechanical behaviour of electron. The interaction of electron with the material was obtained due to the inherent nature of electron which is a quantum mechanical object. Since the electrons have both wave and particle nature and the de Broglie wavelength of electrons are significantly smaller than that of light and so they have higher resolution capability. This enables the instrument's user to examine fine detail—even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution, nanotechnology, and semiconductor research.

The major purpose of this project is to comprehensively cover the aspects of TEM. The history behind successful development of first TEM is described next.

Transmission electron microscopy is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image.
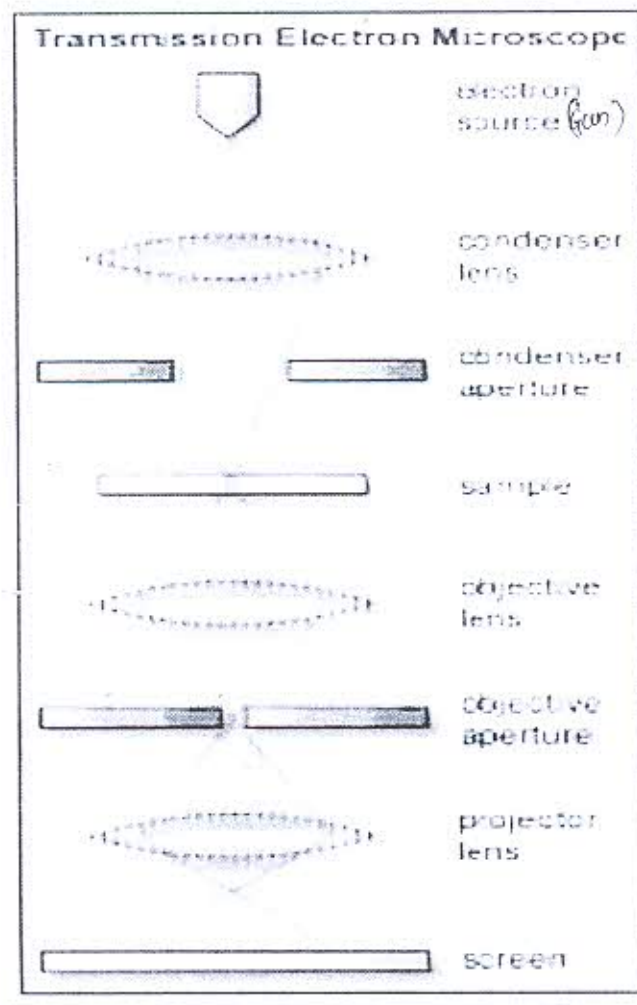
*Dense Material - Iron, lead or platinum*
*Porous Material - Rocks & soil, biological tissues*
*man made material ( cement,    (bones, wood*
*ceramics)          cork )*

# Working Principle

TEM works like a slide projector. A projector shines a beam of light which transmits through the slide. The patterns painted on the slide only allow certain parts of the light beam to pass through. Thus the transmitted beam replicates the patterns on the slide, forming an enlarged image of the slide when falling on the screen.

TEMs work the same way except that they shine a beam of electrons (like the light in a slide projector) through the specimen (like the slide). However, in TEM, the transmission of electron beam is highly dependent on the properties of material being examined. Such properties include density, composition, etc. For example, porous material will allow more electrons to pass through while dense material will allow less. As a result, a specimen with a non-uniform density can be examined by this technique. Whatever part is transmitted is projected onto a phosphor screen for the user to see.

# Construction



Transmission Electron Microscope

- electron source (gun)
- condenser lens
- condenser aperture
- sample
- objective lens
- objective aperture
- projector lens
- screen

ATOMIC FORCE MICROSCOPE

**Park Nanoscience Lab Inauguration**

July 25, 2018

*Park*

These differences provide information on the structure, texture, shape and size of the sample.

To obtain a TEM analysis, samples need to have certain properties. They need to be sliced thin enough for electrons to pass through, a property known as electron transparency.

Samples need to be able to withstand the vacuum chamber and often require special preparation before viewing.

Types of preparation include dehydration, sputter coating of non-conductive materials, cryofixation, sectioning and staining.

## TEM Applications

A Transmission Electron Microscope is ideal for a number of different fields such as life sciences, nanotechnology, medical, biological and material research, forensic analysis, gemology and metallurgy as well as industry and education.

TEMs provide topographical, morphological, compositional and crystalline information.

The images allow researchers to view samples on a molecular level, making it possible to analyze structure and texture.

This information is useful in the study of crystals and metals, but also has industrial applications.

TEMs can be used in semiconductor analysis and production and the manufacturing of computer and silicon chips.

Technology companies use TEMs to identify flaws, fractures and damages to micro-sized objects; this data can help fix problems and/or help to make a more durable, efficient product.

Colleges and universities can utilize TEMs for research and studies.

Although electron microscopes require specialized training, students can assist professors and learn TEM techniques.

Students will have the opportunity to observe a nano-sized world in incredible depth and detail.

## Advantages

A Transmission Electron Microscope is an impressive instrument with a number of advantages such as:

- TEMs offer the most powerful magnification, potentially over one million times or more
- TEMs have a wide-range of applications and can be utilized in a variety of different scientific, educational and industrial fields
- TEMs provide information on element and compound structure
- Images are high-quality and detailed
- TEMs are able to yield information of surface features, shape, size and structure
- They are easy to operate with proper training

## Disadvantages

- Some cons of electron microscopes include:
- TEMs are large and very expensive
- Laborious sample preparation
- Potential artifacts from sample preparation
- Operation and analysis requires special training
- Samples are limited to those that are electron transparent, able to tolerate the vacuum chamber and small enough to fit in the chamber
- TEMs require special housing and maintenance

CCD camera
charge-coupled
Device

Gemology = (Gemstone / Natural & artificial material)
— Branch of minerals

topographical = physical features of an area

morphology = study of the forms of things

- Images are black and white

Electron microscopes are sensitive to vibration and electromagnetic fields and must be housed in an area that isolates them from possible exposure.

A Transmission Electron Microscope requires constant upkeep including maintaining voltage, currents to the electromagnetic coils and cooling water.

## What is the Cost?

TEMs are manufactured by companies such as Zeiss, Jeol, Philips and Hitachi and are extremely expensive.

Examples of prices for new TEM models include $95,000 for a Jeol 1200EXII, $95,000 for a Philips EM10 and $100,000 for a Hitachi 7000.

A Transmission Electron Microscope produces images via the interaction of electrons with a sample.

TEMs are costly, large, cumbersome instruments that require special housing and maintenance.

They are also the most powerful microscopic tool available to-date, capable of producing high-resolution, detailed images 1 nanometer in size.

TEMs have a wide-range of applications in a variety of scientific, education, research and industrial fields.

Now, read about the Scanning Electron Microscope here.

Also Cryo-Electron Microscopy and check out our article on the Virtual Electron Microscopy.

Check out DNA under the Microscope too

Return from Transmission Electron Microscope to Electron Microscope

Return from Transmission Electron Microscope to Best Microscope Home
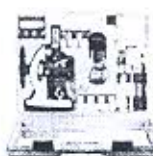
4 people like this. Sign Up to see what your friends like.

## New! Comments

Have your say about what you just read on MicroscopeMaster! Leave me a comment in the box below.

There are two types of electron microscopic techniques—transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM uses electrons transmitted through a thin sample, whereas SEM uses backscattered electrons from the thick surface of the specimen for imaging. Interaction of electrons with the solid specimen results in backscattering of electrons, production of Auger electrons, UV and visible light, X-rays, etc., and the defocusing of the incident electron beam. Electron microscopy poses several limitations such as vibration, contamination, and damage to the specimen due to the intense electron beam or disintegration in high vacuum, aberration of the magnetic lenses used to focus the electron beam, etc.

### Ernst August Friedrich Ruska (1906–1988)

Ernst August Friedrich Ruska, a German physicist, shared the Nobel Prize for Physics in 1986 for his work in electron optics and the design of the first electron microscope with Gerd Binnig and Heinrich Rohrer who won a quarter each for their design of the scanning tunneling microscope.

Ruska studied at the Technical University of Berlin from 1925 to 1927. Here, he began the studies that led to his invention of the electron microscope. Ruska posited that electrons could be focused on a specimen in the same way as light and could yield a magnification greater than conventional light microscopes. In 1931, he demonstrated that a magnetic coil could act as an electron lens and used several coils in a series to build the first electron microscope in 1933. Ruska continued to work in the field of electron optics and was involved in developing the first commercially produced electron microscope in 1939.

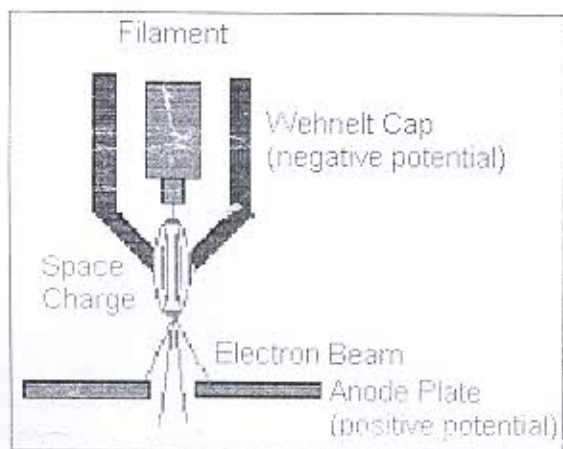### 13.4.1 Transmission Electron Microscopy

TEM is a microscopy technique in which a high energy electron beam is made to pass through a very thin sample in order to visualize its structure at the atomic level. A beam of electron generated by thermal emission from a tungsten filament or by electron field emission is accelerated by an electric potential to several hundred kV and focused using electrostatic and electromagnetic lenses on a thin sample (less than 200 nm) in vacuum and the image is created from the interaction between the electrons and the specimen, which is observed on a fluorescent screen and recorded by a CCD camera. A schematic representation of TEM is presented in Fig. 13.3. Electrons are scattered into wide as well as small angles, leading to a difference in their amplitude, thereby creating a contrast. Larger angle electrons are cut off by an objective aperture. A vacuum (low pressure of the order of $10^{-4}$ to $10^{-8}$ kPa) is important to avoid the absorption or scattering of electrons by air. Sections of TEM are subjected to a different quality of vacuum with the help of gate valves, which act as a preventive measure against the loss of vacuum in critical locations like the electron gun upon the insertion of the specimen in the stage inside the TEM. Generally, the sample grid used for loading the specimen during the TEM analysis is made of brass with a thickness of 100 μm and a diameter of 3 mm.



Electron gun
Condensor lens
Sample
Objective lens
Back focal
Image
Movable s
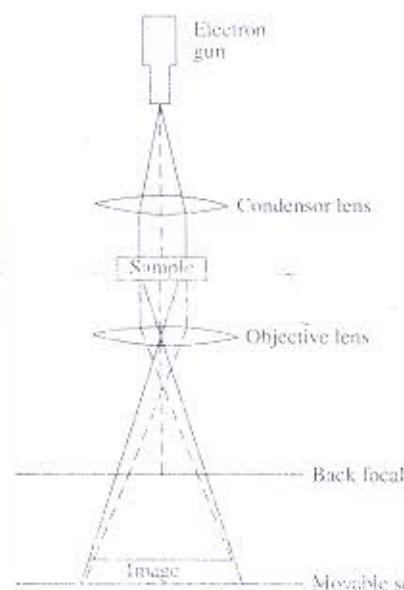
TEM operates in two different
TEM image depends on these mod
the bright field imaging. In this m
or particles and crystalline areas) c
(with no particles) appear bright. I
focal plane of the objective lens th
which interacts with the sample.
the other hand, in the dark field, th
diffracted beam passes through the
beam interacts strongly with the
faults, or particle size.

Optic axis

(a)
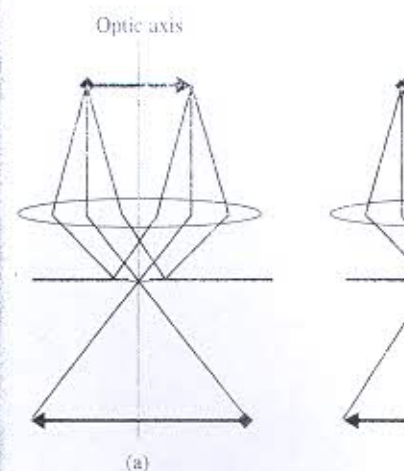
# 1) ELECTRON SOURCE (GUN):-



The first and basic part of the transmission electron microscope is the source of electrons. It is usually a V-shaped filament made of LaB6 or W (tungsten) that is wreathed with Wehnelt electrode (Wehnelt Cap). Due to negative potential of the electrode, the electrons are emitted from a small area of the filament (point source). A point source is important because it emits monochromatic electrons (with similar energy).

In this, a positive electrical potential is applied to the anode, and the filament (cathode) is heated until a stream of electrons is produced. The electrons are accelerated by the positive potential down the column, and because of the negative potential of cap, all electrons are repelled toward the optic axis. A collection of electrons occurs in the space between the
Filament tip and Cap , which is called a space charge. Those electrons at the bottom of the space charge (nearest to the anode) can exit the gun area through the small (<1 mm) hole in the Wehnelt Cap and then move down the column to be later used in imaging.

## 2) CONDENSER LENS:-
The stream of the electron from the electron gun is then focussed to a small, thin, coherent beam by the use of condenser lenses.
The first lens determines the "spot size"; the general size range of the final spot that strikes the sample.
The second lens actually changes the size of the spot on the sample.

constant
phase diff- same frequency
and same waveform.

### 3) CONDENSER APERTURE:-

A condenser aperture is a thin disk or strip of metal with a small circular through-hole. It is used to restrict the electron beams and filter out unwanted scattered electrons before image formation.

### 4) SAMPLE: -

The beam from the condenser aperture strikes the sample and the electron-sample interaction takes place in three different ways. One is unscattered electrons (transmitted beam), elastically scattered electrons (diffracted beam) and inelastically scattered electrons.

### 5) OBJECTIVE LENS: -

The main function of the objective lens is to focuses the transmitted electron from the sample into an image.

### 6) OBJECTIVE APERTURE:-

Objective aperture enhances the contrast by blocking out high-angle diffracted electrons.

### 7) SELECTED APERTURE:-

It enables the user to examine the periodic diffraction of electron by ordered arrangements of atoms in the sample.

### 8) PROJECTOR LENS:-

The projector lens are used to expand the beam onto the phosphor screen.

### 9) SCREEN:-

Imaging systems in a TEM consists of a phosphor screen, which may be made of fine (10-100 micro meter) particulate zinc sulphide, for direct observation by the operator.

### 10) IMAGE PATTERN:-

The image strikes the phosphor screen and light is generated, allowing the users to see the image.

The darker areas of the image represent those areas of the sample that fewer electrons are transmitted.

The lighter areas of the image represent those areas of the sample that more electrons were transmitted.

Applications —

# Advantages and disadvantages of TEM

## Disadvantages

- Low sampling volume and rather slow process of obtaining information.
- High capital and running cost.
- Special training required for the operation of the equipment.
- Difficult sample preparation. Possibility of electron beam damage.
- Samples which are not stable in vacuum are difficult to study.
- Magnetic samples require special care.
- Non-conducting samples require gold or carbon coating.
- Difficulty in the interpretation of images. In usual mode of operation information is integrated along the beam direction.

## Advantages

- Real (Image) and reciprocal space (diffraction pattern) information can be obtained from same region of sample.
- Chemical information via EDX and EELS possible (with additional attachments). Energy filtered images possible via EELS filter.
- High resolution imaging possible (via HRTEM & HAADF in STEM).
- Possible to obtain amplitude and phase contrast images. Many different kinds of phase contrast images can be obtained.

The following is the basic concept of the STM, it has a metal needle that scans a sample by moving back & forth over it, gathering information about the curvature of the surface.

STMs use a sharpened, conducting tip with a bias voltage applied bet'n the tip & the sample. When the tip is brought within about $10\text{\AA}$ of the sample, electrons from the sample begin to "tunnel" through the $10\text{\AA}$ gap into the tip or viceversa, depending upon the sign of the bias voltage. The resulting tunneling current varies with tip-to-sample spacing & it is the signal used to create an STM image.

The tunneling current is an exponential form of distance, if the separation bet'n the tip & the sample changes by 10% (on the order of $1\text{\AA}$), the tunneling current changes by an order of magnitude. This exponential dependence gives STMs their remarkable sensitivity. STMs can image the surface of the sample with sub-angstrom precision vertically & atomic resolution laterally.

8,

(1A) STM — The is an instrument for imaging surfaces at first SPM technique the atomic level.

① · 1981
· Gerd Binning & Heinrich Rohrer
· Imperfections in thin Metal oxides

operates in · vacuum
  · Air
  · Temp. 0°K —

Requirements — sharp, conductive probe
  — conductive sample surface
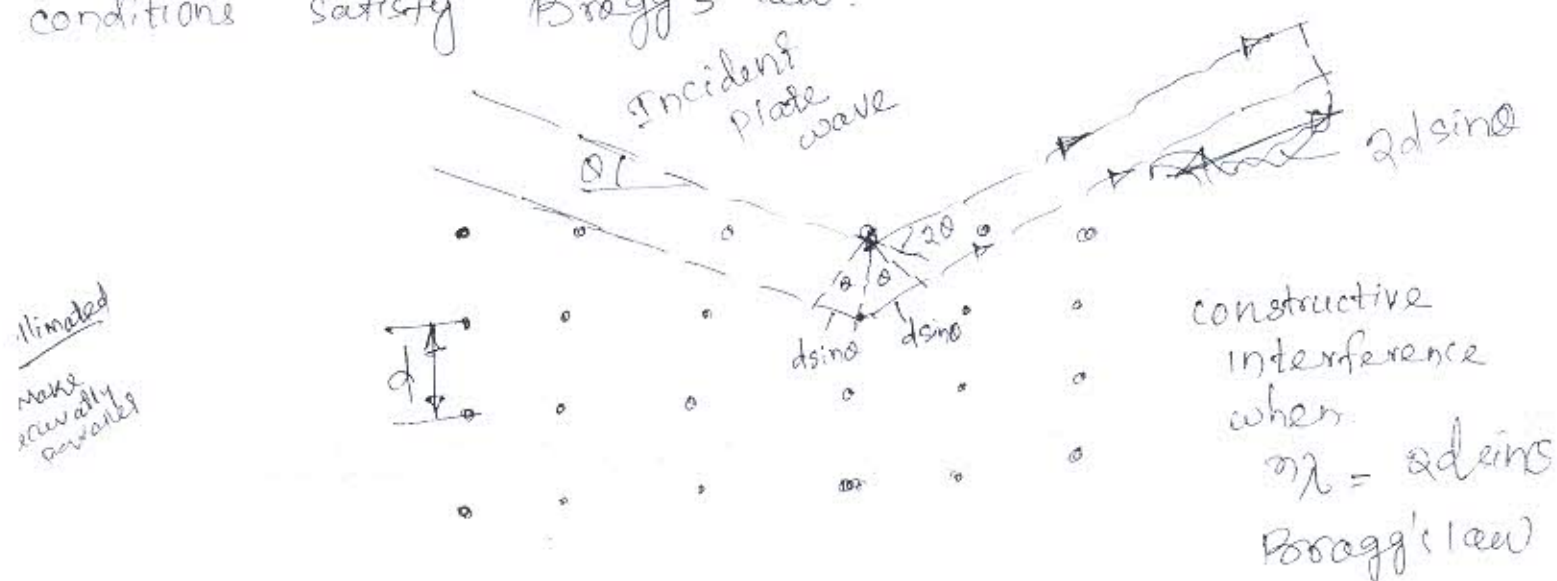  — clean surface
  — vibration control

Advantages = Resolution
  — Sample preparation
  — Operates in a variety of ambients

Disadvantages — Requires conductive samples
  — Flat samples

shree maa

**XRD Principle** - X-ray diffraction is based on constructive
) interference of monochromatic x-rays and a crystalline sample
These x-rays are generated by a cathode ray tube, filtered
to produce monochromatic radiation, collimated to concentrate &
directed towards the sample. The interaction of incident rays
with the sample produces constructive interference when
conditions satisfy Bragg's law.

Incident
plate
wave

$2d\sin\theta$

collimated

make
equally
parallel

$d\sin\theta$   $d\sin\theta$

constructive
interference
when

$$n\lambda = 2d\sin\theta$$

Bragg's law

## Applications of XRD

① Structure of crystals

② Polymer characterisation

③ State of anneal in metals

⑤ Applications of diffraction
Methods to complexes

④ Particle size determination
  - Spot counting method
  - Broadening of diffraction
    lines
  - low-angle scattering

⑥ Miscellaneous applications

**Advantages**
  - X-ray Measurement under atm. po.
  - XRD is Non-destructive technique, easily
    sample preparation

- X-ray diffraction structure analysis can be applied for
  single crystal.
- X-ray are not observed very much by air, so the
  specimen need not be in evacuated chamber.

**Disadvantages** - they do not interact very strongly
with lighter elements.
- The intensity is $10^8$ times less than that of electron

Incident beam

Diffracted beam

Diffraction Pattern recorded

$2\theta$

$\gamma$

Crystalline material

Transmitted beam
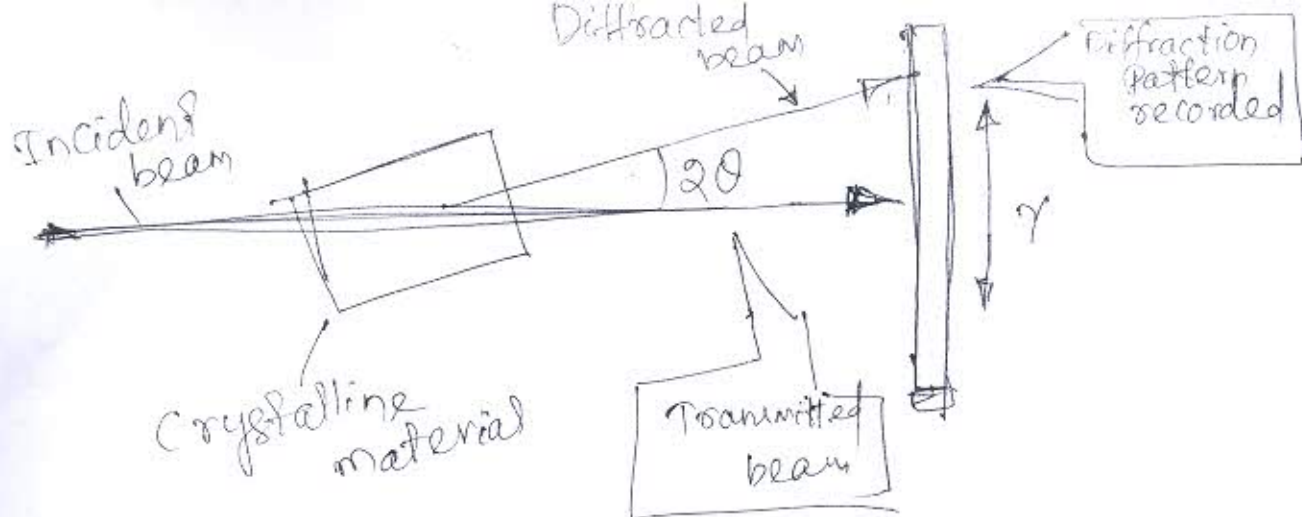
# Chapter 2

## Physical Methods for Characterizing Solids

uses

(1) Distinguishing both crystalline & amorphous materials.

(2) Determination of the structure of crystalline materials.

(3) Determination of electron distribution within the atoms & throughout the unit cell.

(4) Determination of the orientation of single crystals.

(5) Determination of the texture of polygrained materials.
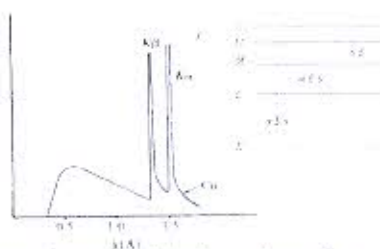
(6) Measurement of strain & small grain size.

### X-ray diffraction

X-rays were discovered by Wilhelm Rontgen, a German physicist in 1895.

To generate x-rays, three things are needed.
• a source of electrons
• a means of accelerating the electrons at high speeds
• a target material to receive the impact of the electrons and interact with them.

X-ray tube

Frequency (wavelength) depends on the anode metal, often Cu, Mo, Co.

Lines occur because bombarding electrons knock out e⁻ from K shell (n = 1), which are filled by electrons in higher shells. Electrons falling from L shell (n = 2) give rise to K lines, whereas e⁻ from M shell (n = 3) give the $K_b$ lines. ($K_{a1}$ and $K_{a2}$ doublets, etc.)
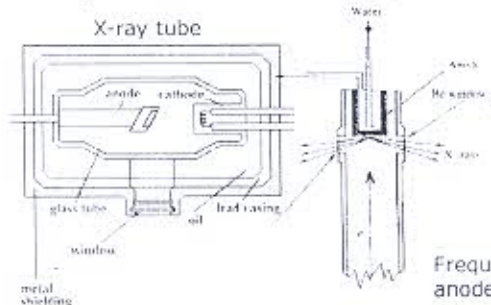
Typical cathode element is W.

Potential difference is 20-50 kV.

Anode must be water cooled.

Angle for coherent and incoherent scattering from a crystal lattice

Incident x-rays

Diffracted x-rays

$\theta$   $\theta$

$d$

1

Electron gun

Electron beam

First condenser lens

Spray aperture

cond condenser lens

X-ray detecto

Deflection coils

Objective ler

Final lens aperture

Backscatter electron detector

Sample

Vacuum pump

Secondary electron detector
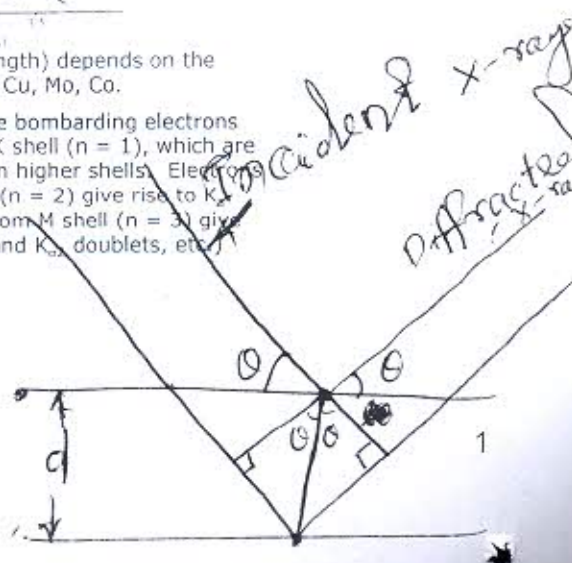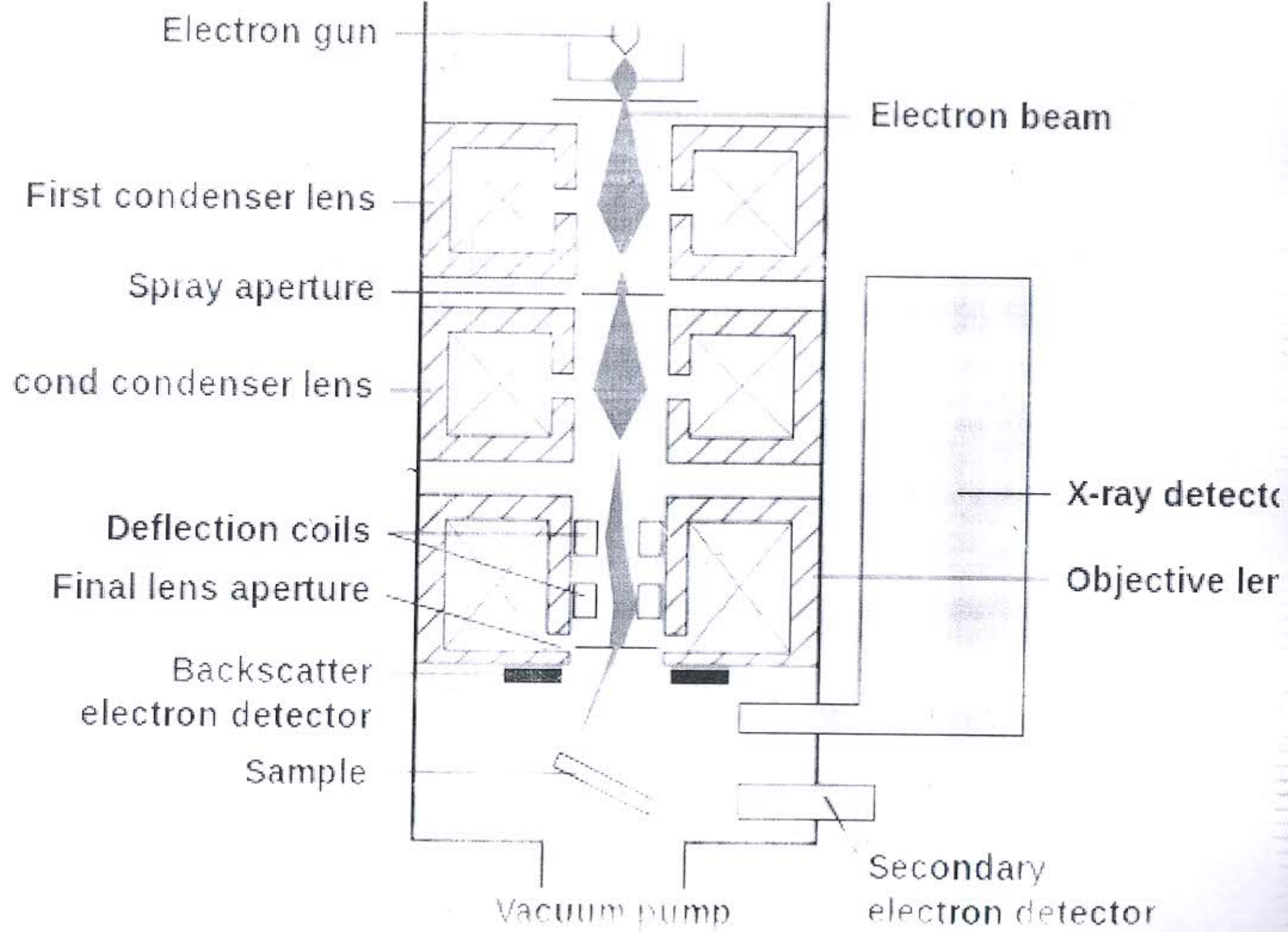
1) **Scanning probe microscopy (SPM)** :- SPM is a branch of microscopy that forms images of surfaces using a physical probe that scans the specimen.

— scanning Tunneling microscopy (STM)

— Atomic force microscopy (AFM)

- AFM or scanning force microscopy (SFM) is a very-high-resolution type of SPM, with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit.

* scanning probe microscopy (SPM) is a technique involving the formation of images of the sample surface by the interaction of a scanning probe with the surface. It can be used to visualize the structure and properties of almost all solid surfaces.

# Introducing Cryo Scanning Electron Microscopy

## 1. Basics

Cryo scanning electron microscopy is effective in imaging of samples containing moisture without causing drying artifacts. Figure 1-1 shows an external view of a general cryo SEM.
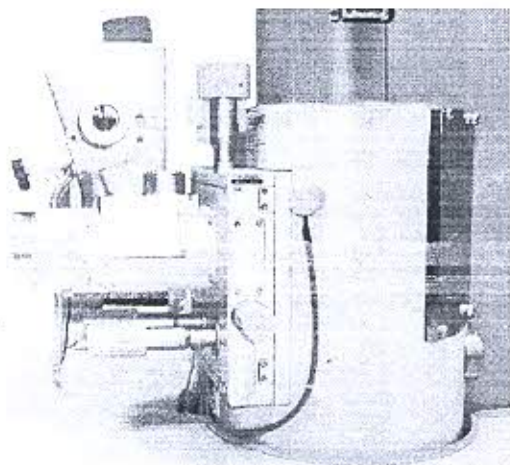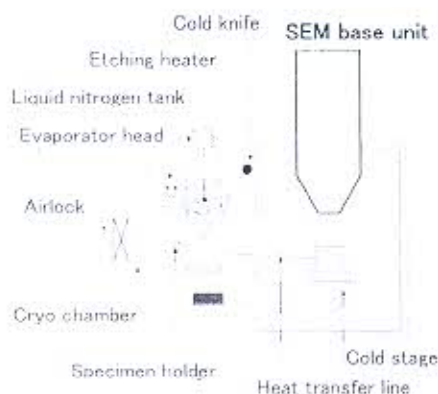


Figure 1-1. External view of general cryo SEM

Figure 1-2 shows the components of this general cryo SEM.



The cryo SEM comprises a cryo chamber for cleaving ( separate )

Figure 1-2. Components of general cryo SEM

and coating of frozen samples and a cold stage for SEM imaging. The system in the figure integrates the cryo chamber and the cold stage, allowing a single liquid nitrogen tank to cool the chamber and the stage. The cryo chamber incorporates a resistance heating vacuum evaporator to coat samples with gold. It also incorporates a heater for etching (subliming) the ice formed in samples. Figure 1-3 shows a typical operating procedure of this cryo SEM. A moisture containing sample needs to be rapidly frozen with liquid nitrogen (physical fixation) before it is loaded into the cryo SEM. The frozen sample is loaded onto the specimen process stage through the airlock system of the cryo chamber. The sample can be cleaved with a cold knife integrated in the chamber for imaging of its internal structure. The cleaved surface is etched in a controlled manner to remove the ice using the heater (ice sublimation) as needed, and is coated with Au for SEM imaging (or can be imaged at low kV without metal coating). There are two crucial points in the operating procedure. One is the etching process where the ice formed inside the sample is sublimated. And the other is the preliminary freezing (physical fixation) technique. These will be described in detail below.
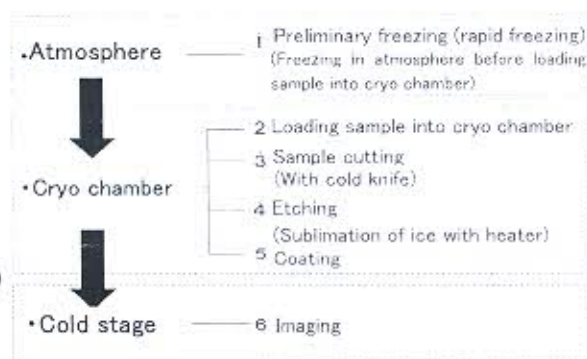


Figure 1-3. Operating procedure of cryo SEM

## 2. Etching

This process controls the temperature of the frozen sample in vacuum, allowing only the ice

1/3

# Cryo Scanning Electron Microscopy (cryo SEM)

cryo SEM is a form of electron microscopy where a hydrated but cryogenically fixed sample is imaged on a SEM cold stage in a cryogenic chamber. The cooling is usually achieved with liquid nitrogen.

weak london dispersion forces
and strongest di dipole
dipole dipole forces

van der waals forces is a general
term used to define the attraction
of intermolecular forces both molecules.

# Atomic force microscopy (AFM)

- Invented 1986

- Commercially available 1989

- Gerber, Binnig and Quate

- Conductive and non-conductive samples

# STM summary

- **Advantages**
  - Resolution
  - Sample preparation
  - Operates in a variety of ambients
- **Drawbacks**
  - Requires conductive samples
  - Flat samples

| STM | AFM |
|---|---|
| images indirectly by observing tunnelling current | vander waals force direct contact |
| – small gap beth two | – AFM, tip touches the surface |
| – less resolution | – better resolution |
| – requires conducting surface & high vacuum condition | – requires liquid&gas environment ball conductor & should |

Applications

1. Examination of surface topography of an electrically conductive sample surface in air, liquid or ultra-high vacuum with minimal sample preparation is possible

2. can be used in spectroscopy mode to obtain information about the outer-shell electron distribution.

STM - scanning tunnelling microscopy is a technique which probes the electrical tunnelling current bet^n the conducting surface of the sample & Metallic trip of the probe in vacuum to image the surface topography.

# STM working principle

(the arrangement of the natural and artificial physical features of an area.
(study of area



a macroscopic scale

tunneling voltage

$U_T$

scanning direction

tungsten tip

sample

b: atomic scale

tip atoms

current $I_T$

sample atoms
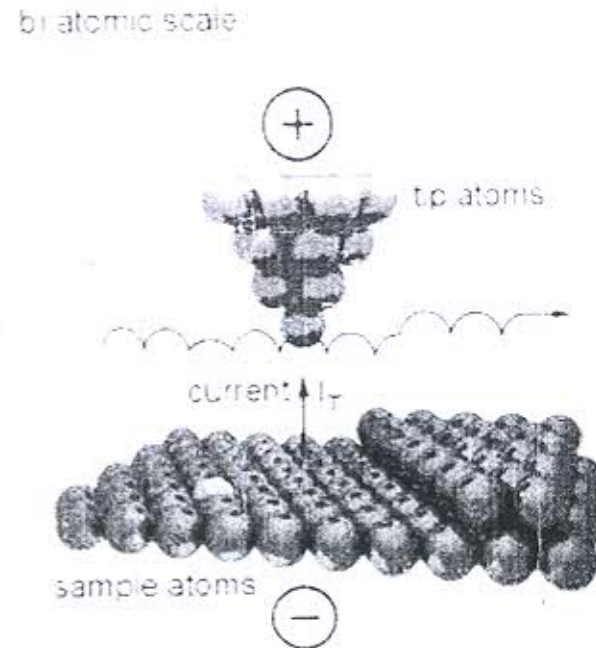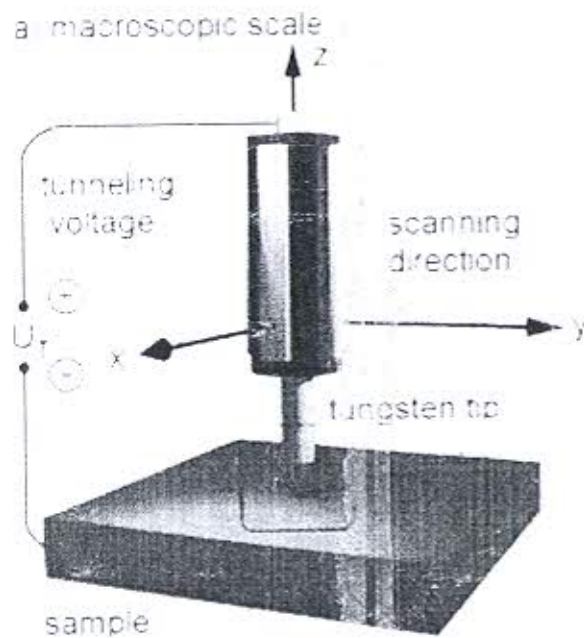
Applications → Examination of surface Topography of conductive as well as non-conductive sample is possible as it does not require an electrically conductive sample surface.

2. can be used for near-atomic resolution and imaging of biological samples.

## AFM working principle
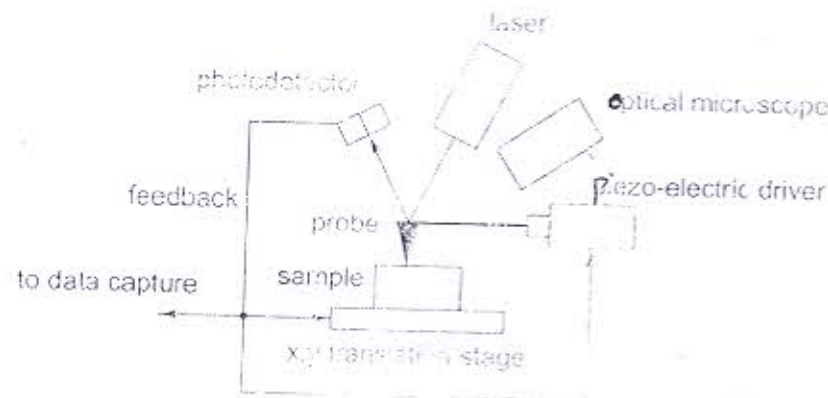


AFM is a technique to study the surface topography of a sample in which a sharp needle attached to the end of a cantilever is pushed across the surface of the sample making direct contact with the surface at a constant force, measuring the vander Waals forces both the tip & the sample

11
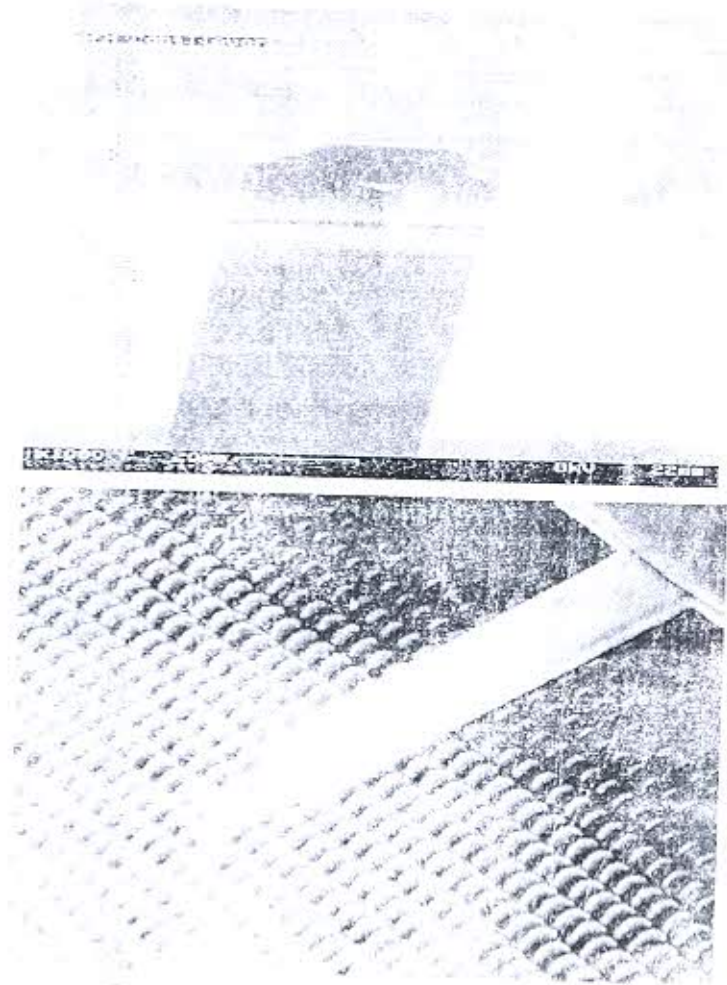
# AFM summary

- Advantages

  - Works on any material

  - Wide range of ambients

  - Little sample preparation

- Drawbacks

  - Resolution compared to STM

  - Finite probe lifetime

  - Requires flat samples

*Heinrich Rohrer (1933–2013)*

Heinrich Rohrer was a Swiss physicist. In 1951, he joined the Swiss Federal Institute of Technology where he got his education from eminent scientists such as Wolfgang Pauli and Paul Scherrer

In 1963, he joined the IBM Research Laboratory in Rüschlikon where he studied magnetic phase diagrams. In 1974, he spent a sabbatical year at the University of California studying nuclear magnetic resonance with Vince Jaccarino and Alan King. He shared a quarter of the Nobel Prize for Physics with Gerd Binnig for the design of the scanning tunnelling microscope in 1986.

## 13.5.2 Atomic Force Microscopy

An AFM is an instrument that can be used to produce a near atomic resolution. Basic components of AFM are presented in Fig. 13.37. In this technique, a sharp needle attached to the end of a cantilever is pushed across the surface of the sample with a constant force. The distance travelled by a laser beam reflected from a mirror fixed to the top of the needle up to the detector is recorded, which gives information about the vertical motion of the needle tip and hence the exact position of the tip. Thus, AFM monitors the force exerted between the surface and the probe tip and is sensitive to the vertical component of the surface forces.

AFM can operate in contact mode in which core-to-core repulsive forces dominate as well as in non-contact mode in which the van der waals forces dominate. Alternatively, a four-quadrant photodetector can be used to sense torsion of the AFM cantilever, which results from a sideways frictional force producing an image. The image produced is basically a map of the local coefficient of friction.

AFM cantilevers are made from silicon nitride by photolithography in large quantities and can be easily replaced when damaged. Materials which store magnetic data can be visualized directly by modifying the tip of the sample to measure the magnetic field.
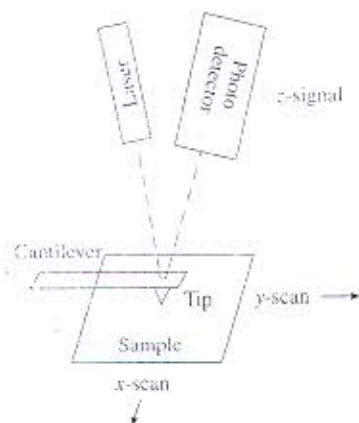


FIG. 13.37 Basic components of AFM

of STM: it can operate in liquid and gas environments and it is also useful for both conductors and insulators unlike STM which needs a conducting surface and a high vacuum condition. In addition, AFM provides topographic contrast and superior surface features.

Apart from this, other techniques such as scanning ion conductance microscopy (SICM), scanning capacitance microscopy (SCM), etc., are used. SICM utilizes an electrode as the probe tip for the determination of surface topography of non-conducting samples up to nanometre-range structures in conducting electrolytes. SCM uses a narrow probe electrode to measure a change in the electrostatic capacitance between the surface and the probe.

## 13.5.1 Scanning Tunnelling Microscopy

Gerd Binnig and Heinrich Rohrer developed scanning tunnelling microscopy at the IBM Zürich Laboratory in 1982 and were awarded the Nobel Prize for Physics in 1986. The quantum mechanical principle of electron tunnelling is the driving force for this technique. According to this principle, there exists a non-zero probability of the movement of an electron from a region of low potential energy to another region of low potential energy even in the absence of sufficient energy to overcome the energy barrier between the two regions. Thus, STM probes the electrical tunnelling current between the surface of the sample and tip of the probe.



FIG. 13.9   Sketch of STM

In this technique, a sharp conducting needle (probe) is brought at a distance of about 1 nm (with the help of a piezoelectric drive) to the conductive surface of the specimen to be studied and a small potential difference of about 1 V is applied to it. Figure 13.9 shows a sketch of STM. Electrons from the surface of a conductive specimen tunnel across the gap, setting up a measurable tunnelling current of ~1 nA. Quantum mechanical tunnelling arises due to the wavelike characteristic of electrons.
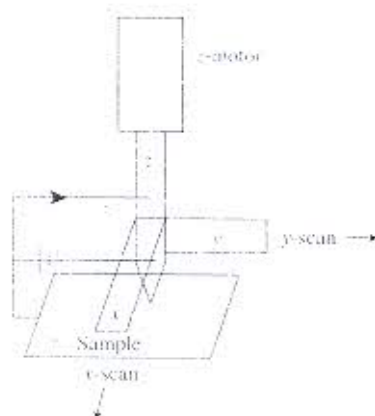
STM can image surface topology in two ways—constant height mode and constant current mode as shown in Fig. 13.10. In constant current mode, the tip is scanned across the surface while keeping the tunnelling current constant. The surface is scanned by moving the needle in x- and y-directions in a raster pattern with the help of a piezoelectric drive. During this process, a constant tunnelling current is maintained by regulating the height of the needle by the movement of its tip in the z-direction along the morphology of the surface (surface topography). Thus, in this mode, the tip keeps moving up and down slightly as it passes over a surface atom and the hollow surface sites. The differential heights of the needle at each position can be used to obtain a picture of the surface topography.

Tungsten filament

Tungsten crystal
with pointed end

Extraction anode

Anode

Anode

(a)

(b)
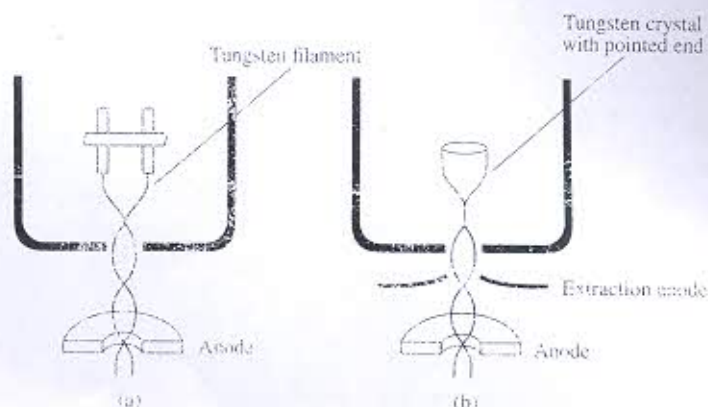
FIG. 13.8   Schematic representation of types of electron guns (a) Thermionic electron gun
(b) Field emission gun

## Applications

Some important applications of SEM are listed as follows.

1. Analysis of chemical composition is possible because the energy or wavelength
   of the X-rays is proportional to the concentration of the element.
2. Information on the crystal orientation and crystalline structure is obtained as it
   generates a 2D electronic map of the sample.
3. Can be used to image the external morphology of a thick sample as the
   information on the distribution of different elements in a sample is provided by
   the backscattered electron images.

## 13.6  SCANNING PROBE MICROSCOPY

Scanning probe microscopy (SPM) refers to the microscopic technique involving
the formation of images of sample surfaces with the help of scanning by a physical
probe. An SPM raster scans the tip over the surface and records values at discrete
points. The resolution of the probe techniques can reach the atomic scale due to the
precision of the piezoelectric actuators to act on electronic command and control
the motions at the atomic level. The probe in SPM should possess a very sharp tip
as the resolution is directly related to its sharpness. In fact, atomic resolution can
be obtained if the tip is terminated by a single atom.

To visualize three-dimensional (3D) real space images as well as localized
measurement of structure and properties of almost all solid surfaces (hard or soft
and conductive or not), scanning probe microscopy (SPM) becomes essential.
SPM comprises of two techniques on the basis of the probe force used—atomic
force microscopy (AFM) and scanning tunnelling microscopy (STM). STM forms
images indirectly by observing the tunnelling current between the metallic tip and
the conducting sample. However, in AFM, the van der Waals force between the tip
and the sample is considered and the probe makes direct contact with the surface.
Usually in AFM, the tip slightly touches the surface, whereas in STM there is a
very small gap between the two. The resolution of AFM is a little better than that

Diffraction Techniques

Diffraction refers to various phenomena that occur when a wave encounters an obstacle. It is defined as the bending of waves around the corners of an obstacle or aperture into the region of geometrical shadow of the obstacle.

EX:- closed spaced tracks on a CD or DVD.
hologram on a credit card ; circular waves generated by diffraction from the narrow entrance of a frocked cave coastal quarry (फोटो भी).

→ we study onny XRD, synchrotron)

\* X-ray Diffraction :-

- The atomic planes of a crystal cause an incident beam of x-rays to interfere with one another as they leave the crystal. The phenomenon is called X-ray Diffraction.

- XRD is used to study the structure, composition & physical properties of materials.

why XRD -(1) Measure the avg. spacings bet? layers or rows of atoms.
(2) Determine the orientation of a single crystal or grain
(3) Find the crystal structure of an unknown material
(4) Measure the size, shape & internal stress of small crystalline regions.
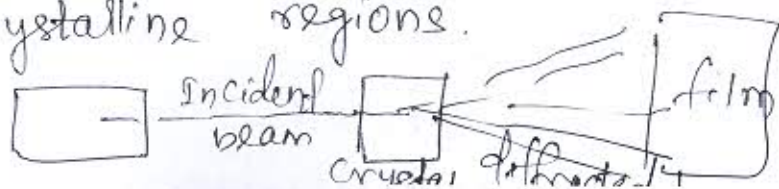
✱ The diffraction process occurs when the Bragg's law (condition) is satisfied. It is expressed as

$$n\lambda = 2d\sin\theta$$

where $\lambda$ = wavelength of X-rays

$d$ = Interplanar spacing

$\theta$ = X-ray angle

$n$ = integer

- **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

1) TOP down approach refers to dicing or successive cutting of a bulk material to get nano-sized particle

2) In top-down technique, the starting material is solid state.

physical processing methods

① Mechanical methods — cutting, etching, grinding
ball milling,

② Lithographic techniques - photo lithography
electron beam lithography

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

## Bottom-up approach

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 approach

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.

physical techniques — PVD : involves
condensation of vapor phase species
- Evaporation, plasma arcing, laser ablation
(surgical removal of tissu)

chemical techniqu — CVD : ~~pha~~ Deposition of tissu)
of vapour phase of reaction species
assembled monolayer (electrolytic deposition ..... ......... )

# Top down approach

## Advantages

- Large scale production deposition over a large substrate is possible.

- chemical purification is not required.



process such as etching & nanolithography starting from bulk material.
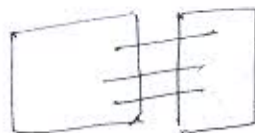
Top-down approach (lithography)

## Dis

1. Broad size distribution
2. varied particle shapes or geometry
3. Expensive technique
4. Impurities - stresses, defects & imperfections get introduced
5. control over deposition parameters is difficult to achieve

## Bottom-up approach



## Advantages

1. ultra-fine nanoparticles, nanoshells, nanotubes can be prepared.
2. Deposition parameters can be controlled.
3. Narrow size distribution possible (1 - 20 nm)
4. cheaper technique

Bottom-up approaches (for example self-assembly molecular patterning

## Dis

1. chemical purification of nanoparticles is required.
2. Large scale production is difficult.
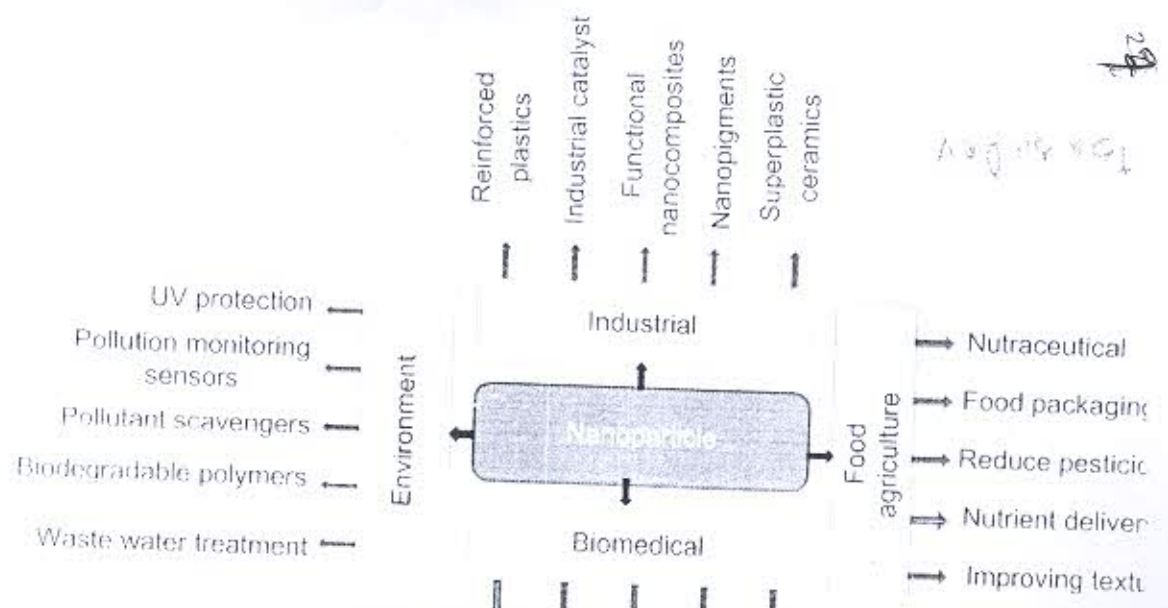
Reinforced plastics
Industrial catalyst
Functional nanocomposites
Nanopigments
Superplastic ceramics

UV protection
Pollution monitoring sensors
Pollutant scavengers
Biodegradable polymers
Waste water treatment

Industrial

Environment

**Nanoparticle**

Food agriculture

Nutraceutical
Food packaging
Reduce pestici
Nutrient deliver
Improving textu

Biomedical

Cancer therapy
Imaging
Aggregation
Drug delivery
Antibacterial

As protein aggregation inducer

As protein aggregation inhibitor

Industrial
- Reinforced plastics
- Industrial catalyst
- Functional nanocomposites
- Nanopigments
- Superplastic ceramics

Environment
- UV protection
- Pollution monitoring sensors
- Pollutant scavengers
- Biodegradable polymers
- Waste water treatment

Nanoparticle

Food agriculture
- Nutraceutical
- Food packaging
- Reduce pesticides
- Nutrient delivery
- Improving texture

Biomedical
- Cancer therapy
- Imaging
- Protein aggregation
- Drug delivery
- Antibacterial

As protein aggregation inducer ← → As protein aggregation inhibitor
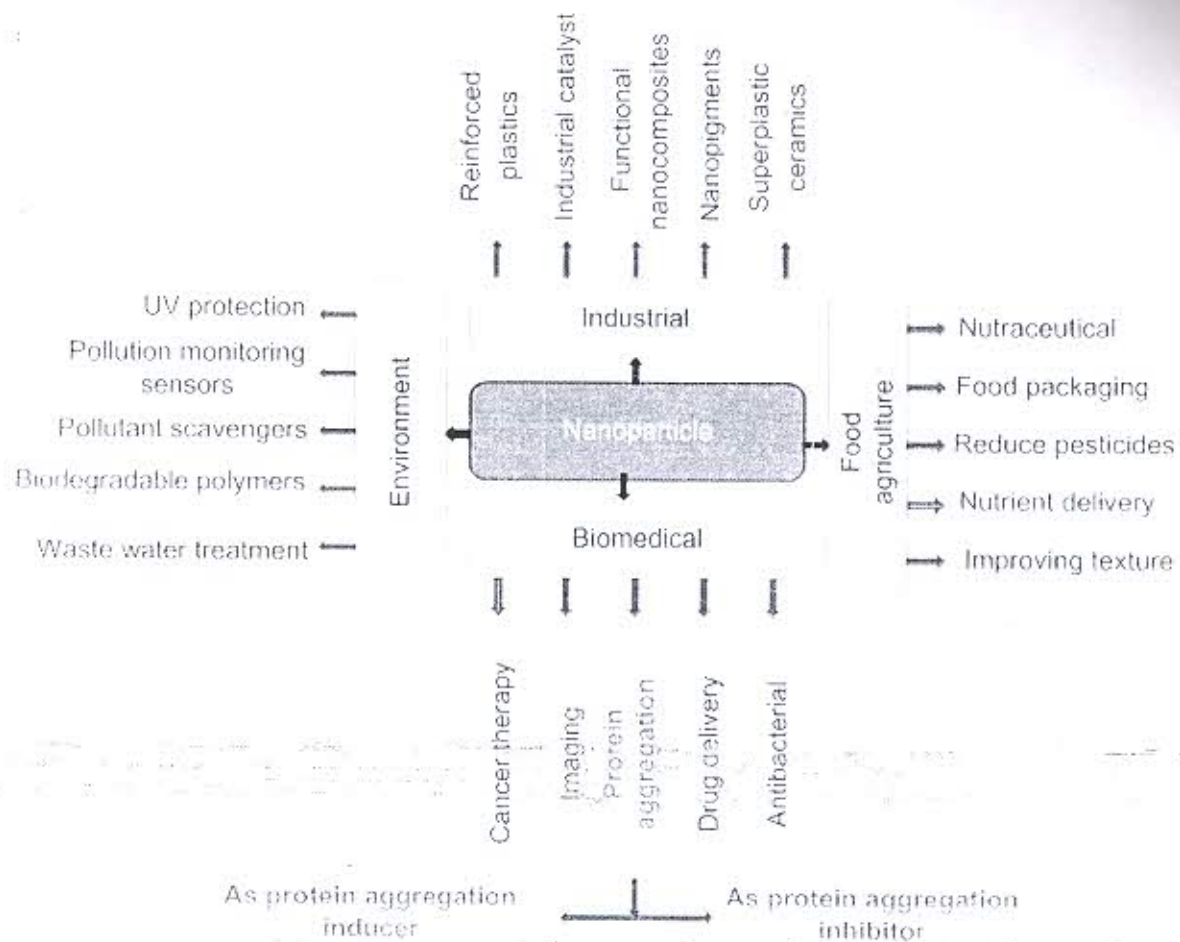
## Type

Several specialized types of synchrotron machines are used today:

- A storage ring is a special type of synchrotron in which the kinetic energy of the particles is kept constant.
- A synchrotron light source is a combination of different electron accelerator types, including a storage ring in which the desired electromagnetic radiation is generated. This radiation is then used in experimental stations located on different beamlines. In addition to the storage ring, a synchrotron light source usually contains a linear accelerator (linac) and another synchrotron which is sometimes called *booster* in this context. The linac and the booster are used to successively accelerate the electrons to their final energy before they are magnetically "kicked" into the storage ring. Synchrotron light sources in their entirety are sometimes called "synchrotrons", although this is technically incorrect.
- A cyclic collider is also a combination of different accelerator types, including two intersecting storage rings and the respective pre-accelerators

## Principle of operation

The synchrotron evolved from the cyclotron, the first cyclic particle accelerator. While a classical cyclotron uses both a constant guiding magnetic field and a constant-frequency electromagnetic field (and is working in classical approximation), its successor, the isochronous cyclotron, works by local variations of the guiding magnetic field, adapting the increasing relativistic mass of particles during acceleration.

In a synchrotron, this adaptation is done by variation of the magnetic field strength in time, rather than in space. For particles that are not close to the speed of light, the frequency of the applied electromagnetic field may also change to follow their non-constant circulation time. By increasing these parameters accordingly as the particles gain energy, their circulation path can be held constant as they are accelerated. This allows the vacuum chamber for the particles to be a large thin torus, rather than a disk as in previous, compact accelerator designs. Also, the thin profile of the vacuum chamber allowed for a more efficient use of magnetic

# SYNCHROTRON

A **synchrotron** is a cyclic particle accelerator in which a charge particle is accelerated to very high energies in the presence of an alternating electric field while confined to a constant circular orbit by a magnetic field.

A **synchrotron** is a particular type of cyclic particle accelerator, descended from the cyclotron, in which the accelerating particle beam travels around a fixed closed-loop path. The magnetic field which bends the particle beam into its closed path increases with time during the accelerating process, being *synchronized* to the increasing kinetic energy of the particles. The synchrotron is one of the first accelerator concepts to enable the construction of large-scale facilities, since bending, beam focusing and acceleration can be separated into different components. The most powerful modern particle accelerators use versions of the synchrotron design. The largest synchrotron-type accelerator, also the largest particle accelerator in the world, is the 27-kilometre-circumference (17 mi) Large Hadron Collider (LHC) near Geneva, Switzerland, built in 2008 by the European Organization for Nuclear Research (CERN). It can accelerate beams of protons to energy of 6.5 teraelectronvolts (TeV).
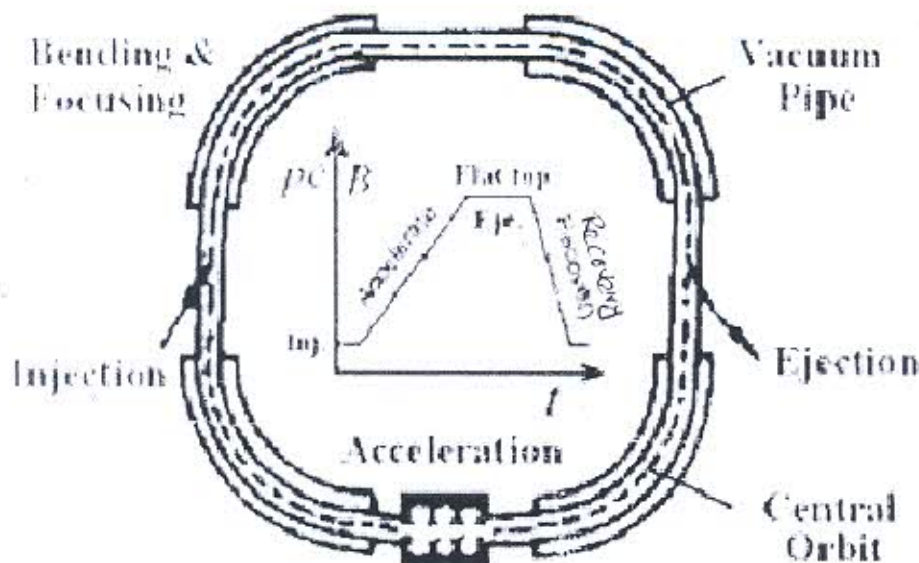
fields than in a cyclotron, enabling the cost-effective construction of larger synchrotrons.

While the first synchrotrons and storage rings like the Cosmotron and ADA strictly used the toroid shape, the strong focusing principle independently discovered by Ernest Courant and Nicholas Christofilos allowed the complete separation of the accelerator into components with specialized functions along the particle path, shaping the path into a round-cornered polygon. Some important components are given by radio frequency cavities for direct acceleration, dipole magnets (*bending magnets*) for deflection of particles (to close the path), and quadrupole / sextupole magnets for beam focusing.

The combination of time-dependent guiding magnetic fields and the strong focusing principle enabled the design and operation of modern large-scale accelerator facilities like colliders and synchrotron light sources. The straight sections along the closed path in such facilities are not only required for radio frequency cavities, but also for particle detectors (in colliders) and photon generation devices such as wigglers and undulators (in third generation synchrotron light sources).

The maximum energy that a cyclic accelerator can impart is typically limited by the maximum strength of the magnetic fields and the minimum radius (maximum curvature) of the particle path. Thus one method for increasing the energy limit is to use superconducting magnets, these not being limited by magnetic saturation. Electron/positron accelerators may also be limited by the emission of synchrotron radiation, resulting in a partial loss of the particle beam's kinetic energy. The limiting beam energy is reached when the energy lost to the lateral acceleration required to maintain the beam path in a circle equals the energy added each cycle.

More powerful accelerators are built by using large radius paths and by using more numerous and more powerful microwave cavities. Lighter particles (such as electrons) lose a larger fraction of their energy when deflected. Practically speaking, the energy of electron/positron accelerators is limited by this radiation loss, while this does not play a significant role in the dynamics of proton or ion accelerators. The energy of such accelerators is limited strictly by the strength of magnets and by the cost.

## Applications

- Life sciences: protein and large-molecule crystallography
- LIGA based microfabrication

- Drug discovery and research
- X-ray lithography
- Analysing chemicals to determine their composition
- Observing the reaction of living cells to drugs
- Inorganic material crystallography and microanalysis
- Fluorescence studies
- Semiconductor material analysis and structural studies
- Geological material analysis
- Medical imaging
- Particle therapy to treat some forms of cancer

## Advantages

- Continuous spectrum
- High Flux and brightness
- High coherence
- Able to detect nanoscale particles

## Disadvantages

- Beam line instability
- Travel to beam line
-

# Synthesis

Physical     chemical     Biological     Hybrid

Biological
→ Using biomolecules
biomembranes
micro-organism
plants

Hybrid
→ Electrochemical
chemical vapour
deposition,
particle arrestin (
in glass or
Zeolites or
Polymers

Mechanical     Vapour

Vapour
→ Physical vapor deposition
Laser ablation, sputter deposition
Electric arc deposition, ion ~~implantation~~
implantation

Mechanical
→ High energy
ball milling, melt mixing

- Nanoparticle synthesis refers to methods for creating nanoparticles. Nanoparticles can be derived from larger molecules or synthesized by "bottom-up" methods. for example nucleate and grow particles from fine molecular distribution in liquid or vapour phase. Synthesis can also include
  ⊙ functionalization by conjugation to bioactive molecules.

⊢ Entanglement is a quantum effect, Radioactive decay is a quantum
ι Interference bet$^n$ electrons is in this sense a effect
  quantum effect.
· In physics, a quantum is the minimum amount of any
  physical entity (physical property) involved in an
  interaction.

)Mechanical
properties

**Nanocomposite coating**
- enhanced toughness
- Lubrication and wear-resistence
- energy - absorbing -
  - particle/Matrix interfacial interaction
    - particle agglomeration

**Mechanical properties**

- hardness
- elastic Modulus
- adhesion
- friction
- movement

- Force
- electrostatic force
- capillary force

Interfacial interaction

- particle rolling
- particle sliding
- particle delamination
- particle agglomeration
  - lubricant additive

- particle collision in dry hydrodynamic film
- abrasive grinding of particle direct
- particle adhesion contact
  cleaning in part
  in Nanomanufacturing

1) Thermal properties — It is well-known fact that Metal nanoparticles have thermal conductivities higher than those of fluids in solid form.

2) Magnetic properties — The uneven electronic distribution in NPs leads to magnetic property. At low scale the magnetic properties of NPs dominated effectively, which make these particle priceless & can be used in different applications.

4) electronic & optical properties

# PROPERTIES

Nanoparticles are of great scientific interest as they are, in effect, a bridge between bulk materials and atomic or molecularstructures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of the surface in relation to the percentage of the volume of a material becomes significant. For bulk materials larger than one micrometer (or micron), the percentage of the surface is insignificant in relation to the volume in the bulk of the material. *The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material.*

Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. For example, gold nanoparticles appear deep-red to black in solution. Nanoparticles of yellow gold and grey silicon are red in color. Gold nanoparticles melt at much lower temperatures ($\sim$300 °C for 2.5 nm size) than the gold slabs (1064 °C). Absorption of solar radiation is much higher in materials composed of nanoparticles than it is in thin films of continuous sheets of material. In both solar PV and solar thermal applications, controlling the size, shape, and material of the particles, it is possible to control solar absorption. Recently, the core (metal)-shell (dielectric) nanoparticle has demonstrated a zero backward scattering with enhanced forward scattering on Si substrate when surface plasmon is located in front of a solar cell. The core-shell nanoparticles can support simultaneously both electric and magnetic resonances, demonstrating entirely new properties when compared with bare metallic nanoparticles if the resonances are properly engineered.

Other size-dependent property changes include quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials. What would appear ironic is that the changes in physical properties are not always desirable. Ferromagnetic materials smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, thus making them unsuitable for memory storage.

Suspensions of nanoparticles are possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences, which otherwise usually result in a material either sinking or floating in a liquid.

The high surface area to volume ratio of nanoparticles provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. In theory, this does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles to agglomerate complicates matters. Moreover, nanoparticles have been found to impart some extra properties to various day to day products. For example, the presence of titanium dioxide nanoparticles imparts what we call the self-cleaning effect, and, the size being nano-range, the particles cannot be observed. Zinc oxide particles have been found to have superior UV blocking properties compared to its bulk substitute. This is one of the reasons why it is often used in the preparation of sunscreen lotions, is completely photostable and toxic.

Clay nanoparticles when incorporated into polymer matrices increase reinforcement, leading to stronger plastics, verifiable by a higher glass transition temperature and other mechanical property tests. These nanoparticles are hard, and impart their properties to the polymer (plastic).

Nanoparticles have also been attached to textile fibers in order to create smart and functional clothing.

Metal, dielectric, and semiconductor nanoparticles have been formed, as well as hybrid structures (e.g., core–shell nanoparticles). Nanoparticles made of semiconducting material may also be labeled quantum dots if they are small enough (typically sub 10 nm) that quantization of electronic energy levels occurs. Such nanoscale particles are used in biomedical applications as drug carriers or imaging agents with work being done to try to understand the fluid dynamic properties (e.g. drag forces) in nanoscale applications. This has shown the relationship between the fluid forces on nanoparticles and the fluid Reynolds and Knudsen numbers.

Semi-solid and soft nanoparticles have been manufactured. A prototype nanoparticle of semi-solid nature is the liposome. Various types of liposome nanoparticles are currently used clinically as delivery systems for anticancer drugs and vaccines.

Nanoparticles with one half hydrophilic and the other half hydrophobic are termed Janus particles and are particularly effective for stabilizing emulsions. They can self-assemble at water/oil interfaces and act as solid surfactants.

Hydrogel nanoparticles made of N-isopropylacrylamide hydrogel core shell can be dyed with affinity baits, internally. These affinity baits allow the nanoparticles to isolate and remove undesirable proteins while enhancing the target analytes.

# Synthesis

There are several methods for creating nanoparticles, including gas condensation, attrition, chemical precipitation, ion implantation, pyrolysis and hydrothermal synthesis. In attrition, macro- or micro-scale particles are ground in a ball mill, a planetary ball mill, or other size-reducing mechanism. The resulting particles are air classified to recover nanoparticles. In pyrolysis, a vaporous precursor (liquid or gas) is forced through an orifice at high pressure and burned. The resulting solid (a version of soot) is air classified to recover oxide particles from by-product gases. Traditional pyrolysis often results in aggregates and agglomerates rather than single primary particles. Ultrasonic nozzle spray pyrolysis (USP) on the other hand aids in preventing agglomerates from forming.

A thermal plasma can deliver the energy to vaporize small micrometer-size particles. The thermal plasma temperatures are in the order of 10,000 K, so that solid powder easily evaporates. Nanoparticles are formed upon cooling while exiting the plasma region. The main types of the thermal plasma torches used to produce nanoparticles are dc plasma jet, dc arc plasma, and radio frequency (RF) induction plasmas. In the arc plasma reactors, the energy necessary for evaporation and reaction is provided by an electric arc formed between the anode and the cathode. For example, silica sand can be vaporized with an arc plasma at atmospheric pressure, or thin aluminum wires can be vaporized by exploding wire method. The resulting mixture of plasma gas and silica vapour can be rapidly cooled by quenching with oxygen, thus ensuring the quality of the fumed silica produced.

In RF induction plasma torches, energy coupling to the plasma is accomplished through the electromagnetic field generated by the induction coil. The plasma gas does not come in contact with electrodes, thus eliminating possible sources of contamination and allowing the operation of such plasma torches with a wide range of gases including inert, reducing, oxidizing, and other corrosive atmospheres. The working frequency is typically between 200 kHz and 40 MHz. Laboratory units run at power levels in the order of 30–50 kW, whereas the large-scale industrial

units have been tested at power levels up to 1 MW. As the residence time of the injected feed droplets in the plasma is very short, it is important that the droplet sizes are small enough in order to obtain complete evaporation. The RF plasma method has been used to synthesize different nanoparticle materials, for example synthesis of various ceramic nanoparticles such as oxides, carbours/carbides, and nitrides of Ti and Si (see Induction plasma technology).

Inert-gas condensation is frequently used to make nanoparticles from metals with low melting points. The metal is vaporized in a vacuum chamber and then supercooled with an inert gas stream. The supercooled metal vapor condenses into nanometer-size particles, which can be entrained in the inert gas stream and deposited on a substrate or studied in situ.

Nanoparticles can also be formed using radiation chemistry. Radiolysis from gamma rays can create strongly active free radicals in solution. This relatively simple technique uses a minimum number of chemicals. These including water, a soluble metallic salt, a radical scavenger (often a secondary alcohol), and a surfactant (organic capping agent). High gamma doses on the order of $10^4$ Gray are required. In this process, reducing radicals will drop metallic ions down to the zero-valence state. A scavenger chemical will preferentially interact with oxidizing radicals to prevent the re-oxidation of the metal. Once in the zero-valence state, metal atoms begin to coalesce into particles. A chemical surfactant surrounds the particle during formation and regulates its growth. In sufficient concentrations, the surfactant molecules stay attached to the particle. This prevents it from dissociating or forming clusters with other particles. Formation of nanoparticles using the radiolysis method allows for tailoring of particle size and shape by adjusting precursor concentrations and gamma dose.

## Sol–gel

The sol–gel process is a wet-chemical technique (also known as chemical solution deposition) widely used recently in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (sol, short for solution), which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers.

Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form either a network "elastic solid" or a colloidal suspension(or dispersion) — a system composed of discrete (often amorphous) submicrometer particles dispersed to various degrees in a host fluid. Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. Thus, the sol evolves toward the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks.

In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in a number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation.

Removal of the remaining liquid (solvent) phase requires a drying process, which typically causes shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes implemented during this phase of processing. Afterward, a thermal treatment, or firing process, is often necessary in order to favor

further polycondensation and enhance mechanical properties and structural stability via final sintering, densification, and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.

The precursor sol can be either deposited on a substrate to form a film (e.g., by dip-coating or spin-coating), cast into a suitable container with the desired shape (e.g., to obtain a monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g., microspheres, nanospheres). The sol–gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth metals, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol–gel derived materials have diverse applications in optics, electronics, energy, space, (bio)sensors, medicine(e.g., controlled drug release) and separation (e.g., chromatography) technology.

## Ion implantation

Ion implantation may be used to treat the surfaces of dielectric materials such as sapphire and silica to make composites with near-surface dispersions of metal or oxide nanoparticles. See ion implantation Ion implantation-induced nanoparticle formation.

**Ion implantation** is low-temperature process by which ions of one element are accelerated into a solid target, thereby changing the physical, chemical, or electrical properties of the target. Ion implantation is used in semiconductor device fabrication and in metal finishing, as well as in materials science research. The ions can alter the elemental composition of the target (if the ions differ in composition from the target) if they stop and remain in the target. Ion implantation cause also chemical and physical changes when the ions impinge on the target at high energy. The crystal structure of the target can be damaged or even destroyed by the energetic collision cascades, and ions of sufficiently high energy (10s of MeV) can cause nuclear transmutation.

## Applications

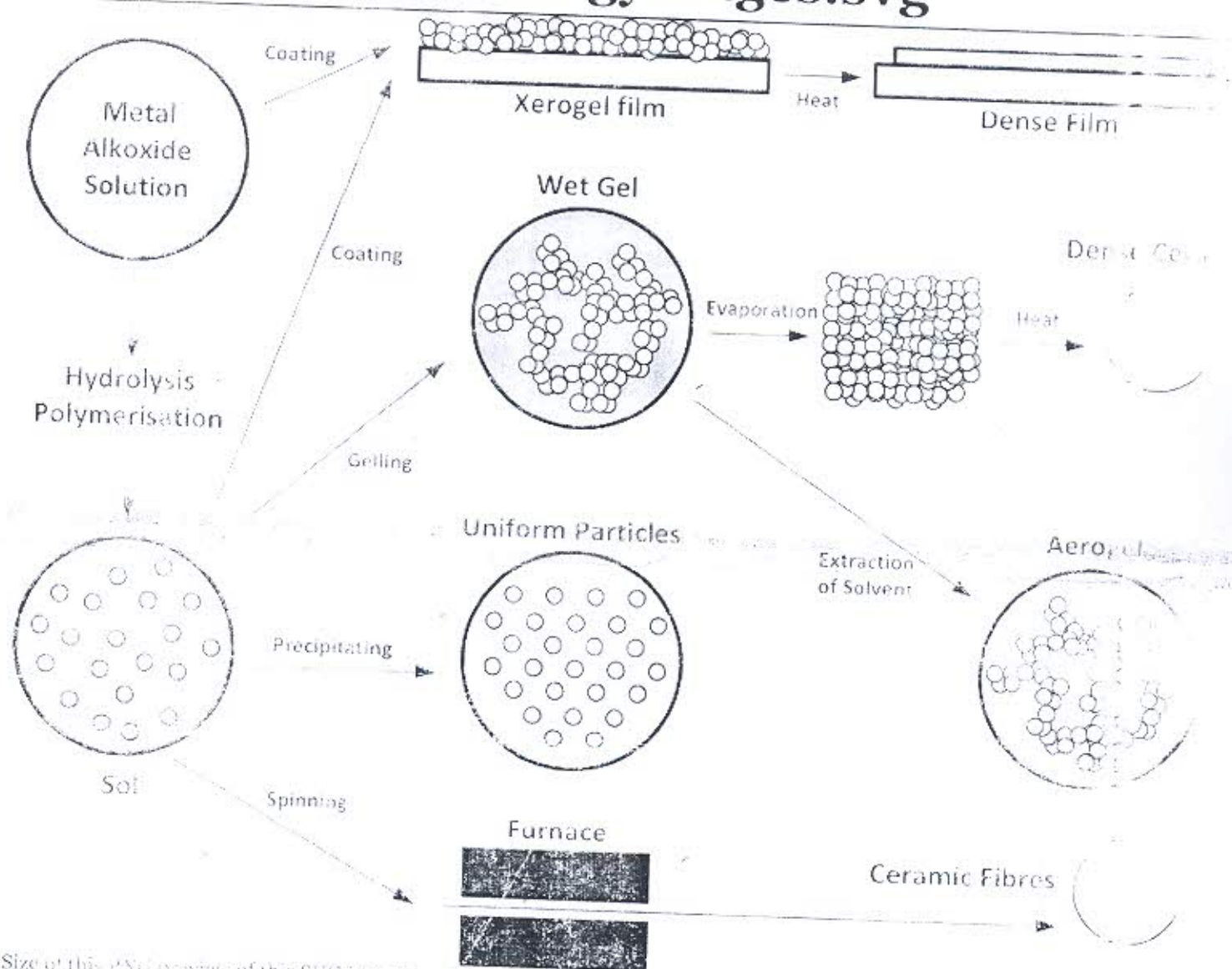(Scientific research on nanoparticles is intense as they have many potential applications in medicine, physics,optics, and electronics.) The U.S. National Nanotechnology Initiative offers government funding focused on nanoparticle research.

The use of nanoparticles in laser dye-doped poly(methyl methacrylate) (PMMA) laser gain media was demonstrated in 2003 and it has been shown to improve conversion efficiencies and to decrease laser beam divergence.Researchers attribute the reduction in beam divergence to improved dn/dT characteristics of the organic-inorganic dye-doped nanocomposite. The optimum composition reported by these researchers is 30% w/w of $SiO_2$ (~ 12 nm) in dye-doped PMMA.

(Nanoparticles are being investigated as potential drug delivery system. Drugs, growth factors or other biomolecules can be conjugated to nano particles to aid targeted delivery. This nanoparticle-assisted delivery allows for spatial and temporal controls of the loaded drugs to achieve the most desirable biological outcome. )

(Nanoparticles are also studied for possible applications as dietary supplements for delivery of biologically active substances, for example mineral elements.)

# File:SolGelTechnologyStages.svg



Metal Alkoxide Solution

Coating

Xerogel film

Heat

Dense Film

Wet Gel

Coating

Evaporation

Dense Co...

Heat

Hydrolysis Polymerisation

Gelling

Uniform Particles

Aero...

Extraction of Solvent

Sol

Precipitating

Spinning

Furnace

Ceramic Fibres

Size of this PNG preview of this SVG file: 769 × 599 pixels.
Original file ... nominally 1:1.5 × 90 pixels, file size: 86 KB)

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# Summary

| | |
|---|---|
| **Description** | **English:** Schematic representation of the different stages and routes of the sol-gel technology. |
| **Date** | 26 November 2013, 19:14:44 |
| **Source** | Own work , inspired in Brinker and Scherer book ("Sol-gel Science: The Physics and Chemistry of Sol-gel Processing") and in several images found online. |

# File:Ion implanter schematic.png

substrate

ion magnet

$U_{decell}$

$U_{accell}$

ion source

No higher resolution available.

Ion_implanter_schematic.png (500 × 486 pixels, file size: 32 KB, MIME type: image/png)

**Open in Media Viewer**

This is a file from the Wikimedia Commons. Information from its description page there is shown below.

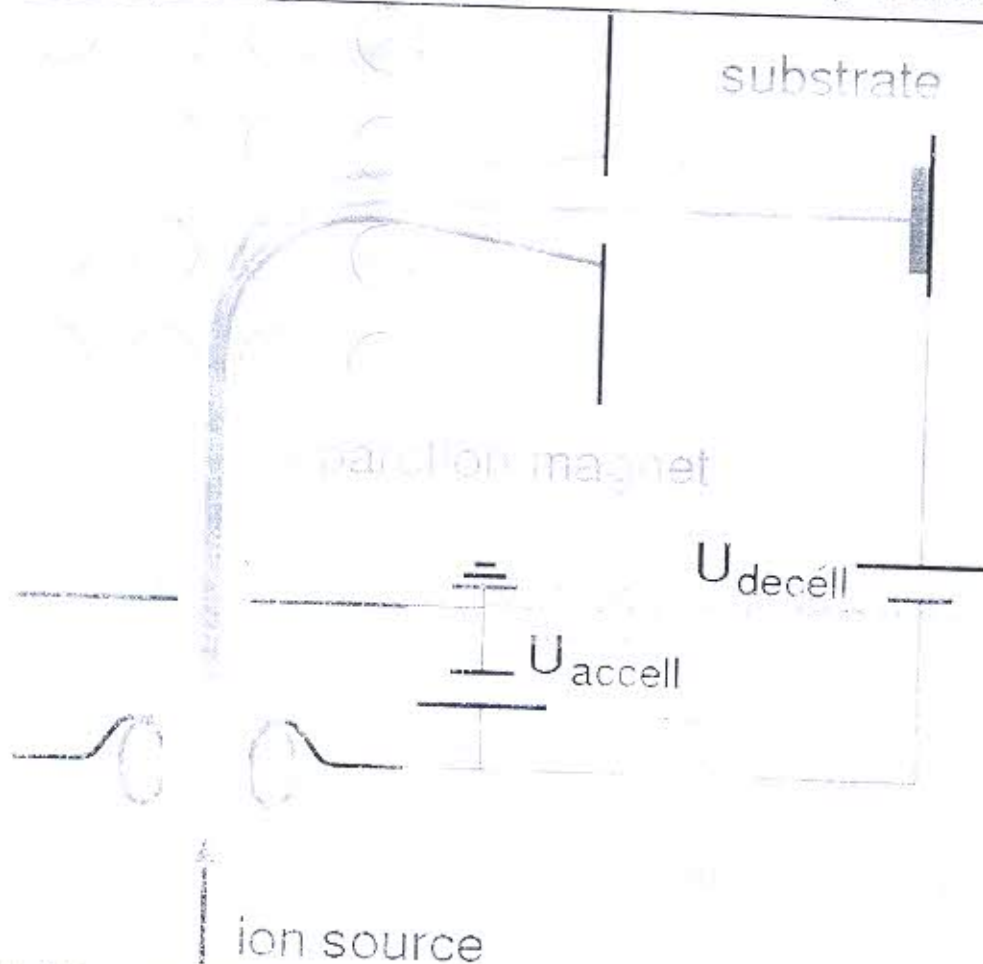Commons is a freely licensed media file repository. You can help.

**Description** English: Schematics of an mass separating implantation/deposition setup. Ion energy at the substrate is determined by the difference of $U_{accell}$ and $U_{decell}$. Image created using Tgif.

**Date** 3 July 2005

**Source** Own work

**Author** Daniel Schwen

Sanyam in the self (I) - feeling of responsibility for Nurturing

Bio - Device & application

Bio - nanostructures ( nanofibers, nanotubes nanocellulose)

Biological nanomachines Ribosomes photosynthesis systems, Near-field Bioimaging

A nanostructure is a structure of intermediate size betn microscopic & molecular structures. Nanostructures refer to materials or structures that have at least one dimension betn 1 and 100 nm.

Nanofiber - Nanofibers are fibers with diameters in the nanometer range. Nanofibers can be generated from different polymers and herre have different physical properties & application potentials. Examples of natural polymers include collagen, cellulose, silk fibroin, keratin, gelatin & polysaccharides such as chitosan & alginate. Examples of synthetic polymers include poly Lactic acid (PLA), poly or polycaprolactone (PCL), polyurethane (PU)

poly ethylene-co-glycolic acid (PLGA)

- The diameters of nanofibers depend on the type of polymer used & the method of production.

- All polymer nanofibers are unique for their large surface area-to-volume ratio, high porosity, appreciable mechanical strength and flexibility in functionalization compared to their microfiber counterparts

- There exist many different methods to make nanofibers including drawing electrospinning, self-assembly, template synthesis and thermal-induced phase separation.

**Applications** - Nanofibers have many possible technological & commerical applications. They are used in tissue engineering, drug delivery, cancer diagnosis, lithium-air battery, optical sensors & air filtration, oil-water separation, sportswear textile

# Applications of CNTs

1. Aligned MWNTs show potential as field-emission devices such as electronic flat-panel displays.
2. Field effect transistors can be designed using CNTs, which can be used for gas sensing.

3. composite CNTs can be used as light-weight shielding material for electronic devices to protect them from electromagnetic radiations.
4. CNTs can be used as battery electrodes.
5. supercapacitors can be fabricated using CNTs.
6. The CNTs may be used for hydrogen storage and fuel cell applications.
7. CNTs can be used to develop nano-biometric devices.
8. Nanotube fluorescence has been investigated for the purpose of imaging and sensing in biomedical applications.
9. light-emitting diodes & photo-detectors can be made based on a single nanotube with narrow selectivity in emission wavelength and the possibility of its fine tuning through the nanotube structure.
10. electroluminescent devices have been produced from single nanotubes.

A CNT is a 1D system, which can be considered as a rolled sheet of graphene. Its diameter lies within 1–2 nm, whereas the length can vary reaching up to 100–1000 nm. Thus, the nanotube aspect ratio can be very high (132,000,000:1), making the properties of the CNTs anisotropic and tunable, relative to those of typical semiconductors. Nanotubes possess a high strength to weight ratio, about 100 times more than steel. Density of an SWNT is about 0.8 g/cm³ and that of an MWNT is about 1.8 g/cm³. Surface area of nanotubes ranges between 10 m²/g and 20 m²/g.

Carbon nanotubes exhibit a wide diversity in structure and structure-related properties. They have low density which makes them intrinsically lightweight. Depending upon the orientation of the hexagonal rings on the walls of the nanotubes, these may be metallic or semiconducting.

SWNTs are thermally stable up to about 1500 °C in an inert atmosphere. In air or oxygen, SWNTs burn in the range of 450 to 620 °C. Due to a difference in the strain energy, smaller diameter tubes burn at lower temperatures in comparison with larger diameter tubes.

The properties of CNTs depend on the tube diameter. Bandgap is determined by the circumferential quantum confinement. Elastic properties are affected by tube diameter, tube chirality, and the number of tube layers. Hence, the results for MWNTs generally vary with the number of carbon shells. For simple understanding, some properties of SWNTs are summarized in Table 6.1.

Table 6.1  Properties of SWNTs

| Property | Value for metallic SWNT | Value for semiconducting SWNT |
|---|---|---|
| Diameter | | 1–2 nm |
| Length | | 100–1000 nm |
| Elastic modulus | | 1000–3000 GPa |
| Thermal conductivity at 300 K | | 20–3000 W/mK |
| Bandgap | 0 eV | 0.5 eV |
| work function | | 5 eV |
| current density | | $10^7$–$10^8$ A/cm² |
| field emission current density | | 10–2000 mA/cm² |

Mechanical properties — Elastic Modulus, Hardness, viscoelastic properties, creep, stress relaxation, Interfacial Adhesion, fracture roughness.

Electrical   —   conductivity

optical   —   color, transparency

chemical   —   reactivity, reaction rates

# PHYSICAL PROPERTIES OF CNT

A CNT is a 1D system, which can be considered as a rolled sheet of graphene. Its diameter lies within 1-2 nm, whereas the length can vary reaching up to 100-1000 nm. Thus, the nanotube aspect ratio can be very high (132,000,000:1), making the properties of the CNTs anisotropic and tunable, relative to those of typical semiconductors. Nanotubes possess a high strength to weight ratio, about 100 times more than steel. Density of an SWNT is about $0.8 \text{ g/cm}^3$ and that of an MWNT is about 1.8 $\text{g/cm}^3$. Surface area of nanotubes ranges between $10 \text{ m}^2/\text{g}$ and $20 \text{ m}^2/\text{g}$.

Carbon nanotubes exhibit a wide diversity in structure and structure-related properties. They have low density which makes them intrinsically lightweight. Depending upon the orientation of the hexagonal rings on the walls of the nanotubes, these may be metallic or semiconducting.

SWNTs are thermally stable up to about 1560 °C in an inert atmosphere. In air or oxygen, SWNTs burn in the range of 450 to 620 °C. Due to a difference in the strain energy, smaller diameter tubes burn at lower temperatures in comparison with larger diameter tubes.

The properties of CNTs depend on the tube diameter. Bandgap is determined by the circumferential quantum confinement. Elastic properties are affected by tube diameter, tube chirality, and the number of tube layers. Hence, the results for MWNTs generally vary with the number of carbon shells. For simple understanding, some properties of SWNTs are summarized in Table 6.1.

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| *field emission current density* | | $10 - 9000 \text{ mA/cm}^3$ |

# Applications of CNTs

1. Aligned MWNTs show potential as field-emission devices such as electronic flat-panel displays.

2. Field effect transistors can be designed using CNTs, which can be used for gas sensing.

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5. Supercapacitors can be fabricated using CNTs.

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7. CNTs can be used to develop nano-biometric devices.

8. Nanotube fluorescence has been investigated for the purpose of imaging and sensing in biomedical applications.

9. Light-emitting diodes & photo-detectors can be made based on a single nanotube with narrow selectivity in emission wavelength and the possibility of its fine tuning through the nanotube structure.

10. Electroluminescence devices have been produced from single nanotube.

Allotropes of carbon (Graphite
& diamond
structure)

## KEY TERMS

Achiral

**Achiral** A molecule is said to be achiral if it can be superimposed on its mirror image. Usually achiral molecules possess a plane of symmetry or a center of symmetry. In case of carbon nanotubes, $(n, 0)$ and $(n, n)$ tubes are achiral and are identical to their mirror image.

**Armchair nanotubes** Armchair nanotubes are nanotubes made by rolling in the direction of axes parallel to the C-C bonds of carbon hexagons.

**Carbon nanotubes** CNTs are allotropes of carbon having a cylindrical nanostructure and large length to diameter ratio (upto 132000000:1). The basic structure of a CNT is that of a rolled-up sheet of graphene. The sheet is arranged in a hexagonal structure with each carbon atom connected to three neighbouring carbon atoms by $sp^2$ hybridization with $D_{6h}$ point group symmetry. CNTs have extraordinary thermal conductivity, mechanical, electrical, optical properties, etc.

**Chiral** The term chirality is derived from a Greek word which means hand. A molecule or a system is said to be chiral if it can be distinguished from its mirror image. In other words, a chiral molecule cannot be superimposed on its mirror image. In case of carbon nanotubes, any tube other than $(n, 0)$ and $(n, n)$ is chiral and non-superimposable of its mirror image.

**Endohedral functionalization** Endohedral functionalization refers to functionalization inside the surface. In case of CNTs, it is the filling of the nanotubes with atoms or molecules.

**Exohedral functionalization** Exohedral functionalization refers to functionalization on

the outer surface. In case of CNTs, it comprises functionalization both at the termini and on the side walls.

**Functionalization of nanotubes** Functionalization of nanotubes is also known as derivatization of nanotubes. It is defined as the addition of chemical functional groups to the ends and sidewalls of the nanotubes, post production. Functionalization improves the solubility and processability of nanotubes.

**Inorganic nanotubes** Inorganic nanotubes are nanotubes are made up of metal oxides, chalcogenides, nitrides, etc. and possess a morphology similar to that of CNTs.

**Multi walled carbon nanotube** Multi walled carbon nanotube (MWNT) is composed of many layers of graphene sheets rolled up concentrically or several tubes stacked one within the other. In other words, MWNTs are made up of a number of concentrically formed SWNTs having different diameter.

**Nanotubes** Nanotubes are long, hollow, cylindrical tube-like structures having an inner and an outer diameter. Nanotubes have diameter in the nanosize range and a high length to diameter ratio.

**Single walled carbon nanotube** A single walled carbon nanotube (SWNT) is a seamless cylindrical tube rolled from a single sheet of graphene. The diameter of an SWNT is about 1-2 nm.

**Zigzag nanotubes** Zigzag nanotubes are nanotubes made by rolling in the direction of nanotubes made by rolling in the direction of $(n, 0)$ or folded at an angle of $30°$ from the direction of C-C bond.

## EXERCISES
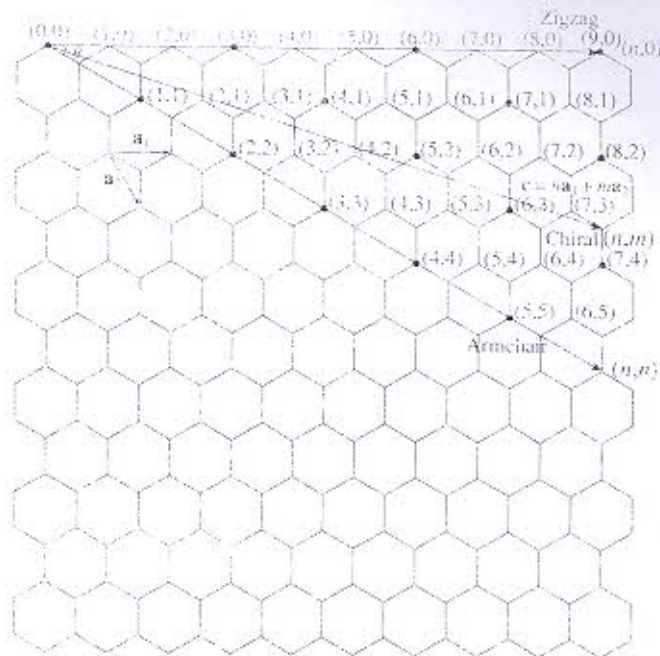
physical Structure of CNT

**FIG. 6.4** Basic vectors of the 2D unit cell, wrapping vectors, and patterns in electronic character shown in a graphitic sheet to be rolled up to form a CNT [($\theta$ = chiral angle, with • - metallic nanotubes, and without • - semiconducting nanotubes) ($\theta$ = 0 or ($n$, 0) tubes - zigzag, $\theta$ = 30° or ($n$, $n$) tubes - armchair, any other value for $\theta$ - chiral)].

Based on the direction of rolling, achiral or chiral nanotubes can be generated. $(n, 0)$ and $(n, n)$ tubes are achiral, whereas the rest are chiral. Spiral rows of carbon atoms appear to coil around the tube axis on looking down a chiral tube. Chiral tubes can be left- or right-handed. $(n, 0)$ nanotubes or tubes folded at an angle of 30° from the direction of a C–C bond are called zigzag tubes. Note that the chiral angle ($\theta$) is zero for zigzag tubes. $(n, n)$ nanotubes or nanotubes folded in the direction parallel to the C–C bonds of carbon hexagon are called armchair due to the configuration of the carbon–carbon bonds along the direction of wrapping. The chiral angle ($\theta$) for armchair tubes is 30°. Zigzag and armchair nanotubes possess a plane of symmetry perpendicular to the tube axis. Armchair, zigzag, and chiral nanotubes are shown in Fig. 6.5.
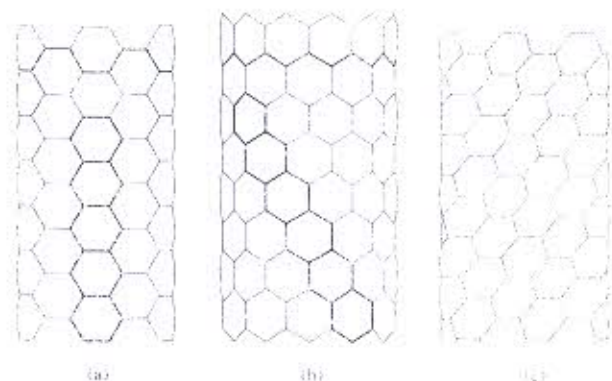


FIG. 6.5    Types of carbon nanotubes (a) Armchair (b) Zigzag (c) Chiral

Different structured CNTs formed by different rolling directions or of different electronic properties. Certain nanotubes are metallic, whereas others are semi-conducting. These patterns in electronic character are also depicted in Fig. 6.5. When $m - n = 3k$ (where $k$ is an integer), the tube is metallic, whereas if $m - n = 3k \pm 1$, the tube is semiconducting. The nanotube diameter $d$ is related to $m$ and $n$ as

$$d = \frac{a}{\pi} \sqrt{n^2 - nm + m^2}$$

where, $a = 0.246$ nm is the magnitude of either unit vector $a_1$ or $a_2$.

## 6.3.1  Types of Nanotubes

Two types of nanotubes are known—single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). 'C' is omitted in the abbreviated forms as it is implied that the nanotubes are composed of carbon. An SWNT consists of a single sheet of graphene rolled into a seamless cylinder whereas an MWNT can be understood as many layers of graphene rolled up concentrically or several tubes stacked one within the other. We can also say that MWNTs are

ernor.

rrect steering? Sketch and show the two main types of
eir relative advantages.

l of 240 rpm. Four masses of magnitude 100 kg, 150 kg,
ively are rigidly attached to the shaft. The masses are
he corresponding radii of rotation are 400 mm, 300 mm,
tively. The angles made by these masses with horizontal
ctively. Find

ancing mass.
cing mass if the radius of rotation is 400 mm.

g engine has the following data:
stroke= 320 mm; mass of reciprocating parts= 45 kg and
kg at crank radius. If 60% of the reciprocating parts and all
balanced, the find:

uired at a radius of 300 mm.
on the crank has rotated 60° from top dead centre.

ent and the ratio of any two consecutive amplitude of a
sists of a mass of 3.5 kg, a spring of stiffness 2.5 N/mm
-efficient 0.018 N-s/mm.

### Part-III

uestions (Answer Any Two out of Four)                    (8)

m for a multi cylinder engine has been drawn to a scale of
and 1 mm = 2.4° horizontally. The intercepted area between
ean resistance line taken in order from one end are 342,
7, 104 mm², when the engine is running at 150 rpm. If the
0 kg and the total fluctuation of speed does not exceed 3%
minimum value of radius of gyration.

$$CH_3$$
$$|$$
$$H - C - Cl$$
$$|$$
$$Br$$

chiral

$$CH_3$$
$$|$$
$$H - C - H$$
$$|$$
$$Br$$
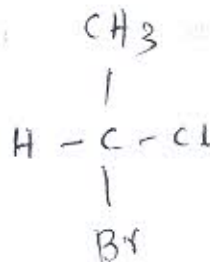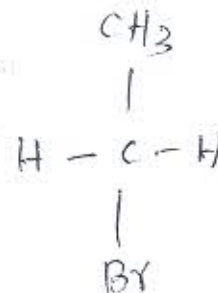
number of concentrically formed SWNTs having different diameters. Figure 6.6 depicts their difference. Due to wrapping of graphene, the usual planar orientation of $sp^2$-hybridized orbitals becomes disturbed, creating a strain. For this reason, the rolling into a tube having a tiny radius of curvature (less than 1 nm) becomes difficult due to energy considerations. In fact, nanotubes having greater diameter are much more stable than those with lesser diameter. In the case of an MWNT, it is not feasible to fit any tube into another due to space restriction. It is necessary to have a gap of 3.44 Å between the two layers. In other words, the diameter of the outer tube must have a diameter equal to or greater than [(2 × 3.44) + diameter of the inner tube]. This gap matches the interlayer distance between the two layers in graphite.

As we understand that MWNTs contain at least two to hundred SWNTs placed one within the other, they possess larger diameters (upto 50 nm) as compared to a typical SWNT. Electrical and mechanical properties of MWNTs are primarily contributed by the outer wall only. Thus, the same effect can be produced by a much lower loading of SWNTs in comparison with MWNTs. Comparing the two types, the properties of SWNTs are more exciting and incredible as they depict great strength, unique optical properties, show high electrical conductivity or semiconductivity, thermal conductivity at room temperature, etc. Their surface area per unit mass is also greater than that of MWNTs.
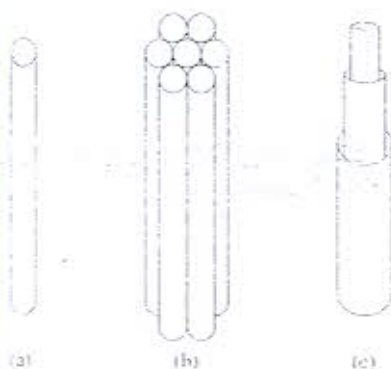


FIG. 6.6 Difference among the types of nanotubes (a) SWNT (b) Bundles of SWNT (c) MWNT

CNTs show excellent van der Waals adhesion with each other as well as with the other molecules. SWNTs spontaneously aggregate into crystalline bundles known as ropes (Fig. 6.6), generally 10 to 30 nm in diameter and a few microns in length. This adhesion arises as a result of the fluctuating and induced dipole moment due to the delocalized π orbitals on the surface of CNT. Both SWNTs and MWNTs can be grown in entangled as well as ordered, close packed structures. Packing depends on thermodynamic considerations and kinetics of entanglement during growth and aggregation and it is found that only CNTs of similar diameter but varying chiralities crystallize together. In fact, the major issue with utilizing SWNTs on a large scale is their exfoliation and untangling.

## 6.4 SYNTHESIS OF CNT

Carbon nanotubes have been synthesized in sizable quantities using various approaches, such as arc discharge, laser ablation, catalysed decomposition, and chemical vapour deposition (CVD). As has been discussed in Section 6.3.1, SWNTs appear more exciting due to their remarkable properties and so are in greater demand as compared to the MWNTs. Their synthesis is difficult and expensive in comparison with MWNTs. Also, SWNT production is desired in larger quantities. Most methods can be used to produce an MWNT as well as SWNT. The primary difference lies in the use of a metallic catalyst for the synthesis of SWNT. The present synthesis methods produce small yields and very high cost SWNTs. Methods based on chemical deposition developed for large scale synthesis majorly produce MWNTs. Similar scaling up of SWNTs is required for decreasing the cost and realizing the immense application potentials of CNTs.

### 6.4.1 Synthesis Methods

The synthesis methods being used are summarized in the following subsections with an emphasis on the synthesis of SWNT.

#### Krätschmer–Huffman Process

The chance discovery of MWNTs was made when Iijima observed nanotubes in the soot produced by the graphite electrodes during the production of fullerenes by arc discharge method. A 30V DC voltage was applied between two graphite electrodes, maintaining a current of about 180 A under 130 torr helium atmosphere, causing the breakdown of the gas molecules, thus producing an electric discharge at about 3000°C in Krätschmer–Huffman process. The carbon atoms at the anode vaporized and got redeposited on the cathode as well as the walls of the chamber as amorphous carbon, graphite, fullerene, and MWNTs. Nanotubes appeared as empty cylinders lying perpendicular to the electron beam.

#### Arc Discharge Method

Arc discharge method produces both the MWNT and SWNT. The arc discharge setup consists of an inert atmosphere in which two graphitic electrodes are used to generate a DC arc discharge (Fig. 6.7). This method could yield SWNTs when the anode was cored and filled with metal catalyst and a mixture of graphite. SWNT growth was catalysed by alloying Co, Ni, Fe, Y, and Gd in atomic percentage. This method yields about 30% by weight, nanotubes which appeared in the form of ropes of 5 to 100 individual SWNTs up to 50 micrometers in length having very little structural defects.
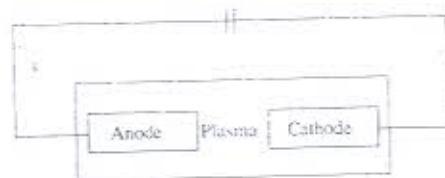
FIG. 6.7 Schema of arc discharge method

Laser ablation or photoablation is the process of removing material from a solid.

Graphene – It is a thin and almost transparent sheet of a single layer of tightly packed carbon atoms that are bonded together in a hexagonal honeycomb lattice. Graphite is formed by the stacking of graphene sheets.
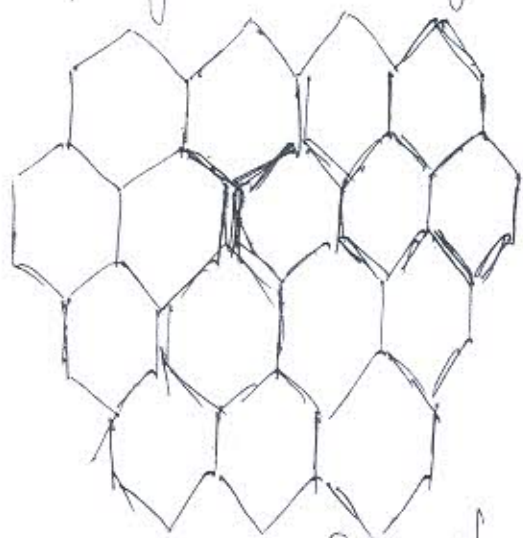
- Graphene forms the basic structure of many other carbon-based materials such as graphite, fullerene and carbon nanotubes. It can be wrapped up to form fullerenes, rolled up to give carbon nanotubes, or stacked up to produce graphite.

structure of graphene

Synthesis of Graphene – Graphene can be synthesized by a number of techniques ranging from chemical methods to physical methods.
* Scotch Tape Method, CVD, By Dissolution of carbon using methane, Reduction method, Sonication Method, chemical cleavage Method

**Graphene** — The carbon-carbon bond length in graphene is about 0.142 nanometers. Graphene sheets stack to form graphite with an interplanar spacing of 0.335 nm, which means that a stack of three million sheets would be only one nm thick. Graphene is the basic structural element of some carbon allotropes including graphite, charcoal, carbon nanotubes & fullerenes.

## chemical vapour Deposition (CVD)

CVD is a vacuum deposition Method used to produce high quality, high-performance solid materials. The process is often used in the semiconduct industry to produce thin films.

Large-scale synthesis of graphene films that can easily be transferred onto other substrates is possible using chemical vapour deposition. However the disadvantage of this method is that a mixture of single & Multilayers is formed.

## Konstantin Sergeevich Kostya Novoselov (1974)

Konstantin Sergeevich Kostya Novoselov is a Russo-British physicist who shared the Nobel Prize for Physics in 2010 with Andre Geim for their work on graphene. Together, they isolated individual graphene planes by using adhesive scotch tape in 2004. Novoselov has written more than 100 papers on Hall magnetometry, subatomic movements of magnetic domain walls, the discovery of gecko tape, and graphene.

He was conferred upon with numerous awards and honours like Nicholas Kurti European Science Prize in 2007, in recognition of his work on high magnetic fields and the Europhysics Prize in 2008 'for discovering and isolating a single free-standing atomic layer of carbon (graphene) and elucidating its remarkable electronic properties'.

### 5.4.3 Properties of Graphene

The term graphene was propounded by Hanns Peter Boehm in 1962 by combining graphite and the suffix 'ene', due to graphene being an indefinitely large aromatic molecule. An aromatic compound contains a planar ring with $(4n + 2)$ $\pi$ electrons, $n$ being a non-negative integer. The carbon–carbon bond length in graphene is $0.142$ nm. It is the thinnest ($0.34$ nm) and the strongest material ever measured. It is very light, weighing only about $0.77$ mg/m². Its density is only about $1.5$-$2.0$ g/cm³ and its specific surface area is up to $2600$ m²/g. For a size less than about $6000$ atoms, graphene is thermodynamically unstable in comparison with other fullerenes. As its size increases to larger than $24,000$ atoms, it becomes most stable. However, the largest isolated graphene consists of about $222$ atoms. Occurrence of free-standing atomic planes of graphene is difficult to obtain due to their thermodynamic instability on the nanoscale and thus, they exhibit a tendency to scroll and buckle.

The atomic structure of graphene consists of a honeycomb lattice. Suspended graphene depicts a rippling of the flat graphene sheet by about 1 nm. These ripples have been reported both due to intrinsic properties of graphene as well as extrinsic reasons. The intrinsic reason is the instability of 2D crystals and the thermal fluctuations in graphene, whereas the extrinsic reason is the presence of impurities or adsorbates like the photoresist residue used in lithographic techniques. Graphene can repair the holes in its sheets by itself when bombarded with carbon atoms which fit into the gaps and align into the hexagonal geometry. Intrinsic graphene is a semi-metal or zero bandgap semiconductor.

Electronic band structure, that is, the Dirac cone structure has been observed in graphene. It shows an unusual low-energy electronic structure in which the electron and hole conical bands meet each other at the Dirac points. Electrons and holes are known as Dirac fermions and the six corners of Brillouin zone are known as Dirac points. Electrons and holes near the six points behave in a similar way as the relativistic particles described by Dirac equation ($E = h\nu_F\sqrt{(k_x^2 + k_y^2)}$), where $E$ is energy, h is the reduced Planck's constant, $\nu_F$ is the Fermi velocity in graphene, $k_x$ and $k_y$ are wave vectors) showing linear dispersion relation for low energies. Massless Dirac fermions have been shown by graphene on SiC even without being transferred. Although graphene is just one-atom thick, it is visible to the naked eye, as it absorbs about 2-3% of white light. It shows high opacity in vacuum due to its Dirac cone structure.

Graphene depicts very high electron mobility at room temperature. Graphene produced by both the drawing method and epitaxial method, shows extremely large temperature-independent mobility in the temperature range of 10K to 100K. At room temperature, the value of mobility ranges from 15000cm²/Vs to 200000cm²/Vs. For graphene on $SiO_2$, the mobility observed does not exceed 40000cm²/Vs as the scattering of electrons by optical phonons of $SiO_2$ exceeds the scattering by graphene phonons. The high value of mobility in graphene shows very low, in fact, lowest resistivity at room temperature. Electron mobility in graphene is about 10 times faster than commercial silicon wafers. Due to its symmetry, the mobility of holes and electrons is similar in graphene. The most dominant mechanism observed is defect scattering. Charge carriers in graphene show ballistic transport under ambient conditions. Doping (the method of adding impurities to something) does not show an observable change in carrier mobility up to a high concentration. However, doping with potassium in ultra-high vacuum at low temperature decreased the mobility by about 20times, which was recoverable on heating of graphene to remove potassium.

Graphene shows a minimum conductivity of the order of $4e^2/h$ or greater, which is twice the conductance quantum $2e^2/h$ (quantized unit of electrical conductance). The appearance of minimum conductivity in graphene, despite the zero carrier density around the Dirac points, is probably due to the production of local puddles of carriers by the rippling of graphene sheets or by the presence of impurities. In general, the thermal conductivity in graphene is phonon dominated. However, in the case of a gated graphene strip, the application of a gate bias causes a Fermi energy shift that is significantly greater than $k_BT$, thus increasing the electronic contribution over phonon contribution at low temperatures. The thermal conductivity in graphene ranges from about $4.40 \times 10^3$ to $5.78 \times 10^3 Wm^{-1} K^{-1}$ near room temperature, which is much higher as compared to graphite, carbon nanotubes, and diamond, and the lower limit of ballistic thermal conductance per unit circumference of carbon nanotubes is equal to the ballistic thermal conductance of graphene, which is isotropic. Graphene produced by graphite oxide film shows high electrical conductivity and superconducting properties. Intercalation of potassium atoms in between planes of sheets of crystalline graphite makes it superconducting at extremely low temperatures of about 0.1K.

Graphene possessed an optical transmission rate of more than 98%, which is higher than that of indium tin oxide films (85%). Graphene as well as graphene oxide exhibit electrochromic nature, allowing the tuning of linear and ultrafast optical properties. The bandgap of graphene can be tuned from 0 to 0.25 eV. Ultrafast optical response of graphene can be tuned electrically. Optical response of graphene nanoribbons is also tunable by applying a magnetic field. Graphene shows nonlinear optical behaviour in the form of saturable absorption, whereby the absorption becomes saturated on increasing the input optical intensity above a threshold value known as saturation fluence. It shows a nonlinear phase shift due to optical nonlinear Kerr effect (a Kerr coefficient of $10^{-7} cm^2 W^{-1}$) when exposed to intensive laser illumination.

Graphene demonstrates very high mechanical properties, being one of the strongest materials produced. It is harder than even diamond. It possesses a tensile

modulus of 1 TPa, Young's modulus of 0.5 TPa, a spring constant in the range of 1 to 5 Nm$^{-1}$, and shows a hundred times greater breaking strength as compared to steel of the same thickness.

Graphene exhibits anomalous quantum Hall effect in the presence of a magnetic field, which can be measured even at room temperature. The Hall conductivity for graphene is given by $\sigma_{xy} = \pm 4 (N + \frac{1}{2}) e^2/h$, where $N$ is the Landau level. It is shifted by $\frac{1}{2}$ and a factor of 4 in comparison with the standard $(Ne^2/h)$. This unique behaviour is a result of the massless Dirac electrons in graphene. The spectrum of graphene shows a Landau level with energy at the Dirac point. Factor $\frac{1}{2}$ arises due to the half-filled Landau level in graphene, while factor 4 arises due to the double valley and double spin degeneracy. In strong magnetic fields above 10 Tesla, additional plateaus of Hall conductivity are observed at $\sigma_{xy} = ve^2/h$, where $v = 0, \pm 1, \pm 4$.

Graphene, being the lightest and strongest material and possessing a very high thermal and electric conductivity, can be integrated into a huge number of applications. Graphene is being used to help in improving the performance and efficiency of the existing materials.

## Applications of Graphene

Graphene finds its applications in various fields. Some of them are mentioned as follows.

1. Graphene can be used to make lighter and stronger automobiles and aircrafts, being the lightest and strongest material ever produced.

2. Graphene can be used to produce both n-type and p-type thin transistors operating at GHz frequencies as the type and concentration of carriers (electron or holes) can be controlled by the addition of molecules or metals. 2D electron gas in a doped graphene possesses high mobility at room temperature, thus helping to produce field effect transistor at room temperature.

3. Due to the high mechanical properties of graphene, NEMS such as pressure sensors and resonators can be made as these meet out the stability requirements.

4. By varying the magnetic field, the edge states in graphene could be turned on and off, thus making it feasible to design circuits and transistors out of the material. Due to spin selectivity, electrons are transmitted along the edges with almost no imperfections, even if the edges are dirty, thus making it useful in quantum computers.

5. Solar cells can be made using graphene, as it possesses a high electrical conductivity as well as optical transparency.

6. Small bandgap and numerous Dirac points in graphene exhibit graphene's potential in microwave and terahertz photonics devices.

7. As graphene possesses zero bandgap and universal optical absorption, it can be saturated in the visible to near-infrared range by excitation leading to the possibility of fullband mode locking of fibre lasers using graphene-based saturable absorber.

8. Graphene does not possess nuclear magnetic moment and possesses a small spin orbit interaction, thus showing a potential in the area of spintronics.

9. Bragg's grating based on graphene shows excitation of surface electromagnetic waves in a periodic structure.
10. Transparent conducting electrodes for touch screens, liquid crystal displays, organic light-emitting diodes, organic photovoltaic cells, etc., are all possible due to graphene's high conductivity, optical transparency, mechanical strength, and flexibility.
11. Graphene–metal composites can be used as thermal interface materials for thermal management applications.
12. As graphene shows nonlinear Kerr effect, it can be used in graphene-based nonlinear Kerr photonics.
13. Graphene oxide membranes are selectively permeable to water, while being impermeable to other liquids and gases; so it can be useful in desalination and distillation processes.

## 5.5 CARBON FULLERENES—BUCKYBALLS

The name fullerene is assigned to any molecule composed entirely of carbon which is in the form of a hollow sphere. $C_{60}$-molecule, a 60-carbon atom ball, was first designed by American architect R. Buckminster Fuller in his geodesic dome. In his honor, $C_{60}$ was named as buckminsterfullerene, or buckyball. Solid crystalline fullerenes are also referred to as fullerites. $C_{60}$ is the most well-known of the fullerenes due to its maximum symmetry, high spherical shape, and high relative yield. Neighbouring carbon atoms are connected in a three-fold coordination by $sp^2$ bonds. $C_{60}$ is made up of 12 pentagonal and 20 hexagonal faces arranged in the same icosahedral geometrical configuration as a soccer ball as shown in Fig. 5.6. Twelve pentagons connected by 20 hexagons arise by the truncation of 12 points of the icosahedron at an appropriate depth. The bond lengths in $C_{60}$ depend upon the depth of truncation and the edge length of pentagons and hexagons may be different from each other. icosahedral point group has the highest symmetry in a 3D Euclidean space. Icosahedral symmetry of $C_{60}$ molecule is confirmed by the observation of four vibrational absorption bands in IR spectroscopy.



FIG. 5.6 Structure of fullerene ($C_{60}$)

## Definition

**Carbon nanotubes** are large molecules of pure **carbon** that are long and thin and shaped like tubes, about 1-3 nanometers (1 nm = 1 billionth of a meter) in diameter, and hundreds to thousands of nanometers long.

A carbon nanotube is a small cylindrical carbon structure made out of graphene. The tube comprises hexagonal structures. Despite their very small size, carbon nanotubes are very strong. They are currently used for structural reinforcement in applications such as concrete rebar, but could also be used as semiconductors.

Carbon nanotubes are also known as "Buckytubes" because they resemble R. Buckminster Fuller's geodesic domes.

Multiwall tubes, are sometimes called *buckytubes*, were developed from the fullerene, a molecular device similar to the geodesic domes.

Carbon nanotubes are allotropes of carbon with a cylindrical nanostructure. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology.

## Types of carbon nanotubes and related structures

- Single-walled.
- Multi-walled.
- Junctions and cross linking.
- Other morphologies.
- Extreme carbon nanotubes.

## METHODS OF PRODUCTIONS OF CNTS:

1. PLASMA BASED SYNTHESIS METHODS:
   a. Arc Discharge Method
   b. Laser Ablation Method:

2. Thermal Synthesis Process:
   a. Chemical vapor deposition (CVD)
   b. Plasma Enhanced CVD (PECVD)
   c. Alcohol Catalytic CVD (ACCVD)

3. The Hydrothermal Methods:

# Synthesis

Techniques have been developed to produce nanotubes in sizable quantities, including arc discharge, laser ablation, chemical vapor deposition (CVD) and high-pressure carbon monoxide disproportionation (HiPCO). Among these arc discharge, laser ablation, chemical vapor deposition (CVD) are batch by batch process and HiPCO is gas phase continuous process. Most of these processes take place in a vacuum or with process gases. The CVD growth method is

ablation- surgical of body tissue

*Morphology* - 'the study of form, shape or structure
*HiPCO* - High pressure carbon monoxide method.

popular, as it yields high quantity and has a degree of control over diameter, length and morphology. Using particulate catalysts, large quantities of nanotubes can be synthesized by these methods, but achieving the repeatability becomes a major problem with CVD growth. The HiPCO process advances in catalysis and continuous growth are making CNTs more commercially viable. The HiPCO process helps in producing high purity single walled carbon nanotubes in higher quantity. The HiPCO reactor operates at high temperature 900-1100°C and high pressure ~30-50 bar. It uses carbon monoxide as the carbon source and Nickel/ iron penta carbonyl as catalyst. These catalyst acts as the nucleation site for the nanotubes to grow.

Vertically aligned carbon nanotube arrays are also grown by thermal chemical vapor deposition. A substrate (quartz, silicon, stainless steel, etc.) is coated with a catalytic metal (Fe, Co, Ni) layer. Typically that layer is iron, and is deposited via sputtering to a thickness of 1-5 nm. A 10-50 nm underlayer of alumina is often also put down on the substrate first. This imparts controllable wetting and good interfacial properties. When the substrate is heated to the growth temperature (~700 °C), the continuous iron film breaks up into small islands... each island then nucleates a carbon nanotube. The sputtered thickness controls the island size, and this in turn determines the nanotube diameter. Thinner iron layers drive down the diameter of the islands, and they drive down the diameter of the nanotubes grown. The amount of time that the metal island can sit at the growth temperature is limited, as they are mobile, and can merge into larger (but fewer) islands. Annealing at the growth temperature reduces the site density (number of CNT/mm$^2$) while increasing the catalyst diameter.

The as-prepared carbon nanotubes always have impurities such as other forms of carbon (amorphous carbon, fullerene, etc.) and non-carbonaceous impurities (metal pcs used for catalyst). These impurities need to be removed to make use of the carbon nanotubes in applications.

# Properties
## Mechanical

Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp$^2$ bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotube was tested to have a tensile strength of 63 gigapascals (9,100,000 psi). (For illustration, this translates into the ability to endure tension of a weight equivalent to 6,422 kilograms-force (62,980 N; 14,160 lbf) on a cable with cross-section of 1 square millimetre (0.0016 sq in).) Further studies, such as one conducted in 2008, revealed that individual CNT shells have strengths of up to ~100 gigapascals (15,000,000 psi), which is in agreement with quantum/atomistic models. Since carbon nanotubes have a low density for a solid of 1.3 to 1.4 g/cm$^3$, its specific strength of up to 48,000 kN·m·kg$^{-1}$ is the best of known materials, compared to high-carbon steel's 154 kN·m·kg$^{-1}$.

Although the strength of individual CNT shells is extremely high, weak shear interactions between adjacent shells and tubes lead to significant reduction in the effective strength of multi-walled carbon nanotubes and carbon nanotube bundles down to only a few GPa. This limitation has been recently addressed by applying high-energy electron irradiation, which crosslinks inner shells and tubes, and effectively increases the strength of these materials to ~60 GPa for multi-walled carbon nanotubes and ~17 GPa for double-walled carbon nanotube bundles. CNTs are not nearly as strong under compression. Because of their hollow structure and high aspect ratio, they tend to undergo buckling when placed under compressive, torsional, or bending stress.

On the other hand, there was evidence that in the radial direction they are rather soft. The first transmission electron microscope observation of radial elasticity suggested that even the van der Waals forces can deform two adjacent nanotubes. Later, nanoindentations with atomic force microscope were performed by several groups to quantitatively measure radial elasticity of multiwalled carbon nanotubes and tapping/contact mode atomic force microscopy was also performed on single-walled carbon nanotubes. Young's modulus of on the order of several GPa showed that CNTs are in fact very soft in the radial direction.

## Electrical

Unlike graphene, which is a two-dimensional semimetal, carbon nanotubes are either metallic or semiconducting along the tubular axis. For a given $(n,m)$ nanotube, if $n = m$, the nanotube is metallic; if $n - m$ is a multiple of 3 and $n \neq m$ and $nm \neq 0$, then the nanotube is quasi-metallic with a very small band gap, otherwise the nanotube is a moderate semiconductor.[42] Thus all armchair $(n = m)$ nanotubes are metallic, and nanotubes (6,4), (9,1), etc. are semiconducting. Carbon nanotubes are not semimetallic because the degenerate point (that point where the $\pi$ [bonding] band meets the $\pi^*$ [anti-bonding] band, at which the energy goes to zero) is slightly shifted away from the $K$ point in the Brillouin zone due to the curvature of the tube surface, causing hybridization between the $\sigma^*$ and $\pi^*$ anti-bonding bands, modifying the band dispersion.

The rule regarding metallic versus semiconductor behavior has exceptions, because curvature effects in small diameter tubes can strongly influence electrical properties. Thus, a (5,0) SWCNT that should be semiconducting in fact is metallic according to the calculations. Likewise, zigzag and chiral SWCNTs with small diameters that should be metallic have a finite gap (armchair nanotubes remain metallic). In theory, metallic nanotubes can carry an electric current density of $4 \times 10^9$ A/cm$^2$, which is more than 1,000 times greater than those of metals such as copper, where for copper interconnects current densities are limited by electromigration. Carbon nanotubes are thus being explored as interconnects, conductivity enhancing components in composite materials and many groups are attempting to commercialize highly conducting electrical wire assembled from individual carbon nanotubes. There are significant challenges to be overcome, however, such as undesired current saturation under voltage, the much more resistive nanotube-to-nanotube junctions and impurities, all of which lower the electrical conductivity of the macroscopic nanotube wires by orders of magnitude, as compared to the conductivity of the individual nanotubes.

Because of its nanoscale cross-section, electrons propagate only along the tube's axis. As a result, carbon nanotubes are frequently referred to as one-dimensional conductors. The maximum electrical conductance of a single-walled carbon nanotube is $2G_0$, where $G_0 = 2e^2/h$ is the conductance of a single ballistic quantum channel.

Due to the role of the $\pi$-electron system in determining the electronic properties of graphene, doping in carbon nanotubes differs from that of bulk crystalline semiconductors from the same group of the periodic table (e.g. silicon). Graphitic substitution of carbon atoms in the nanotube wall by boron or nitrogen dopants leads to p-type and n-type behavior, respectively, as would be expected in silicon. However, some non-substitutional (intercalated or adsorbed) dopants introduced into a carbon nanotube, such as alkali metals as well as electron-rich metallocenes, result in n-type conduction because they donate electrons to the $\pi$-electron system of the nanotube. By contrast, $\pi$-electron acceptors such as FeCl$_3$ or electron-deficient metallocenes function as p-type dopants since they draw $\pi$-electrons away from the top of the valence band.

Intrinsic superconductivity has been reported, although other experiments found no evidence of this, leaving the claim a subject of debate.

## Optical

Carbon nanotubes have useful absorption, photoluminescence (fluorescence), and Raman spectroscopy properties. Spectroscopic methods offer the possibility of quick and non-destructive characterization of relatively large amounts of carbon nanotubes. There is a strong demand for such characterization from the industrial point of view: numerous parameters of the nanotube synthesis can be changed, intentionally or unintentionally, to alter the nanotube quality. As shown below, optical absorption, photoluminescence and Raman spectroscopies allow quick and reliable characterization of this "nanotube quality" in terms of non-tubular carbon content, structure (chirality) of the produced nanotubes, and structural defects. Those features determine nearly any other properties such as optical, mechanical, and electrical properties.

Carbon nanotubes are unique "one-dimensional systems" which can be envisioned as rolled single sheets of graphite (or more precisely graphene). This rolling can be done at different angles and curvatures resulting in different nanotube properties. The diameter typically varies in the range 0.4–40 nm (i.e. "only" ~100 times), but the length can vary ~100,000,000,000 times, from 0.14 nm to 55.5 cm. The nanotube aspect ratio, or the length-to-diameter ratio, can be as high as 132,000,000:1, which is unequalled by any other material. Consequently, all the properties of the carbon nanotubes relative to those of typical semiconductors are extremely anisotropic (directionally dependent) and tunable.

Whereas mechanical, electrical and electrochemical (supercapacitor) properties of the carbon nanotubes are well established and have immediate applications, the practical use of optical properties is yet unclear. The aforementioned tunability of properties is potentially useful in optics and photonics. In particular, light-emitting diodes (LEDs)and photo-detectors based on a single nanotube have been produced in the lab. Their unique feature is not the efficiency, which is yet relatively low, but the narrow selectivity in the wavelength of emission and detection of light and the possibility of its fine tuning through the nanotube structure. In addition, bolometer and optoelectronic memory devices have been realised on ensembles of single-walled carbon nanotubes.

Crystallographic defects also affect the tube's electrical properties. A common result is lowered conductivity through the defective region of the tube. A defect in armchair-type tubes (which can conduct electricity) can cause the surrounding region to become semiconducting, and single monatomic vacancies induce magnetic properties.

## Thermal

All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction", but good insulators lateral to the tube axis. Measurements show that an individual SWNT has a room-temperature thermal conductivity along its axis of about 3500 $W \cdot m^{-1} \cdot K^{-1}$; compare this to copper, a metal well known for its good thermal conductivity, which transmits 385 $W \cdot m^{-1} \cdot K^{-1}$. An individual SWNT has a room-temperature thermal conductivity across its axis (in the radial direction) of about 1.52 $W \cdot m^{-1} \cdot K^{-1}$, which is about as thermally conductive as soil. Macroscopic assemblies of nanotubes such as films or fibres have reached up to 1500 $W \cdot m^{-1} \cdot K^{-1}$ so far. The temperature stability of carbon nanotubes is estimated to be up to 2800 °C in vacuum and about 750 °C in air.

Crystallographic defects strongly affect the tube's thermal properties. Such defects lead to phonon scattering, which in turn increases the relaxation rate of the phonons. This reduces the mean free path and reduces the thermal conductivity of nanotube structures. Phonon transport simulations indicate that substitutional defects such as nitrogen or boron will primarily lead to scattering of high-frequency optical phonons. However, larger-scale defects such as Stone Wales's defects cause phonon scattering over a wide range of frequencies, leading to a greater reduction in thermal conductivity

# Applications

1. Carrier for Drug delivery: Carbon nanohorns (CNHs) are the spherical aggregates of CNTs with irregular horn like shape. Research studies have proved CNTs and CNHs as a potential carrier for drug delivery system.

2. Functionalized carbon nanotubes are reported for targeting of Amphotericin B to Cells.

3. They can be used as lubricants or glidants in tablet manufacturing due to nanosize and sliding nature of graphite layers bound with Van der Waals forces.

4. In Genetic Engineering:

5. Biomedical applications

6. Artificial implants.

7. Preservative.

8. Diagnostic tool.

9. As catalyst.

10. As Biosensors

Field Emitters/Emission: • Conductive or reinforced plastics • Molecular electronics: CNT based non volatile RAM • CNT based transistors • Energy Storage • CNT based fibers and fabrics • CNT based ceramics • Biomedical applications etc

**Structural** CNTs possesses remarkable properties and qualities as structural materials.(a) **Textiles**—CNTs can produce waterproof and tear-resistant fabrics. (b) **Body armor**—CNT fibers are being used as combat jackets. The jackets are used to monitor the condition of the wearer and to provide protection from bullets. (c) **Concrete**—CNTs in concrete increases its tensile strength and halt crack propagation. (d) **Polyethylene**—CNT fibers can be used as polyethylene. The CNT based polyethylene can increase the elastic modulus of the polymers by 30 %. (e) **Sports equipment**—Golf balls, golf clubs, stronger and lighter tennis rackets, bicycle parts, and baseball bats. (f) **Bridges**—CNTs may be able to replace steel in suspension and bridges. (g) **Flywheels**—The high strength/weight ratios of CNTs enable very high rotational speeds. (h) **Fire protection**—Thin layers of buckypaper can potentially protect the object from

fire. The dense, compact layer of CNT or carbon fibers in the form of buckypaper can efficiently reflect the heat.

**Electromagnetic** CNTs can be fabricated as electrical conductors, semiconductors and insulators. Such applications include: (a) **Buckypaper**—Thin nanotube sheets are 250 times stronger and 10 times lighter than steel. They can be used as heat sink for chipboards, backlight for LCD screens, or Faraday cage to protect electrical devices/aeroplanes. (b) **Light bulb filament**—CNTs can be used as alternative to tungsten filaments in incandescent lamps (c) **Magnets**—A strong magnetic field can be generated using multi-walled CNTs coated with magnetite. (d) **Solar cells**—Germanium CNT diode exploits the photovoltaic effect. In some solar cells, nanotubes are used to replace the ITO (indium tin-oxide) to allow the light to pass to the active layers and generate photocurrent. (e) **Electromagnetic antenna**—CNTs can act as an antenna for radio and other electromagnetic devices due to its durability, light weight and conductive properties. The skin effect in CNTs is negligible at high frequencies due to additional kinetic inductance. This results in low power dissipation, resulting in high antenna efficiency.

**Electroacoustic-** The application of CNT in the field of electroacoustic is: Loudspeaker—Loudspeakers can be manufactured from sheets of parallel CNTs. Such a loudspeaker can generate sound similar to the sound of lightening producing thunder.

**Chemical** CNTs finds tremendous applications in the chemical field also, few of them are as follows: (a) **Air pollution filter**—CNTs are one of the best materials for air filters because they possess high adsorption capacity and large specific area. The conductance of CNTs changes when polluted gas comes in its contact. This helps in detecting and filtering the polluted air. CNT membranes can successfully filter carbon dioxide from power plant emissions. (b) **Water filter**—CNT membranes can aid in filtration. It can reduce distillation costs by 75 %. These tubes are so thin that small particles (like water molecules) can pass through them, while blocking larger particles (such as the chloride ions in salt). CNTs have high active site and controlled distribution of pore size on their surface. This increases not only its sorption capabilities, but also its sorption efficiency. CNTs have effective sorption capacity over broad pH range (particularly for 7 to 10 pH) . (c) **Chemical Nanowires**—The CNTs finds their applications in nanowire manufacturing using materials such as gold, zinc oxide, gallium arsenide, etc. The gold based CNT nanowires are very selective and sensitive to hydrogen sulphide ($H_2S$) detection. The zinc oxide (ZnO) based CNT nanowires can be used in applications for light emitting devices and harvesters of vibrational energy . (d) **Sensors**—CNT based sensors can detect temperature, air pressure, chemical gases (such as carbon monoxide, ammonia), molecular pressure, strain, etc. The operation of a CNT based sensor is primarily dependent on the generation of current/voltage. The electric current is generated by the flow of free charged carrier induced in any material. This charge is typically modulated by the adsorption of a target on the CNT surface.

**Mechanical** The potential application of CNTs can be found in the following areas of mechanical engineering as well : (a) **Oscillator**—Oscillators based on CNTs have achieved higher speeds than other technologies (>50 GHz) . Researchers reported a molecular oscillator

with frequencies upto several gigahertz. The operation of this oscillator is primarily based on the low friction and low wear bearing properties of a multi-walled CNT with a diameter ranging from 1 nm to a few tens of nanometers. (b) **Waterproof**—CNTs can be used to prepare superhydrophobic cotton fabric by dip-coating approach. This approach is solely based on the chemical reactions caused by UV-activated nitrene solution. The solution is used to transform the cotton fabric surface from hydrophilic to superhydrophobic with an apparent water contact angle of 154°. Since CNTs are covalently attached on the surface of the cotton fabric, the superhydrophobicity possesses high stability and chemical durability.

**Optical** Carbon nanotubes are grown like a field of grass, where each nanotube is separated like a blade of grass. Thus, a particle of light bounces between the nanotubes. In this process, light is completely absorbed and it is converted to heat. Therefore, the absorbance of CNT is extremely high in wide ranges from FUV to FIR.

**Electrical Circuits** CNTs are attractive materials in fundamental science and technology. They have demonstrated unique electrical properties for building electronic devices, such as CNT field-effect transistors (CNTFETs) and CNT diodes. CNTs can be used to form a p–n junction diode by chemical doping and polymer coating. These types of diodes can be used to form a computer chip. CNT diodes can potentially dissipate heat out of the computer chips due to their unique thermal transmission properties.

**Interconnects** Carbon nanotubes (CNTs) have emerged as one of the most potential interconnect material solutions in current nanoscale regime. The higher current density of 1000 MA/sq-cm of an isolated CNT can eliminate the electromigration reliability concerns that plagues the current nanoscale copper interconnects. Therefore, CNT interconnects can potentially offer immense advantages over copper in terms of crosstalk, delay and power dissipation.

**Transistors** CNTs can form conducting channels in transistor . Two different device architectures have been developed for the transistor configuration. In both cases, CNTs connect the source and drain electrodes and show excellence behavior in the area of memory designing, amplifiers, sensors and detectors, etc. In one device architecture, the source and the drain are connected by a single nanotube. In other device architecture, a random array of nanotubes.

Laser **ablation** is the process by which layers are removed from solid metals & industrial compounds using a laser beam for ultimate precision.

**PVD** describes a variety of vacuum deposition methods which can be used to produce thin films & coatings.

**CVD** is deposition method used to produce high quality, high performance, solid materials typically under vacuum. The process is often used in the semiconductor industry to produce thin films.
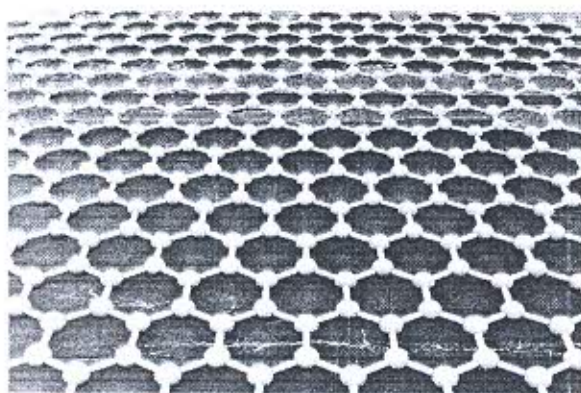
# GRAPHENE

Graphene" is a combination of "graphite" and the suffix -ene, named by Hanns-Peter Boehm and colleagues, who produced and observed single-layer carbon foils in 1962.

Boehm et al. introduced the term *graphene* in 1986 to describe single sheets of graphite. Graphene can be considered an "infinite alternant" (only six-member carbon ring) polycyclic aromatic hydrocarbon.

**Graphene** a form of carbon consisting of planar sheets which are one atom thick, with the atoms arranged in a honeycomb-shaped lattice.

Graphene is a semi-metal with small overlap between the valence and the conduction bands. It is an allotrope of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice.



# Structure

Graphene is a crystalline allotrope of carbon with 2-dimensional properties. Its carbon atoms are densely packed in a regular atomic-scale chicken wire (hexagonal) pattern.

Each atom has four bonds: one σ bond with each of its three neighbors and one π-bond that is oriented out of plane. The atoms are about 1.42 Å apart. $(1 e^{-10} m)$

Graphene's hexagonal lattice can be regarded as two interleaving triangular lattices. This perspective was successfully used to calculate the band structure for a single graphite layer using a tight-binding approximation.

Graphene's stability is due to its tightly packed carbon atoms and a $sp^2$ orbital hybridization – a combination of orbitals s, $p_x$ and $p_y$ that constitute the σ-bond. The final $p_z$ electron makes up the π-bond. The π-bonds hybridize together to form the π-band and π*-bands. These bands are responsible for most of graphene's notable electronic properties, via the half-filled band that permits free-moving electrons.

Graphene sheets in solid form usually show evidence in diffraction for graphite's (002) layering. This is true of some single-walled nanostructures. However, unlayered graphene with only (hk0) rings has been found in the core of presolar graphite onions. TEM studies show faceting at defects in flat graphene sheets and suggest a role for two-dimensional crystallization from a melt.

Graphene can self-repair holes in its sheets, when exposed to molecules containing carbon, such as hydrocarbons. Bombarded with pure carbon atoms, the atoms perfectly align into hexagons, completely filling the holes.

The atomic structure of isolated, single-layer graphene was studied by TEM on sheets of graphene suspended between bars of a metallic grid. Electron diffraction patterns showed the expected honeycomb lattice. Suspended graphene showed "rippling" of the flat sheet, with amplitude of about one nanometer. These ripples may be intrinsic to the material as a result of the instability of two-dimensional crystals, or may originate from the ubiquitous dirt seen in all TEM images of graphene. Atomic resolution real-space images of isolated, single-layer graphene on $SiO_2$ substrates are available via scanning tunneling microscopy (STM). Photoresist residue, which must be removed to obtain atomic-resolution images, may be the "adsorbates" observed in TEM images, and may explain the observed rippling. Rippling on $SiO_2$ is caused by conformation of graphene to the underlying $SiO_2$ and is not intrinsic.
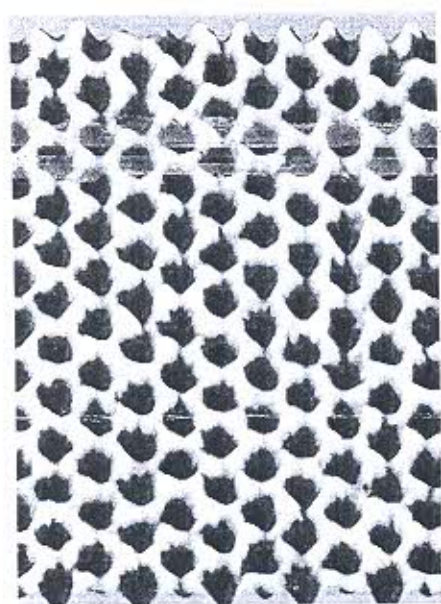


# Properties

## Electronic

Graphene is a zero-gap semiconductor, because its conduction and valence bands meet at the Dirac points, which are six locations in momentum space, on the edge of the Brillouin zone, divided into two non-equivalent sets of three points. The two sets are labeled K and K'. The sets give graphene a valley degeneracy of $gv = 2$. By contrast, for traditional semiconductors the primary point of interest is generally Γ, where momentum is zero. However, if the in-plane direction is confined, in which case it is referred to as a nanoribbon, its electronic structure is different. If it is "zig-zag", the bandgap is zero. If it is "armchair", the bandgap is non-zero (see figure).

Graphene displays remarkable electron mobility at room temperature, with reported values in excess of 15000 $cm^2 \cdot V^{-1} \cdot s^{-1}$. Hole and electron mobilities were expected to be nearly identical. The mobility is nearly independent of temperature between 10 K and 100 K, which implies that the dominant scattering mechanism is defect scattering. Scattering by graphene's

acoustic phonons intrinsically limits room temperature mobility to $200000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at a carrier density of $10^{12} \text{ cm}^{-2}$, $4.5 \times 10^3$ times greater than copper.

The corresponding resistivity of graphene sheets would be $10^{-6} \Omega \cdot \text{cm}$. This is less than the resistivity of silver, the lowest otherwise known at room temperature. However, on $SiO_2$ substrates, scattering of electrons by optical phonons of the substrate is a larger effect than scattering by graphene's own phonons. This limits mobility to $40000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. Charge transport is affected by adsorption of contaminants such as water and oxygen molecules. This leads to non-repetitive and large hysteresis I-V characteristics.

Electrons propagating through graphene's honeycomb lattice effectively lose their mass, producing quasi-particles that are described by a 2D analogue of the Dirac equation rather than the Schrödinger equation for spin-$\frac{1}{2}$ particles.

Superconductivity has been observed in twisted bilayer graphene.

## Optical

Graphene's unique optical properties produce an unexpectedly high opacity for an atomic monolayer in vacuum, absorbing $\pi\alpha = 2.3\%$ of red light, where $\alpha$ is the fine-structure constant This is a consequence of the "unusual low-energy electronic structure of monolayer graphene that features electron and hole conical bands meeting each other at the Dirac point... [which] is qualitatively different from more common quadratic massive bands." Based on the Slonczewski–Weiss–McClure (SWMcC) band model of graphite, the interatomic distance, hopping value and frequency cancel when optical conductance is calculated using Fresnel equations in the thin-film limit.

Although confirmed experimentally, the measurement is not precise enough to improve on other techniques for determining the fine-structure constant.

Multi-parametric surface plasmon resonance was used to characterize both thickness and refractive index of chemical-vapor-deposition (CVD)-grown graphene films. The measured refractive index and extinction coefficient values at 670 nm wavelength are 3.135 and 0.897, respectively. The thickness was determined as 3.7 Å from a 0.5 mm area, which agrees with 3.35 Å reported for layer-to-layer carbon atom distance of graphite crystals.

The method can be used for real-time label-free interactions of graphene with organic and inorganic substances. The existence of unidirectional surface plasmons in the nonreciprocal graphene-based gyrotropic interfaces has been demonstrated theoretically. By efficiently controlling the chemical potential of graphene, the unidirectional working frequency can be continuously tunable from THz to near-infrared and even visible. Particularly, the unidirectional frequency bandwidth can be 1–2 orders of magnitude larger than that in metal under the same magnetic field, which arises from the superiority of extremely small effective electron mass in graphene. Graphene's band gap can be tuned from 0 to 0.25 eV (about 5 micrometre wavelength) by applying voltage to a dual-gate bilayer graphene field-effect transistor (FET) at room temperature. The optical response of graphene nanoribbons is tunable into the terahertz regime by an applied magnetic field. Graphene/graphene oxide systems exhibit electrochromic behavior, allowing tuning of both linear and ultrafast optical properties.

A graphene-based Bragg grating (one-dimensional photonic crystal) demonstrated its capability for excitation of surface electromagnetic waves in the periodic structure using a 633 nm He–Ne laser as the light source.

## Saturable absorption

Such unique absorption could become saturated when the input optical intensity is above a threshold value. This nonlinear optical behavior is termed saturable absorption and the threshold value is called the saturation fluence. Graphene can be saturated readily under strong excitation over the visible to near-infrared region, due to the universal optical absorption and zero band gap. This has relevance for the mode locking of fiber lasers, where fullband mode locking has been achieved by a graphene-based saturable absorber. Due to this special property, graphene has wide application in ultrafast photonics. The optical response of graphene/graphene oxide layers can be tuned electrically. Saturable absorption in graphene could occur at the Microwave and Terahertz bands, owing to its wideband optical absorption property. The microwave saturable absorption in graphene demonstrates the possibility of graphene microwave and terahertz photonics devices, such as a microwave saturable absorber, modulator, polarizer, microwave signal processing and broad-band wireless access networks.

## Nonlinear Kerr effect

Under more intensive laser illumination, graphene could possess a nonlinear phase shift due to the optical nonlinear Kerr effect. Based on a typical open and close aperture z-scan measurement, graphene possesses a nonlinear Kerr coefficient of $10^{-7}$ $cm^2 \cdot W^{-1}$, almost nine orders of magnitude larger than that of bulk dielectrics.[58] This suggests that graphene may be a powerful nonlinear Kerr medium, with the possibility of observing a variety of nonlinear effects, the most important of which is the soliton. A 2016 study has shown that the nonlinear refractive index of graphene is negative. Thermal lens spectroscopy can be used for measuring the thermo-optic coefficient of graphene and inspecting its thermal nonlinearity.

## Quantum dots

Several techniques can prepare nanostructured graphene. e.g., graphene quantum dots (GQDs), these techniques mainly include electron beam lithography, chemical synthesis, electrochemical preparation, graphene oxide (GO) reduction, C60 catalytic transformation, the microwave assisted hydrothermal method (MAH),the Soft-Template method, the hydrothermal method, and the ultrasonic exfoliation method.

## Thermal

## Thermal conductivity

Thermal transport in graphene is an active area of research which has attracted attention because of the potential for thermal management applications. Early measurements of the thermal conductivity of suspended graphene reported an exceptionally large thermal conductivity of approximately 5300 $W \cdot m^{-1} \cdot K^{-1}$, compared with the thermal conductivity of pyrolytic graphite of approximately 2000 $W \cdot m^{-1} \cdot K^{-1}$ at room temperature. However, later studies have questioned whether this ultrahigh value was overestimated, and instead measured thermal conductivities between 1500–2500 $W \cdot m^{-1} \cdot K^{-1}$ for suspended single layer graphene. The large range can be attributed to large measurement uncertainties as well as variations in the graphene quality and processing conditions. In addition, when single-layer graphene is supported on an amorphous material, the thermal conductivity is reduced to about 500–600 $W \cdot m^{-1} \cdot K^{-1}$ at room temperature as a result of scattering of graphene lattice waves by the substrate, and can be even lower for few layer graphene encased in amorphous oxide. Likewise, polymeric residue can contribute to a similar decrease for suspended graphene to approximately 500–600 $W \cdot m^{-1} \cdot K^{-1}$ for bilayer graphene.

of bulk graphite. These intrinsic properties could lead to applications such as NEMS as pressure sensors and resonators. Due to its large surface energy and out of plane ductility, flat graphene sheets are unstable with respect to scrolling, i.e. bending into a cylindrical shape, which is its lower-energy state.

As is true of all materials, regions of graphene are subject to thermal and quantum fluctuations in relative displacement. Although the amplitude of these fluctuations is bounded in 3D structures (even in the limit of infinite size), the Mermin–Wagner theorem shows that the amplitude of long-wavelength fluctuations grows logarithmically with the scale of a 2D structure and would therefore be unbounded in structures of infinite size. Local deformation and elastic strain are negligibly affected by this long-range divergence in relative displacement. It is believed that a sufficiently large 2D structure, in the absence of applied lateral tension, will bend and crumple to form a fluctuating 3D structure. Ripples have been observed in suspended layers of graphene. It has been proposed that the ripples are caused by thermal fluctuations in the material. As a consequence of these dynamical deformations, it is debatable whether graphene is truly a 2D structure. In 2014 it was shown that these ripples, if amplified through the introduction of vacancy defects, can impart a negative Poisson's ratio into graphene, resulting in the thinnest auxetic material known.

Graphene nanosheets can be incorporated into a nickel matrix through a plating process to form Ni-graphene composites on a target substrate. The enhancement in mechanical properties of the composites is attributed to the high interaction between Ni and graphene and the prevention of the dislocation sliding in the Ni matrix by the graphene.

## Fracture toughness

Despite its strength, graphene is also relatively brittle, with a fracture toughness of about 4 MPa$\sqrt{m}$. This indicates that imperfect graphene is likely to crack in a brittle manner like ceramic materials, as opposed to many metallic materials that have fracture toughnesses in the range of 15–50 MPa$\sqrt{m}$. Graphene shows a greater ability to distribute force from an impact than any known material, ten times that of steel per unit weight. The force was transmitted at 22.2 kilometres per second (13.8 mi/s).

## Biological

In 2011 graphene was shown to accelerate the osteogenic differentiation of human mesenchymal stem cells without the use of biochemical inducers.

In 2015 graphene was used to create biosensors with epitaxial graphene on silicon carbide. The sensors bind to 8-hydroxydeoxyguanosine (8-OHdG) and is capable of selective binding with antibodies. The presence of 8-OHdG in blood, urine and saliva is commonly associated with DNA damage. Elevated levels of 8-OHdG have been linked to increased risk of several cancers. A commercial version of a graphene biosensor has been used as a protein binding sensor platform.

In 2016 uncoated graphene was shown to serve as a neuro-interface electrode without altering or damaging properties such as signal strength or formation of scar tissue. Graphene electrodes in the body stay significantly more stable than electrodes of tungsten or silicon because of properties such as flexibility, bio-compatibility and conductivity.

# Potential applications

It has been suggested that the isotopic composition, the ratio of $^{12}C$ to $^{13}C$, has a significant impact on thermal conductivity. For example, isotopically pure $^{12}C$ graphene has higher thermal conductivity than either a 50:50 isotope ratio or the naturally occurring 99:1 ratio. It can be shown by using the Wiedemann–Franz law, that the thermal conduction is phonon-dominated. However, for a gated graphene strip, an applied gate bias causing a Fermi energy shift much larger than $k_B T$ can cause the electronic contribution to increase and dominate over the phonon contribution at low temperatures. The ballistic thermal conductance of graphene is isotropic.

Potential for this high conductivity can be seen by considering graphite, a 3D version of graphene that has basal plane thermal conductivity of over 1000 $W \cdot m^{-1} \cdot K^{-1}$ (comparable to diamond). In graphite, the c-axis (out of plane) thermal conductivity is over a factor of $\approx 100$ smaller due to the weak binding forces between basal planes as well as the larger lattice spacing. In addition, the ballistic thermal conductance of graphene gives the lower limit of the ballistic thermal conductances, per unit circumference and length of carbon nanotubes.

Despite its 2-D nature, graphene has 3 acoustic phonon modes. The two in-plane modes (LA, TA) have a linear dispersion relation, while the out of plane mode (ZA) has a quadratic dispersion relation. Due to this, the $T^2$ dependent thermal conductivity contribution of the linear modes is dominated at low temperatures by the $T^{1.5}$ contribution of the out-of-plane mode. Some graphene phonon bands display negative Grüneisen parameters (GPs). At low temperatures (where most optical modes with positive GPs are still not excited) the contribution from the negative GPs will be dominant and thermal expansion coefficient (which is directly proportional to GPs) negative. The lowest negative GPs correspond to the lowest transverse acoustic ZA modes. Phonon frequencies for such modes increase with the in-plane lattice parameter since atoms in the layer upon stretching will be less free to move in the z direction. This is similar to the behavior of a stretched string that has vibrations of smaller amplitude and higher frequency. This phenomenon, named "membrane effect", was predicted by Lifshitz in 1952.

## Melting point

A prediction that was published in 2015 suggested a melting point of $\approx 4125$ K. more sophisticated modelling has increased this temperature to at least 5000 K. At 6000 K (the sun's surface having an effective temperature of 5,777 K) graphene melts into an agglomeration of loosely coupled doubled bonded chains, before becoming a gas.

## Mechanical

The carbon–carbon bond length in graphene is about 0.142 nanometers. Graphene sheets stack to form graphite with an interplanar spacing of 0.335 nm.

Graphene is the strongest material ever tested, with an intrinsic tensile strength of 130.5 GPa and a Young's modulus of 1 TPa (150000000 psi). The Nobel announcement gave the strength as 42 N/m; the mass of 1 $m^2$ as 0.77 mg. and the electrical resistance of a square as 31 $\Omega$.

Large-angle-bent graphene monolayer has been achieved with negligible strain, showing mechanical robustness of the two-dimensional carbon nanostructure. Even with extreme deformation, excellent carrier mobility in monolayer graphene can be preserved.

The spring constant of suspended graphene sheets has been measured using an atomic force microscope (AFM). Graphene sheets were suspended over $SiO_2$ cavities where an atomic force microscope (AFM) tip was used to apply a stress to the sheet to test its mechanical properties. Its spring constant was in the range 1–5 N/m and the stiffness was 0.5 TPa, which differs from that

Nanophotonics or nano-optics is the study of the behavior of light on the nanometer scale, and of the interaction of nanometer-scale objects with light. It is a branch of optics, optical engineering, electrical engineering, and nanotechnology.

The term "nano-optics", just like the term "optics" usually refers to situations involving ultraviolet, visible, and near-infrared light.

A photonic crystal is a periodic optical nanostructure that affects the motion of photons in much the same way that ionic lattices affect electrons in solids. Photonic crystals occur in nature in the form of structural coloration and animal reflectors, and, in different forms, promise to be useful in a range of applications.

Photonic crystals can be fabricated for one, two, or three dimensions. One-dimensional photonic crystals can be made of layers deposited or stuck together. Two-dimensional ones can be made by photolithography, or by drilling holes in a suitable substrate. Fabrication methods for three-dimensional ones include drilling under different angles, stacking multiple 2-D layers on top of each other, direct laser writing, or, for example, instigating self-assembly of spheres in a matrix and dissolving the spheres.

structural coloration – peacock tail feathers are pigmented bro
  └ microscopic structure ( reflect blue, ⊗ turquoise &
      green light ., iridescent            ਅਫ਼ਫ਼ਗ਼ਸਾ

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# Nanofluidics

**Nanofluidics** is the study of the behavior, manipulation, and control of fluids that are confined to structures of nanometer (typically 1–100 nm) characteristic dimensions (1 nm = $10^{-9}$ m). Fluids confined in these structures exhibit physical behaviors not observed in larger structures, such as those of micrometer dimensions and above, because the characteristic physical scaling lengths of the fluid, (e.g. Debye length, hydrodynamic radius) very closely coincide with the dimensions of the nanostructure itself.

When structures approach the size regime corresponding to molecular scaling lengths, new physical constraints are placed on the behavior of the fluid. For example, these physical constraints induce regions of the fluid to exhibit new properties not observed in bulk, e.g. vastly increased viscosity near the pore wall; they may effect changes in thermodynamic properties and may also alter the chemical reactivity of species at the fluid-solid interface. A particularly relevant and useful example is displayed by electrolyte solutions confined in nanopores that contain surface charges, i.e. at electrified interfaces, as shown in the nanocapillary array membrane (NCAM) in the accompanying figure.

All electrified interfaces induce an organized charge distribution near the surface known as the electrical double layer. In pores of nanometer dimensions the electrical double layer may completely span the width of the nanopore, resulting in dramatic changes in the composition of the fluid and the related properties of fluid motion in the structure. For example, the drastically enhanced surface-to-volume ratio of the pore results in a preponderance of counter-ions (i.e. ions charged oppositely to the static wall charges) over co-ions (possessing the same sign as the wall charges), in many cases to the near-complete exclusion of co-ions, such that only one ionic species exists in the pore. This can be used for manipulation of species with selective polarity along the pore length to achieve unusual fluidic manipulation schemes not possible in micrometer and larger structures.
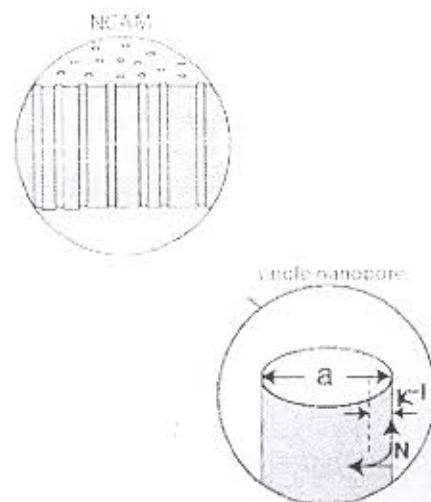


Schematic diagram of one particular realization of nanofluidics in a nanocapillary array membrane, or NCAM. The NCAM is composed of a large number of parallel nanocapillaries, each of which have a pore radius, a/2, which is approximately the same size as the Debye length, $\kappa^{-1}$. The electrical double layer is characterized by a counter-ion distribution, N, which is largest at the pore wall and decays toward the center of the pore.

## Contents

Applications – Nanofluidics have also have a significan impact in biotechnology, medicine and clinical diagnosti with the development of lab-on-a-chip devices for PCR and related techniques.

# Theory

In 1965, Rice and Whitehead published the seminal contribution to the theory of the transport of electrolyte solutions in long (ideally infinite) nanometer-diameter capillaries.[1] Briefly, the potential, $\phi$, at a radial distance, $r$, is given by the Poisson-Boltzmann equation,

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\phi}{dr}\right) = \kappa^2\phi,$$

where $\kappa$ is the inverse Debye length,

$$\kappa = \sqrt{\frac{8\pi n e^2}{\epsilon k T}},$$

determined by the ion number density, $n$, the dielectric constant, $\varepsilon$, the Boltzmann constant, $k$, and the temperature, $T$. Knowing the potential, $\varphi(r)$, the charge density can then be recovered from the Poisson equation, whose solution may be expressed as a modified Bessel function of the first kind, $I_O$, and scaled to the capillary radius, $a$. An equation of motion under combined pressure and electrically-driven flow can then be written,

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dv_z}{dr}\right) = \frac{1}{\eta}\frac{dp}{dz} - \frac{F_z}{\eta},$$

where $\eta$ is the viscosity, $dp/dz$ is the pressure gradient, and $F_z$ is the body force driven by the action of the applied electric field, $E_z$, on the net charge density in the double layer. When there is no applied pressure, the radial distribution of the velocity is given by,

$$v_z(r) = \frac{\epsilon\phi_0}{4\pi\eta}E_z\left[1 - \frac{I_0(\kappa r)}{I_0(\kappa a)}\right].$$

From the equation above, it follows that fluid flow in nanocapillaries is governed by the $\kappa a$ product, that is, the relative sizes of the Debye length and the pore radius. By adjusting these two parameters and the surface charge density of the nanopores, fluid flow can be manipulated as desired.

# Fabrication

Nanostructures can be fabricated as single cylindrical channels, nanoslits, or nanochannel arrays from materials such as silicon, glass, polymers (e.g. PMMA, PDMS, PCTE) and synthetic vesicles.[2] Standard photolithography, bulk or surface micromachining, replication techniques (embossing, printing, casting and injection molding), and nuclear track or chemical etching,[3][4][5] are commonly used to fabricate structures which exhibit characteristic nanofluidic behavior.

# Applications

Because of the small size of the fluidic conduits, nanofluidic structures are naturally applied in situations demanding that samples be handled in exceedingly small quantities, including Coulter counting, analytical separations and determinations of biomolecules, such as proteins and DNA, and facile handling of mass-limited samples. One of the more promising areas of nanofluidics is its potential for integration into microfluidic systems, i.e. micrototal analytical systems or lab-on-a-chip structures. For instance, NCAMs, when incorporated into microfluidic devices, can

## NanoFluid

( A nanofluid is a fluid containing nanometer-sized particles, called nanoparticles. These fluids are engineered colloidal suspensions of nanoparticles in a base fluid. The nanoparticles used in nanofluids are typically made of metals, oxides, carbides, or carbon nanotubes. Common base fluids include water, ethylene glycol and oil. )

( Nanofluids have novel properties that make them potentially useful in many applications in heat transfer, including microelectronics, fuel cells, pharmaceutical processes, and hybrid-powered engines, engine cooling/vehicle thermal management, domestic refrigerator, chiller, heat exchanger, in grinding, machining and in boiler flue gas temperature reduction. They exhibit enhanced thermal conductivity and the convective heat transfer coefficient compared to the base fluid) Knowledge of the rheological behaviour of nanofluids is found to be critical in deciding their suitability for convective heat transfer applications. Nanofluids also have special acoustical properties and in ultrasonic fields display additional shear-wave reconversion of an incident compressional wave; the effect becomes more pronounced as concentration increases.

In analysis such as computational fluid dynamics (CFD), nanofluids can be assumed to be single phase fluids; however, almost all new academic papers use a two-phase assumption. Classical theory of single phase fluids can be applied, where physical properties of nanofluid is taken as a function of properties of both constituents and their concentrations. An alternative approach simulates nanofluids using a two-component model. The spreading of a nanofluid droplet is enhanced by the solid-like ordering structure of nanoparticles assembled near the contact line by diffusion, which gives rise to a structural disjoining pressure in the vicinity of the contact line. However, such enhancement is not observed for small droplets with diameter of nanometer scale, because the wetting time scale is much smaller than the diffusion time scale.

## Synthesis

Nanofluids are produced by several techniques:

1. Direct Evaporation (1 step)
2. Gas condensation/dispersion (2 step)
3. Chemical vapour condensation (1 step)
4. Chemical precipitation (1 step)

Thermophysical properties of nanofluids
① Density ② sp. heat capacity ③ viscosity ④ thermal conductivity

* colloid is a mixture in which one substance of microscopically dispersed insoluble particles is suspended throughout another substance

## Applications

(Nanofluids are primarily used for their enhanced thermal properties as coolants in heat transfer equipment such as heat exchangers, electronic cooling system(such as flat plate) and radiators.) Heat transfer over flat plate has been analyzed by many researchers. However, they are also useful for their controlled optical properties. Graphene based nanofluid has been found to enhance Polymerase chain reaction efficiency (Nanofluids in solar collectors is another application where nanofluids are employed for their tunable optical properties. )

## Nanopores

A **nanopore** is a pore of nanometer size. It may, for example, be created by a pore-forming protein or as a hole in synthetic materials such as silicon or graphene.

When a nanopore is present in an electrically insulating membrane, it can be used as a single-molecule detector. It can be a biological protein channel in a high electrical resistance lipid bilayer, a pore in a solid-state membrane or a hybrid of these – a protein channel set in a synthetic membrane. The detection principle is based on monitoring the ionic current passing through the nanopore as a voltage is applied across the membrane. When the nanopore is of molecular dimensions, passage of molecules (e.g., DNA) cause interruptions of the "open" current level, leading to a "translocation event" signal. The passage of RNA or single-stranded DNA molecules through the membrane-embedded alpha-hemolysin channel (1.5 nm diameter), for example, causes a ~90% blockage of the current (measured at 1 M KCl solution).

It may be considered a Coulter counter for much smaller particles.

## Debye Length

In plasmas and electrolytes, the **Debye length** (also called **Debye radius**), named after the Dutch physicist and physical chemist Peter Debye, is a measure of a charge carrier's net electrostatic effect in solution and how far its electrostatic effect persists. A **Debye sphere** is a volume whose radius is the Debye length. With each Debye length, charges are increasingly electrically screened

## Nano - capillary



Roughness equivalent porous medium layer

fluid

central line of tube
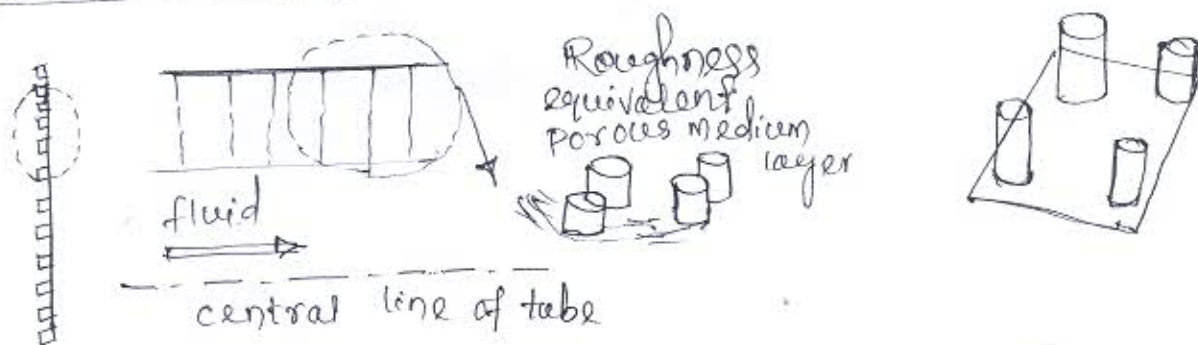
A model of a nano-capillary. The cylinders depict the inherent roughness of the surface of the capillary wall.

# Quantum wire

In mesoscopic physics, a quantum wire is an electrically conducting wires in which quantum effects influence the transport properties. Usually such effects appear in the dimension of nanometers, so they are also referred to as nanowires.

nanowires can be defined as structures that have a thickness or diameter constrained to tens of nanometers or less and an unconstrained length.

Many diff. types of nanowires exist, including superconducting (YBCO) (yttrium barium copper oxide), Metallic (Ni, Pt, Au), silicon nanowires (SiNWs, InP, GaN)

Nickel, platinum, gold

Indium phosphide
Gallium nitride

insulating ($SiO_2$, $TiO_2$) (silicon dioxide, titanium dioxide

Synthesis
[ Top-down
  Bottom-up

## Applications

Electronic devices, Nanowire lasers, sensing of proteins and chemicals using semiconductor nanowires

## Quantum dot

A semiconductor crystal of nanometre dimensions with distinctive conductive properties determined by its size.

Quantum dots are very small semiconductor particles, only several nanometres in size, so small that their optical and electronic properties differ from those of larger particles. They are a central theme in nanotechnology.

**Quantum dots (QDs)** are tiny semiconductor particles a few nanometres in size, having optical and electronic properties that differ from larger particles due to quantum mechanics. They are a central topic in nanotechnology. When the quantum dots are illuminated by UV light, an electron in the quantum dot can be excited to a state of higher energy. In the case of a semiconducting quantum dot, this process corresponds to the transition of an electron from the valence band to the conductance band. The excited electron can drop back into the valence band releasing its energy by the emission of light. This light emission (photoluminescence) is illustrated in the figure on the right. The color of that light depends on the energy difference between the conductance band and the valence band.

Potential applications of quantum dots include single-electron transistors, solar cells, LEDs, lasers, single-photon sources, second-harmonic generation, quantum computing, and medical imaging. Their small size allows for some QDs to be suspended in solution, which may lead to use in inkjet printing and spin-coating. They have been used in Langmuir-Blodgett thin-films. These processing techniques result in less expensive and less time-consuming methods of semiconductor fabrication.

## Production

- Colloidal synthesis
- Plasma synthesis
- Fabrication
- Viral assembly
- Electrochemical assembly
- Bulk-manufacture
- Heavy-metal-free quantum dots

Applications:- potential applications of quantum dots include single-electron transistors, solar cells, LEDs, lasers, single-photon sources, medical imaging, quantum computing, inkjet printing & spin-coating.

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# Nanomechanics

**Nanomechanics** is a branch of *nanoscience* studying fundamental *mechanical* (elastic, thermal and kinetic) properties of physical systems at the nanometer scale. Nanomechanics has emerged on the crossroads of biophysics, classical mechanics, solid-state physics, statistical mechanics, materials science, and quantum chemistry. As an area of nanoscience, nanomechanics provides a scientific foundation of nanotechnology.

Nanomechanics is that branch of nanoscience which deals with the study and application of fundamental mechanical properties of physical systems at the nanoscale, such as elastic, thermal and kinetic material properties.

Often, nanomechanics is viewed as a *branch* of nanotechnology, i.e., an applied area with a focus on the mechanical properties of *engineered* nanostructures and nanosystems (systems with nanoscale components of importance). Examples of the latter include nanomachines, nanoparticles, nanopowders, nanowires, nanorods, nanoribbons, nanotubes, including carbon nanotubes (CNT) and boron nitride nanotubes (BNNTs); nanoshells, nanomebranes, nanocoatings, nanocomposite/nanostructured materials, (fluids with dispersed nanoparticles); nanomotors, etc.
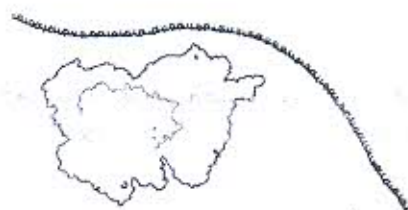
A ribosome is a biological machine that utilizes protein dynamics on nanoscales

Some of the well-established *fields of nanomechanics* are: nanomaterials, nanotribology (friction, wear and contact mechanics at the nanoscale), nanoelectromechanical systems (NEMS), and nanofluidics.

As a fundamental science, nanomechanics is based on some empirical principles (basic observations), namely general mechanics principles and specific principles arising from the smallness of physical sizes of the object of study.

General mechanics principles include:

- Energy and momentum conservation principles
- Variational Hamilton's principle
- Symmetry principles

Due to smallness of the studied object, nanomechanics also accounts for:

- *Discreteness* of the object, whose size is comparable with the interatomic distances
- Plurality, but *finiteness*, of degrees of freedom in the object
- Importance of *thermal fluctuations*
- Importance of *entropic effects* (see configuration entropy)
- Importance of *quantum effects* (see quantum machine)

These principles serve to provide a basic insight into novel mechanical properties of nanometer objects. Novelty is understood in the sense that these properties are not present in similar macroscale objects or much different from the properties of those (e.g., nanorods vs. usual macroscopic beam structures). In particular, smallness of the subject itself gives rise to various surface effects determined by higher surface-to-volume ratio of nanostructures, and thus affects mechanoenergetic and thermal properties (melting point, heat capacitance, etc.) of nanostructures. Discreteness serves a fundamental reason, for instance, for the dispersion of mechanical waves in solids, and some special behavior of basic elastomechanics solutions at small scales. Plurality of degrees of freedom and the rise of thermal fluctuations are the reasons for thermal tunneling of nanoparticles through potential barriers, as well as for the cross-diffusion of liquids and solids. Smallness and thermal fluctuations provide the basic reasons of the Brownian motion of nanoparticles. Increased importance of thermal fluctuations and configuration entropy at the nanoscale give rise to superelasticity, entropic elasticity (entropic forces), and other exotic types of elasticity of nanostructures. Aspects of configuration entropy are also of great interest in the context self-organization and cooperative behavior of open nanosystems.

Quantum effects determine *forces of interaction* between individual atoms in physical objects, which are introduced in nanomechanics by means of some averaged mathematical models called *interatomic potentials*.

Subsequent utilization of the interatomic potentials within the classical multibody dynamics provide deterministic mechanical models of nano structures and systems at the atomic scale/resolution. Numerical methods of solution of these models are called *molecular dynamics* (MD), and sometimes *molecular mechanics* (especially, in relation to statically equilibrated (still) models). Non-deterministic numerical approaches include Monte Carlo, Kinetic More-Carlo (KMC), and other methods. Contemporary numerical tools include also hybrid *multiscale approaches* allowing concurrent or sequential utilization of the atomistic scale methods (usually, MD) with the continuum (macro) scale methods (usually, field emission microscopy) within a single mathematical model. Development of these complex methods is a separate subject of applied mechanics research.

Quantum effects also determine novel electrical, optical and chemical properties of nanostructures, and therefore they find even greater attention in adjacent areas of nanoscience and nanotechnology, such as nanoelectronics, advanced energy systems, and nanobiotechnology.

## See also

{ Bias voltage is the amount of voltage that an electronic device needs in order to power on & function

- Molecular machine
- Geometric phase (section Stochastic Pump Effect)
- Nanoelectromechanical relay

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Quantum electronics - Quantum electronics is the area of physics dealing with the effects of quantum mechanics on the behaviour of electrons in matter.

Single Electron Devices - SEDs are based on the controlled transfer of single electrons bet'n small conducting islands

Coulomb Blockade (CB) named after Charles-Augustin de Coulomb electrical force, is the decrease in electrical conductance at small bias voltages of a small electronic device comprising at least one low-capacitance tunnel junction. A tunnel junction is a barrier ... a thin insulating layer ...

## 9.3 SINGLE ELECTRON DEVICES

Single electron devices are based on the controlled transfer of single electrons between small conducting islands. The basic principles behind single electron devices, such as the two-terminal single electron box, three-terminal single electron transistor (SET), and SET and their applications, are presented here. These devices are opening new avenues in the development of fundamental understanding of new quantum phenomena based on the control of single electron transportation and SET, which offers prospects of replacing conventional MOS transistor involving a vast number of electrons in charge transportation. A modification of an electron box with a one-dimensional (1D) array of two or more quantum islands separated by tunnel barriers, called single-electron trap, offers a new feature of internal memory (bi- or multi-stability) with a retention capacity of several hours. Thus, several single electron devices are possible that may find practical applications in digital integrated circuits.

### ~~9.3.1~~ Coulomb Blockade in Nanocapacitors

In case of a single electron transistor, the tunnelling current flows between two leads through the QD, which is merely a small material region, also called the quantum or Coulomb island, as shown in Fig. 9.3. To understand the basic concepts behind the working of an SET, it has to be known why an electron transfer into a quantum island requires a minimum charging energy, what causes a Coulomb blockade, how much energy is needed to transfer the next electron, and what the importance of the physical dimensions and the materials of the elements is.



FIG. 9.3 Schematic shows the two leads and a QD in the middle that form an important part of a single electron transistor. Both the leads are separated from the QD by a thin insulating layer (a tunnel barrier) and form nanocapacitors. When biased, the current flows between the leads via the QD by the tunneling process across these insulating barriers.

We, therefore, must analyse the charging behaviour and electron tunnelling between the plates of a tunnelling capacitor, which are depicted in Fig. 9.4.
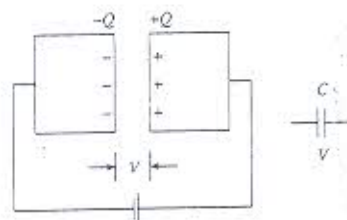


FIG. 9.4 A parallel plate charged capacitor with two metal electrodes, representing a lead and the QD island, with a thin insulator in between them under applied voltage, V

The charge stored in a parallel plate capacitor between two electrodes of area A separated by an insulator of thickness d at an applied voltage V is given as follows.

$$Q = CV = \left( \frac{\varepsilon_r \varepsilon_0}{d} A \right) V$$

where, $\varepsilon_r$ and $\varepsilon_0$ are the relative dielectric constant and the permittivity of the free space ($8.85 \times 10^{-12}$ F/m) respectively. Thus, the stored charge Q depends on the capacitance (C) of the structure and the applied voltage. Since the thickness d of the tunnel barriers has to be kept within the tunnel range ≤ 10 nm, the use of thicker insulator in keeping the capacitance small is not suitable for tunnel devices. The QDs are normally a few nm across and the capacitance value for the matching lead cross-section is extremely small. As an example, the capacitance value for a $5 \times 5$ nm$^2$ parallel plate capacitor with 2 nm air separation is ~$1.1 \times 10^{-19}$ F. The electrostatic energy E, stored in the capacitor, required to separate the charges initially when applying voltage across the conducting electrodes, is

$$E = \frac{1}{2}CV^2 = \frac{Q^2}{2C} \tag{9.1}$$

The energy change for a single-electron transfer ($\Delta Q = q_e$) to the nanoscale capacitor in the aforementioned example is ~0.73 eV, which is significantly larger as compared to the energy change (negligible) for a macrocapacitor with an area of $5 \times 5$ mm$^2$, keeping the electrode separation of 2 nm. Thus, it is evident that a single-electron transfer involves large energy change for a nanocapacitor; whereas it is negligibly small for macro or gross capacitors. The potential difference established at the electrode interfaces of a charged capacitor is caused by polarization of the dielectric medium as a result of the relative displacement of positive ions and negative electronic charges, distributed across the insulator, resulting in a net effective polarity between the plates. In addition, the macrocapacitors carry charging current in milliamperes or higher values involving a vast number of electrons. Recall that an ampere current flow amounts to one Coulomb or 6.25 × 10$^{18}$ unit charges passing per second. Even if the electronic charges are discrete in nature, the large number of electrons transfer coupled with the distribution of the polarization charges in the medium, leads to a continuous variation of the electrostatic potential at the interfaces in a large capacitor.

Consider a nanocapacitor that undergoes change from an initial state with charges −Q and +Q to a final state with charges [−Q −$q_e$] and [+Q +$q_e$] on the two plates, respectively, due to tunnelling of an electron from the positive to negative plate. It can be shown using Eq. 9.1 that the difference of energy $\Delta E$ between the two states to be greater than zero for tunnelling to occur, leads to a condition

$$Q > -\frac{q_e}{2} \quad \text{or} \quad V > -\frac{q_e}{2C} \tag{9.2}$$

Conversely, for tunnelling to occur in the reverse direction, we obtain a condition

$$V < \frac{q_e}{2C} \tag{9.3}$$

Combining Eqs 9.2 and 9.3, we yield

$$-\frac{q_e}{2C} < V < \frac{q_e}{2C} \tag{9.4}$$

Thus, a sufficiently large change in the voltage should occur for tunnelling to take place in a nanocapacitor, that is, $|V| > |q_e|/2C$. This effect is known as the *Coulomb blockade*. For transferring $n$ electrons en bloc, we need to replace the term for single-electron charge $q_e$ by $nq_e$ in Eq. 9.4.

The charging energy $E_C$ required for adding a single electron to the capacitor, against the repulsive force, is

$$E_C = q_e V_c = \frac{q_e^2}{2C} \quad \text{or} \quad V_c = \frac{q_e}{2C}$$

The current flow between the nanocapacitor plates will remain zero until the charging voltage $V_c$ is reached for a single electron to tunnel. The I–V characteristics illustrating the Coulomb blockade in a small capacitor are shown in Fig. 9.5.



FIG. 9.5 I–V characteristics of a nanocapacitor, illustrating the Coulomb blockade effect, with no current-flow until charging voltage exceeds the Coulomb blockade

The aforementioned analysis holds good at $T = 0\,K$. At $T > 0\,K$, the charging energy must be more than the thermal energy of the electron, that is, $E_C > 1/2\,k_BT$, which applies well at practical working temperatures for nanocapacitors. Coulomb blockade is, therefore, observable even at room temperature for a nanocapacitor. However, in case of macrocapacitors, this condition requires use of extremely low temperatures close to 0 K, which can be difficult to achieve, to observe the effect.

Classically, an ideal capacitor stores and releases electrical energy, without incurring any resistive loss. It also does not allow electron tunnelling events to occur. In reality, however, a capacitor may have imperfections and can be considered to be leaky, which involves loss of energy. The electron tunnelling through an insulating barrier is a quantum mechanical phenomenon, which must be differentiated from the leakage in a normal capacitor. In case of electron tunnelling, an ideal capacitor can be modelled as a capacitor $C$ in parallel with an appropriately high but finite tunnel resistance $R_t$, which is related to the energy barrier width between the capacitor plates. Such a parallel combination of a capacitor and tunnel resistance is called a *tunnel junction* (TJ) or *tunnel element*, as shown in Fig. 9.6.
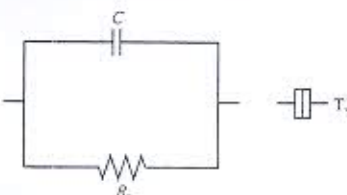


FIG. 9.6 Equivalent circuit of a tunnel junction (TJ) modelled as a parallel network of an ideal capacitor C and tunnel resistance $R_t$

The time constant of the tunnel junction circuit is

$$\tau = R_t C$$

On observing the quantum Coulomb blockade encountered in electron tunnelling, Heisenberg's uncertainty principle imposes a condition that the energy uncertainty must be less than the charging energy of the nanocapacitor. The uncertainty principle states that

$$\Delta E \Delta t \geq \frac{\hbar}{2} \quad \text{or} \quad \Delta E \geq \frac{\hbar}{2\Delta t} \quad \text{or} \quad \Delta E \geq \frac{\hbar}{2R_t C} \quad (9.5)$$

where, uncertainty in time has been equated to the time constant of the tunnel element. The condition for observing Coulomb blockade, therefore, becomes

$$E_C = \frac{q_e^2}{2C} \gg \frac{\hbar}{2R_t C}$$

or

$$R_t \gg \frac{\hbar}{q_e^2}$$

Substituting the values of the parameters in the aforementioned relation, we get $R_t \approx 4.1\,k\Omega$.

### 9.3.2 Coulomb Blockade in Quantum Dot Circuit

Forming a major part of the SET system, a QD is coupled to external leads, as shown in Fig. 9.3. It can be modelled as a metallic charge island isolated from the leads by the separation between the dot and the leads of the two tunnel junctions A and L. A voltage source $V_S$ is connected across the terminals, as shown in Fig. 9.7. Since an elaborate mathematical description of the model of the QD circuit is beyond the scope of this chapter, only the salient features of the QD circuit are presented here. It is assumed that the QD is isolated from the external environment, as the junctions are tunnel leaky, as discussed previously in the case of a nanocapacitor, and their tunnel resistances are unequal to make the circuit asymmetrical to observe the Coulomb blockade in the I–V characteristics.
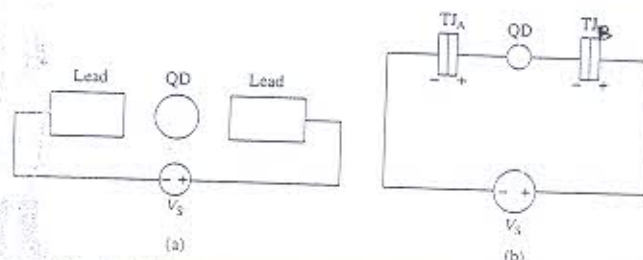


FIG. 9.7 Schematic (a) Block diagram of a QD circuit with tunnel junctions TJA and TJB, and the voltage source $V_S$ (b) Equivalent circuit diagram