# 1

# Nanomaterials—Definition and Methods of Preparation

## 1.1 DEFINITION OF NANOMATERIALS AND NANOTECHNOLOGY

Though nanomaterials have taken the centre stage of materials research today an exact definition of nano materials is still a point of contention. This is evident from the following definitions provided by different researchers from their points of view. (Only the essential lines from each of these definitions are reproduced here and for the original full text of the definitions the readers can look uphttp://www.nanowerk.com/ nanotechnology/introduction/introduction_to_nanotechnology_1.html).

"For me, nanotechnology is all about building things. Judging by current rates of progress in fields as diverse as protein engineering and nanoelectronics, the emergence of atomic-precision manufacturing on an industrial scale is still some decades away… "***Thomas Theis*** is director of physical sciences at the IBM Watson Research Center.

"One way of defining nanotechnology is to talk about length scales. A different way is to see it as an upcoming economic, business and social phenomenon. Nano-advocates argue it will revolutionize the way we live, work and communicate. If it will dramatically affect everyone, shouldn't everyone have a say in what developments take place — with what impacts, under whose control, and with who benefiting (and losing)?……" ***Doug Parr,*** *is the chief scientist for Greenpeace in the UK*

"There isn't just one nanotechnology; there are many nanotechnologies and these are primarily enabling technologies and not end products in themselves. It would not surprise me if the term nanotechnology disappeared from general use in the next decade, with the terms nanomaterials and nanobiotechnology assuming greater currency….." ***Peter Binks*** *is chief executive officer of Nanotechnology Victoria, a consortium of four research organizations focused on the commercialization of nanotechnologies in Australia.*

"I see nanotechnology as a toolbox that provides nanometre-sized building blocks for the tailoring of new materials, devices and systems. The nanometre length scale (that is < 100 nm) offers unique size-dependent properties in physico–chemical phenomena….. "***Jackie Ying*** *is the executive director of the Institute of Bioengineering and Nanotechnology in Singapore, and adjunct professor of chemical engineering at the Massachusetts Institute of Technology.*

"Nanoscience and nanotechnology can be regarded as areas defined by a chosen boundary, but I find it more fruitful to see them as directions united by shared objectives. Central among these is the atomistic understanding and control of an increasing range of physical systems and phenomena....." ***K. Eric Drexler*** *wrote Nanosystems and Engines of Creation and is chief technical advisor to Nanorex.*

"Nanoscience is a very handy word for rather small things with a rather big impact. Why should we care about such small things? We may find properties that are useful for everyday life...." ***Elisabeth Schepers*** *is in the department of museums education at the Deutsches Museum in Munich, where she has recently been working for the EU Nanodialogue project.*

"......that invention is truly the watershed between nanotechnology and everything really small, like molecules, which came before but were, in the main, only accessible collectively....." ***Kary Mullis*** *shared the Nobel Prize for Chemistry in 1993 for his work on the polymerase chain reaction technique. He is currently working on chemical methods to control and direct immune responses.*

"The converging interests of nanotechnology foresee the precise control of individual atoms or molecules, leading to an unprecedented ability to design material and device capabilities....." ***Chunli Bai*** *is executive vice president of the Chinese Academy of Sciences, director of the China National Center for Nanoscience and Technology, and chief scientist of the China National Steering Committee for Nanoscience and Nanotechnology.*

"Indeed, one could reasonably argue that it is meaningless to refer to the innate properties of nanoscale systems without due reference to the influence of environmental factors such as surface termination, substrate interactions and electrical and mechanical contacts. Although this sensitivity is a challenge for nanoscale materials processing, it brings with it the potential for unprecedented levels of control of material and device properties......." ***John J. Boland*** *is professor of chemistry and director of the Centre for Research on Adaptive Nanostructures and Nanodevices at Trinity College, Dublin, Ireland.*

"Nanotechnology is concerned with work at the atomic, molecular and supramolecular levels in order to understand and create materials, devices and systems with fundamentally new properties and functions because of their small structure...." *Robert Langer is the Institute Professor at the Massachusetts Institute of Technology, the recipient of the 2002 Draper Prize and a member of the National Academies of Sciences and Engineering and the Institute of Medicine.*

"Actually, nanotechnology has been around for over a hundred years. Irving Langmuir was one of the first to truly develop the technology in the General Electric labs in the 1920s and 1930s. Nanoscience is a label given now to the new work emerging from the technology we have developed to manipulate, visualize and make atomic and molecular structures. It would have been called surface science in the 1960s and 1970s. In the immediate future, we will see incremental changes in materials for energy generation and storage, improved and safer cosmetics and other domestic products, and new methodologies for healthcare, water treatment and pollution control......" ***Peter Dobson*** *of Oxford University has recently started two companies that use nanotechnology: Oxonica and Oxford Biosensors.*

"I want to be sure that the benefits of nanoscience reach all mankind. Although the research is being carried out in only a few countries and laboratories, I do hope that the poorest of the poor will benefit from the results of research in nanoscience and nanotechnology." ***C. N. R. Rao*** *is a national research professor and the honorary president of the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India.*

"My bottom line, however, is that the field should worry less about self-serving definitions (including my own!), and more about how to be of true benefit to humankind..........." ***Mauro Ferrari*** *is professor of molecular medicine at the University of Texas Health Science Center, of experimental therapeutics at the M. D. Anderson Cancer Center, and of bioengineering at Rice University.*

For generating a working definition of nanotechnology, it can be defined as "development and utilization of structures and devices with organizational features at the intermediate scale between individual molecules and about 100 nanometers where novel properties occur as compared to the bulk materials." Though the term nanotechnology was first employed by Tokyo Science University Prof. Norio Taniguchi of Tokyo Science University in 1974 to describe the precision manufacture of materials with nanometer tolerances, the idea has been around for many centuries and it is often credited to Prof Richard Feynman for his 1959 lecture at Cal Tech titled there is plenty of room at the bottom. It is interesting to quote a few lines of this famous lecture.

"People tell me about miniaturization and how far it has progressed today (1959). They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing' that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that any body began seriously to move in this direction. Why cannot we write the entire 24 volumes of Enclopedia Brittanica on the head of a pin?" How true his prophesy for 2000 has come true.

However, it has often been credited to K. Eric Drexler as the reinvetor (1980) of the term nano technology, since he used this term in his 1986 book on Engines of creation where he expanded the term into nanosystems to mean molecular machinery, manufacturing and computation.

In spite of all these definitions from the point of perceptions of different people it is necessary to have a working definition for nanomaterials and nanotechnology. The accepted definition is "the design, characterization, production, and application of structures, devices, and systems by controlled manipulation of size and shape at the nanometer scale (atomic, molecular, and macromolecular scale) that produces structures, devices, and systems with at least one novel/superior characteristic or property".

## 1.2 SIZE DEPENDENT PROPERTIES OF NANOMATERIALS

It is therefore clear that nanomaterials and nanotechnology, depend on size dependent properties. In general they can be recognized as follows:

(i) Chemical properties – reactivity, catalysis
(ii) Thermal property – melting temperature
(iii) Mechanical property – adhesion, capillary forces
(iv) Optical properties – absorption and scattering of light
(v) Electrical properties – tunneling of current
(vi) Magnetic properties – super paramagnetic effect.

This list can be extended to include many other sensing and biochemical properties and functions. Normally the size of a nanometer is compared to that of the human hair which is 80,000 nm wide. To illustrate the comparison, in Fig. 1.1. the human hair fragment together with a net work of single-walled carbon nanotubes is given.

## 1.3 ALTERNATE APPROACHES FOR THE PREPARATION OF NANOMATERIALS

Nanochemistry, as opposed to nanophysics is an emerging constituent of solid state materials chemistry. It emphaseized the synthesis rather than the engineering aspects of preparing minute pieces of matter with

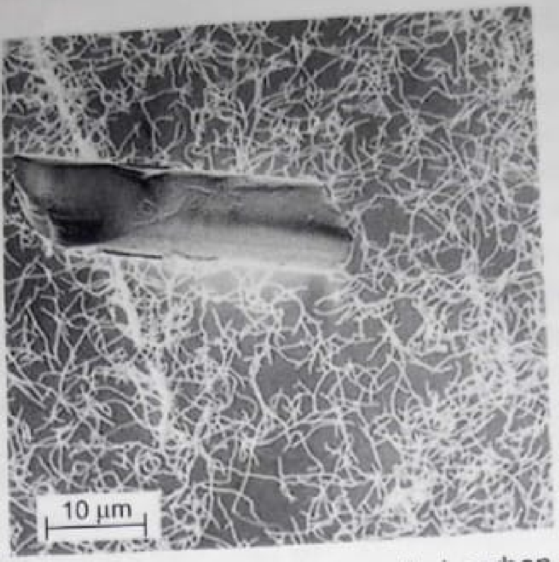


**Fig. 1.1** Human hair fragment and a network of single-walled carbon nanotubes (reproduced from: http://www.nanowerk.com/nanotechnology/introduction/introduction_to_nanotechnology_1.html)

nanometer sizes in one or two or three dimensions. Chemists strive towards this objective from the "atom Up" while nano-physicists operate from the "bulk down". A pictorial representations of these two processes is shown in Fig. 2. Building and organizing nano-objects under mild and controlled conditions one atom at a time instead of manipulating the bulk in principle provide the chemist with simple, reproducible and cost effective synthetic approaches to materials of perfect atom sizes and shapes rather than having to use the complex and sophisticated instrumental techniques of the engineering physicist.

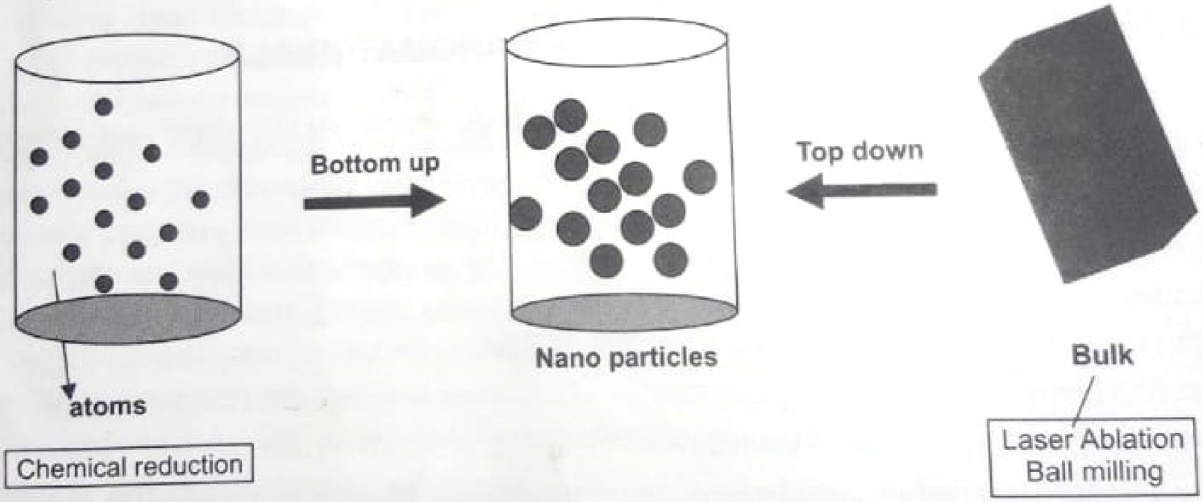


**Fig. 1.2** Pictorial representation of the two approaches

The evolving nanophysics fabrication methods include molecular beam epitaxy, scanned optical, X-ray, ion and electron beam lateral engineering (lithographic) techniques which could produce sub micrometer-scale objects with any desired architecture.

Chemists pride themselves in being able to synthesize small and perfect molecular size objects. However, to prepare routinely and reproducibly, atomically perfect nano-structures, chemists have to develop new types of synthetic approaches that have the ability to assemble and position these tiny particles in appropriately organized arrays with uniform size and space distribution. Two exemplary approaches involve" patterning and templating" principles. In patterning, nanolithography is used to spatially define physically or chemically active foundation sites usually on planar substrates upon which subsequent site – specific chemical synthesis allows the growth of the nano scale objects. Templating on the other hand, exploits the preexisting perfectly periodic, singe-size and single shape void spaces found in porous materials for performing host-guest inclusion chemistry.

## 1.4 SYNTHETIC STRATEGIES

In this section we shall briefly consider the various synthetic strategies adopted for the preparation of nano materials. Even though this section is subdivided in subsections, it should be remarked that there exists a certain overlap between the different methods.

### 1.4.1 Gas Phase Evaporation Method

This technique is based on the vapourizaton of metals in a pressure of static inert gas. Vapourization can be achieved by using resistive heating, electron beam or laser vapourization. Cluster growth occurs in gas phase and depends on the gas temperature and pressure. The clusters formed can be condensed on suitable substrates.

### 1.4.2 Matrix Isolation Technique

Matrix isolation is based on the con-condensation of metal vapours with weakly interactive supports such as inert gases (Ar, Kr, Xe) at low temperatures. This has been widely used to isolate small and well defined ligand free metal clusters.

### 1.4.3 Metal Vapour-colvent Codeposition Method

Co-Condensation of metal vapours with organic compounds as weakly coordinated solvents followed by warming to room temperature is adopted method to produce solvated metal particles. Co-condensation is usually carried out at surfaces cooled to low temperatures (say 77 K). At these temperatures almost all organic substances are in the solid state, so upon co-condensation, metals atoms and clusters are embedded into solid organic matrices. A variation of this method is to react the metal atoms with reactive organic substrates (like arenes) and this will result in formation of metal arene complex thus resulting in cluster arene complex containing strained ring substituents. Other variations are metal vapour deposition into a polymer, decomposition of organo-metal compounds and cluster complexes for the preparation of metal clusters.

### 1.4.4 Sol Gel Processing

One of the most successful methods adopted for the synthesis of nano materials is the sol gel processing route under appropriate experimental conditions.

The sol gel process involves the combination of chemical reactions which turns a homogeneous solution of reactants into an infinite molecular weight polymer. This polymer is a three dimensional interconnected pores. The polymer is isotropic, homogeneous and uniform and it replicates its mold exactly and miniaturizes all features without distortion. Thus the polymer net works provide nanostructure and nanophase porosity. A pictorial representation of this technique is shown in Fig. 1.3.

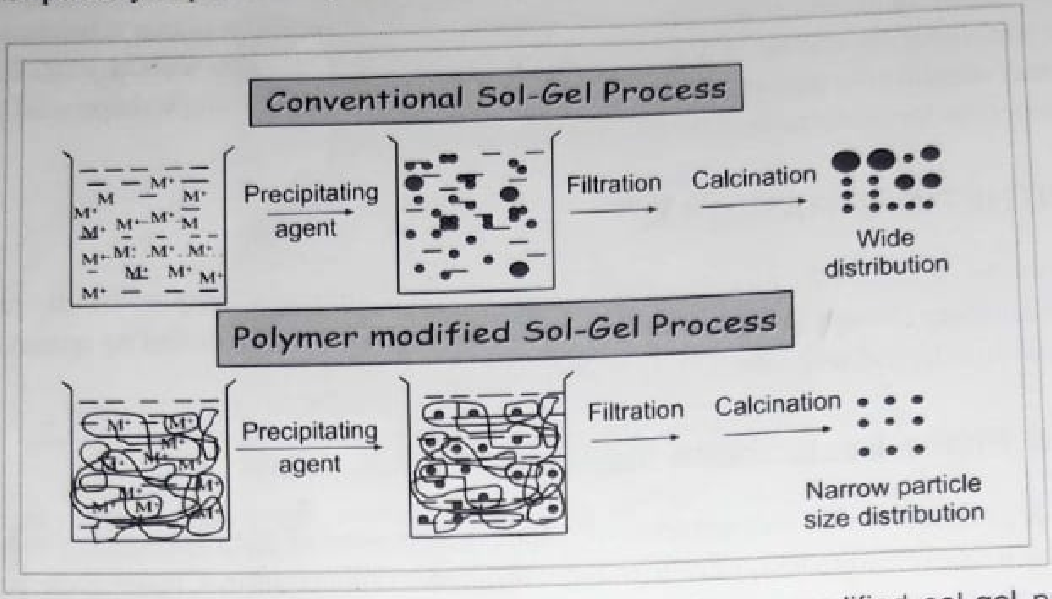


**Fig. 1.3** Pictorial representation of conventional and polymer modified sol-gel process

A variety of reaction conditions are employed for suitably architecturing the nano materials. In the case of metal nanomaterials preparation with various capping agents are employed and a pictorial representation of the same is shown in Fig. 1.4.

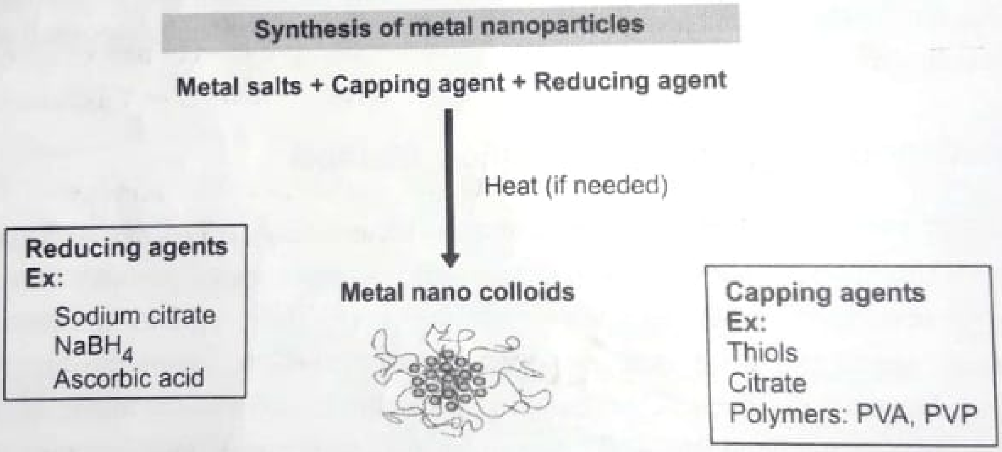


**Fig. 1.4** Pictorial representation of the formation of metal nanoparticles employing capping agents

The factors that control the nucleation and growth routes of the nano particles formed are given in Table 1.1.

**Table 1.1** Governing factors for the growth of nanostructures

- Kinetics of nucleation and growth
- Concentration of stabilizing agent
- Structure of the stabilizing agent
- Nature of the capping agent
- pH of the medium employed and temperature

The nucleation and growth of the particles are the crucial factors for controlling the size of the nano particles formed. This is usually achieved by choice of the suitable capping agents and also the functionality of the capping agents, their hydrophobic and hydrophilic parts interacting suitably with the particles formed and thus preventing the growth mechanism. The nucleation and growth kinetics is determined by various factors and this is illustrated pictorially in Fig. 1.5.

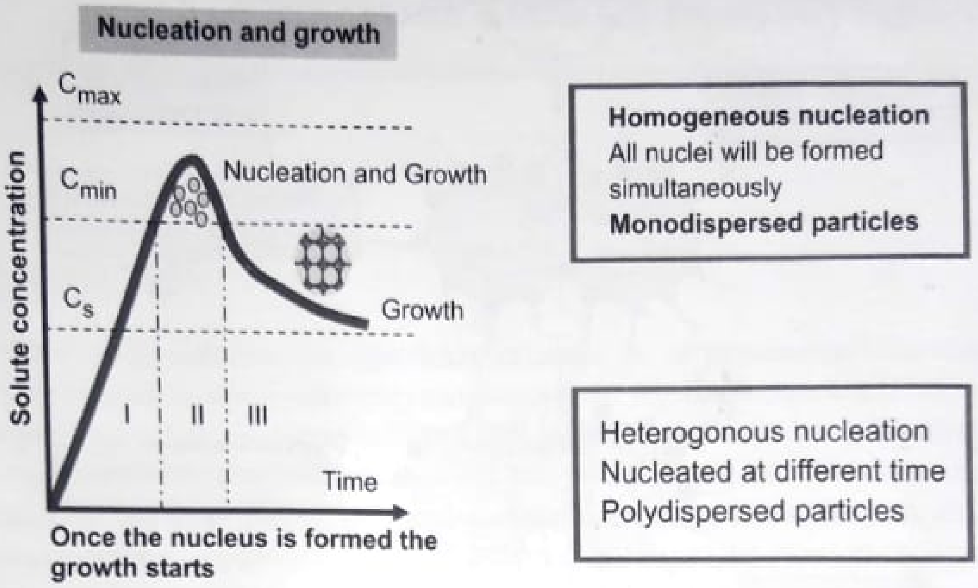


**Fig. 1.5** The Nucleation and Growth curve and concentration dependence

There are various other methods that can be employed for the preparation of nano materials. One of the methods is termed as reverse micellar technique. A pictorial representation of this method is shown in Fig.1.6.

The reactivity of nano materials is usually attributed to the ratio of the number of surface to bulk species. This number can be as high as 60 % in the case of nanomaterials. This can be illustrated with the following data.

## 1.5 SURFACE VERSUS BULK SPECIES

A typical material possesses approximately $10^{23}$ atoms/cm$^3$ (volume density) and approximately $10^{15}$ atoms /cm$^2$ (surface density). For a cube with a side length of 1 nm the total number of atoms is $\sim 10^{23}$ atoms/cm$^3$ $\times (10^{-7}\text{ cm})^3 \sim 100$ whereas the number of surface atoms is $\sim 10^{15}$ atoms/cm$^2 \times 6 \times (10^{-7}\text{cm})^2 \sim 60$ and this gives a ratio of surface to total atoms of 60%. Since surface atoms possess more energy than bulk atoms and hence the surface atoms are chemically more reactive.

Nanomaterials thus exhibit remarkable reactivity and this can be exploited in a number ways. It is envisaged that nanomaterials find applications in every sector of human life requirements. The book attempts to outline some of the applications of nano materials in a few of the essential sectors of human life in the subsequent chapters.

# 2

# Properties of Nanomaterials

## 2.1 INTRODUCTION

The particles size of the material has significant influence on its physical and chemical properties. Especially, when the particle size is reduced to nanometer scale, it behaves completely different form their bulk counterpart. Unusual physico-chemical properties of nanoparticles are due to three main reasons. (i) The size of nanoparticles is comparable to the Bohr radius of the excitons. This significantly alters the optical, luminescent and redox properties of nanoparticles when compared to the bulk material. (ii) The surface atoms constitute a considerable fraction of the total number of the atoms of the nanoparticle. The surface atoms contribute largely to the thermodynamic characteristics of solids and also determine the melting temperature and structural transitions of nanoparticles in the bulk material, atoms are evenly surrounded and the cohesive forces between the atoms tend to balance. However, there are atoms on only one side of a free nanoparticle surface, and there is an internal cohesive force. As the particle size decreases, the net internal cohesive force increases, and as a consequence the surface energy that depends on the internal cohesive force should increase with decreasing particle size. (iii) The natural size of the nanoparticles is comparable with the size of molecules. This determines the peculiarities of the kinetics of chemical processes on the surface of nanoparticles.

In general, it is easily noticeable that, the reduction in the particle size results in

1. Increase in surface to bulk atom ratio
2. Increase in the surface area

The increases in the surface area can be understood from the following example. The total surface area proportional to a given 1cm$^3$ volume filled by particles with 1cm$^3$cube in size is 6 cm$^2$, whereas when the particle size is reduced to 1μm$^3$ cubes and 1nm$^3$ cubes in size, the surface area increases to 6 m$^2$ and 6000 m$^2$ respectively. Similarly the proportion of number of surface atoms to bulk atoms in 1cm$^3$ cube and 1mm$^3$ cube particles is < 10 %. While, in the case of particles in the nanometer range, *i.e.* 1nm$^3$ cube, 80% of atoms will be present on the surface. This is shown in a pictorial representation in Fig. 2.1.

It can be seen from the figure that when the number of shells increases, the % of surface atom decreases, the decrease in the cluster size results exposure of more number of surface atoms when compared to the bulk clusters. In many cases, it is observed that 80- 95 % surface atoms can be achieved when the size of the particle is reduced to nanometer range. The increase in the number of surface atoms alters the physical and chemical properties of the corresponding materials.

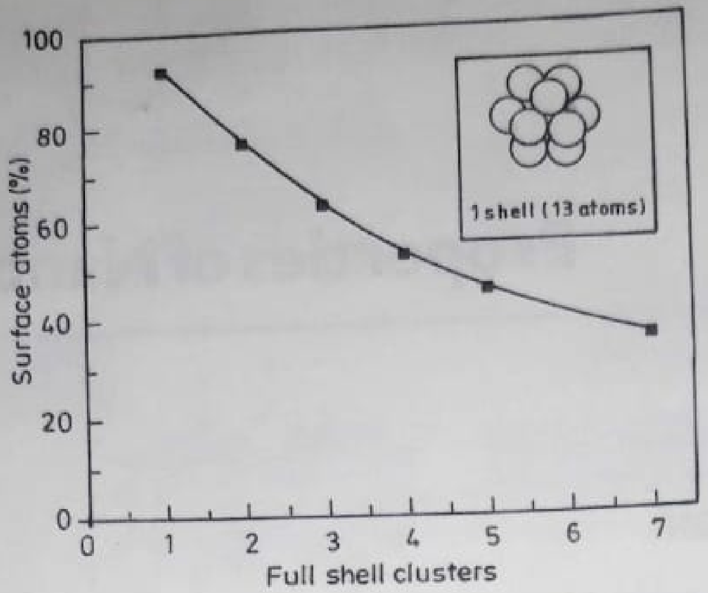


Fig. 2.1 Variation of surface atom (%) with respect to number of clusters [1]

### 2.1.1 Formation of Dangling Bonds

The presence of dangling bonds is due to the missing of one or two adjacent atoms or the unsaturation existing in the coordination. It is well known that, surface atoms are suffering due to the unsaturatiuon in the coordination. The increase in the number of surface atom results in an increase in the presence of so-called "Dangling bonds". Generally the dangling bond arises when an atom is missing a neighbor to which it would be able to bind. Such dangling bonds are defects that disrupt the flow of electrons and that are able to collect the electrons. Dangling bonds are generally found on the surface of most of the crystalline materials due to the absence of lattice atoms on the surface. The Si (001) surface would have two dangling bonds per surface atoms. The greater the number of dangling bonds the higher the surface free energy. Therefore, it is energetically favorable for a structural rearrangement of the surface to occur that will lower

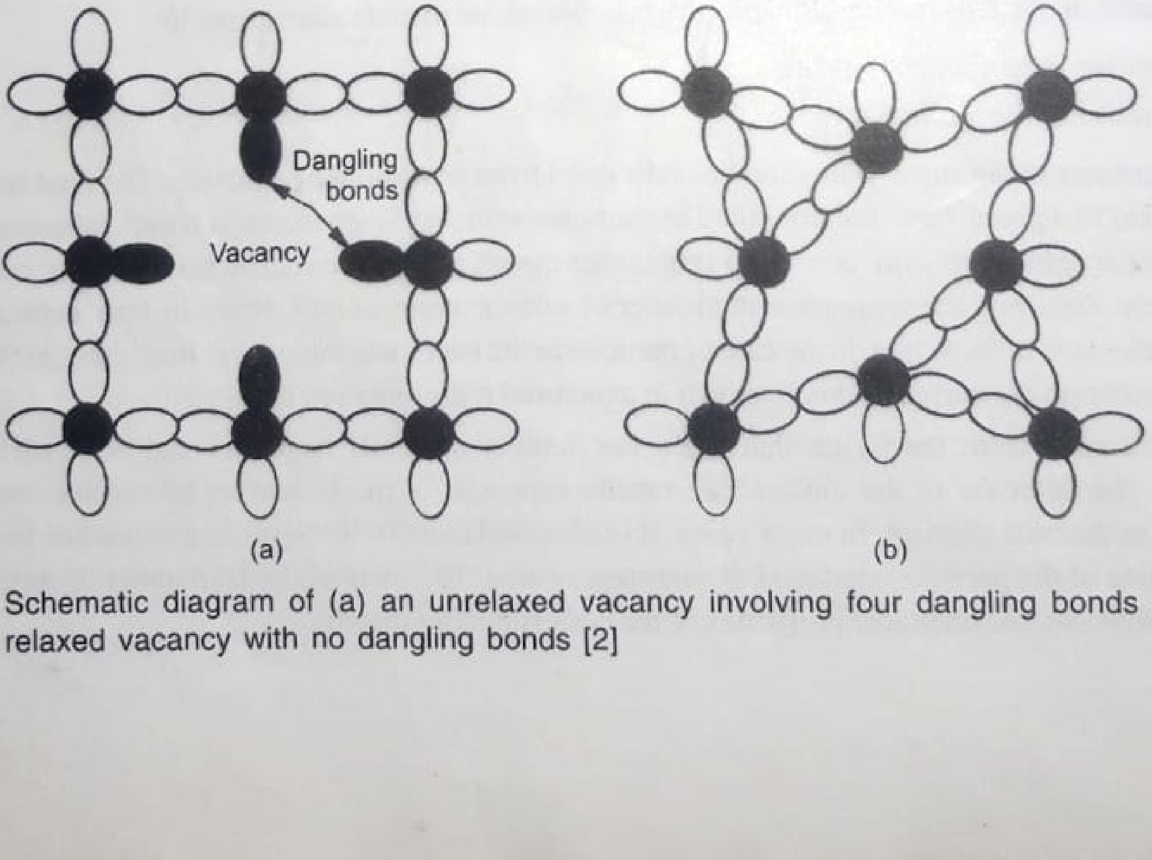


Fig. 2.2 Schematic diagram of (a) an unrelaxed vacancy involving four dangling bonds and (b) a relaxed vacancy with no dangling bonds [2]

the number of dangling bonds and thereby reduce the surface free energy. A wide range of surfaces undergo such a structural change or relax or reconstruct and/or adsorb atoms to reduce the surface energy. Similarly, the dangling bonds can also arise by lattice relaxation in deep centers. That is the missing of an atom in the bulk will also lead to the formation of dangling bonds (Fig. 2.2a). The four dangling bonds can be rearranged by forming two pairs of bonds among neighboring dangling bonds. The distances between atoms with dangling bonds are larger than the bond lengths in the perfect crystal, atoms with dangling bonds have to move closer to each other in order to form new bonds (Fig. 2.2b).

The energy required for this displacement of neighboring atoms is compensated by the lowering of the energy of the four electrons originally in the dangling bonds. Since each new bond can accommodate two electrons in the bonding state, the decrease in the energy of each electron in the dangling bond is proportional to the overlap parameters (extent of overlapping) [2].

### 2.1.2 Atom Like Behavior of Nanoparticles

When the particle size is reduced to nanorange, the particle behaves like in individual atoms due to the formation of discrete energy level rather than the continuum in the energy levels. When conduction electrons are confined within a particle smaller than about 10 nm in diameter, it is not appropriate to use the usual assumption that the electronic energy levels inside the metal form a continuum of states. The energy spacing between the "electrons-in-a-box" quantum levels can be greater than the thermal energy, $k_BT$, at low temperature, so that the energy levels must be considered as discrete energy levels. Fig. 2.3 shows the pictorial representation of atom like behavior when the particle size is decreased. When the particle in the 3 D nature the energy levels are continuous, where as when moving from 3 dimension to zero dimension, formation discrete energy levels occurs which results in the atom like behavior of the nanoparticles [1].

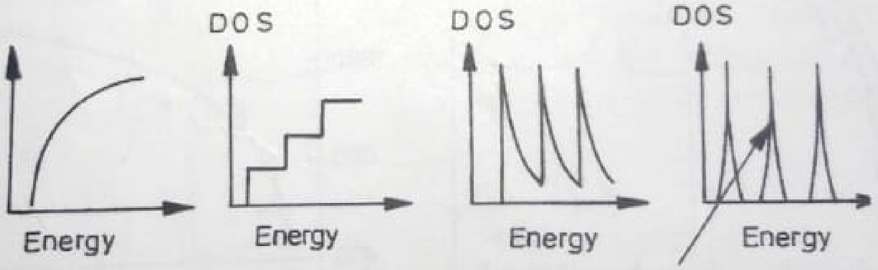


**Fig. 2.3** Formation of zero-dimensional (0D) quantum dots by formal reduction of dimension, correlating with continuing the discretization of the energy states [1]

## 2.2 PHYSICOCHEMICAL PROPERTIES

The physical properties of nanostructured materials differ fundamentally from that of the corresponding bulk materials. This is due to the reduced dimensionality on the one hand, and to the modification of fundamental properties on the other hand as the system size approaches quantum mechanical scale. Optimization of geometry, structure, morphology and the electronic, mechanical, and optical properties of nanometer-sized systems are of fundamental importance for the design of nanostructures with favorable properties. Essentially, the reduction in the particle size from bulk to nanosize results in an increase in the proportion of surface energy and also alters the interparticle spacing.

The variation in the interplanar distance with respect to particle size is shown in Fig. 2.4 for $Cu_n$ particles. Also, the reduction in the particle size alters the thermal behavior. It is observed that the decreases in the melting point with respect to decreases in particle size. Examples are shown in Fig. 2.5 for $Au_n$ and in Fig. 2.5 b for CdS nano particle for the change in melting point as a function of size [3].

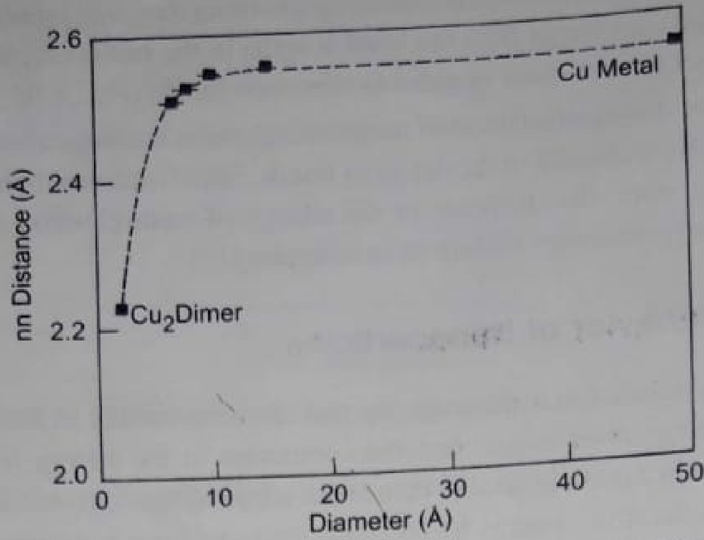
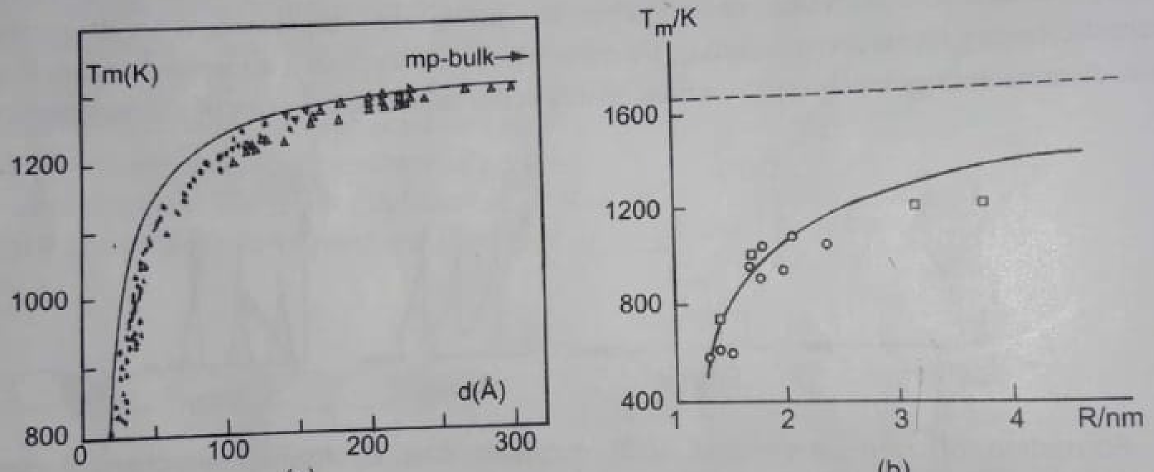


**Fig. 2.4** Variation in the interplanar distance with respect to particle size [3]



(a)

(b)

**Fig. 2.5** Variation in the melting point with respect to decreases in particle size (a) $Au_n$ Cluster (b) CdS naoparticle [3]

## 2.3 OPTICAL PROPERTIES OF NANOMATERIALS

Nanocrystalline systems have attracted interest for their novel optical properties, which differ remarkably from bulk crystals. The factors include quantum confinement of electrical carriers within nanoparticles, efficient energy and charge transfer over nanoscale distances and in many systems a highly enhanced role of interfaces. With the growing technology of these materials, it is essential to understand the detailed basis for photonic properties of nanoparticles. The linear and nonlinear optical properties of such materials can be finely tailored by controlling the crystal dimensions, and the chemistry of their surfaces, fabrication technology becomes a key factor for the applications.

The size dependence of optical properties has been explained by the following example, in which the luluminescence spectra of $Eu^{3+}$: $Y_2O_3$ nanocrystals has been shown for various particle sizes [4].

Fig. 2.6 shows the broad-band $^7F_0 \rightarrow {}^5D_0$ excitation spectra of bulk and nanocrystalline 0.1% Europium-doped $Y_2O_3$. The spectrum (a) shows three lines at 579.41, 582.72, and 582.86 nm for the bulk material. For nanoparticles, the same peaks were observed. One can see two significant changes in the broad-band excitation spectra as the particle size decreases. When the particle size decreases from 15 nm to 7 nm, the widths of the three sharp lines become broader. This broadening could be explained due to disorder induced by the increase in the surface area with decreasing particle size. Also, decreasing particle size results in the appearance of additional phases or sites at 580.6 nm. The spectrum of the 7-nm sample (d) shows a narrow line at 580.6 nm, which is the $C_2$ site in cubic-phase of $Y_2O_3$. But, there is an overlap between the first two excitation lines. This broad band can be seen in the spectra of the 10- and 7-nm particles, but it is also present in the 15- and 13-nm samples with weaker intensity.

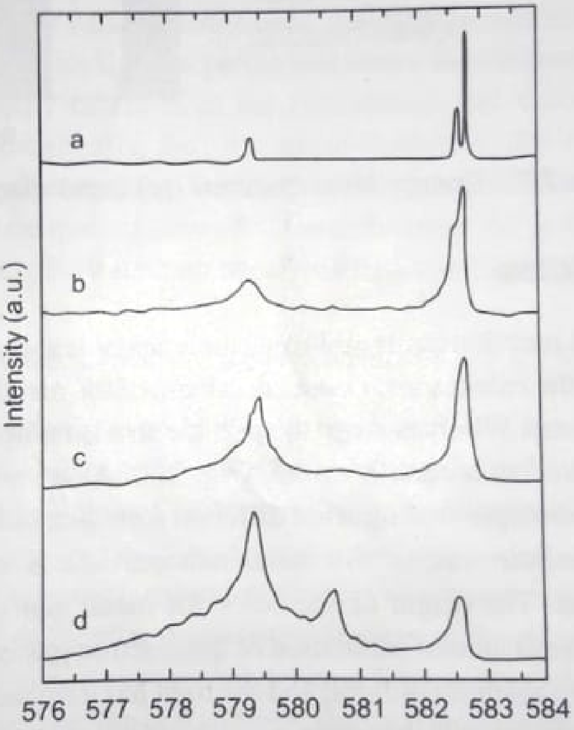


**Fig. 2.6** $^7F_0 \rightarrow {}^5D_0$ excitation spectra of 0.1% $Eu^{3+}$: $Y_2O_3$. The spectra were recorded with monochromator at 614 nm. (a) Bulk; (b) 15 nm; (c) 13 nm; (d) 7 nm.

## 2.3.1 Semiconductor Nanoparticles

The reduction in the particle size in the case of semiconductors results in the increase in the band gap which results in the shift of the light absorption towards in the high-energy region (blue shift). In addition, the band edge position of valence and the conduction bands are stabilized and destabilized respectively. This leads to an increase in the oxidation and reduction ability of the semiconductor. Certainly, the rate of recombination of photoexcited electron-hole pair is also reduced greatly. The energy level diagram for various orbitals in the molecules, clusters and semiconductors are shown in Fig. 2.7 [1].

It can be seen form the figure that the reduction in the number of atoms or particle size results in an increase of the band gap in the case of semiconductor nanoparticles.

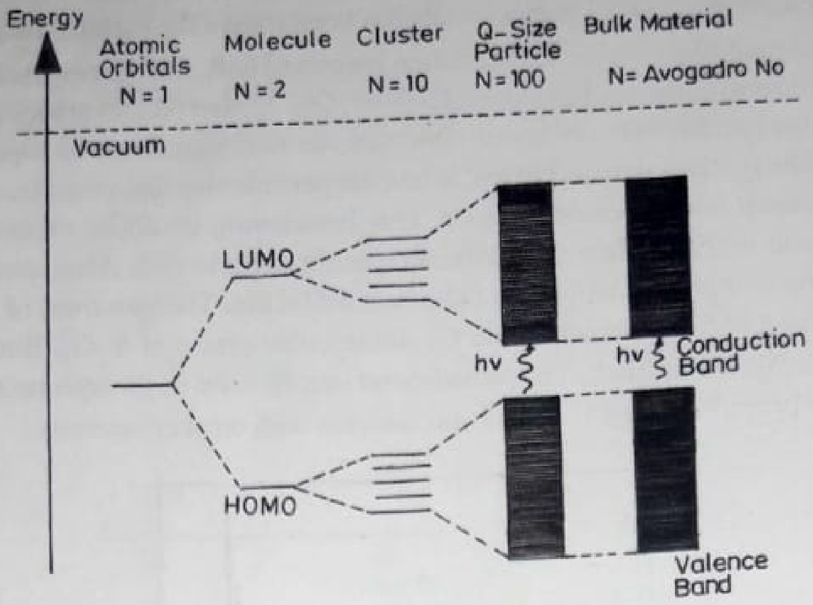


**Fig. 2.7** Energy level diagram (or) band diagram

### 2.3.2 Metal Nanoparticles

When the particle size of the metal atom is reduced, the energy levels are altered like in the case of semiconductor. In bulk metal, the valence and conduction band of the metal are overlapping, which results in the continuous electronic states. Whereas when the particle size is reduced, the valence and conduction band energy levels are separated to a certain extent (Fig. 2.8). As a result, the movement of electron (conductivity) and the optical absorption of light are different form that of the bulk metal. It can be seen in many cases that when the particle size of the metal nanoparticle is varied, the color of the metal nanoparticles are also changed. The origin of the color for metal nanoparticles is due to the surface plasmons. The surface plasmon is a natural oscillation of the electron gas inside a given nanosphere. If the sphere is small compared to a wavelength of light, and the light has a frequency close to that of the surface plasmons, then the surface plasmons will absorb energy. The frequency of the surface plasmons depends on the dielectric function of the nanomaterial, and the shape of the nanoparticle. For a gold spherical

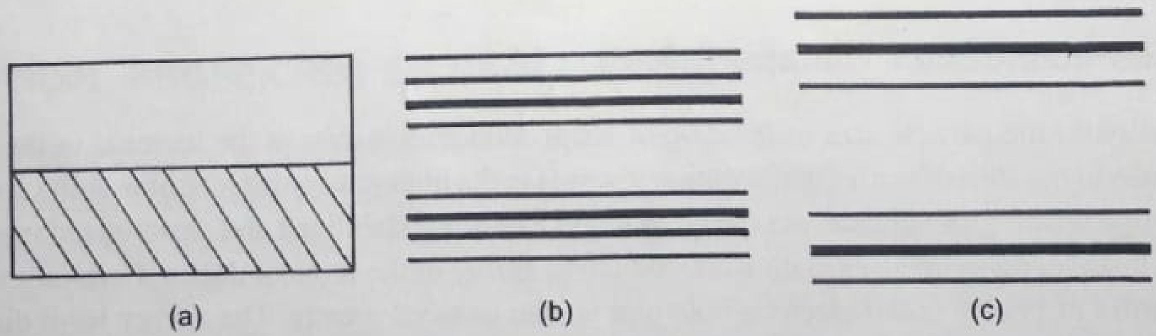

(a) (b) (c)

**Fig. 2.8** Energy level diagram of (a) bulk metal (b) large metal cluster and (c) small metal cluster [1] particle, the frequency is about half of the bulk plasma frequency. Thus, although the bulk plasma frequency is in the UV region, the surface plasmon frequency is in the visible region (close to 520 nm). Suppose we have a suspension of nanoparticles in a host. If a wave of light is applied, the local electric field may be hugely enhanced near surface plasmons resonance. If so, one expects various nonlinear susceptibilities, which depend on higher powers of the electric field, to be enhanced even more. Surface plasmons of metals like Au, Ag are discussed in detail in the subsequent chapters.

## 2.4 ELECTRICAL AND ELECTRONIC PROPERTIES

It is well known that the electrical conductivity of the solids is determined by its electronic structure or band structure. Generally in solids, the valence band is completely filled by electrons and separated form the empty conduction band with the energy gap of $E_g$ (band gap). For metals, $E_g = 0$, which results in the mixing of the valence and conduction bands. In the case of semiconductors, the value of $E_g$ is small. The electrons can be excited from the valence band to conduction band using light or heat, which results in partial conductivity. In insulator, the $E_g$ is high and the electrical conductivity is restricted. The conducting nature of the solids can be affected by various factors like, temperature and particle size. When the particle size is reduced to nanometer range, the $E_g$ is increases and hence the conductivity is reduced. In the case of metal nanoparticles, the density of states in the conduction and valence bands are reduced and electronic properties changed drastically, *i.e.*, the quasi-continues density of states is replaced by quantized levels with a size dependent spacing. In this situation, the metal does not exhibit bulk metallic or semiconducting behavior. This size quantization effect may be regarded as the onset of the metal to non-metal transition. The size at which the transition occurs depends on the nature of the metal.

### 2.4.1 Electronic Properties of Carbon Nanotubes

Carbon based materials are extensively used in the electronic industry due to its high conductivity and mechanical stability. Recently, the carbon nanostructured materials like carbon nanotubes have several applications in various fields. The electronic property of carbon nanotubes depends on their helicity and diameter. The armchair tubes are metallic, and zigzag and chiral tubes can be either metallic or semiconductor. Generally, the electronic conduction process in nanotubes is quantum confined, since in the radial direction, the electrons are confined in a singular plane of the graphite sheet. In armchair tubes, the valence and conduction bands always cross each other at Fermi energy for certain wave vector, which results the metallic behavior. Whereas, the chiral tubes, shows a gap at Fermi energy and hence behaves like semiconductor. When the diameter of the tubes increases, the band gap is decreased, yielding a zero-gap semiconductor, which is essentially equivalent to the planar graphitic sheet.

Also, the nanomaterials can hold or store considerably more energy than conventional materials because of their large grain boundary (surface) area. They are materials in which an optical absorption band can be introduced, or an existing band can be altered by the passage of current through these materials, or by the application of an electric field.

## 2.5 REDOX PROPERTIES

The reduction in the particle size always shows significant shift in the position of the electron energy levels (valence and conduction band), this will result in change in the Fermi energy level of the metal, semiconductor and insulator. It is well known that the changes in the Fermi energy levels are associated with the redox properties of the particular system.

The shift in the Fermi levels can be obtained from the shift in the flat band potential. Fig. 2.9 shows the flat band potential of $TiO_2$-Au composite materials [5]. It is observed with $TiO_2$/Au composite, shift in the flat band potential is seen when compared to pure $TiO_2$ films. Also, a larger shift can be seen with smaller particles, which are parallel to the Fermi level shift with particle size.

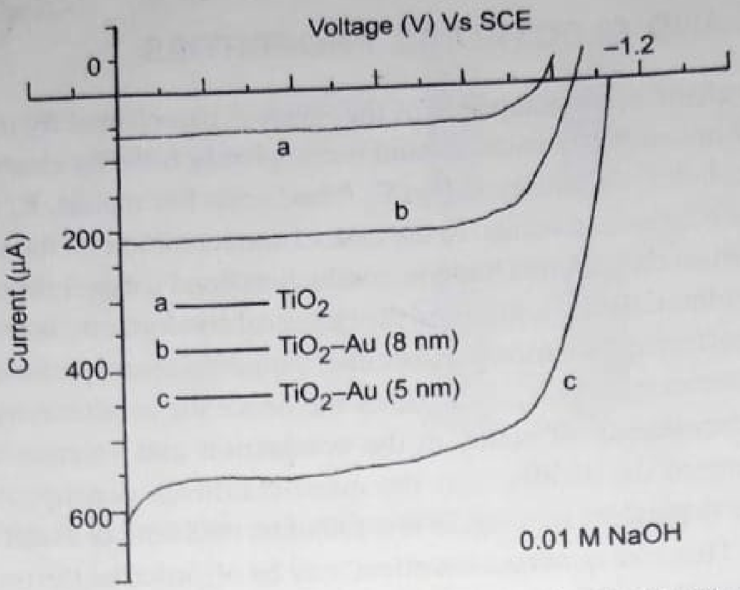


**Fig. 2.9** Particle size effect on the shift in the flat band potential

### 2.5.1 Semiconductor Nanoparticles

Changes in the semiconductor particle size results in the change in the band position of valence and conduction band energy levels, which have an effect on the formation of electron – hole pair and redox properties of semiconductor. Generally, the conduction and valence bands are shifted towards more negative and more positive potentials, respectively by decreasing the size of semiconductor size. It can be explained by the following band diagram of CdTe nanocrystals with various particle size (Fig. 2.10) [6]. It can be seen that, the decrease in the size of particles affects more strongly on the position of the energy levels.

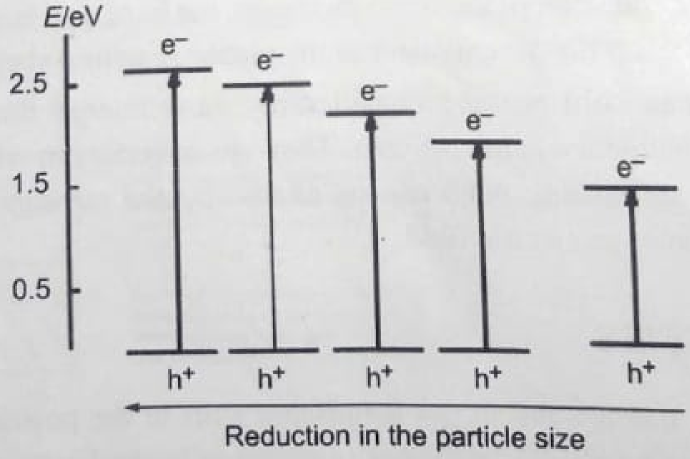


**Fig. 2.10** The energy diagram of various sizes CdTe nanoparticle

## 2.6 MECHANICAL PROPERTIES

Because the nanosize, many of the mechanical properties of the materials are modified, among others, hardness and elastic modulus, fracture toughness, scratch resistance, fatigue strength, and hardness. Cutting tools made of nanomaterials, such as tungsten carbide, tantalum carbide, and titanium carbide, are harder, more wear-resistant, erosion-resistant, and last longer than their conventional (large-grained) counterparts. Similarly, ductile nature of the ceramics materials is also modified when the particle size is reduced to nanometer scale. Generally, ceramics are very hard, brittle, and hard to machine even at high temperatures. However, with a reduction in grain size, the properties change drastically that, the nanocrystalline ceramics can be pressed and sintered into various shapes at significantly lower temperatures. Energy dissipation, mechanical coupling within arrays of components, and mechanical nonlinearities are influenced by structuring components at the nanometer scale [7].

One of the essential properties required for the aircraft components is the fatigue strength, which decreases with the component's age. The fatigue strength increases with a reduction in the grain size of the material. Nanomaterials provide such a significant reduction in the grain size over conventional materials that the fatigue life is increased by an average of 250 %.

## 2.7 MAGNETIC PROPERTIES

Many properties of magnetic systems are fundamentally determined by the underlying electronic structure. Magnetic behavior, electronic transport, and even structural stability are intimately related to electronic properties. Reducing the size or dimension of magnetic systems changes the electronic properties by reducing the symmetry of the system and by introducing a quantum confinement. The strength of a magnet is measured in terms of coercivity and saturation magnetization values. These values increase with a decrease in the grain size and an increase in the specific surface area (surface area per unit volume) of the grains.

Nanoparticles exhibit magnetic properties that are different from bulk materials. These are due to the following reasons: (i) As the size of these systems reaches the typical lengths of few nanometers, it is expected that the response of the system depends on the boundary conditions (which are no longer periodic, but determined by the particle size) and therefore, to be different from bulk material. (ii) Because of the large ratio of surface to volume atoms in nanoparticless, the surface energy becomes important when compared with volume energy, and therefore, the equilibrium situation can be different that for bulk materials. The energy barrier to overcome for magnetization inversion is KV, where K is the anisotropy constant and V the particle volume. In the case of nanoparticles, the volume is so small, therefore the thermal energy ($K_B T$) is enough to invert the magnetization with relaxation times as low as few seconds. Thus, the material looses coercivity and remanence, giving rise to the so-called superparamagnetic behaviour.

Fig. 2.11 presents the room temperature saturation magnetization ($M_s$) and coercive field ($H_c$) versus the average particle size D. It can be seen from the figure that, $M_s$ and $H_c$ drop sharply as the average particle size decreases below 12 nm. A fit of the experimental data for $H_c$ to the relation $H_c \alpha [1 - (Dp/D)^{3/2}]$ defines the critical size of $D_p$ is equal to 8.6 nm, below which the particles become super paramagnetic behavior [8].

Therefore, it is difficult to get nanoparticles exhibiting ferromagnetism at room temperature. However controversial results have been published [9].

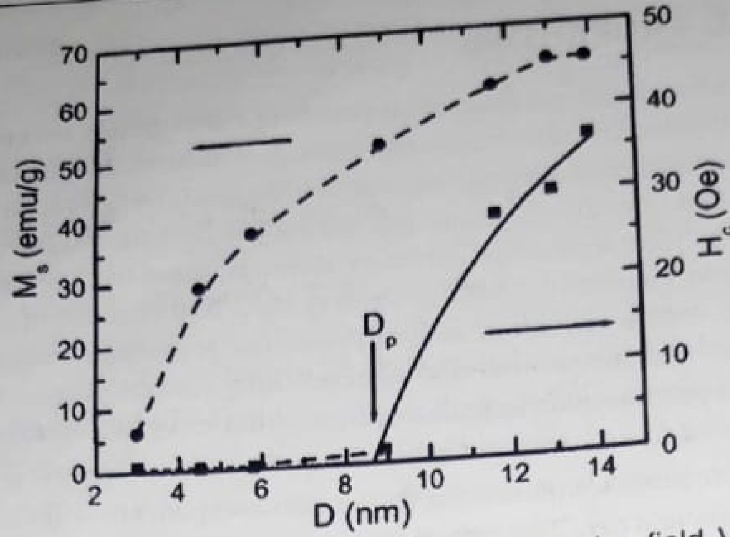


**Fig. 2.11** Room temperature saturation magnetization and coercive field Vs average particle size

## 2.7.1 Magnetic Properties of $Fe_2O_3$ Nanoparticles

Magnetite ($Fe_3O_4$) is a ferrimagnetic iron oxide. It has cubic inverse spinel structure, in which the oxygen anions forming face centered closed packing and iron (cations) located at the interstitial tetrahedral sites and octahedral sites. The electron can hop between $Fe^{2+}$ and $Fe^{3+}$ ions in the octahedral sites at room temperature imparting semi metallic property to magnetite. The magnetic moment of the unit cell comes only due to the presence of $Fe^{2+}$ ions. This has the magnetic moment of 4μB. As the particle size decreases, there is a relative decrease in amount of oxygen ion content in the sample, which consequently, leads to the lowering of the valance state of the cations, *i.e.*, some of the $Fe^{3+}$ ions are converted into $Fe^{2+}$ ion, which results in an increase in the number of $Fe^{2+}$ ions in the unit cell. Consequently, due to the larger size of the $Fe^{2+}$ ions compared to $Fe^{3+}$ ions (ionic radius of $Fe^{2+}$ (0.74 Å) is larger than $Fe^{3+}$ (0.64 Å)), it is observed that the increase in unit cell volume with reduction in particle size of $Fe_3O_4$ particles. Since the resultant magnetic moment in $Fe_3O_4$ is observed is due to the divalent ions ($Fe^{2+}$), the increase in magnetization with decrease in size could be explained. Nevertheless, this explanation does not hold good for sizes below 10 nm. Since, when the particle size is decreased to certain extent, the surface effects are more predominant. When the size of the particle is reduced the ratio of surface to bulk atoms increases, when particles $< 5$ nm, more than 80% of the atoms lie on the surface and, therefore, the effects are more prominent. Even in the bulk particles, the magnetization near the surface is generally lower than that in the interior.

In addition to the increase in the magnetic moment, the reduction in particle size creates negative pressure on the lattice due to lattice cell volume expansion and the magnetic transition temperature ($T_{(M)}$) also decreases. This may be attributed to negative pressure exerted on the lattice due to unit cell volume expansion. The decreases in the $T_{(M)}$ are attributed due to its sensitivity to pressure.

## 2.8 CATALYTIC ACTIVITY

It is well known that the reduction in the particle size results in higher surface area and number surface atoms. The increase in surface area is always associated with increase in the catalytic activity in many cases. Essentially, increase in the surface area provides increased adsorption of reactant molecules on its

# 12

# Composite Materials

## 12.1 INTRODUCTION

Nanomaterials have become increasingly important in the development of new materials for enhanced applications. Despite extensive innovation, there remains a need for improvement to match the ever-growing demand for multifunctional materials. Nanocomposites are a versatile class of materials for this purpose. The notation of nanocomposites defines organization presenting one of its components of nanometric scale. Nature's remarkable feature has been producing nanocomposites for millions of years. It has ability to combine at the nanoscale (bio) organic and inorganic components allowing the construction of smart natural materials that found a compromise between different properties or functions (mechanics, density, permeability, color, hydrophobia, etc.). Such a high level of integration associates several aspects: miniaturization whose object is to accommodate a maximum of elementary functions in a small volume, hybridization between inorganic and organic components optimizing complementary possibilities, functions and hierarchy. Current examples of natural organic–inorganic composites are crustacean carapaces or mollusc shells and bone or teeth tissues in vertebrates. As far as man-made materials are concerned, the possibility to combine properties of organic and inorganic components for materials design and processing is a very old challenge that likely started since ages (Egyptian inks, green bodies of china ceramics, prehistoric frescos, etc.).

By controlling the properties of a material by engineering it on the nanoscale offers wide area of new uses of conventional materials. There is an immense quest for the composite materials containing nanomaterials for securing or alterering the properties of two or more materials to create a material designed for a specific purpose with high efficiency. In this chapter, we shall see in a systematic way various nanocomposites starting from the fundamentals.

## 12.2 WHAT ARE COMPOSITE MATERIALS?

A composite material is a combination of two or more separate materials that has characteristics not shown by either of the materials separately. Or it can be defined as two or more materials combined on a macroscopic scale to form a useful material.

### 12.2.1 What are Nanocomposite Materials?

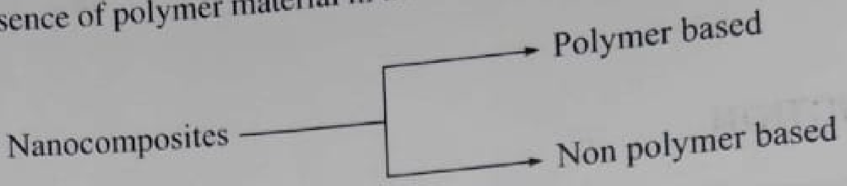
Materials derived by the combination of two or more building blocks in one material, containing, atleast one of the components in the nanometer length scale, are entitled nanocomposites materials.

### 12.2.2 Why to go for Nanocomposite Materials?

Nanoparticles and nanocomposites offer unique properties that arise from their small size, large surface area, and the interactions of phases at their interfaces, and are attractive for their potential to improve performance of drugs, biomaterials, catalysts and other high-value-added materials.

## 12.3 CLASSIFICATION OF NANOCOMPOSITES

Many composite materials that are available can be simply classified into the following main classes based on the presence or absence of polymer material in the composite.



### 12.3.1 Nonpolymer Based Nanocomposites

Nonpolymer based nanocomposite materials can further be classified as follows:

#### *12.3.1.1 Metal/Metal Nanocomposites*

The discovery of new alloys has often been accompanied by major developments in the history of mankind; for example, the era of bronze was initiated by the discovery that intimate mixing of copper and tin yielded a much stronger metal than copper itself. Years later, yet stronger alloy was to be discovered by heating iron in the presence of charcoal. The ancestor of steel was born, which owes its hardness and toughness to controlled solubilization of carbon in iron. Yet, only with the invention of steam engines could the massive and controlled production of steel begin. Four thousand years of practice and recent scientific understanding culminate in the development of super ductile and super resistant alloys. Today, plastics might be going through similar revolutions, though at a much higher pace. There is insatiable demand for new nanocryatalline alloy materials with new compositions for purposeful construction of nanomaterials with structures and properties able to meet the demands of tomorrow's needs.

There are many ways to synthesize nanocrystalline alloys, one of which is mechanical alloying (MA) or mechanical milling (MM). Because MA needs a secondary process to form bulk alloys, degradation in mechanical properties caused by grain growth during the secondary processing becomes a main concern in this process. It is therefore important to understand grain growth behavior in ultrafine and nanocrystalline materials to optimize the grain-size-dependent properties. Some recent investigations on the stability of grain size have been carried out using various nanocrystalline materials such as pure metals, oxides, compounds and composites. Regardless of methods of synthesis, most nanocrystalline based metal –metal nanocomposites exhibit a remarkable resistance to grain growth. Thermal stability and the mechanisms involved in nanocrystalline materials are not only associated to the microstructural and compositional parameters but also related to porosity, impurity, grain size distribution, texture and microstrain resulted during the processing of nanocrystalline materials. The structure of grain boundaries and hence the diffusion behavior can vary strongly depending on the processing method even within the same class of nanocrystalline material.

Bimetallic nanoparticles, either in the form of an alloy or in core–shell structures, are being investigated in some depth because of their improved catalytic properties and changes in the electronic/optical properties relative to the individual, separate metals. It is postulated that their interesting physicochemical properties result from the combination of two kinds of metals and their fine structures. So far, as alloy nanoparticles are concerned, the combination of gold and palladium is popular since these metals are miscible at any ratio. Due to the high catalytic activity of Pd and Pt, bimetallic colloids of gold and silver in combination with Pd and Pt (Ag–Pd, Ag–Pt, Au–Pt, and Au–Pd) have been studied in great detail. Bimetallic nanoparticles as alloys are conveniently synthesized by simultaneous reduction of two or more metal ions. Pt- Ru based alloy nanoparticles when supported on carbon was resulted as efficient anode electrocatalyst compared to Pt alone supported on carbon. This is due to the enhanced CO tolerance ability of Pt-Ru alloy nanoparticles rather than Pt alone nanoparticles. Alloy nanoparticles have also excelled the simple metal nanoparticles based electrocatalysts in terms of activity and for many electrochemical processes. The simple mixing of two different metal nanoparticles also will end up with new properties. However, a major problem in utilizing mixture of different nanoparticles is that they often lose their high surface area due to agglomeration of the individual nanoparticle constituents. Preclusion of nanoparticles during mixing of metal nanoparticles is the current field of interest. Gas fluidization is one of the best techniques available to disperse and process dry powders without agglomeration of the particles. Or we have to introduce an external force such as vibration, sound waves, magnetic excitation and/or a centrifugal field, by using a rotating fluidized bed. This can significantly improve the fluidization of cohesive nanopowders, reducing the minimum fluidization velocity, eliminating plug formation, channeling and spouting, and resulting in a smooth, homogeneous, virtually bubbleless fluidization with negligible elutriation.

### 12.3.1.2 Metal/Ceramic Nanocomposites

In metal-ceramic composites the electric, magnetic, chemical, optical and mechanical properties of both phases are combined. Size reduction of the components to the nano-scale causes improvement of the above-mentioned properties and leads to new applications (e.g. non-linear optical response). The polymer precursor technique offers an attractive route to such composites providing a chemically inert and hard ceramic matrix. Noble metal nanoparticles showing surface plasmon resonance can easily be introduced into the ceramics. The incorporation of iron-containing nanoparticles in preceramic polymer leads to super paramagnetic composites and is interesting for high-frequency applications. One special effect of polymer-derived metal-ceramic nanocomposites is the *in-situ* formation of nanotubes and more complicated nanostructures with their potential ability to reinforce the desired material and control the electrical and optical properties. Polysilazane/polysiloxane derived nanocomposites are potentially useful for high frequency and bio-medical applications.

Metal/ceramic nanocomposite components have numerous potential applications where enhanced strength and stiffness with excellent high temperature properties are the major criteria for materials selection. There exist a number of disparities and conflicting views on the processing and successful consolidation of nanoparticles retaining their nanoscale structure to harness the beneficial properties. The process know-how will be scaled up to make real components, which can be evaluated by putting in service for novel applications and the design, synthesis and characterization of high-toughness (crack-resistant) ceramic nanocomposites that retain superior properties to high temperatures is a major technological challenge of great need for applications from the aerospace industry to structural materials, and nano-scale composite ceramics offer an opportunity to realize such materials.

Various important steps involved in the preparation of these nanocomposites are:

#### 12.3.1.2.1 *Powder Development*

Synthesis of the nanoparticles will be done through a sol-gel process route to yield narrow size distribution and agglomerate-free particles. The mixture of ceramic and metallic oxide particles will be partially reduced to form pre-sintering powder mix of ceramic oxides and metallic nanoparticles by hydrogen reduction at suitable temperatures based on the thermodynamic principle. Also an electroless coating technique will be adopted to incorporate metals in ceramic matrix to produce metal/oxide mix. Using this method, it is possible to deposit ultrathin continuous and clusters of nanoparticles.

#### 12.3.1.2.2 *Optimization of Process Parameters*

Powder Synthesis process and consolidation processes will be optimized for their process parameters to yield nanosized, monodispersed powders and corresponding compact with uniform and closed to the 99% of the theoretical density of each system. The design of experiment methodology may be used for such parametric optimization.

Infiltration by a melt is an attractive but rarely utilized technique of synthesis of composite materials. When applying pressures in the GPa range the technique allows for a synthesis of multi-phase nanomaterials. The process is done in a toroid high-pressure high-temperature cell at pressures up to 7.7 GPa and temperatures up to $2000^0$C. The nanoporous matrix is prepared by compacting nanopowders of high-hardness materials such as $Al_2O_3$, SiC, or diamond. The infiltrating material can be any substance with the melting temperature (at a given pressure) below the processing temperature.

When the infiltrant melts the pressure forces it to fill the pores in the matrix. The resulting composite contains a continuous network of solidified injected material with embedded grains of the ceramic powder. The crystallite size of the secondary phase depends on the grain size of the ceramic powder used and can be as low as 10 nm. The technique proved successful with metals (Mg, Sn, Zn, Al, Ag, Cu), semiconductors (Si, Ge, GaAs, CdTe), and ionic glasses as the injected material. Under certain p-T conditions the infiltrating material can chemically react with the matrix. In such cases the interfaces between the nanograins of the two components become chemically bonded which improves mechanical properties of the material. High-plasticity of some metals under pressure allows for their infiltration below the melting point. Depending on the matrix-infiltrant system and the processing conditions the technique may produce materials serving different objectives. The process can produce nanograins of a given material embedded in an ambient matrix. Such composites are used to study electrical, optical and magnetic properties of nanoparticles of metals and semiconductors. Chemically-bonded composites are primarily the subject of investigations of the effect of the crystallite size on the material mechanical properties.

### 12.3.1.3 Ceramic/Ceramic Nanocomposites

A typical example where in a ceramic/ceramic nanocomposite is exploited for the fabrication of articial joint is illustrated below.

## What Makes Polymer Nanocomposites Unique?

The small size of nanofillers leads to several factors that distinguish nanocomposites from traditional composites. First of all, nanofillers are small mechanical, optical, and electrical defects compared to micron-scale fillers. This addition of nanofillers to a polymer does not necessarily lead to a decrease in the ductility of the polymer and in some cases can increase it. It also means that below about 50 nm, many types of filler do not scatter light significantly. Thus it is possible to make composites with altered electrical or mechanical properties that maintain their optical clarity. Finally, as small electrical defects, nanofillers do not concentrate electromagnetic fields as sharply as micron-scale fillers and indeed may act to trap charge and increase the electrical breakdown strength of polymers.

Secondly, although many properties of a material are said to be intrinsic, they often depend upon matter being assembled above a critical length scale. When the nanoparticle decrease below this size, the properties of the particles can differ significantly from the bulk material; thus variations in melting temperature, color, magnetization and charge capacity are often observed.

Third, the small size of the fillers leads to an exceptionally large interfacial area in the composites. If one compares the surface area of 10-micrometer carbon fiber to that of a 1 nm single walled nanotube for the same total volume of the two, the surface area increases by a factor of 10,000. In addition the inter-particle spacing decreases such that at small volume fractions of filler, the inter-particle spacing is similar to the radius of gyration of the polymer (~100 A). The high surface area becomes even more significant when one coincides that there is an interaction zone (IZ) surrounding the filler. This is a region in which the structure and properties have been altered because of the presence of the filler. It could be the region of altered chemistry, polymer conformation, chain mobility, and degree of cure or crystallinity. This zone of affected polymer has been approximated to be between 2 and 9 nm thick but may be much larger if we assume that this zone is about 10 nm in thickness, then at 2.5 vol% of a 20nm equiaxed nanoparticle well dispersed, 37% of the polymer. Therefore the IZ can be a significant portion, if not the entire bulk, of the matrix. Thus nanofillers can alter the expected properties of the composite considerably.

Carbon nanotubes have considerable potential for composite fabrication. In recent years they have been an enormous number of important developments in this area. The interest in nanotubes as the "ultimate carbon fiber" arises from the very desirable mechanical properties with the potential for a very high Young's modulus which can be close to that of in-plane value for perfect graphite, some 10 to 100 times greater than currently available carbon fibers. Single wall nanotubes have good flexibility unlike carbon fibers, and thus composites with such nanotubes would be unlikely to fracture when exposed to compressive stress along the axis of the fiber, in contrast to carbon fibers reinforced composites.

There has been little success so far in replacing carbon fibers with carbon nanotubes in composite fabrication. The principal problem is the difficulty of getting good interaction between the carbon nanotube and the matrix.

Polymer based nanocomposite materials can be further classified as follows:

### *12.3.2.1 Polymer/Ceramic Nanocomposites*

Nanocomposites consist of single ceramic layers (1 nm thick) homogeneously dispersed in a continuous matrix. The host ceramic layers tend to orient themselves parallel to each other due to dipole-dipole interaction.

A passive device is defined as a device that does not require an energy source for operation. They can be resistive, capacitive, or inductive; others may include diodes, optical fibers, cables, wires, filters, and glass lenses. Integral passive offers numerous advantages such as increased silicon efficiency, improved electrical performance, elimination of separate packaging (no assembly to board soldering and thus increased reliability), and efficient circuit design. However, these benefits demand extremely high product yield at reduced cost.

The polymer-ceramic Nanocomposites technology as a highly favorable low-cost option for embedded capacitors in organic laminates because of its low processing temperature (<200°C) and cost advantages. Nanocomposite dielectrics are essentially dispersions of nano-sized particles (< 200nm) in a polymeric phase. The cornerstone of this technology is the development of defect-free thin films (<2 microns) with a high packing density of the ceramic filler. High ceramic filler content (>50 vol%) is needed in order to achieve a high dielectric constant. Capacitors integrated on low-loss organic package substrates can find numerous applications (such as bandpass filters), in which IC chips are flip-chip mounted on the package substrate. To address the high capacitance density requirements of integral capacitors, a series of organic and inorganic based materials that are compatible to organic based laminate process has been developed. A capacitance density of ~30 nF/cm$^2$ has been achieved in polymer/ceramic nanocomposites through optimization of particle dispersion. For higher capacitance densities (>200 nF/cm$^2$), hydrothermal synthesis of barium titanate particles and deposition of non-stoichiometric inorganics by metal-organic chemical vapor deposition showed promising results.

Significant size reduction and improvement in electrical performance of microelectronic systems can be realized through integration of passive elements like capacitors, resistors and inductors. Integration of capacitors poses unique challenges because of the need for a wide range of capacitances (from 0.1 pF to 10 μF) and low dielectric losses. Nearly 50 % of these capacitors will be used as decoupling capacitors, which requires 0.1 – 10 μF, and are the hardest to integrate on organic boards. A number of existing material systems, like polymers with low dielectric constant and loss stable with frequency, can be used for embedding small capacitance values. Further, these polymers can be filled with ferroelectric powder, resulting in a polymer-matrix composite with processable capacitance density up to 5-10 nF/cm$^2$.

### 12.3.2.2 *Inorganic/Organic Polymer Nanocomposites*

Metal/polymer nanocomposites attract attention because of unique properties of metal clusters, which are dispersed in polymer matrix. The typical size of such metal cluster is approximately 1-10nm. The properties of clusters and nanoparticles (band gap, spectral properties, the transport of electrons) are very different from those of bulk materials and individual atom or molecules. It is often advantageous to incorporate them into a matrix material, e.g., a polymer solution or melt, or an elastomer, in order to obtain a 'nanomaterial' with additional properties brought in by the filler particles. One of the basic but nonetheless crucial properties is the mechanical strength of such polymer nanocomposites, whose rheological (or mechanical) properties are usually better than those of the pure matrix. The precise origin of this mechanical reinforcement effect, however, remains unclear. Zero valent metal nanopartices can readily be dispersed in an inert polymer thin film matrix inorder to study a variety of physical and chemical properties as a function of size, shape especially volume fraction of such nano particles composites. Advances in nanoscience and technology are closely linked to the development of new methods for the synthesis and assembly of nano particles. Atomic and molecular assemblies at the nanoscale are important candidates for a wide range of

A highly versatile method for the preparation of long polymer-based nanofibers is electrospinnning. Polymer nanofibers of different dimensions, shapes and porosity can be obtained by variation of spinning parameters and polymer characteristics. Fiber properties can be further modified by spinning and modification of polymer blends and block copolymers. In addition, numerous additives such as catalysts, nanoparticles, and enzymes etc., can be loaded. Variation of fibers properties can be also accomplished by chemical variation of functional polymers. Electrospun polymer fibers have been utilized for specialty filters and are on the edge to application in the fields of drug release, tissue engineering, catalysis, textiles and crop protection.

Polymer nanofibers can also be utilized foe the preparation of long polymer nanotubes by the TUFT-process (TUFT = tubes by fiber templates) simply by coating of polymer nanofibers acting as templates and subsequent selective removal of fictionalized template nanofibers or by multistep coatings including nanopolymer coatings such as metals or ceramics. These polymer nanotubes are of interest for release applications or applications in catalysis.

Rubber is a polymer and a composite made by using rubber as a component is also a task of interest. Metal Rubber is a unique self-assembled nanocomposite material that combines the high electrical conductivity of metals with the low mechanical modulus of elastomers. Self-assembly processing allows the simultaneous modification of both conductivity and modulus during manufacturing. It has wide range of possible applications, from mechanically flexible electrical interconnections and electromagnetic shielding to the measurement of large mechanical deformations.

### 12.3.2.3 *Inorganic/Organic Hybrid Nanocomposites*

Hybrid organic–inorganic materials are not simply physical mixtures. They can be broadly defined as nanocomposites with organic and inorganic components, intimately mixed. Indeed, hybrids are either homogeneous systems derived from monomers and miscible organic and inorganic components, or heterogeneous systems (nanocomposites) where at least one of the components' domains has a dimension ranging from some Å to several nanometers. It is obvious that properties of these materials are not only the sum of the individual contributions of both phases, but the role of the inner interfaces could be predominant. The nature of the interface has been used to grossly divide these materials into two distinct classes. In class I, organic and inorganic components are embedded and only weak bonds (hydrogen, Van der Waals or ionic bonds) give the cohesion to the whole structure. In class II materials, the two phases are linked together through strong chemical bonds (covalent or iono-covalent bonds).

Considering the industrial era, successful commercial hybrid organic–inorganic polymers have been part of manufacturing technology since the 1950s. The wide increase of work on organic–inorganic structures was pursued with the development of the polymer industry. The concept of "hybrid organic–inorganic" nanocomposites exploded in the eighties with the expansion of soft inorganic chemistry processes. Indeed the mild synthetic conditions offered by the sol–gel process (metallo-organic precursors, organic solvents, low processing temperatures, processing versatility of the colloidal state) allows the mixing of inorganic and organic components at the nanometric scale. Since then, the study of so-called functional hybrid nanocomposites became a mushrooming field of investigation yielding innovative advanced materials with high added value. These materials being at the interface of organic and inorganic realms are highly versatile offering a wide range of possibilities to elaborate tailor-made materials in terms of processing and chemical and physical properties.

applications, including those in electronics and photonics. Metal nano particles are known to be promising materials for the development of optical limiters. The 'bottom-up' approach to the synthesis of metal nanoparticles have largely relied on the colloidal route involving reduction of metal ions by appropriate chemical reagents and stabilization of the metal nanopartilces by suitable surfactants. However, several factors including potential device applications and health hazard issues make it advantageous to fabricate and assemble nanoparticles in matrices such as polymers. Techniques, which concurrently satisfy further significant requirements of particle size tuning, control of size/shape distribution and simplicity of fabrication procedure, are rare. Among the number of possible synthetic approaches, plasma enhanced vapour deposition of polymer and simultaneous sputtering of any metal is especially well studied to make a large variety of such composite metal/polymer thin films using low temperature processing throughout. Pulsed laser deposition (PLD) is a suitable technique for the growth of polymer/metal nano composites with different morphologies in a one-step process. In this an excimer laser of certain nanometer wavelength is used to first deposit polymer and then metallic nanoclusters on the polymer surface by island growth. Depositing a second polymer layer on to the size of the metal can embed these. The number of laser pulses used can systematically adjust the size of the metal clusters. For small clusters, facetted grains or spherical clusters are observed. While coalescence processes in some cases leads to a bimodal size distribution. The size and grains depends on mobility of the metal atoms on the polymer surface. For example in the case of polymethyl methacrylate(PMMA) polymer the cluster size depends on the amount of crosslinking of the polymer, which obviously changes the mobility of the metal atoms.

Optical, electrical, magnetic and mechanical properties reflect dramatic changes as a function of size and volume fraction of this nano particle composite. Especially when reaching the onset percolation.

Post deposition annealing above the glass/rubber transition temperature of the polymer matrix leads to metal nanoparticle migration and coalescence. Irradiating such polymer composite films with spatially confined, scanning heat sources can lead to a variety of applications such as circuit writing or single domain ferromagnetic arrays.noble metal and transition metal dispertion in hydrocarbon and fluorocarbon thin film matrices will be described as prototype systems for this approach.

Conducting polymers and nanoparticles are two classes of materials with distinct properties. Recently, an interesting electrical bistable behavior was observed with a polymer film containing metallic nanoparticles sandwiched between two electrodes. This bistability does not exist in either of the individual materials.Promising application areas for polymer metal-nanowires composites are asymmetric conductive transparent foils, coatings with a low metal filling factor that can be produced by wet chemistry or isolated metal nanowires with contacts for sensor devices. Typical advantages of polymer are large area production, low costs and mechanical flexibility. To maintain these advantages for the composites, complicated structuring techniques cannot be applied. In this procedure first one will create surface nanowires and is based on thin film fracture. A brittle film, e.g., modified photo resist, is deposited on a polymer foil. Subsequent fracture can be carried out, e.g., by creating uniaxial stress by bending the substrate foil. As thin film cracks will relax stress only in a limited area. A template consisting of parallel racks can be produced in this manner. A filling of cracks with metal and a removal of the brittle thin film together with the excess material create metal nanowires on the polymer surface. By modifying the process more complicated structures can be realized.

The above described process needs a solid substrate and creates nanowires on the top of the polymer film. Often embedded wires and a wet chemical processing are desired.

#### 12.3.1.3.1 Ceramic Nanocomposites in Artificial Joint

Ceramic nanocomposites could solve the problem of fracture failures in artificial joint implants. This would extend patient mobility and eliminate the high cost of reparative surgery. Today, more than 500 000 hip- and knee-joint replacements are fitted annually throughout the world. Such procedures are extremely successful in restoring mobility to sufferers from arthritic and other degenerative conditions. However, the average lifetime of a hip prosthesis, for example, is around 10 to 15 years – with active and heavyweight patients being particularly prone to premature failure. This clearly poses a quality-of-life problem for younger and other vulnerable recipients. Moreover, revisionary surgery adds a further 70 to 100% to the cost of the original operation. It raises medical costs. The hip joint has a 'ball-and-socket' structure, in which the spherical head of the thighbone (femur) moves inside a cup-shaped hollow socket (acetabulum) in the pelvis. To duplicate this action, a total hip replacement implant has three parts: a metallic stem fits into the femur and provides stability; a ball replaces the spherical head of the femur and a cup lines the worn-out hip socket.

Acetabular cups are typically faced with polyethylene having an ultra-high molecular weight, while the femoral heads are made either of cobalt/chromium alloys or of ceramics. Because the wear resistance of the head is a key factor in implants longevity, durable ceramics formed from zirconia or alumina has tended to supersede metallic construction. Yet neither of these materials is optimal for the task, as they are relatively brittle and susceptible to crack propagation at the sites of small surface defects. Even without complete failure, such surfaces irregularities can also cause wear in the polymer cup, releasing particles of debris that give rise to irritation and possible osteolytic changes. The use of zirconia-toughened alumina nanocomposites to form ceramic-ceramic implants with potential life spans of more than 30 years. In these composites polymers also plays an important role so we can see these composites in polymer ceramic composites in elaborate manner.

## 12.3.2 Polymer Based Nanocomposites

Polymer nanocomposites are composites with a polymer matrix and filler with at least one dimension less than 100nm. The fillers can be plate-like (clays), high aspect ratio nanotubes and lower aspect ratio or nanopartilces. While some nanofilled composites (carbon black and fumed silica filled polymers) have been used for over a century, in recent years the dedicated research and development of nanofilled polymers has greatly increased. This is due to our increased ability to synthesize and manipulate a broad range of nanofillers and significant investment by government and industry in this field.

Current interest in nanocomposite has been generated and maintained because nanoparticle and carbon nanotube filled polymers exhibit unique combination of properties not achievable with traditional composites. For example, the inclusion of equiaxed nanoparticles in thermoplastics and particularly in semicrystalline thermoplastics increases the yield stress, the tensile strength and young's modulus compared to pure polymer. Other examples include scratch resistant transparent amorphous thermoplastic coatings. This combination of properties can be achieved because of the small size of the fillers, the large surface area the fillers provide and in many cases the unique properties of fillers themselves. As will be shown, in many cases these large changes in the material properties require small to modest nanofiller loadings. Unlike traditional micron-filled composites, these novel fillers often alter the properties of the entire polymer matrix while, at the same time, imparting new functionality because of their chemical composition and nanoscale size.

#### 12.3.2.3.1 *Photorefractivity at Communication Wavelengths*

Photorefractivity, a multifunctional property derived from the combination of photoconductivity and electrooptic activity, has been the focus of an extensive body of research due to its potential application to real-time optical information processing; beam clean up and amplification, dynamic interferometry, phase conjugation, and pattern recognition. Due to their large optical nonlinearities, low dielectric constants and low cost, polymeric photorefractive (PR) materials in particular have attracted a significant amount of attention during the past 10 years, and tremendous progress has been made in their development. Although many dyes are well suited for visible wavelengths, none have been reported to photosensitize PR polymeric composites at the infrared wavelengths of 1.31 or 1.55 µm, commonly used in optical communications. Although considerable effort has been made to alter the absorption spectra of recognized organic photosensitizers through fictionalization of the parent chromophore, the observed spectral shifts have been meager and unpredictable.

With the advent of nanocrystal (NC) technology, a new means by which to photosensitize polymer composites has been realized, establishing a novel class of inorganic-organic hybrid photoconductive materials. Perhaps the primary advantage gained through this approach concerns the ease with which the spectral properties of NCs are modified, made possible by the quantum size effect where the magnitude of the optical bandgap is inversely proportional to the size of the nanocrystal. This characteristic in conjunction with the wide range of materials available, including narrow band-gap semiconductors, permits this approach to be used for ultra-violet and visible as well as for applications involving infrared wavelengths. In addition, superior photocharge generation efficiency, ¼, associated with inorganic semiconductor materials incorporated into these hybrid composites, may result in a notable PR figure-of-merit obtained with a relatively small applied electric field. Photorefractivity in the visible spectral range has been obtained using nanocomposites of a polymer, poly *N*-vinylcarbazole (PVK), and CdS nanocrystals. the incorporation of narrow band-gap semiconductor NCs into a PR polymeric matrix to produce, to our knowledge for the first time, photorefractivity at a communication wavelength (1.3 ím in the present case). Two composites were studied; in both cases the photoconductor, PVK, was the primary continuous medium for the transport of the photogenerated charge-carriers (holes).

### 12.3.2.4 Polymer/Layered Silicate Nanocomposite

Polymer/layered silicate nanocomposite materials are attracting considerable interest in polymer science research. In recent years polymer/layered silicate (PLS) nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties when compared with virgin polymer or conventional micro- and macro-composites. These improvements can include high moduli increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymers. On the other hand, there has been considerable interest in theory and simulations addressing the preparation and properties of these materials, and they are also considered to be unique model systems to study the structure and dynamics of polymers in confined environments.

Hectorite and montmorillonite are among the most commonly used smectite-type layered silicates for the preparation of nanocomposites. Smectites are valuable mineral class for industrial applications because of their high cation exchange capacities, surface area, surface reactivity, adsorptive properties, and, in the case of hectorite, high viscosity and transparency in solution. In their pristine form they are hydrophilic in nature, and this property makes them very difficult to disperse into a polymer matrix. The most common way to remove this difficulty is to replace interlayer cations with quarternized ammonium or phosphonium cations, preferably with long alkyl chains.

In general, polymer/layered silicate nanocomposites are of three different types, namely (1) *intercalated nanocomposites*, for which insertion of polymer chains into a layered silicate structure occurs in a crystallographically regular fashion, with a repeat distance of few nanometers, regardless of polymer to clay ratio, (2) *flocculated nanocomposites*, for which intercalated and stacked silicate layers flocculated to some extent due to the hydroxylated edge–edge interactions of the silicate layers, and (3) *exfoliated nanocomposites*, for which the individual silicate layers are separated in the polymer matrix by average distances that depend only on the clay loading. This new family of composite materials frequently exhibits remarkable improvements of material properties when compared with the matrix polymers alone or conventional micro- and macro-composite materials. Improvements can include a high storage modulus, both in solid and melt states, increased tensile and flexural properties, a decrease in gas permeability and flammability, increased heat distortion temperature, an increase in the biodegradability rate of biodegradable polymers, and so forth.

Although the intercalation chemistry of polymers when mixed with appropriately modified layered silicate and synthetic layered silicates has long been known and, the field of PLS nanocomposites has gained momentum recently. Two major findings have stimulated the revival of interest in these materials: first, Nylon-6 (N6)/montmorillonite (MMT) nanocomposite, for which very small amounts of layered silicate loadings resulted in pronounced improvements of thermal and mechanical properties; and second, that it is possible to melt-mix polymers with layered silicates, without the use of organic solvents. Today, efforts are being conducted globally, using almost all types of polymer matrices.

### 12.3.2.5 Polymer/Polymer Nanocomposites

In this era of portability and rapid technological advances, polymers are more than ever under pressure to be cheap and offer tailored property profiles. Often, the key lies in designing blends and alloys carefully structured at the appropriate scale (preferably less than a micrometre) from existing polymers. Block copolymers — two or more different polymer chains linked together — have long been thought to offer the solution. Local segregation of the different polymer blocks yields molecular-scale aggregates of nanometre size. Recent progress in synthetic chemistry has unveiled unprecedented opportunities to prepare tailored block copolymers at reasonable cost. Over twenty years of intense academic research and the advent of powerful statistical theories and computational methods should help predict the equilibrium and even non-equilibrium behaviour of copolymers and their blends with other polymers. The gap between block copolymer self-assembly and affordable nanostructured plastics endowed with still-unexplored combinations of properties is getting narrower.

Very few instances of complete miscibility between different polymers have been readily exploited to prepare superior plastics through blending. Noryl, amiscible blend commercialized by General Electric, combines the heat resistance, dimentional stability and ductility of poly(*p*-phenylene oxide) to the low cost and fluidity of polystyrene. In most cases, however, macromolecules are not keen on mixing. Mixtures of different polymers often phase separate, even when their monomers mix homogeneously. This comes from the very low entropy of mixing two polymer chains of N momomers each, roughly 1/N smaller than that of mixing the monomers they are made of. Yet, over 50 years of research and practise have led to rich expertise on how to exploit this immiscibility to create novel heterogeneous plastics with sometimes radically improved combinations of mechanical, flow, optical, barrier or other physico-chemical properties from polymers. In other applications, blending facilitates processing, lowers material costs, or is the mere consequence of plastic scrap recycling. In all cases, control over dispersion, morphology and adhesion between immiscible phase is essential. Dispersion of a polymer A in an immiscible polymer B is typically achieved by intense mechanical stirring. When it comes to block copolymers they also have the properties like composites. Most block copolymers used today are prepares by living anionic polymerization. This has been the method of choice for preparing block copolymers of controlled architecture through precise sequencing of two, three or even more monomers. In this process, each copolymer chain is grown from a single reactive site through sequential additions and polymerization of, say, A and B monomer batches, for a simple A-B diblock. This requires that the growing polymer chains remain alive throughout the polymerization process, that is, they are free of termination or transfer reactions.

With the progressive democratization of block copolymer synthesis, the past decade has witnessed an unprecedented blooming of nanostructures and copolymers. Already on their own, some of these present truly superior combinations of properties that might justify commercial development. They further open up unexplored opportunities to nanostructure all kinds of commodity or engineering plastics at the nanoscle by judisciously choosing copolymer architecture and degrees of interaction between copolymer blocks and homopolymers. Moleculaer disorder and selfassembly happily coexist to yield unique combinations of properties in commercially viable nanostructured block copolymer/homopolymer blends. Predicting the future of polymeric materials has always been a very tricky business. Yet this is a strong message of hope for the future of commodity or engineering polymer blends nanostructured by affordable copolymers.

### 12.3.3 Biocomposites

The field of biomaterials is extensive, covering all divisions of materials science and many other scientific disciplines. Metals and metal alloys are used in orthopaedics, dentistry and other load bearing applications; ceramics are used with emphasis on either their chemically inert nature or their high bioactivity; polymers are used for soft tissue replacement and used for many other non-structural applications. All biomaterials are used to maintain a balance between the mechanical properties of the replaced tissues and the biochemical effects of the material on the tissue. Both areas are of great importance and key to a materials clinical success. However, in most (if not all) biological systems a range of properties is required, biological activity, mechanical strength, chemical durability etc. Therefore, often a material that exhibits a complex combination of properties can only fulfill a clinical need. Use of composite technology has enabled biomedical material researchers to develop a wide range of new, tailored materials, 'biocomposites', which offer the promise to greatly improve the quality of life of many people. The quality of natural tissues is usually a key factor in governing people's quality of life, and because 'the quality of life' is something that concerns us all, there is a large amount of research on biocomposites.

Naturally occurring composites are within us all. On the macro scale, soft and hard tissues are formed from a complex structural array of organic fibres and matrix. Soft tissues are formed from elastic (elastin) and non-elastic fibres (collagen) with a cellular matrix between the fibres. Biological structures such as tendon, linking muscles to bone, are low in elastin thus allowing muscle movement to be translated to the bone. However, ligaments, linking bone to bone, are high in elastin allowing movement between bones but retaining sufficient support to stop joints dislocating. It is at the microstructural level that the natural tissues truly have the advantage over synthetic materials. Collagen is a highly abundant and varied protein with more than 14 types discovered. All variations are formed from tropocollagen molecules, which are inelastic. The tropocollagen molecule is formed from three peptide chains. Each chain is formed from 1/

# UNIT II

## 2.1.QUANTUM PHENOMEN:

What are Low-Dimensional Structures?

When one or more of the dimensions of a solid are reducedficiently,suf its physicochemical characteristics notably depart from those of the bulk solid. With reduction in size, novel electrical, mechanical, chemical, magnetic, and optical properties can be introduced. The resulting structure is then called a low-dimensional structure (or system). The confinement of particles, usually electrons or hoes,l to a low-dimensional structure leads to a dramatic change in their behaviour and to the manifestation of size effects that usually fall into the category of quantum-size effects.

The low dimensional materials exhibit new physicochemical properties not shown by the corresponding large-scale structures of the same composition. Nanostructures constitute a bridge between molecules and bulk materials. Suitable control of the properties and responses of nanostructures can lead to new devices and technologies.

## 2.2. CLASSIFICATION OF LOW-DIMENSIONAL MATERIALS

Low-dimensional structures are usually classified according to the number of reduced dimensions they have. More precisely, the dimensionality refers to the number of degrees of freedom in the particle momentum. Accordingly, depending on the dimensionality, the following classification is made:

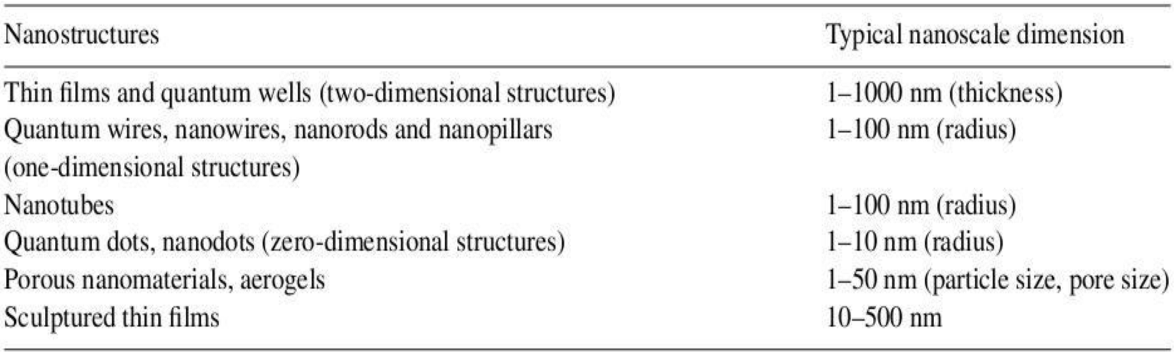
**Three-dimensional (3D) structure or bulk structure:** No quantization of the particle motion occurs, i.e., the particle is free.

**Two-dimensional (2D) structure or quantum well**: Quantization of the particle motion occurs in one direction, while the particle is free to move in the other two directions.

**One-dimensional (1D) structure or quantum wire**: Quantization occurs in two directions, leading to free movement along only one direction.

**Zero-dimensional (0D) structure or quantum dot (sometimes called "quantum box")**: Quantization occurs in all three directions.

**Table 1. Nanostructures and their typical nano scale dimensions**



| Nanostructures | Typical nanoscale dimension |
|---|---|
| Thin films and quantum wells (two-dimensional structures) | 1–1000 nm (thickness) |
| Quantum wires, nanowires, nanorods and nanopillars (one-dimensional structures) | 1–100 nm (radius) |
| Nanotubes | 1–100 nm (radius) |
| Quantum dots, nanodots (zero-dimensional structures) | 1–10 nm (radius) |
| Porous nanomaterials, aerogels | 1–50 nm (particle size, pore size) |
| Sculptured thin films | 10–500 nm |

Tradition has determined that reduced-dimensionality structures are labeled by the remaining degrees of freedom in the particle motion, rather than by the number of directions with confinement.

**Why we need Quantum Mechanics?**

As a spatial dimension approaches the atomic scale, a transition occurs from the classical laws to the quantum-mechanical laws of physics. Phenomena that occur on the atomic or subatomic scale cannot be explained outside the framework of quantum-mechanical laws.

For example, the existence and properties of atoms, the chemical bond, and themotion of an electron in a crystal cannot be understood in terms of classical laws. Moreover, many phenomena exhibited on a macroscopic scale reveal underlying quantum phenomena. It is in this reductionist sense that quantum mechanics is proclaimed as the basis of our present understanding of all natural phenomena studied and exploited in chemistry, biology, physics, materials science, engineering, etc.

Physical behaviour at the nanoscale is accurately predicted by quantum mechanics, as represented by the Schrödinger equation, which therefore provides a quantitative understanding of the properties of low-dimensional structures.

In quantum mechanics, the trajectory of a moving particle loses its meaning when the distance over which potential energy varies is on the order of the de Broglie wavelength:

$$\lambda = \frac{2\pi}{2me}\hat{h} \tag{1}$$

where $\hat{h}$ is the reduced Planck constant, m is the mass of the particle, and E is its energy. In other words, a basic characteristic of all matter at the nanoscale is the manifestation of the wave–particle duality—a fundamental quantum-mechanical principle that states that all matter (electrons, nuclei, photons, etc.) behaves as both waves and particles.. The quantum effects of confinement become significant when at least one of the dimensions of a structure is comparable in length to the deBroglie wavelength. If at least one dimension of a solid is comparable to the de Broglie wavelength of the particle, a quantum-mechanical treatment of particle motion becomes necessary. In the Schrödinger description of quantum mechanics, an elementary particlee.g., an electron, a hole and a photon—or even a physical system such as an atom is described by a wave function Ψ (r t), which depends on the variables describing the degrees of freedom of the particle (system). Thesquare of the wave function is interpreted as the probability of finding a particle at spatial location ŕ =( $x$ , $y$ , $z$) and time t.

The wave function contains all of the information that may be obtained about a physical entity and is sufficient to describe a particle or syste m of particles. In other words, if the wave function of, for example, an ensemble of electrons in a device, is known, it is possible in principle—though limited by computational abilities—to calculate all of the macroscopic parameters that define the electronic performance of that device.

The wave function of an uncharged particle with no spin satisfies the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right)\psi(\vec{r},t) = i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t},$$

where, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian operator, i= $\sqrt{-1}$, and V(r t) is the spatio temporally varying potential influencing the particle's motion. The particle's mass m in the equation has to be carefully handled. For a particle (electron or hole) in a solid, this mass is its effective mass m, which is usually less than the mass of an isolated electron. In the above equation the action of Hamiltonian operator

$$H(\vec{r},t) \equiv -\hbar^2 /2m\nabla^2 + V(\vec{r},t)$$

on the wave function yields the total energy of the particle. The first part of $H(r, t)\psi(r, t)$ is the kinetic energy, and the second part is the potential energy. For many real systems, the potential does not depend on time, ie V(r,t)=V(r). Then, the dependences on time and spatial coordinates of $\psi(z)$ (r t) are separated as

$$\psi(\vec{r}, t) = \mathrm{Re}\left[e^{-iEt/\hbar}\psi(\vec{r})\right],$$

Where $\psi(r)$ is a complex-valued function of space only, and E is the energy of the system. Using this representation of the wave function in the Schrödinger equation, the time harmonic Shcrodinger equation is obtained and can be written as,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\psi(\vec{r}) = E\psi(\vec{r})$$

Analytical solutions of the time-harmonic Schrödinger equation can be obtained for a variety of relatively simple.

Molecular vibrations are often approximated as harmonic oscillators. Several of the more common analytical solutions are for a free (isolated) particle: a particle in a box, finitea potential well, 1D lattice, ring, or spherically symmetric potential; the hydrogen atom or hydrogen-like atom; the quantum harmonic oscillator; the linear rigid rotor; and the symmetric top.

For many systems, however, there is no analytic solution to the Schrödinger equation, and the use of approximate solutions becomes necessary. Some commonly used numerical techniques are: perturbation theory, density functional theory, variational methods (such as the popular Hartree–Fock method which is the basis of many post-Hartree–Fock methods), quantum Monte Carlo methods, the Wentzel– Kramers–Brillouin (WKB) approximation, and the discrete delta- potential method. The interested reader is encouraged to consult specialized books on these methods.

## 2.3.FERMI'S GOLDEN RULE

The transition rate and probability of observing the system in a state $k\backslash$ after applying a perturbation to !\from the constant first-order perturbation doesn't allow for the feedback between quantum states, so it turns out to be most useful in cases where we are interested just the rate of leaving a state. This question shows up commonly when we calculate the transition probability not to an individual eigenstate, but a distribution of eigenstates. Often the set of eigen states form a continuum of accepting states, for instance, vibrational relaxation or ionization.

Transfer to a set of continuum (or bath) states forms the basis for a describing irreversible relaxation. You can think of the material Hamiltonian for our problem being partitioned into two portions, $H \square H_S \square H_B \square V_{SB} \square t \square$, where you are interested in the loss of amplitude in the $H_S$ states as it leaks into $H_B$ . Qualitatively, you expect deterministic, oscillatory feedback between discrete quantum states. However, the amplitude of one discrete state coupled to a continuum will decay due to destructive interferences between the oscillating frequencies for each member of the continuum.

So, using the same ideas as before, let's calculate the transition probability from !
\to a distribution of final states: $P_k$ .

! $\square E_k \square$:Density of states—units in $1/E_k$, describes distribution of finalstates—
all eigenstates of $H_0$

If we start in a state the total transition probability is a sum of probabilities

## 2.4. THE INDEPENDENT QUANTUM APPROXIMATION METHODS

### 2.4.1. INTRODUCTION

In Quantum Mechanics as in Classical Mechanics exactly solvable problems are rare and one must frequently resort to approximation. Approximations are therefore expected to play an important part. So various methods of approximate solution of the wave equation have been devised, leading to the more or less accurate approximate evaluation of energy values and wave-functions. Of these methods the first and in many respects the most interesting is simple wave mechanical perturbation theory developed by Schroedinger. Perturbation theories are to two kinds: time independent or stationary perturbation theory and time dependent. In this chapter we shall discuss several time independent quantum approximation methods and apply them to problems.

### 2.4.2.STATIONARY PERTURBATION THEORY (NON-DEGENERATE CASE) :

The stationary perturbation theory is concerned with finding the changes in the energy levels and eigen functions of a system when a small disturbance is applied. In such cases, the Hamiltionian can be broken up into two parts, one of which is large and represents a system for which the Schroedinger equation can be solved exactly, while other part is small and can be treated as perturbation term. If the potential energy is disturbed by the influence of additional forces, the energy levels are shifted and for a weak perturbation, the amount of shift can be estimated if the original unperturbed states are known.

Consider a physical system subjected to a perturbation which shifts the energy levels slightly : of course the arrangement remains the same : Mathematically the effect of perturbation is to introduce additional terms in the Hamiltonian of the unperturbed system (or unchanged system). This additional term may be constant or it may be a function of both the space and momentum co-ordinates.

In other words, the Hamiltonian H in the Schroedinger equation can be written as the sum of two parts ; one of these parts $H^0$ corresponds to unperturbed system and other $H'$ corresponds to perturbation effect. Let us write Schroedinger wave equation.

$$H\psi = E\psi \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

in which Hamiltonian $\hat{H}$ represents the operator

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 + V \qquad \ldots\ldots\ldots(2)$$

Let E be the eigen value and $\psi$ is eigen function of operator $\hat{H}$ . $\hat{H}$ is the sum of two terms $H^0$ and $H'$ already defined.

$$H = H^0 + H' \quad \ldots\ldots \qquad \ldots\ldots\ldots\ldots(3)$$

where $H'$ is small perturbation term.

Let $\psi_k^o$ and $E_k^o$ be particular orthonormal eigen function and eigen value of unperturbed Hamiltonian $H^0$, i.e.,

$$H^0\psi_k{}^0 = E_k{}^0\psi_k{}^0$$

If we consider non-degenerate system that is the system for which there is one eigen function corresponding to each eigen value. In the stationary system, the Hamiltonian H does not depend upon time and it is possible to expand H in terms of some parameter $\lambda$ yielding the expression.

$$H = H^0 + \lambda H' + \lambda^2 H'' + \ldots. \qquad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

in which $\lambda$ has been chosen in such a way that equation (1) for $\lambda$ = 0 reduces to the form

$$H^0\psi^0 - E^0\psi^0 = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

It is to be remembered that there is one eigen function $\psi$ and energy level $E^0$ corresponding to operator $H^0$. Euqation (5) can be directly solved. This equation is said to be the 'wave equation of unperturbed system" while the terms $\lambda H' + \lambda^2 H'' + \ldots.$ are called the perturbation terms.

The unperturbed equation (5) has solutions

$$\psi_0{}^0, \psi_1{}^0, \psi_2{}^0, \ldots\ldots, \psi_k{}^0 \ldots\ldots.$$

Called the unperturbed eigen functions and corresponding eigen values are

$E_0{}^0, E_1{}^0, E_2{}^0, \ldots\ldots, E_k{}^0 \ldots\ldots.$

The functions $\psi_k^o$ form a complete orthonormal set, i.e. they satisfy the condition

$$\int \psi_i{}^{0*}\psi_j{}^0 \, d\tau = \delta_{ij} \quad \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Where $\delta_{ij}$ is Kronecker delta symbol defined as

$$\begin{aligned} \delta_{ij} &= 0 \ \ for \ \ i \neq j \\ &= 0 \ \ for \ \ i = j \end{aligned}$$

Now let us consider the effect of perturbation. The application of perturbation does not cause large changes : hence the energy values and wave-functions for the perturbed system will be near to those for the unperturbed system. We can expand the energy E and the wave-function $\psi$ for the perturbed system in terms of $\lambda$, so

$$\psi_k = \psi_k{}^0 + \lambda\psi_k{}' + \lambda^2\psi_k{}''.+ \quad \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

$$E_k = E_k{}^0 + \lambda E_k{}' + \lambda^2 E_k{}''+\ldots\ldots \quad \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

If the perturbation is small, then terms of the series (7) and (8) will become rapidly smaller i.e., the series will be convergent.

Now substituting (6), (7) and (8) in equation (1), we get

$$= (H^0 + \lambda H' + \lambda^2 H''+\ldots)\ (\psi_k{}^0 + \lambda\psi_k{}' + \lambda^2\psi_k{}''+\ldots..) \ = \ (E_k{}^0 + \lambda E_k{}' + \lambda^2 E_k{}''.+\ldots.)(\psi_k{}^0 + \lambda\psi_k{}' + \lambda^2\psi''+\ldots)$$

On collecting the coefficients of like powers of $\lambda$

$$(H_0\psi_k{}^0 - E_k{}^0\psi_k{}') + (H^0\,\psi_k{}' + H'\,\psi_k{}^0 - E^0{}_k\psi_k{}' - E_k{}'\psi_k{}^0)\,\lambda + (H^0\,\psi_k{}'' + H'\,\psi_k{}'' + H'\,\psi_k{}^0 - E_k{}^0\psi_k{}'' - E_k{}'\psi_k{}' - E_k{}''\psi_k{}^0)\,\lambda^2 + \ldots. = 0$$

If this series is properly convergent i.e., equal to zero for all possible values of $\lambda$ , then coefficients of various powers of $\lambda$ must vanish separately. These equations will have successively higher orders of the perturbation. The coefficient of $\lambda^{0}$ gives.

$$(H^0 - E_k{}^0)\ \psi_k{}^0 = 0 \qquad \text{................ (10a)}$$

The coefficient of $\lambda$ gives the equation.

$$(H^0\psi_k{}' + H'\psi_k{}^0 \ - E_k{}^0\psi_k{}' - E_k{}'\psi_k{}^0) \ = 0$$

$$(H^0 - E_k{}^0) + \psi_k{}' + (H' - E_k{}')\psi_k{}^0) = 0 \qquad \text{................ (10b)}$$

The coefficient of $\lambda^{2}$ gives the equation

$$(H^0\psi_k{}'' + H'\psi_k{}' + \psi_k{}' \ + H''\psi_k{}^0 \ - E_k{}^0\ \psi_k{}'' - E_k{}'\ \psi_k{}' - E_k{}''\psi_k{}^0) = 0$$

$$(H^0 - E_k{}^0) + \psi_k{}'' + (H' - E_k{}')\psi_k{}^0 = 0 \qquad \text{................ (10c)}$$

Similarly, the coefficient of $\lambda^{3}$ yield

$$(H^0 - E_k{}^0)\ \psi_k{}''' + (H' - E'_k)\ \psi_k{}'' + (H'' - E''_k)\ \psi_k{}' + (H''' - E_k{}''')\ \psi_k{}^0 = 0 \quad \text{........ (10d)}$$

But if we limit the total Hamiltonian $\lambda H'$ upto , i.e., if we put $H = H^0 + \lambda H'$ , then equations (10) will be modified as

$$(H^0 - E_k{}^0)\ \psi_k{}^0 = 0 \qquad \text{..... (a)}$$

$$(H^0 - E_k{}^0)\ \psi_k{}' + (H' - E_k{}')\ \psi_k{}^0 = 0 \qquad \text{..... (b)}$$

$$(H^0 - E_k{}^0)\ \psi_k{}'' + (H' - E_k{}')\ \psi_k{}' - E_k{}''\ \ \psi_k{}^0 = 0 \qquad \text{..... (c)}$$

$$(H^0 - E_k{}^0)\ \psi_k{}'' + (H' - E_k{}')\ \psi_k{}'' - E_k{}''\ \ \psi_k{}' - E_k{}'''\ \ \psi_k{}^0 = 0 \qquad \text{..... (d) ...........(11)}$$

**First order perturbation:** Equation (11b) is

$$(H^0 - E_k{}^0)\ \psi_k{}' + (H' - E_k{}')\ \psi_k{}^0 = 0$$

To solve this equation we use expansion theorem. As perturbation is very small, the deviations form unperturbed state are small, therefore the first order perturbation correction function $\psi_k{}'$ can be expanded in terms of unperturbed functions $\psi_1{}^0,\ \psi_2{}^0, .....,\psi_1{}^0, ....,$ $\sin ce\ \psi_1{}^0$ form a normalized orthonormal set. Hence we write

$$\psi_k{}' = \sum_{l-0}^{\infty} a_l\ \psi_l{}^0 \qquad ……………..(12)$$

Substituting $\psi_k{}'$ from (12) in (11b), we get

$$(H^0 - E_k{}^0)\ \sum_l\ a_l\ \psi_l{}^0 + (H' - E_k{}')\ \psi_k{}^0 = 0$$

i.e $$\sum_l\ a_l\ \psi_l{}^0 - E_k{}^0\ \sum_l a_l\ \psi_l{}^0 + (H' - E_k{}')\ \psi_k{}^0 = 0$$

Using $H^0\ \psi_l{}^0 = E_l{}^0\ \psi_l{}^0$ ,we get

$$\sum_l\ a_l\ \psi_l{}^0 - E_k{}^0\ \sum_l\ a_l\ \psi_l + (H' - E_k{}')\ \psi_k{}^0 = 0$$

$$\sum_l\ a_l\ (E_l{}^0\ - E_k{}^0)\ \psi_k{}^0 = (E_k{}' - H')\ \psi_k{}^0 \qquad ……………..(13)$$

Multiplying above equation by $\psi_m{}^{0*}$ and integrating over configuration space, we get

$$\sum_i\ a_l\ (E_l{}^0\ - E_k{}^0)\int \psi_m{}^{0*}\ \psi_l{}^0\ d\tau = \int \psi_m{}^{0*}(E_k{}' - H')\ \psi_k{}^0\ d\tau$$

.

Using the condition of orthonormalisation of $\psi_0$'s,

i.e $\int \psi_i^{0*} \psi_j^0 \, d\tau = \delta_{ij} = \begin{cases} 0 \;\; for \; i \neq j \\ 1 \;\; for \; i = j \end{cases}$

we get $\sum_i a_l (E_l^0 - E_k^0)\, \delta_{ml} = \int \psi_m^{0*} \, E_k^{'} \, \psi_k^0 \, d\tau - \int \psi_m^{0*} \, H' \, \psi_k^0 \, d\tau$

$= E_k^{'} \, \delta_{mk} - \int \psi_m^{0*} \, H' \, \psi_k^0 \, d\tau$ Using this notation $\int \psi_m^{0*} \, H' \, \psi_k^0 \, d\tau \; = <m|H'|k>$ we get .

$$\sum_i a_l \, (E_l^0 - E_k^0)\, \delta_{ml} \;= E_k^{'} \, \delta_{mk} \; - \; <m|H'|k> \quad \ldots\ldots\ldots..(14)$$

**Evaluation of first order energy $E_k^{'}$ :** Setting m = k in eqn. (14), we observe that

$\sum_i a_l \, (E_l^0 - E_k^0)\, \delta_{kl} \; = 0 \; always$

Since for $l = k, \; E_l^0 - E_k^0 = 0 \; and \;\; for \; l \neq k, \; \delta_{kl} = 0$ so that, we get

$0 = E'_k - <km|H'|k>$

Or $$E'_k = <k|H'|k> = \int \psi_k^{0*} \, H' \, \psi_k^0 \, d\tau \qquad \ldots\ldots\ldots\ldots\ldots..(15)$$

This expression gives first order perturbation energy correction. Accordingly the "first order perturbation energy correction for a non-degenerate system is just th expectation value of first order perturbed hamiltonian (H′) over the unperturbed state of the system."

### 2.4.3. EVALUATION OF FIRST ORDER CORRECTION TO WAVEFUNCTION:

Equation (14) may be expressed as

$$a_m \, (E_m^0 - E_k^0) = E_k^{'} \, \delta_{mk} - <m|H'|k> \qquad \ldots\ldots\ldots\ldots\ldots..(16)$$

$$Since\ \delta_{ml} \begin{cases} 0 & for\ l \neq m \\ 1 & for\ l = m \end{cases}$$

For $m \neq k$, equation (16) gives

$$a_m\ (E_m^0 - E_k^0) = -<m|H'|k>$$

.

Or $$a_m\ \frac{<m|H'|k>}{E_m^0 - E_k^0} = \frac{<m|H'|k>}{E_k^0 - E_m^0}$$

Setting

$$m = l,\ a_l\ \frac{<l|H'|k>}{E_k^0 - E_l^0} \qquad \text{……………..(17)}$$

If we retain only first order correction terms, then

$$\begin{aligned} E_k &= E_k^0 + \lambda E_k^{'} & ....(a) \\ \psi_k &= \psi_k^0 + \lambda \psi_k^{'} & ....(b) \end{aligned} \qquad \text{……………..(18)}$$

Keeping in view equation (12) and (17), we get from (18b)

$$\psi_k = \psi_k{}^0 + \lambda \sum_l{}' \frac{<l|H'|k>}{E_k{}^0 - E_l{}^0}\ \psi_l{}^0 + \lambda a_k\ \psi_k{}^0 \quad \text{……………..(19)}$$

where prime (or dash) on summation indicates that the term $l = m$ has been omitted from the summation (or it reminds that $l \neq k$ ).

The value of constant $a_k$ may be evaluated by requiring that is normalised, i.e.

$$\int \psi_k^* \ \psi_k d\tau = 1 \qquad \text{……………..(20)}$$

Substituting $\psi_k$ from (19) and retaining only first order terms in $\lambda$ : we get

$$\int \psi_k^{0*}\ \psi_k^0\, d\tau + \lambda a_k \int \psi_k^{0*}\psi_k^0\, d\tau + \lambda a_k^* \int \psi_k^{0*}\ \psi_k^0\, d\tau + \lambda \sum_l{}' \frac{<l|H'|k>}{E_k^{\ 0} - E_l^0}\ \delta_{lk} + \lambda \sum_l{}' \frac{[<l|H'|k>]^*}{E_k^{\ 0} - E_l^0}\ \delta_{lk} = 1$$

Or $$\lambda a_k + \lambda a_k^* = 0 \ \ i.e.\ a_k + a_k^* = 0 \qquad \ldots\ldots\ldots\ldots\ldots..(21)$$

This equation indicates that the real part of a$_k$ is zero and still it leaves an arbitrary choice for the imaginary part.

Let us take $a_k = i\gamma$ .The wavefunction $\psi_k$ can then be expressed as

$$\psi_k = \psi_k^0 + \lambda i\gamma\ \psi_k^{\ 0} + \lambda \sum_l{}' \frac{<l|H'|k>}{E_k^{\ 0} - E_l^0}\ \psi^0{}_l$$

$$= \psi_k^0\ (1 + \lambda i\gamma) + \lambda \sum_l{}' \frac{<l|H'|k>}{E_k^{\ 0} - E_l^0}\ \psi^0{}_l \qquad \ldots\ldots\ldots\ldots\ldots..(22)$$

The term containing $\gamma$ merely gives a phase shift in the unperturbed function $\psi_k^o$ and for normalisation, this shift can be put equal to zero, so that equation (22) gives.

$$\psi_k = \psi_k^0 + \lambda \sum_l{}' \frac{<l|H'|k>}{E_k^{\ 0} - E_l^0}\ \psi^0{}_l \qquad \ldots\ldots\ldots\ldots\ldots..(23)$$

The arbitrary $\lambda$ can be put equal to 1 and it may be included in symbols, i.e. $\lambda\ H' \to H'$ ; then Eigen values and Eigen functions of the system upto first order perturbation correction terms are expressible as

$$\left.\begin{aligned} E_k &= E_k^{\ 0} + <k|H'|k> && \ldots\ldots\ldots\ldots\ldots..\text{(a)} \\ \text{And }\ \psi_k &= \psi_k^{\ 0} + \sum_l{}' \ \frac{<k|H'|k>}{E_k^{\ 0} - E_l^0}\ \psi_l^0 && \ldots\ldots\ldots\ldots\ldots..\text{(b)} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots..(24)$$

### 2.4.4 PHYSICAL APPLICATIONS OF NON-DEGENERATE PERTURBATION THEORY:

#### (a). Normal Helium Atom (without spin considerations) as an application of first order perturbation theory for a non-degenerate state

A normal helium atom consists of a nucleus of charge z e (z = 2) and two electrons circulating about the nucleus. The potential energy for a system of two electrons 1 and 2 and a nucleus of charge + ze (Fig. 3.1) is

$$V = -\frac{ze^2}{r_1} - \frac{ze^2}{r_2} + \frac{e^2}{r_{12}} \qquad \ldots\ldots(1)$$

where $r_1$ and $r_2$ are the distances of electrons 1 and 2 and $r_{12}$ is the separation of the electrons. Then Hamiltonian of system

$$H = -\frac{\hbar^2}{2m_0}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{ze^2}{r_1} - \frac{ze^2}{r_2} + \frac{e^2}{r_{12}} \ldots\ldots (2)$$

The wave equation for unperturbed Hamiltonian

$$H^0\,\psi^0 = E^0\,\psi^0 \qquad \ldots\ldots\ (3)$$

Can be solved easily, taking as sum of two hydrogen atoms.

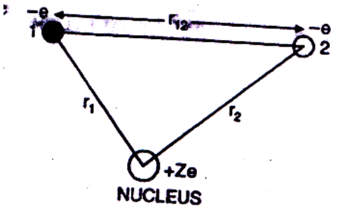


Fig. 3.1 Normal Helium Atom

The wave equation for two electrons in helium atom is

$$H\psi = \left\{-\frac{\hbar^2}{2m_0}\left(\nabla_1^2 + \nabla_2^2\right) + \left(-\frac{ze^2}{r_1} - \frac{ze^2}{r_2} + \frac{e^2}{r_{12}}\right)\right\}\psi = E\psi \qquad \ldots\ldots (4)$$

This equation is a applicable to He, $Li^+$, $Be^{++}$ etc. with z = 2, 3, 4 etc. respectively.

Equation (4) can be written as

$$H\psi = \left(-\frac{\hbar^2}{2m_0}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{ze^2}{r_1} - \frac{ze^2}{r_2}\right)\psi + \frac{e^2}{r_{12}}\,\psi = E\psi$$

if we write the Hamiltonian in the form H = H$^0$ + H′, we note that unperturbed Hamiltonian

$$H^0 = -\frac{\hbar^2}{2m_0}\ (\nabla_1{}^2 + \nabla_2{}^2)\ -\ \frac{ze^2}{r_1}\ -\ \frac{ze^2}{r_2}$$

and perturbation correction term

$$H' = \frac{e^2}{r_{12}}$$

The wave equation for unperturbed state would then be

$$\left(-\frac{\hbar^2}{2m_0}\ (\nabla_1{}^2 + \nabla_2{}^2)\ -\ \frac{ze^2}{r_1}\ -\ \frac{ze^2}{r_2}\right)\psi_0 = E^0\psi^0 \qquad .....(5)$$

If we substitute $\psi_0 = \psi_1{}^0\ \psi_2{}^0$ and energy $E^0 = E_1{}^0 + E_2{}^0$ , then equation (5) may be split into component equations one for each hydrogen like atom, viz.

The equation for $\psi_1{}^0$ is

$$\nabla_1{}^2\ \psi_1{}^0 + \frac{2m_0}{\hbar^2}\left((E_1{}^0 + \frac{ze^2}{r_1})\right)\psi_1{}^0\ = 0 \qquad .....(6)$$

and equation for $\psi_2{}^0$ is

$$\nabla_2{}^2\ \psi_2{}^0 + \frac{2m_0}{\hbar^2}\left(E_2{}^0 + \frac{ze^2}{r_2}\right)\psi_2{}^0\ = 0 \qquad .....(7)$$

These two equations are hydrogen - like wave equations and their solutions for Eigen values and Eigen functions are

$$E_1{}^0 = E_2{}^0 =\ -\ \frac{z^2 m_0 e^4}{2\hbar^2 n^2}\ =\ -\ \frac{z^2 W_H}{n^2} \qquad .....(8)$$

Where , $$W_H = \frac{m_0 e^4}{2\hbar^2} = \frac{e^2}{2a_0} \left( with\ a_0\ \frac{\hbar^2}{m_0 e^2} \right) \qquad \text{.....(9)}$$

And $$\psi_1{}^0 = \sqrt{\left(\frac{z^3}{\pi a_0{}^3}\right)}\ e^{-zr_1/a_0},\ \psi_2{}^0 = \sqrt{\left(\frac{z^3}{\pi a_0{}^3}\right)}\ e^{-zr_2/a_0}$$

So total unperturbed energy is

$$E^0 = E_1{}^0 + E_2{}^0 = -2z^2 W_H\ \ for\ \ n = 1\ (ground\ \ state)$$

The f first order perturbation energy $E'$ is the average value of the perturbation function $H' = e^2 / r_{12}$ over the unperturbed state of the system.

$$E' = \int \psi_0^* \, H' \, \psi_0 \, d\tau = \int \frac{e^2}{r_{12}} |\psi_0|^2 \ d\tau,$$

Where $$\psi_0 = \psi_1{}^0 \, \psi_2{}^0 = \sqrt{\left(\frac{z^3}{\pi a_0{}^3}\right)}\ e^{-zr_1/a_0}\ \sqrt{\left(\frac{z^3}{\pi a_0{}^3}\right)}\ e^{-zr_2/a_0}$$

$$= \left(\frac{z^3}{\pi a_0{}^3}\right)\ e^{-\rho_1/2}\ e^{-\rho_2/2}$$

Where $$\rho_1 = \frac{2zr_1}{a_0},\ \rho_2 = \frac{2zr_2}{a_0}$$

i.e $$\psi_0 = \frac{z^3}{\pi a_0{}^3}\ \exp\left(\frac{-\rho_1 - \rho_2}{2}\right)$$

Volume element for two electrons in spherical polar coordinates $(r, \theta, \Phi)$ is

$$d\tau = r_1{}^2\, dr_1\ \sin\ \theta_1\, d\theta_1\, d\Phi_1\, r_2{}^2\, dr_2\ \sin\ \theta_2\, d\theta_2\, d\Phi_{2,}$$

So that

$$E' = \frac{ze^2}{32\pi^2 a_0} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{e^{-\rho_1} e^{-\rho_2}}{\rho_{12}} \rho_1^2 \, d\rho_1 \, \sin\theta_1 \, d\theta_1 \, d\Phi_1 \times \rho_2^2 \, d\rho_2 \, \sin\theta_2 \, d\theta_2 \, d\Phi_2$$

…..(10)

Where $\rho_{12} = \frac{2zr_{12}}{a_0}$

This may be expressed as

$$E' = \frac{ze^2}{32\pi^2 a_0} \iint \frac{e^{-\rho_1} e^{-\rho_2}}{\rho_{12}} \, dV_1 \, dV_2$$

Where $dV_1 = \rho_1^2 \, d\rho_1 \, \sin\theta_1 \, d\theta_1 \, d\Phi_1$ & $dV_2 = \rho_2^2 \, d\rho_2 \, \sin\theta_2 \, d\theta_2 \, d\Phi_2$

The integral $\left( aside \text{ } the \text{ } factor \text{ } \frac{ze^2}{32\pi^2 a_0} \right)$ represents the mutual electrostatic energy for two spherically symmetrical distribution of electricity with density functions $e^{-\rho_1}$ and $e^{-\rho_2}$ respectively.

The integral may be evaluated by calculating the potential due to first of these by integrating over $dV_1$ and then finding the energy of second charge distribution in that potential field.

The potential at a point r due to a spherical shell of radius $\rho_1$ and $d\rho_1$ thickness ie.. of total charge $4\pi\rho_1^2 e^{-\rho_1} d\rho_1$ falls off with distance outside the shell as if the total charge were concentrated at the centre, so that for $r > \rho_1$ , the potential

$$\Phi \; (r > \rho_1) = \frac{q_1}{r} = \frac{4\pi\rho_1^2 e^{-\rho_1} \, d\rho_1}{r}$$

Within the shell the potential is constant and has value equal to that at shell's surface.

$$= \ 4\pi\rho_1 \, e^{-\rho_1} \, d\rho_1 \, \Phi \ (r \le \rho_1) = \ \frac{4\pi\rho_1{}^2 \, e^{-\rho_1} \, d\rho_1}{\rho_1}$$

The potential due to the whole charge distribution is therefore given by

$$\Phi(r) = \frac{4\pi}{r}\int_0^r e^{-\rho_1} \ \rho_1{}^2 \, d\rho_1 \ + 4\pi\int_r^\infty e^{-\rho_1} \ d\rho_1$$

$$= \frac{4\pi}{r} \ \left[\left(-r^2 - 2r - 2\right)e^{-r} + 2\right] + 4\pi \ [r+1] \ e^{-r}$$

$$= \frac{4\pi}{r} \ \left[\left(-r^2 - 2r - 2 + r + r^2\right)e^{-r} + 2\right]$$

$$= \frac{4\pi}{r} \ \left[2 - e^{-r}\left(r+2\right)\right]$$

The energy of the second charge distribution in this potential is, then

$$\int \Phi \ (\rho_2) e^{-\rho_2} \ dV_2 = \int \ \frac{4\pi}{\rho_2} \ [2 - e^{-\rho_2} \ (\rho_2 + 2)] \ e^{-\rho_2} \ dV_2$$

$$= \int_0^\infty \ \frac{4\pi}{\rho_2} \ [2 - e^{-\rho_2} \ (\rho_2 + 2)] \ e^{-\rho_2} \ 4\pi\rho_2{}^2 \, d\rho_2$$

$$= 16\pi^2 \int_0^\infty \ \left\{2 - e^{-\rho_2} \ (\rho_2 + 2)\right\} \ e^{-\rho_2} \ \rho_2 \, d\rho_2$$

$$= 16\pi^2 \times \frac{5}{4} \ = 20\pi^2 \qquad \ldots \qquad \ldots\ldots..(11)$$

that is the value of integral in equation (10) is $20\pi^2$

hence $E' = \dfrac{ze^2}{32\pi^2 a_0} \times 20\pi^2 = \dfrac{5ze^2}{8a_0} = \dfrac{5}{8} \ \dfrac{ze^2}{\hbar^2 / m_0 e^2} = \dfrac{5}{8} \ . \ \dfrac{zm_0 e^2}{\hbar^2} = \dfrac{5}{4} \ z \, W_H$

Total energy E = $E_0$ + $E'$

$$= -2z^2\, W_H + \frac{5}{4}\, z\, W_H = -\left(2z^2 \;-\; \frac{5}{4} z\right) W_H \qquad \ldots\ldots\ldots\ldots(12)$$

For Helium atom z = 2

$$E = -\left(2\times 4 - \frac{5}{4}\times 2\right) W_H = -\,\frac{11}{2}\, W_H .$$

$$E = -\,\frac{11}{2}\times\frac{m_0 e^4}{2\hbar^2} = -\frac{11}{4}\,\frac{m_0 e^4}{\hbar^2} = -\,\frac{11}{4}\,\frac{e^2}{a_0} = -2.75\,\frac{e^2}{a_0}$$

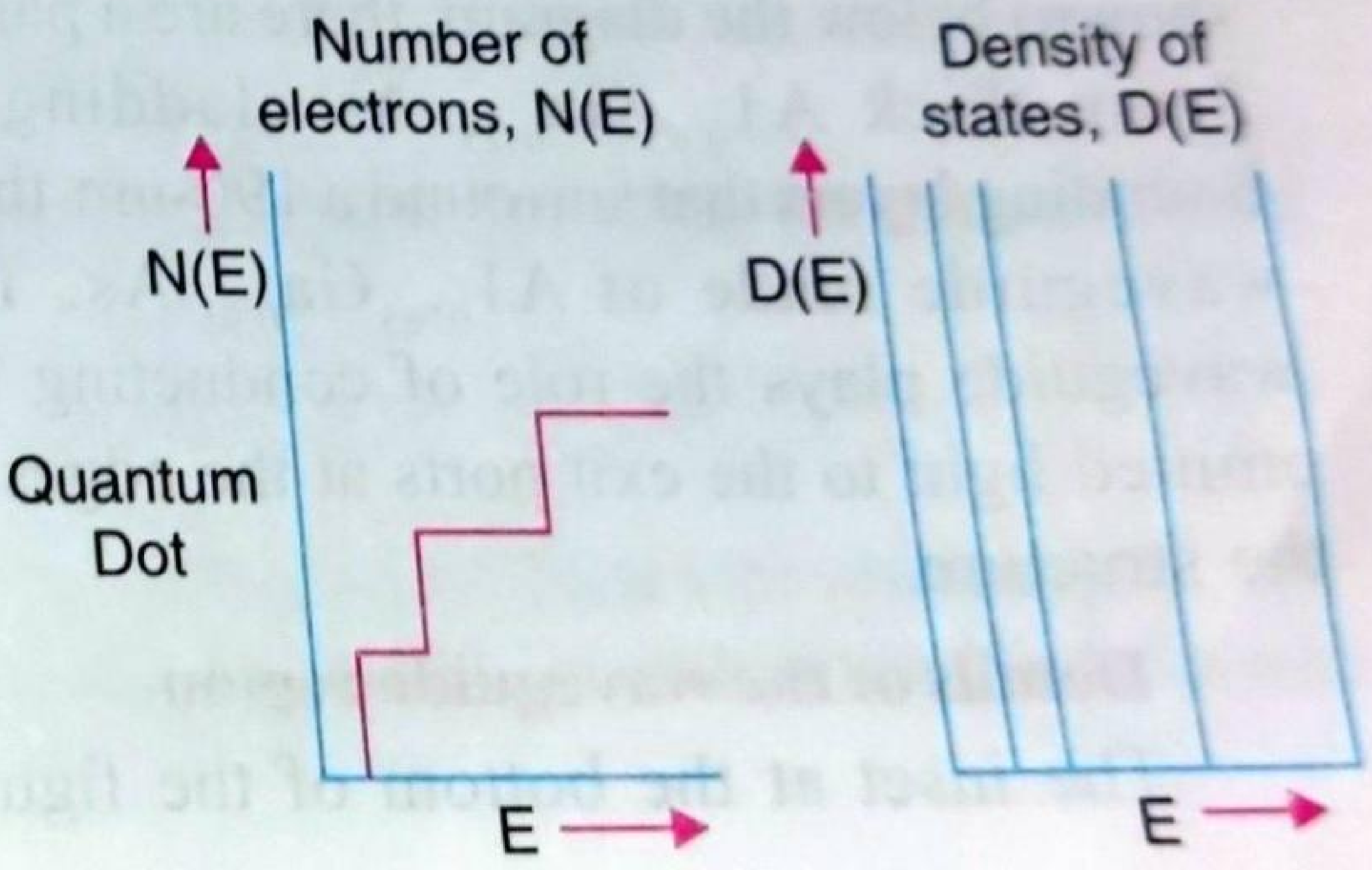
Total energy of helium atom is ground state without perturbation is

$$-\,2z^2\, W_H = -\,8W_H = -\,4\frac{e^2}{a_0}$$

Which is less than the corrected energy by means of perturbation theory.

**Energy dependence curves of Number of electrons and Density of states**

Fig. 79.24 shows number of electrons $N(E)$ (left side) and density of states $D(E)$ (right side) plotted against the energy $E$ for three quantum structures and their bulk counterpart in the square well-Fermi gas approximations.



(*i*) The number of electrons $N(E)$ increases with the energy $E$ for all the four structures. So the four types vary only qualitatively from each other.

(*ii*) The density of states $D(E)$ differ dramatically for each of the three nanostructure types. This means that the nature of the dimensionality and of the confinement associated with a particular nanostructure have a pronounced effect on its properties. These considerations can be used to predict properties of nanostructures. We can also identify types of nanostructures from their properties.

Some of the properties of solids that depend on the density of states are: electron heat capacity, Pauli susceptibility, the intensity of x-ray emission, electron and hole concentrations in semiconductors, the superconducting energy gap, and Josephson junction tunneling in superconductors. Experimental measurements of these various properties permit us to determine the form of the density of states $D(E)$, both at the Fermi level $E_F$ and over a broad range of temperature.

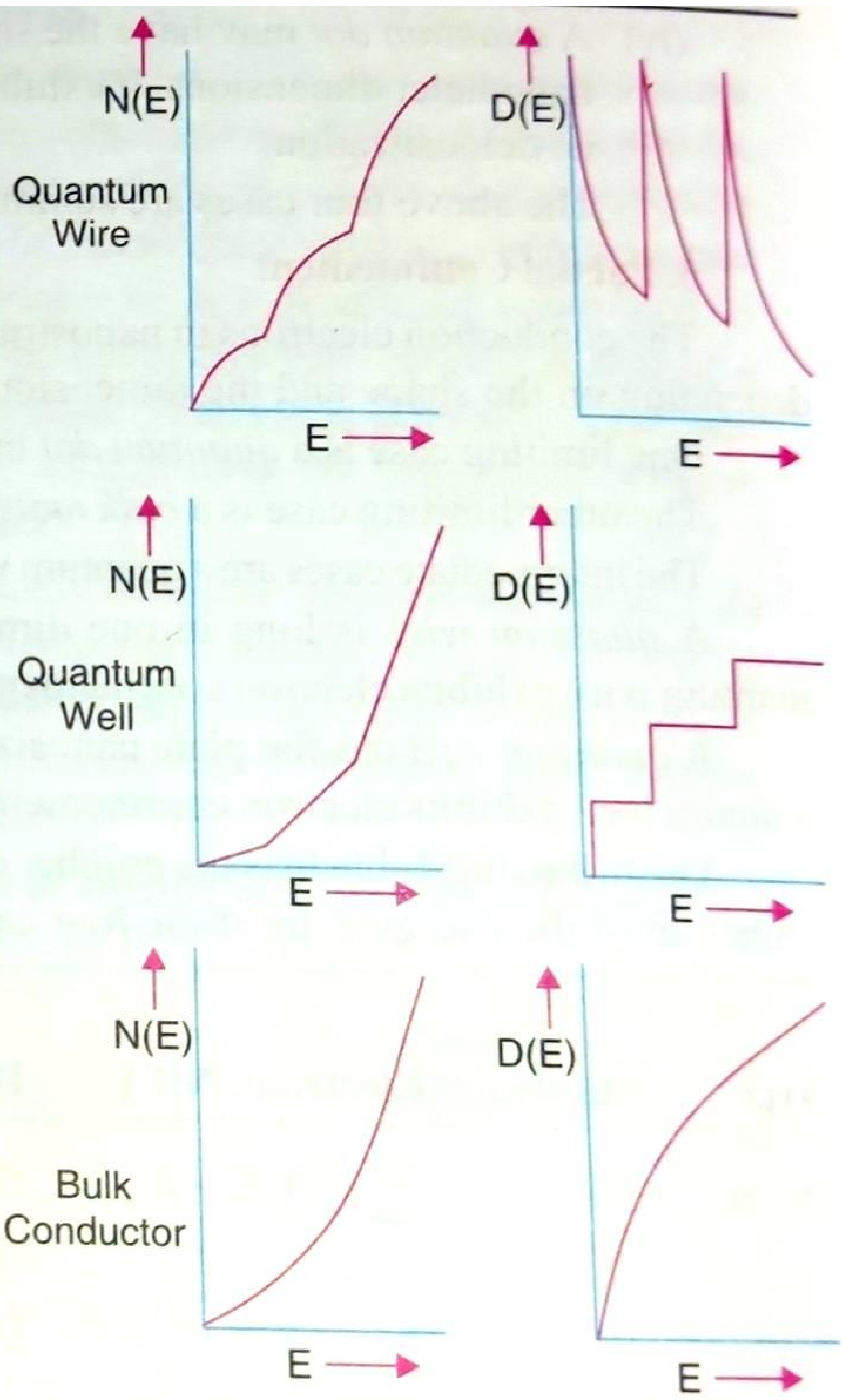


Fig. 79.24

## Nuclear Zeeman Splitting

In an asymmetric electric field there are $M_I$ degenerate states. This degeneracy is removed by placing the absorber in a magnetic field, which arises either internally as in a ferromagnetic material such as metallic iron or $Fe_2O_3$ , or which is generated by an external magnetic field. Nuclear Zeeman splitting is observed in which each nuclear level splits into $\left(2\left|M_I\right|+1\right)$ components (Fig-5.22). The Hamiltonian describing the interaction of the magnetic field of flux density B with nuclear spin is given by

$$H_{mag} = -\mu.B = -g_N\mu_N I.B \qquad 5.75$$

where $\mu_N$ is the nuclear magnetron ($eh/4\pi m_p = 5.04929 \times 10^{-27}$ Am$^2$ or JT$^{-1}$) and $g_N$ is the nuclear g-factor [$= \mu/(I\mu_N)$].

The eigen value of this Hamiltonian is given by

$$E_{mag} = -g_N \mu_N B M_I \qquad 5.76$$

where $M_I$ is the magnetic quantum number $M_I$ = I, (I-1), . . . .-I.

The selection rules for the dipole transition is given by

$$\Delta M_I = 0, \pm 1 \qquad 5.77$$

so that in an absorber with an excited state of I = 3/2 and a ground state of I = ½, a six-line hyperfine will be observed. The intensities of six peaks for a powdered Fe and Sn compounds are in the ratio of 3:2:1:1:2:3. These transitions are shown in Fig-5.22.

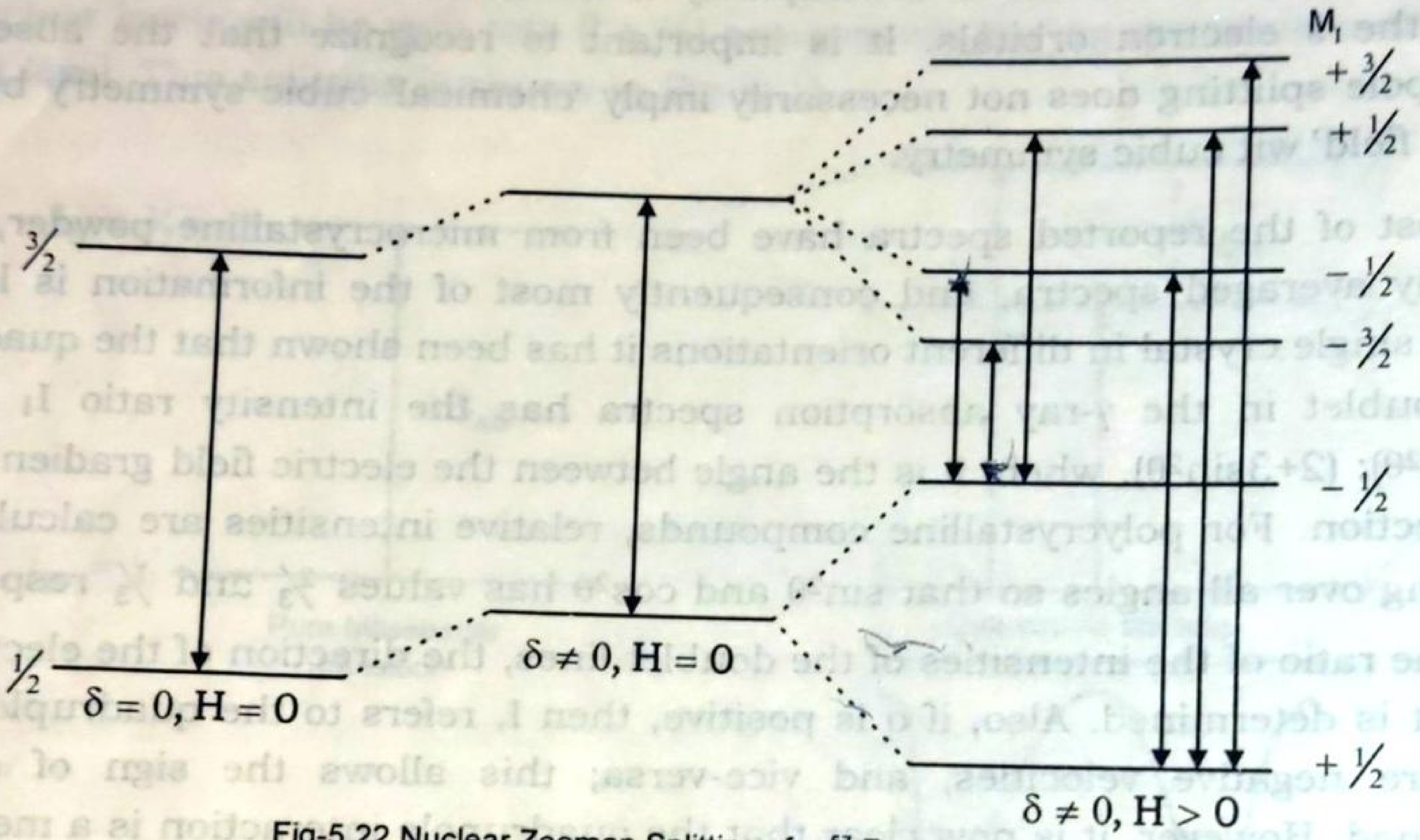


Fig-5.22 Nuclear Zeeman Splittings for $^{57}$Fe

The magnetic hyperfine interaction is a product of a nuclear constant ($g_N$ $\mu_N$) and an external variable ( the flux density B ). The latter may be applied by an external magnet. In case external magnetic field is employed to "calibrate" the spectrum, the magnitude of internal field can be found and by this method fields of 20 – 50 T have been found for various compounds of $^{57}$Fe. These fields are quite large compared with 5 – 10 T fields created by superconducting magnets. Any unpaired electron in an atom induces a slight imbalance in the s-electron spin density at the nucleus because it interacts differently with the parallel and anti-parallel spins of the other electrons, and this results in a large local magnetic field of up to 100 T at the nucleus. In a magnetically ordered solid, the direction of the unpaired spin and thus of the filled are effectively frozen, and the result is magnetic hyperfine splitting. In a paramagnetic solid, the direction of the spin is rapidly changing by electronic spin-relaxation, and the time average of B is usually zero within the life time of the MÖssbauer excited state, so no splitting is seen.

Combined Zeeman and quadrupole splittings are also possible although relatively few compounds show such effects. In general, in order to simplify the spectra, the source material is selected to give a single transition line. For iron this is achieved by using $^{57}Co$ diffused into metallic chromium and no net electric field gradient and magnetic field are present at the cobalt nucleus.

undergoes hydrolysis generating a hydroxyl group on the metal center (M). The hydroxyl group undergoes further condensation reaction progressively generating the silicon network. The R' group provide a handle for imparting various properties to the silica network. In Class-II type hybrids, the interaction that holds the organic and inorganic components can be covalent, iono-covalent or Lewis acid-base.

## 17.3 PREPARATION OF ORGANIC-INORGANIC HYBRIDS

The methods used for making organic-inorganic hybrids are classified into three types. They are: sol-gel methods, self-assembly route and nano-building-block approach.

### 17.3.1 Sol-Gel Methods

**Route 1**: This route involves the hydrolysis of the organically modified alkoxides. The general formula of the alkoxides can be written as $R'M(OR)_{n-1}$, wherein the R' group contains the functionality. The controlled hydrolysis followed by condensation of it leads to silica network with the organic group imparting various properties.

**Route 2**: This method uses bridged siloxanes with the general formula, $X_3Si\text{-}R\text{-}X_3$ (R is an organic spacer, X may be OR, Cl or Br).

**Route 3**: This involves hydrothermal synthesis of materials in polar solvents in the presence of organic templates. The medium is normally a polar solvent, like water or formamide. This method is used to make zeolites.

### 17.3.2 Nano-building Blocks

Nano-building blocks are preformed, perfectly calibrated building units. Nano-building blocks keep their identity in the final material. This path utilises clusters, pre- or post-functionalised nanoparticles or layered materials like layered silicates and layered double hydroxides, in order to disperse the organic component. The use of nano-building blocks leads to a better definition of the inorganic part in the final hybrid material.

### 17.3.3 Self-Assembly

The organic template usually self-assembles to give the mold, over which one can grow the inorganic template. The organic structure-directing agents normally used include surfactants and nano-building blocks.

**Route 1**: The classic example for a hybrid produced by this method is periodic mesoporous silica. This method can produce periodic mesoporous materials with the walls decorated with functional groups.

**Route 2**: In this method, the surfactant provides the template and the bridged silsesquioxane is used as the precursor for the inorganic phase.

the metal ion added may get As a result of this, there can be the presence of uncoated nanoparticles of the first kind, although the objective -shell par Such particles are commonly referred to as core@shell. A typical example is Fe@Au[123,124] syste which the synthesis also gives pure Fe particles.[125] The approach can be extended to get Au@Fe kind of systems.[126,127] The difference between this and the simultaneous reduction approaches i it is very difficult to get conditions by which a less noble metal becomes the core, as in Ag@Au d simultaneous reduction, but such possibilities exist in the microemulsion route.

The core-shell can be made of oxides. $Fe_3O_4$@MnO has been synthesised. The core has 10 diameter and the shell has 2.5 nm thickness.[128] $SiO_2$@$Fe_3O_4$ has been prepared.[129] The compl and variety of the core-shell system can be numerous. One could coat the surface of the nanopa with a polymer that is prepared *in-situ* in the reaction mixture. The polymerisation can occur over nanoparticle surface, which is already coated with an appropriate group on which polymerisation occur. This kind of approach can be used for growing inorganic shells as well. This is the appro used by Liz-Marzan to prepare $SiO_2$ shells over gold nanoparticle.[130] Here, the approach is to coat surface of gold with a monolayer of aminopropyltrimethoxysilane. The amino group binds on to surface of gold and the trimethoxy group can be hydrolysed in the presence of tetraethoxyorthosi (TEOS) resulting in the growth of a thin silica shell. The shell thickness can be increased further using a method of Stöber.[131] This synthetic approach can be used for other nanoparticles as well.

The synthesis of core-shell materials can also be achieved by a single step, in which all materials a reagents are added into one pot. This approach has produced Au@$TiO_2$ and Ag@$TiO_2$ particles. Here, the readuction is achieved by dimethylformamide (DMF) and the precursor species are HAu $AgNO_3$ and titaniumisopropoxide. A similar method can be used for Au@$ZrO_2$ and Ag@$ZrO_2$ whe the Zr precursor is zirconium isopropoxide.[133] Corresponding alloys can also be prepared. All the core-shell materials, namely Au@$SiO_2$, Au@$TiO_2$ and Au@$ZrO_2$, and their Ag analogues are fre dispersible in organic media. In order to increase the dispersibility, the oxide surfaces can be coa with long chain carboxylates. In this case, the material obtained can be taken out of the solution i powder form and stored for extended periods and redispersed.[134]

Colloidal core-shell particles can be used to control the optical absorption of nanoparticles. T assemblies of these structures in various forms are also important ways of controlling optical absor Various aspects of such control are discussed in the article by Liz-Marzan.[135]

## 9.6 SOLVOTHERMAL SYNTHESIS

Solvothermal method refers to conducting the reaction in a closed vessel, in which the solvent h a possibility to achieve its supercritical state. The temperatures and pressures are high (e.g., abo 374°C and 218 atm for water). Although many reactions are not conducted at the supercritical sta the reactions are done in pressure bombs typically with Teflon lining. In the supercritical state, th liquid-vapour boundary disappears. The fluid achieves properties of both the liquid and the g Increased solubility and increased reaction rate favour many reactions, and therefore, processes better done at the supercritical state. However, for many reactions, increased reactivity at higher temperatures in a controlled condition is the sole aspect of interest. If the reaction is done in water, it is called hydrothermal, and in the case of other solvents it is referred to as solvothermal. Several reviews are available on this topic and an interested reader may consult them for details, such as the pressure conditions, experimental apparatus, various materials synthesised, etc.[136–143]

One of the aspects of particular interest in this method is the significant reduction in the reaction temperatures, even for many ceramic materials. Materials thus synthesized are highly crystalline and often post synthetic annealing operations are not necessary. They are monodisperse and often, are suspendable in a suitable medium. Besides, the methodology can be adapted to suit several synthetic conditions and also can be used for large-scale synthesis. The heating process itself can be conducted in a microwave oven making it also energy efficient in addition to the distinct advantages the technique offers.[144] The process can also be adopted to continuos flow conditions.[145] All of these make it an interesting methodology for synthesis. Besides, the synthetic procedures have the advantages of being relatively inexpensive in terms of the solvents used, arguably green (when water is the solvent).[138]

In a typical method, the precursor species are mixed with suitable reagents for reduction, precipitation, etc., in a suitable medium. Often stabilisation and complexation agents are added so that the process takes place happenes at controlled conditions. The synthesis of anatase $TiO_2$ is achieved by controlled hydrolysis of $Ti(OEt)_4$ in ethanol.[146] Monodisperse particles were prepared by this route.[147] The starting material can be $TiCl_4$,[148, 149] and one can also use stabilisers, such as citric acid.[150] Microemulsion-based synthesis often includes a solvothermal step and $TiO_2$ was prepared that way also.[151] Large-scale synthesis of $TiO_2$ is significant in view of its application in photocatalysis, solar cells, etc., $CeO_2$ synthesis has been achieved with[152] and without[153] stabilisers. Complex oxides, such as $\gamma$-$Fe_2O_3$, $CoFe_2O_4$[154] and $ZnFe_2O_4$[139] were prepared by the hydrothermal route. The microwave-hydrothermal route is very useful for many complex oxides, such as the ferrites ($MFe_2O_4$, M=Mn, Co, Ni, Zn),[155] $BaTiO_3$,[144] $\alpha$-$Fe_2O_3$.[156] The methodology is also useful in making several other materials, especially mesoporous solids. The applications of these materials are numerous in catalysis and are extensively covered in other places.

Hydrothermal processes are used to make metal chalcogenides.[157] CdSe particles were made from elemental Cd and Se at 180°C in a hydrothermal route.[158] The products were aggregated in the absence of suitable stabilisers. In presence of TOPO, the synthesis of CdSe produces ~3 nm particles.[159] Many other chalcogenides-$SnS_2$, $NiS_2$, $CoS_2$, $FeS_2$ and $NiSe_2$-have been synthesised.[160, 161]

## 9.7 SYNTHESIS USING SUPPORTS

Various synthetic approaches are available to use supports for the preparation of nanoparticles. These vary from the use of nanoparticles themselves to materials with nano cavities. Particles prepared by one route can be used for subsequent growth. This results in the controlled growth of particles at the nanoparticle surfaces. If the growth of smaller particles is avoided, one can get programmed increase in size. This is possible by the use of suitable reactants. For example, hydroxylamine will reduce $Au^{3+}$, but will do so better on Au particles. As a result, larger particles can be grown by adding $Au^{3+}$ to a

## Chapter 20

# NANOLITHOGRAPHY

> *"I saw the angel in the marble and carved until I set him free."*
>
> Michelangelo
> Bull, George Anthony.
> *Michelangelo: A Biography*. New York: Viking, 1995

*Writing at the nanoscale is nanolithography. This branch has become one of the most important areas of research as nanometer scale structures are the cornerstone of modern devices. This chapter is an illustration of the variety of techniques used for this application. Nanoscale patterns are made with atoms, molecules and even nanomaterials. The kind of patterns derived and the modern research frontiers in this area are briefly outlined.*

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**Learning Objectives**

- What is nanolithography?
- What are the diverse tools in this branch?
- What are clean room facilities?
- How do we create patterns in conventional lithography?
- How is scanning probe microscopy used in lithography?

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## 20.1 NANOLITHOGRAPHY

Nanolithography is the lithography at the nanoscale. Although the basic ideas of lithography are old, the fabrication of structures on the nanometer-length scale has made nanolithography an exciting new field of research during the last one decade or so. The study of quantum phenomena in confined structures demands patterning periodic arrays, gratings or address systems at the nanoscale made of desired materials. This has resulted in a new class of electronic devices with interesting functionalities. Such applications demand the availability of highly sophisticated techniques capable of fabricating reproducible structures and devices in the nanometer regime. Nanolithography, thus, has far-reaching implications in the fabrication and integration of nanodevices, which explains the importance given to it.

Nanolithography has been applied extensively to pattern new materials or to create new and complex structures using known materials and studying the various properties, either individual or collective. Repetitive structures, such as line grating or arrays of dots or nanopillars, have been patterned; while varying structural parameters such the feature size and inter-feature distance. The properties of patterned materials, especially electronic, magnetic and optical, have been studied extensively.[1] Patterned materials have also been used as templates for the catalytic growth of other nanostructures such as carbon nanotubes and nanowires.[2]

Another field of nanoscience where lithography is on high demand, is the fabrication of nanocircuitry. Here, the materials are to be patterned across specified nanoelectrodes and studied for their characteristics. There are a few important issues that come into play, namely,

1. laying nanoelectrodes;
2. placing an active element like a nanotube or a quantum dot at the desired location either by nanomanipulation or by selective masking;
3. soldering to improve the nanoelement-nanoelectrode coupling and finally; and
4. feeding and deriving electrical or optical signals from the nanocircuit.

Indeed, each of these issues has developed into matured fields of research and technology.

Both repetitive and non-repetitive nanopatternings borrow several ideas from conventional microlithography. The lithography beam is essentially a photon or charged particle (electron or ion) beam. In order to achieve the desired resolution, light of smaller wavelength is used—extreme UV and even soft X-ray photons. A new set of techniques unique to nanolithography have emerged in the recent years. These techniques essentially make use of the scanning probe microscopy set-ups. Stamping methods have also been downsized to reach nanoscale dimensions.

## 20.2 LITHOGRAPHY: CONCEPTS AND DEFINITION

In Greek, litho means 'stone' and gráphein means to 'write'. It is virtually creating impressions on any surface. Although, caveman knew writing on the wall, it is was Aloys Senefelder in 1796, who invented a repetitive process of reproducing a drawing on Bavarian limestone, then transferring onto paper. Lithography is a generic term for a process, in which something is printed on a surface that is receptive to 'ink' in some regions and repels 'ink' in other regions. In present-day usage of the term, lithography refers to creating repetitive or non-repetitive patterns of a material on a given substrate with a wide choice for both, the patterns being anywhere between submicron to nanometric in dimension. The processes involved are not very different from creating ink impressions on paper (Fig. 20.1). Writing can be done in three different ways, the easiest of all, is direct writing method, where patterns are created on the surface directly using the ink. The surface, on which the patterns are created, is known as substrate and the ink can be referred to as resist. In another method, the impression of a pattern is first cut-out on a surface, generally known as mask or stencil, which is then used to transfer the pattern onto a substrate using a brush carrying the ink or sprayed on the substrate with the mask. The advantages of using this method is firstly, the stencil or mask, which is cut-out can be used several times to create the same pattern, and secondly, the excess of resist/ink used is removed by lift-off of stencil after the inking process. Yet another way shown in the Fig. 20.1 is to create an impression is to raise a 'mirror pattern' as a mould or stamp, which is inked and stamped to create the impression.

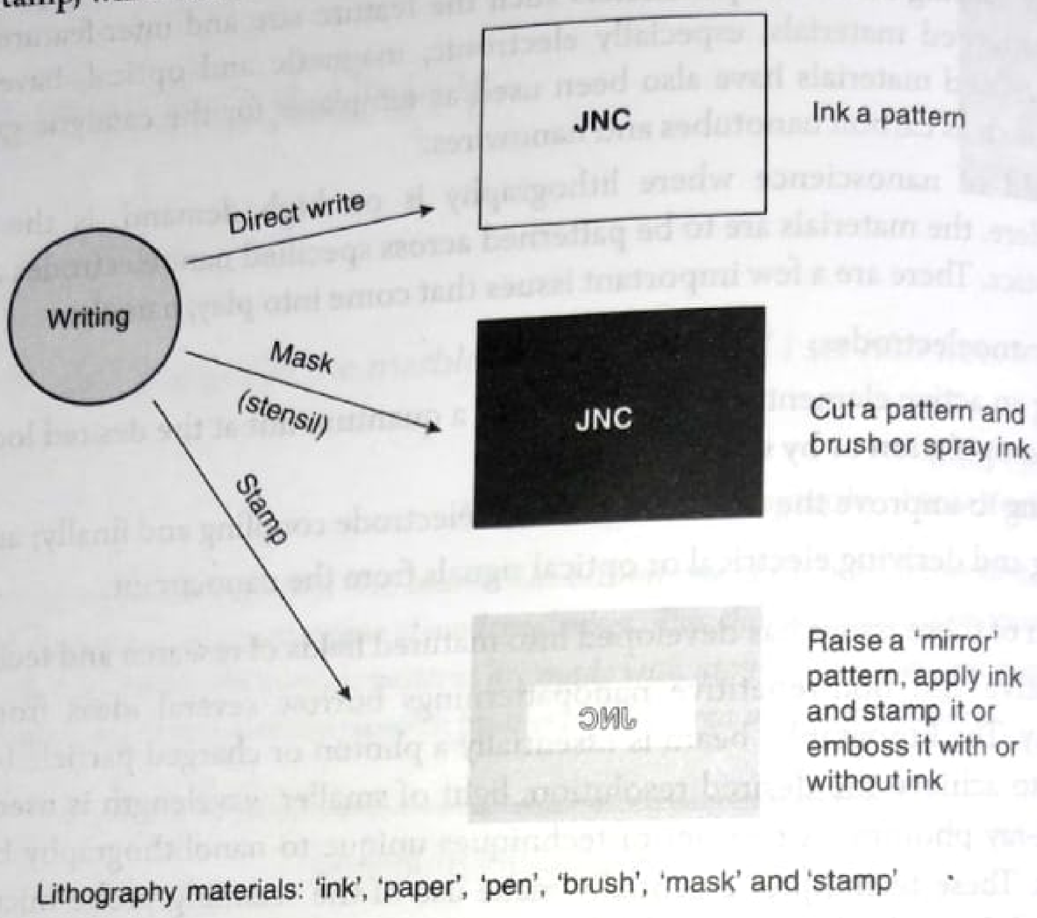


**Fig. 20.1** *Different ways of creating ink impressions on paper.*

## 20.3 CONVENTIONAL LITHOGRAPHY

Microlithography, where the feature size is of the order of microns, is considered conventional, but much of the ingredients and terminology remain similar for nanolithography. Typically, in microlithography based on light, a substrate is coated with a light sensitive resin (resist), which, upon exposure to light, transforms in such regions to another form with different properties so that such regions can be selectively retained or washed away. The active (desired) material such as a metal, is brought in during the second stage to finally create metal patterns on the substrate.

### 20.3.1 Preparing the Substrate

The substrates (also called wafers) used for lithography should be free from contamination. There are several methods to clean the substrate. The most commonly used method is ultrasonication, which physically removes particulate matter from the substrate. The medium can be organic solvents like acetone or alcohols orsimply distilled water. Wet methods include RCA1 and RCA2 cleaning.

The RCA1 cleaning is done to remove the organic dirt while RCA2 is performed to remove metal impurities. The composition of RCA1 and RCA2 reaction mixtures are $NH_3$:$H_2O_2$:$H_2O$::1:1:5 and HCl:$H_2O_2$:$H_2O$::1:1:6, respectively (Caution: this mixture reacts violently with organic matter). The cleaning in each case is done by heating the reaction mixture at 80 °C for 10 min. The distilled water rinse is followed after every chemical treatment. After the cleaning, the substrate is dried under argon or nitrogen gas. Other methods employed for cleaning the substrates are heating the substrates at high temperatures in vacuum or in oxygen or to use plasma etching techniques. The commonly used substrates are Si substrates or Si substrates with thermally grown oxide as a dielectric layer (for electronic applications), quartz, glass, etc. For growing the oxide, the cleaned substrate is subjected to a high temperature (> 850 °C) in the presence of oxygen flow. Depending on the required thickness of the oxide, the temperature and duration of oxidation is controlled.[3]

Once the cleaning process is completed and the substrate is spin-coated with the resist to produce a thin uniform layer. This is a crucial step for effective pattern transfer. The thickness of the resist is varied depending on its application. The volume of resist taken, its viscosity and the spinning rate are crucial for uniform resist film. In some cases, a monolayer of adhesion promoter, hexamethyldisilazane vapours (HDMS) is employed to make the surface hydrophobic. Sometimes, dry film resists, a photosensitive resin in a multilayer configuration with a carrier film and cover films are used in photolithography to form precision patterns.

## 20.3.2 Positive and Negative Resists

The main component to perform lithography is the resist, which undergoes the chemical changes on exposure of light or electron beam. The polymers that on exposure to light undergo chemical transformations are known as photoresists. Polymers undergo chain scission or cross-linking on exposure of light resulting in an effective decrease or increase, respectively in their molecular weight (Fig. 20.2). After exposure to light, these polymers show selective dissolution in some solvents known as developers. Based on this property, photoresists can be classified into two types, positive and negative photoresists. In the case of a positive resist, the region exposed to light solubilises in the developer (due to chain scission and decrease in the molecular weight) and the unexposed regions remains insoluble. In other words, the exposed resist leaves windows of the bare underlying material; hence, "whatever shows, goes". Negative resists behave in just the opposite manner. For a negative resist, the regions exposed to light become relatively insoluble in the developer compared to the unexposed regions (Fig. 20.2).

Originally, the resists were mostly of the negative type, but since 1970s, the positive resists have also come into play. A well-known example of a positive photoresist is polymethylmethylacylate (PMMA). It undergoes chain scission under UV illumination. Sometimes, to increase the sensitivity of the resist, a sensitiser is added. Phenolic Novolak–Diazonapthoquinine is an example of such resist, where diazoquinone ester is the photoactive species and phenolic novolak is the resin. Examples for negative photoresists are Kodak KTFR, which is an azide-sensitised polyisoprene rubber. Similarly, for electron beam lithography, polymers, which undergo chemical change on exposure to electron

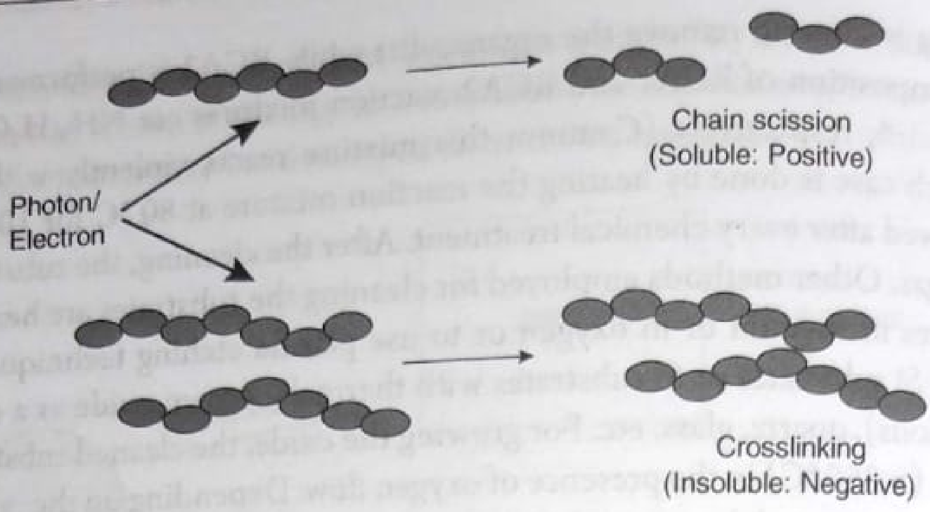


**Fig. 20.2** *Schematic of the chemical changes undergone by positive and negative resist on exposure to photon/electron source.*

beam are used. The best example for a positive e-resist is PMMA and for negative tone, examples are polystyrene and calixarene. There are other commercially available resists for both photolithography and electron beam lithography, such as Shipley, DUV, SU and ZEP series. After spin-coating a resist, the excess of solvent is removed by prebaking or soft baking. This step is performed in order to achieve the maximum adhesion of the resist to the substrate. Over-baking should be avoided as the resist film can decompose or it can degrade the photosensitivity of the resist either by reducing the developer solubility or actually destroying a portion of the sensitizer. Under-baking will prevent the light from reaching the sensitiser.

A "mask" is defined as a tool that contains patterns, which can be transferred to a resist coated substrate or to another mask in a single exposure. A reticle is defined as a tool that contains a pattern image that needs to be stepped and repeated in order to expose the entire wafer or mask. The mask used for a positive resist contains an exact copy of the pattern, which is to remain on the substrate, whereas the mask used for negative photoresist contains the inverse (or photographic "negative") of the pattern to be transferred. Figure 20.3 shows the difference in the patterns generated from the use of positive and negative resist using a same mask.

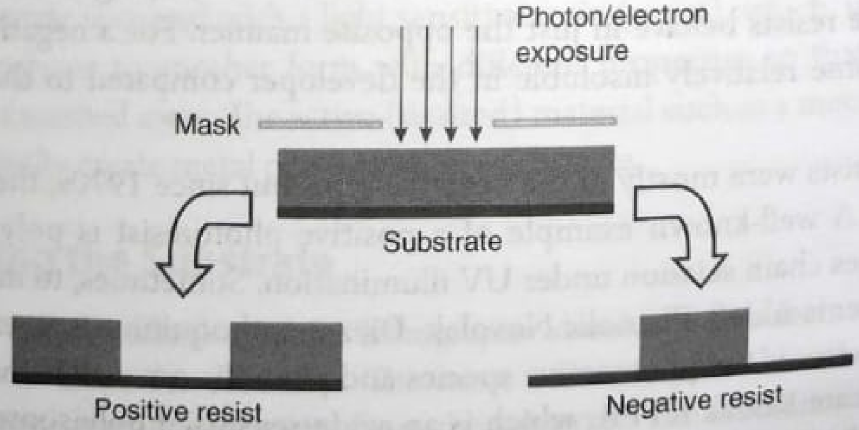


**Fig. 20.3** *Patterns generated on positive and negative resist using a mask.*

Exposure or dosage is a process to bring about the chemical changes in the resist using the light or e-beam. The dosage is very crucial as it decides the quality of patterns on the resist material. Under-exposure may result in incomplete pattern transfer, whereas over-exposure may cause undue broadening of the pattern. In case of photolithography, dosage is defined as the energy (in mJ) dosed per unit area (in cm$^2$), whereas in the case of electron beam, lithography dosage is defined as charge (in $\mu$C) dosed per unit area (in cm$^2$). The exposure can be done in two ways: using a focused scanning beam or using a broad beam to project an entire pattern. The major advantage of the second method is a higher pattern writing speed, compared to serial writing of the focused beam, where only small areas of pattern can be written at a time. Photolithography is more popular, because it is mainly a projection based lithography, and therefore, large areas can be patterned in a very short span of time, whereas the non-optical based techniques which use charged particles like electrons, are mostly focused scanning based, making the patterning process slow.

### 20.3.3 Developing

After the exposure, the substrate is developed in a developing solution. Development is carried out by immersion developing, spray developing or puddle developing. For example, in the case of PMMA, a mixture of methylisobutyl ketone: isopropyl alcohol (MIBK: IPA) in the ratio 1:3 has been found to be the best developing solution. At low-exposure energies, the negative resist remains completely soluble in the developer solution. As the exposure is increased above the threshold energy, more of the resist film remains after development. At exposures two or three times the threshold energy, very little of the resist film is dissolved. For positive resists, the resist solubility in its developer is finite even at zero-exposure energy. The solubility gradually increases until, at some threshold, it becomes completely soluble. Developing time varies from a few seconds to minutes. Higher the developing time, one has a better control for high definition patterns. Regardless of the method used, it should always be followed by thorough rinsing and drying to ensure that the developing action will not continue after the developer has been removed from the wafer surface. In order to remove the excess solvent and to harden the photoresist and improve adhesion of the photoresist, post baking/hard-baking is necessary. There are also physical methods such as reactive ion etching and plasma etching to develop the pattern. In these cases, the polymer does not come in contact with the solvents. This is particularly advantageous in the case of negative photoresists as the swelling of the polymer is avoided.

### 20.3.4 Resolution, Sensitivity and Contrast

The resolution of a resist is defined as the smallest line-width to be consistently patterned. For positive resist, it is related to rate of chain scission and the rate of solubility with the molecular weight. Lower the molecular weight of the polymeric resist, higher the resolution. A disadvantage of negative resists is the fact that their exposed portions swell as their unexposed areas are dissolved by the developer. This swelling, which is simply volume increase due to the penetration of the developer solution into the resist material, results in distortions in the pattern features. This swelling phenomenon can limit the resolution of a negative resist. The unexposed regions of positive resists do not exhibit swelling and

## 20.4 LITHOGRAPHY TECHNIQUES

The different lithography techniques are briefly described in the following sections.

### 20.4.1 Photolithography

The resolution limit in conventional projection optical lithography is largely determined by the well-known Rayleigh's equation. The resolution, R and the corresponding depth of focus (DOF) are given by the following[9],

$$R = k_1\lambda/NA, \text{ and} \tag{10}$$

$$DOF = k_2\lambda/NA^2; \tag{11}$$

where λ is the exposure wavelength, NA is the numerical aperture of the optical system, and $k_1$ and $k_2$ are constants that depend on the specific resist material, process technology, and image formation technique used. High resolution photolithography, therefore relies, photon beam wavelengths shorter than visible range, deep in UV such as from excimer lasers (248 nm and 193 nm) (Fig. 20.7). At such short wavelengths, absorption loss from the optical components and air is considerable and may call for preventive measures using suitable instrumentation involving vacuum. There are many variations of photolithography aimed at circumventing the diffraction limit.

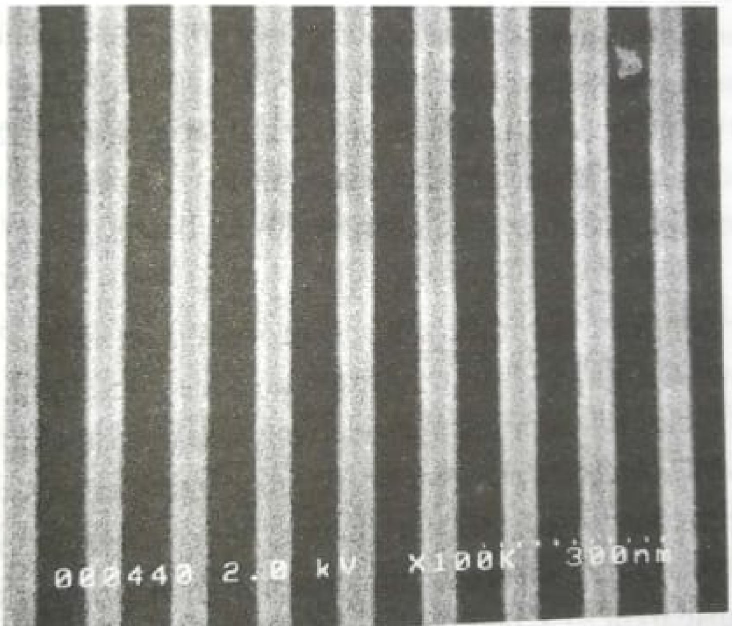


**Fig. 20.7** *Patterns generated on PMMA by EUV microlithography system (reproduced from ref. 10).*

The simplest photolithography technique is contact lithography, wherein the mask and the resist-coated substrate are brought intimate contact and exposed. The resolution purely depends on the mask dimension and diffraction at mask edges. Proximity lithography is a modification of contact lithography, where there is a small gap of 3–50 μm between the mask and the resist-coated substrate. The photon source gets diffracted by the mask patterns and produces the final pattern. In another type projection lithography, the optical system provides an image of the mask on the resist-coated substrate, with reduction projection, features of 1μm can be brought down to 0.2 μm easily.

A method of phase shift lithography includes forming a chromeless phase reticle with a pattern of parallel, spaced phase shifters. The phase shift reticle is placed between an exposure source (e.g., UV light) and a substrate having a layer resist formed thereon. Following an initial exposure, the phase shift reticle is rotated and the substrate is exposed a second time. The resist is then developed to form features in areas of resist that have not been exposed. These areas correspond to the projected points of intersection of the phase shifters. Using a positive tone resist, solid resist features are formed. These solid features can be used as mask blocks for etching the substrate to form field emitter sites for a field emission display. Using a negative tone resist, open areas are formed in the resist and can be used to deposit a material on the substrate, such as a contacts for a semiconductor structure. The method of the invention can also be implemented using two different reticles with intersecting patterns or using a single reticle having intersecting phase shift areas.

The stencil method is based on selective deposition of material through shadow masks (micro- and nanostencils). The main added value of this technique is that it does not rely on photoresist processes. Although photolithography is still the main method used for creating micro- and nanostructures in thin films, it requires several process steps, for example, application of photoresist, exposure, development, evaporation of a thin film, and lift off. The stencil method can create a structured thin film in one process step. The deposited structures can either be used directly, transferred into a sub-layer, combined by lift-off processes, or refined by self-assembly or other growth processes. The stencil method typically uses solid-state membranes with structures in the nanometer range (<100 nm) in combination with micrometer features (>10 μm). These patterns can be transferred to a substrate in a single process step, potentially in a non-contact mode. These specifics make the stencil method applicable to surfaces that are either mechanically unstable, such as cantilevers and membranes, and/or functionalized for, e.g., bio-sensor applications.

Collimated X-rays are also used as source and this process is known as X-ray lithography (XRL). Being much shorter in wavelength (~1 nm), X-rays provide increased lateral resolution and in addition, a higher depth of focus. Scattering is also relatively less in case of X-rays. The most commonly known X-ray resist is PMMA, which is a positive resist and is being extensively used whereas negative resists, such as polyglycidylmethacrylate (PGMA), have also been developed. The mask used for XRL basically consists of a pattern of X-ray absorbing materials, such as Au (high atomic number material) on a substrate relatively transparent to X-rays such as Ti, Si, SiC, $Si_3N_4$, BN and B (low atomic number materials).[11] For resist removal and etching, usually physical methods are employed (Fig. 20.8).

### 20.4.2 Charged Particles-based Techniques

Apart from using light sources for lithography, charged particle beams of electrons, protons or ions are extensively used for patterning the polymeric films. These are preferred over the light-based techniques because the de Broglie wavelengths of these particles are sufficiently short (<0.1 nm) that they minimise the effects of diffraction that currently limit many photolithographic approaches. In addition, they allow high depth and fine focus. These techniques are generally performed in high

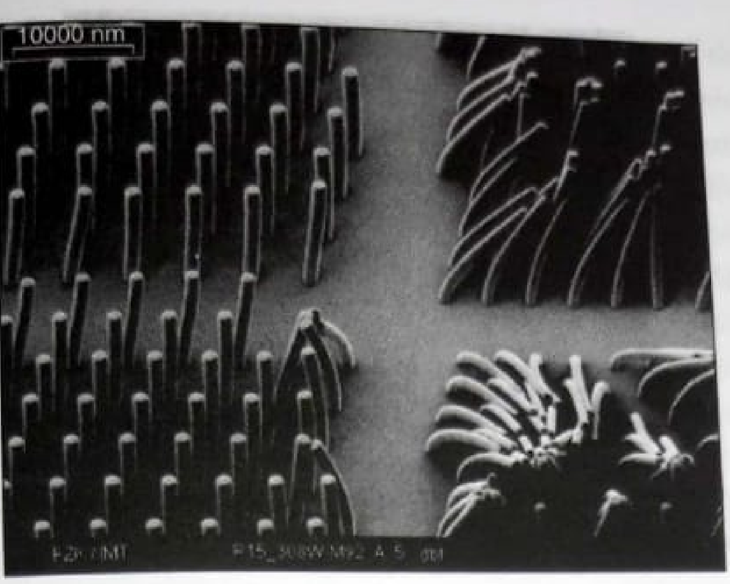


Fig. 20.8 *Patterns generated by X-ray lithography on a 10 µm SU-8 film, fields of columns with different diameter and pitch. Patterns themselves indicate for the limit of stability (reproduced from ref. 11).*

vacuum conditions unlike photolithography. The exposure dose has units of charge deposited by the beam per unit area (µC. $m^{-2}$). Electron beam lithography (EBL), in which a beam of electrons is used as the exposure source, has extremely high-resolution capabilities combined with a large depth of focus. The patterning can be done in serial or parallel method depending on the type of patterns to be generated. Field emission sources are preferred over thermionic guns, because of high achievable beam currents and focus. The beam current is in the range of pico to nanoamperes. The shorter wavelength possessed by the 2–50 kV electrons are not limited by diffraction unlike photolithography. While using a finely-focused electron beam makes it possible to delineate extraordinarily fine patterns down to 10 nm, EBL does suffer from proximity effect due to secondary electrons.[12] Besides, writing of chip-scale patterns with a single e-beam is rather a slow process. According to the pattern complexity, the exposure time for writing also becomes very long, hence low throughput. Therefore, EBL remained as a high-end technique and was primarily employed to make high resolution masks and reticular structures. However, with the advent of high current sources and faster electronics for the last two decades, EBL is now being applied for raised patterns of metals, semiconductors and polymers in fine-scale devices. EBL is also used in the small-scale production of the specialised very high frequency devices (Fig. 20.9).

PMMA was one of the first resists developed for EBL in 1968 and is the highest resolution resists commonly available. PMMA is a chain-scission type resist, which allows for high resolution because of its high contrast. Another popular positive resist is ZEP. Negative resists such as hydrogen silsesquioxane (HSQ), work by cross-linking and in general the patterns they produce in EBL are not as good as those produced with positive resists. The patterns suffer due to swelling during development and bridging between features. The sensitivity of a e-resist is dependent on the beam current and the e-beam voltage. Sol gel precursors are also cast into the patterns generated by EBL (Fig. 20.10). As a rule of thumb, the sensitivity scales proportionally with the acceleration voltage. For example, ZEP

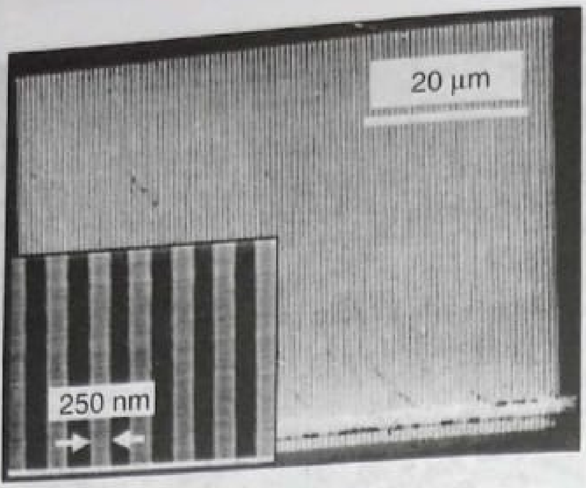


**Fig. 20.9** *SEM image of the stripe-electrode structure fabricated by e-beam lithography, with a detail (reproduced from ref. 13).*

has its sensitivity of 200 μC.cm$^{-2}$ at an acceleration voltage of 100 kV. This dose will be reduced to around 60 μC.cm$^{-2}$ at 30 kV! PMMA can be patterned using electron dosage of 10 μC.cm$^{-2}$ at 30 kV. If the dosage is increased, it behaves like a negative resist, however, the resolution will be degraded to about 50 nm. Generally for most resists, the e-dosage varies from few μC.cm$^{-2}$ to C.cm$^{-2}$. The dosage is calculated based on the dose given per pixel.

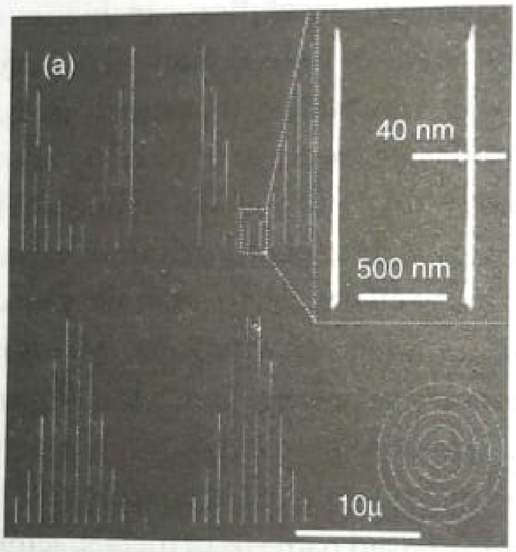


**Fig. 20.10** *Backscattered electron image of ZnO patterns starting with sol-gel precursor on SiO$_2$ substrates annealed in air at 700 °C for 20 min (reproduced from ref. 14).*

$$\text{Area dose} = (\text{beam current} \times \text{exposure time} \times \text{number of passes})/\text{area per pixel} \quad (12)$$

$$\text{Line dose} = (\text{beam current} \times \text{exposure time} \times \text{number of passes})/\text{length of the pixel} \quad (13)$$

By analogy to EBL, focused-ion beam lithography (FIB)[15, 16] scans an ion beam across a surface to form a pattern. Application of a very high electric field onto a liquid metal source, such as Ga, generates ions (Ga$^+$), which are focused by electrostatic lenses. The development of liquid metal ion source (LMIS) is crucial for the development of FIB. The ion beam may be used for directly sputtering the surface, or to induce chemical reactions in the resist layer. Re-deposition of the sputtered material is a common occurrence, which affects the final surface profile. In the case of resist exposure, even though the beam spot size is smaller, secondary electrons limit the achievable resolution to about 30 nm. FIB is commonly used for repair of photomasks, such as Au on Si. PMMA is the commonly used resist for patterning. Other ions used are $H^+$, $He^+$ and $Ar^+$ ions. Of late, $H^+$ based ion beams are increasingly used in lithographic techniques, known as proton beam lithography. Neutral metastable atoms can also be used for particle-based lithography. Neutral atoms are attractive partly, because they do not electrostatically interact with one another. Their neutrality requires, however, development of new types of optics based on light forces. Initial results are encouraging: features as small as ~50 nm have been fabricated in a single step over large areas with stencil masks and ~70 nm features have been produced using directed deposition with light force lenses. 3-D nanostructuring is also done using FIB (Fig. 20.11).

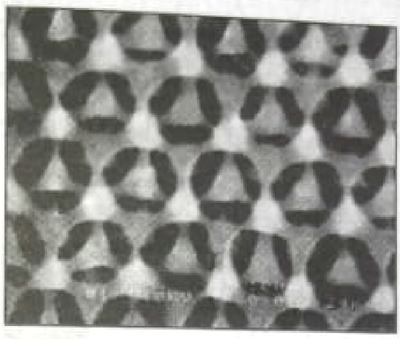


**Fig. 20.11** *3-D inverse cylinder structure created using FIB (reproduced from ref. 17).*

### 20.4.3 Scanning Probe Lithography Techniques

Scanning probe lithography (SPL)[18] encompasses techniques that use sharp (<50 nm) tips scanned near the surface of a sample in the configuration of scanning tunneling microscopes (STMs) and atomic force microscopes (AFMs) or many variations. Although scanning probes were originally designed to provide high-resolution images of surfaces, their lithographic capability was demonstrated in a set of experiments with an STM, just five years after the first STM images were recorded. A large electrical bias applied between a tungsten tip and a Ge surface caused transfer of a single atom from the tip to the surface.[19] Since then, STMs and AFMs are being employed in many different ways to perform sophisticated lithography. Of the two, AFM is more popular due to variations possible.

Advantages of SPL methods include resolution that approaches the atomic level, the ability to generate features with nearly arbitrary geometries, and the capability to pattern over surface topography that deviates significantly from planarity. However, these methods are serial and have writing speeds that are typically limited by the mechanical resonances of the tips and the piezoelectric elements that maintain constant separation between the tips and the sample. This problem is partially overcome in AFM by hosting parallel cantilever tips to perform repetitive patterning.

There are many variations of AFM-based lithography techniques. A biased AFM tip under the influence of water from the ambient can locally oxidise the substrate (usually Si), which is termed as identity of nanopatterns have also been probed. Patterning of Ni catalyst for the selective growth of GaN nanotubes has also been demonstrated. Large-scale patterning is also feasible by employing parallel pen plotters and inkwells. Recently, nanofountain pen technology has been utilised to dispense liquid materials directly on to the substrate (Fig. 20.13).

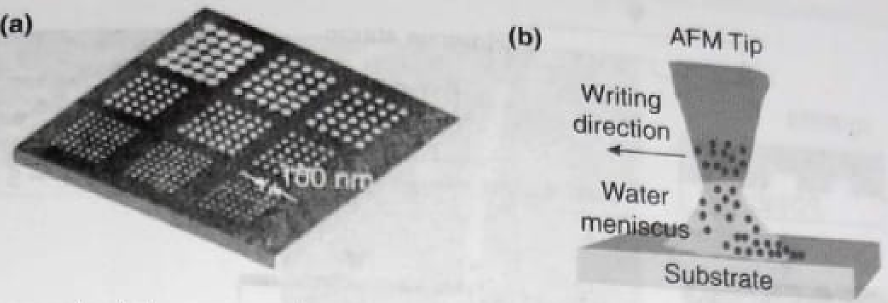


**Fig. 20.13** *(a) Nanoscale dot arrays written on a polycrystalline Au surface with mercaptohexadecanoic acid and (b) A schematic of the DPN technique (reproduced from ref. 25).*

### 20.4.4 Soft Lithography

This is an extension of stamping method to micro and nanolithography. Soft lithography[26, 27] (see Fig. 20.14) is the collective name for a set of lithographic techniques: replica molding (REM), microcontact printing (μCP), micromolding in capillaries (MIMIC), microtransfer molding (μTM), solvent-assisted micromolding (SAMIM), and near-field conformal photolithography using an elastomeric phase-shifting mask. These techniques use a patterned elastomer (usually PDMS) as the mold, stamp, or mask to generate or transfer the pattern with feature sizes down to 100 nm. Soft lithography offers immediate advantages over photolithography and other conventional microfabrication techniques for applications, in which patterning of nonplanar substrates, unusual materials, or large area patterning are the major concerns. It provides a convenient, effective, and low-cost method for the formation and manufacturing of micro- and nanostructures. It is especially promising for microfabrication of relatively simple, single-layer structures for uses in cell culture, as sensors, as microanalytical systems, in MEMS, and in applied optics. The initial success of soft lithography indicates that it has the potential to become an important addition to the field of micro- and nanofabrication. Nanoimprint lithography is a novel method of fabricating nanometer scale patterns. It is a simple process with low cost, high throughput and high resolution. It creates patterns by mechanical deformation of imprint resist and subsequent processes. The imprint resist is typically a monomer or polymer formulation that is cured by heat or UV light during the imprinting. Adhesion between the resist and the template is controlled to allow proper release.

### 20.4.5 Direct Write Techniques

Dip-pen lithography (DPN) is a good example of a direct write technique. Direct write techniques are simple and straightforward. In other words, the number of process steps are minimal, usually 'filling the ink' and 'writing'. Post processing may be as simple as drying in air! EBL or FIB based direct write

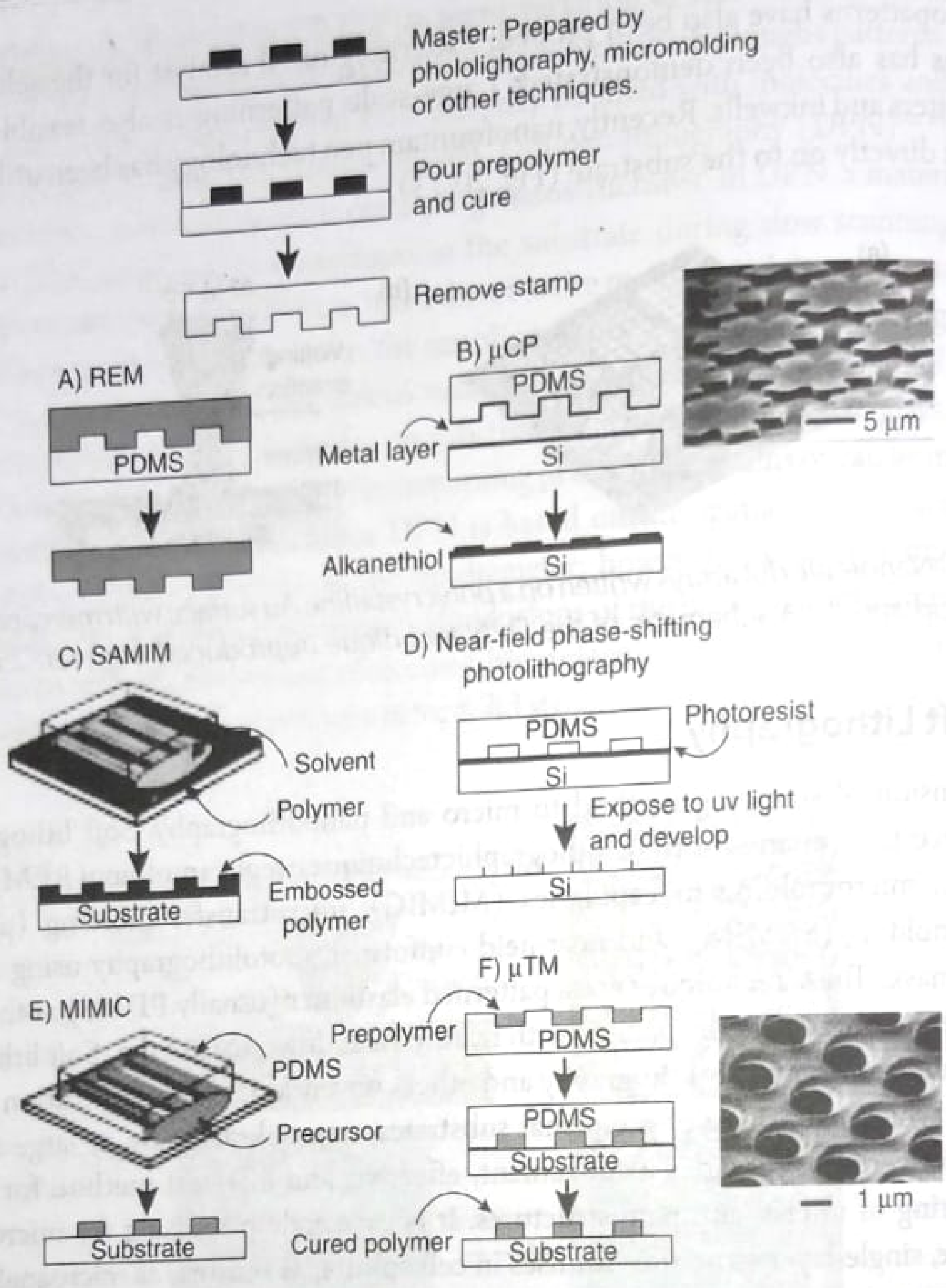


**Fig. 20.14** *Different soft lithographic processes with some typical examples* (reproduced from *ref. 26–31).*

techniques[31–33] have been around for quite some time. Electron or focused ion beam-induced deposition (EBID or FIBID) is a direct-write process, in which a pattern is defined directly by a focused electron (ion) beam, without any additional processes or treatments. In a typical setup, metal-organic precursor molecules (generally of W, Fe, Au and Pt) are directed onto a substrate by a gas nozzle in the e-beam vacuum chamber. Under the influence of a focused e-beam, the adsorbed molecules are dissociated into volatile and non-volatile fragments (Fig. 20.15). Depending on the precursor molecules, these fragments form a metal rich deposit. The volatile components are pumped away by the vacuum system. These techniques are usually employed to define interconnects soldering nanoelements in circuitry. The deposit may have poor electrical characteristics, because of carbon contamination from the organics.

Instead of cracking the vapour phase precursors by the electron beam, there is increasing interest worldwide, to innovatively come up with direct write resist precursors (Fig. 20.16), that may be coated in the solid form on substrates. These resists uniquely possess the ability to pattern (resist action) and at the same time, transform into desired nanomaterial in a single-step processing. Recently, there are innovations in stamping methods that allow direct patterning of the nanomaterial (Fig. 20.17).

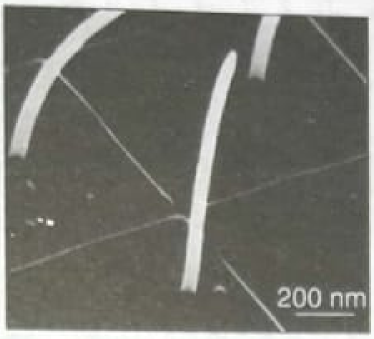


**Fig. 20.15** *Electron beam deposition of 50 nm thin, 1 μm tall, Pt nano-wires (reproduced from ref. 35).*

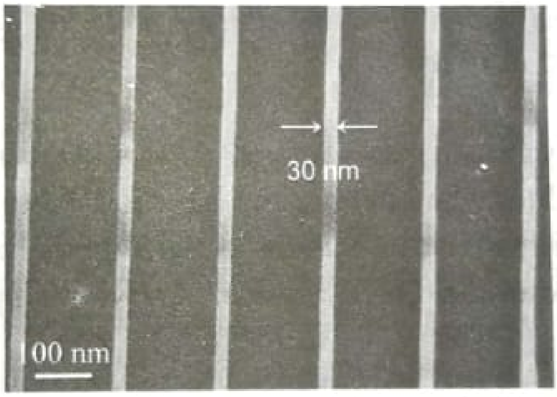
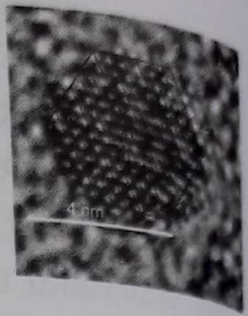


**Fig. 20.16** *SEM image showing thermolyzed Pd nanowires of ~30 nm width (reproduced from ref. 36).*

## 20.4.6 Sub-100-nm Lithography

The terminology, sub-100-nm lithography, is applied to clearly distinguish those recipes, which enable one to perform patterning below 100 nm as against those which do not. Such a distinction is but natural as materials below 100 nm behave differently due to quantum confinement. Accordingly, the implications and their potential applications are of immense importance. The sub-100-nm recipe itself may have been derived from any known lithography technique or from a new combination of techniques. SPL techniques, such as DPN[23] are good examples for sub-100-nm lithography techniques. EBL, EBID and FIBID techniques as well, on routine basis, can reach below 100 nm. The smallest values identified so far are 1.9 nm for lines and 0.72 nm for dots! The de Broglie wavelengths of the charged particles can be sufficiently short (<0.1 nm), keeping broadening due to diffraction effects minimal, unlike many photolithographic approaches. However, phase-contrast photolithography and such methods have intelligently brought the resolution down to below 100 nm. Scientists at IBM have

# Chapter 5



# SELF-ASSEMBLED MONOLAYERS

*Self-assembled monolayers are important nanostructured systems which are two-dimensional nano assemblies. The structure of this assembly is such that it facilitates precise control of molecules. Various spectroscopic, scattering and imaging techniques have been used to understand the structure of self-assembled monolayers in detail. These assemblies have been used in a number of applications, mostly in the area of sensors. A protoptypical molecular nanomachine has been by built by using SAMs. The diversity of SAMs allows almost anything to be grown on them through appropriate chemistry.*

## Learning Objectives

- What are the various kinds of monolayers?
- What are self-assembled monolayers? What are their properties?
- What are their applications?
- How can one use them for nanotechnology?

## 5.1 Introduction

The bottom-up approach of manufacturing nano devices has been demonstrated very well. The most celebrated example is the iron corrals and the molecular abacus made by IBM researchers (Ref. 1). However, the use of such an approach to make devices, i.e. placing atoms one at a time to form a functional structure, cannot have a high throughput. The alternate approaches for making functional nanostructures must involve self-assembly. In this approach, once the process begins, structures are formed without external intervention. The structure organizes itself, on the basis of external conditions. The information required to form the structure is contained in the molecules themselves. The structure is organized by utilizing weak interactions such as hydrogen bonding, and van der Waals interactions, and there are numerous interactions of this kind in a structure which makes it stable. These are the interactions which make and sustain life, and there are numerous examples of such interactions in the world around us.

Monolayers are single-molecule thin layers prepared on surfaces. They can be assumed to be molecularly thin sheets of infinite dimension, just like ultra thin foils. They are among the simplest chemical systems on which nanotechnological approaches can be practised. This feasibility of using monolayers arises from the simplicity of their design and molecular structure and from the user's ability to manipulate them at ease. The possibility of bringing about patterns of nanometer spatial resolution allows one to incorporate multiple functions within a small area.

The concept of monolayers was first introduced by Irving Langmuir in 1917, during his study of amphiphiles in water (Ref. 2). While spreading the amphiphiles on water, he found that the film formed had the thickness of one molecule. Later Katherine Blodgett was able to transfer the monolayer onto a solid support (Ref. 3). The spontaneous formation of a monolayer was first reported by Zisman, *et al.* in 1946 (Ref. 4). They observed the spontaneous monolayer formation of alkyl amines on a platinum surface. The field observed a tremendous growth when in 1983 Nuzzo and Allara found that ordered monolayer of thiols can be prepared on a gold surface by the adsorption of di-*n*-alkyl disulfides from dilute solutions (Ref. 5).

The name self-assembled monolayers (SAMs) indicates that their formation does not require the application of external pressure. The study of SAMs generates both fundamental as well as technological interest. Nature uses the same process of self-assembly to produce complex architectures. One such example is the formation of the cell membrane from lipid molecules through self-assembly. SAMs are ideal systems which can answer fundamental questions related to interfacial properties like friction, adhesion and wetting. They have been used to alter the wetting behavior of the condenser plates in steam engines. This is because the drop-wise condensation of steam enhances the efficiency of the engine as compared to the film-like condensation. In the latter case, the film acts as an insulator between the metal plate and steam. The two approaches used to make a monolayer of a molecule on a metal surface are discussed as follows:

***1. The Langmuir—Blodgett Technique*** The Langmuir film is prepared by spreading amphiphilic molecules on a liquid surface. Considerable order can be achieved in these films by applying pressure. The film is then transferred to a solid substrate. The various steps involved during the preparation of Langmuir–Blodgett (L–B) films are shown in Fig. 5.1.

***2. Self-assembly*** As mentioned earlier, the formation of a self-assembled monolayer does not require the help of an external driving force. Such a monolayer is formed when the metal (or any other substrate) surface is exposed to a solution containing the surfactant (Fig. 5.2).

## 5.2 Monolayers on Gold

Alkanethiolate monolayers (Ref. 6) grown on coinage metals (Au, Ag, Pt)—the molecular sheet is made of thiolate species (with long alkyl chains) and the substrate is one of the above metals—are structurally simple and easy to construct, which is why a larger number of studies have been conducted on them. It is important to mention that there are several other kinds of monolayers and a review of these is available in (Ref. 7).

–0.3 and +1.5 V versus Ag/AgCl in a voltammetric cell. During the positive potential sweep, the surface is oxidized and in the negative sweep, the oxide is reductively removed. Cyclic voltammetric measurements carried out in this way facilitate the calculation of the effective surface area from the peak area.

## 5.2.1 Preparation

SAMs are prepared by dipping substrates such as evaporated gold films into a millimolar solution of the surfactant. The gold films of 500–2000 Å thickness are made on substrates. The solution is normally made in hexane for long-chain surfactants and in ethanol for short chain surfactants. The process of assembly of monolayers on the surface involves two stages. During the first stage, the surfactants are rapidly pinned on the surface, followed by a slow reorganization step, during the second stage, extending over several hours (Ref. 8). The exact kinetics of both these steps depend on parameters such as the concentration of the solution, length of the alkyl chain, etc. It is a standard practice to leave the substrate in the solution, face up ('face' refers to the gold coating), for periods ranging from 12–24 hours for complete self-assembly. Before being used, the monolayer surfaces are washed and blown dry with nitrogen. The kinetics of initial pinning can be monitored by a quartz crystal microbalance whereas the extent of organization can be studied through infrared spectroscopy. A monolayer of a mixture of alkane thiols can be prepared starting with a mixed solution of the concerned thiols. A mixed thiol monolayer can also be formed through a ligand place exchange reaction in which one surfactant molecule replaces another that is already present on the surface. Monolayers can be formed by microcontact printing wherein the thiol solution is used as ink on a stamp that is prepared from a polymer. This approach is especially useful in preparing patterned surfaces (see Section 5.5). Other methods that have been used to make SAMs include vapour phase deposition on molecules, LB methodology and potential-assisted deposition.

## 5.2.2 Structure

Two types of sites are available for the thiol chemisorption on the Au(111) surface, the on-top site and the hollow site. *Ab-Initio* calculations have shown that the charge of sulphur at the hollow site is –0.7e and that at the on-top site is –0.4e. Hence the hollow site is the energetically favorable one from the point of view of charge-transfer. Thiolate can migrate between the two adjacent hollow sites. This can happen either through the on-top site or through the bridge site. In both cases, the excited state will be polar. The excited state during such migration will then be stabilized by polar solvents. This is confirmed by the fact that ordered SAMs are formed in ethanol. Figure 5.3 shows the overlayer structure of the monolayer with sulphur atoms occupying alternative hollow sites above the Au(111) layer, giving a hexagonal $(\sqrt{3} \times \sqrt{3})$ *R*30° unit cell (the symbolism refers to the crystallographic structure of an overlayer).

In this assembly, alkyl chains are in close contact with each other and the chains are fully stretched to form a zig-zag assembly. As a result of this close contact and due to the large distance between the sulphur atoms, the chains tilt. The tilt angle is 34° in the case of Au(111), but it is 5° in Au(100). The chains have rotational freedom at room temperature, which means there is no three-dimensional order in the arrangement of different chains. The adjacent chains are rotationally disordered and this persists at a low temperature. In fact, the freezing of the rotational disorder can be seen in low temperature infrared spectroscopy (Ref. 9). The presence of very bulky groups at the tail end can affect this order, as molecules may not get attached to all the available surface sites. The structure of alkane thiol monolayers on Au(111) is shown schematically in Fig. 5.3.

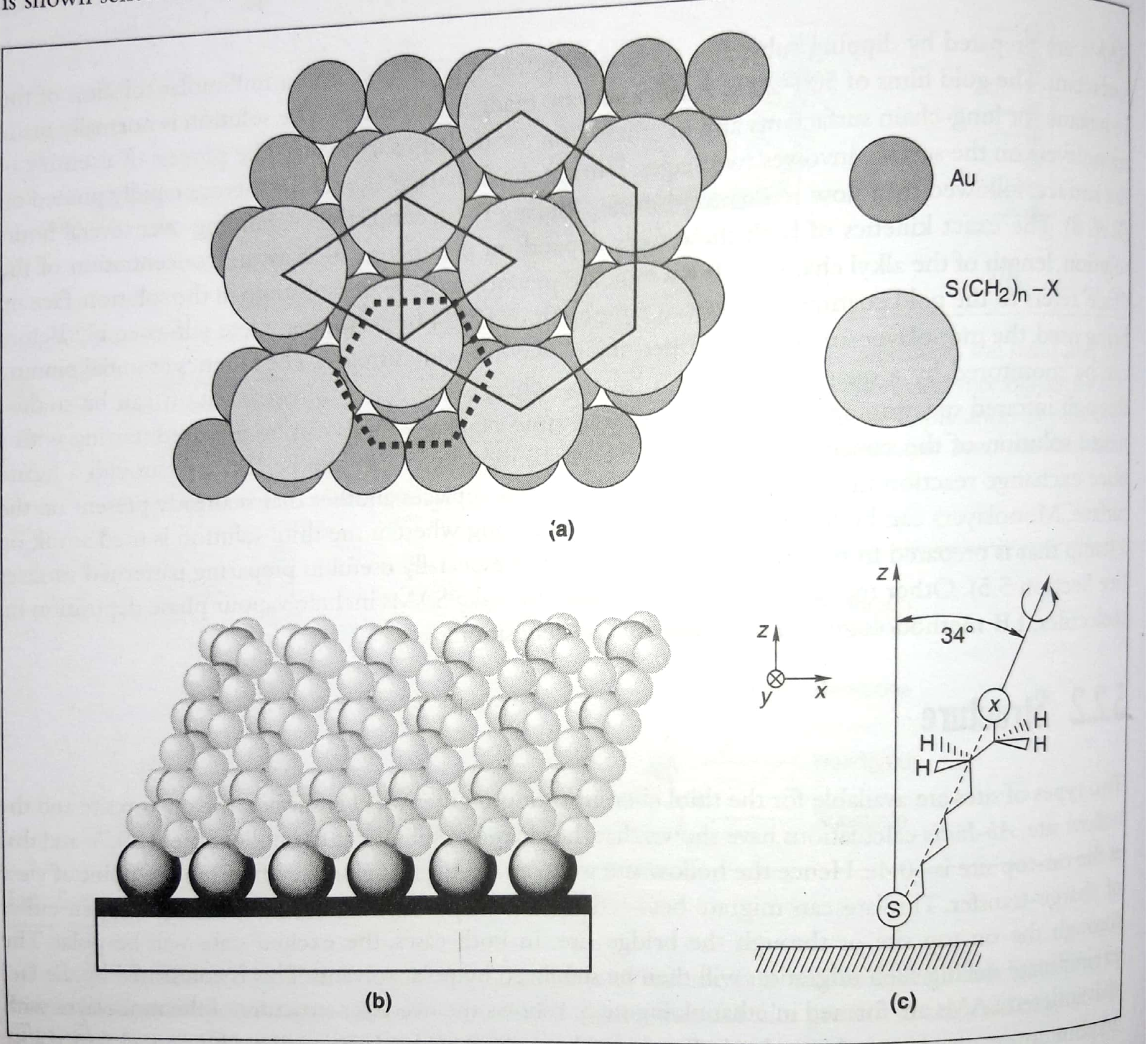


**Fig. 5.3:** *Schematic structure of a monolayer of alkanethiol on Au(111). (a) Layer of hexagonally arranged gold atoms (dotted hexagon). Each corner of this dotted hexagon corresponds to the center of the gold atom. On top of this surface, the alkanethiol molecules chemisorb. The structure of the sulphur atoms is also hexagonal (solid hexagon), as indicated. These atoms sit on three-fold sites created by the gold atoms. (b) Assembly of thiolate chains. This will form a two-dimensional sheet on the surface. (c) Extended chain. It shows a zig-zag assembly. The tilt angle is shown. It is also shown that the chains have rotational freedom. X is a functional group.*

As mentioned above, this structure is present for several hundreds of angstrom square area. The underlying surface itself is not ordered over an extended area and the typical grain size (within this region, the surface structure is uniform) is of the above dimension. This limits the growth of an ordered SAM over the entire area of the substrate. At the edges of the grain, the monolayer structure is not ordered due to defects in the structure of the gold. There are ways to increase the area of the ordered region such as high temperature annealing.

SAMs can be formed on other surfaces such as Cu, Ag, Pt, GaAs, etc. The coverage of molecules on these surfaces is in the order Cu>Ag>Pt>Au>GaAs, which is a direct consequence of the adsorbate structure. On Ag(111), the overlayer structure is the same as that of gold, but the tilt angle is only 12° and not 34°. This reduced tilt angle reduces the contact distance between the chains (4.1 Å and not 4.95 Å). On a GaAs(100) surface, a large tilt angle of 57° is reported (Ref. 10).

The chain length affects the order of the alkyl chain assembly. In the case of chains of longer thiols, the van der Waals interaction between the chains is large to enable all the chains to stand up. This makes the carbon chain assembly all-trans and reduces the number of defects. 'All-trans' means that the carbon atoms on either end of a C–C bond are trans to each other. This makes the alkyl chain appear like a zig-zag ladder-like structure. However, as the chain length decreases, the van der Waals interaction becomes weak and defects occur. These defects imply the incorporation of gauche conformations. The extent of order in the alkyl chain assembly manifested depends on the technique used for its investigation. The best tool to see the order is surface infrared spectroscopy, which shows a red shift in the methylene C–H stretches as a function of order. Peaks at 2918 and 2846 $\text{cm}^{-1}$ are characteristic of ordered alkyl chain assembly. Decreased order is observed when the chain length is less than 11, and when the length is less than 6, the assembly is assumed to be disordered. When the groups at the chain ends have a smaller cross-sectional area than that of the alkyl chain, the hydrocarbon chain assembly is the same as that of the alkyl thiol. This is the case with all monolayers with chain ends such as $-OH$, $-NH_2$, $-CONH_2$, $-CO_2H$, $-CO_2CH_3$ in addition to simple $-CH_3$. However, in the case of larger end groups, the chains cannot pack as efficiently as in the case of simple thiols.

The structure of the monolayer varies with the structure of the gold below it. Au(111) is thermodynamically the most stable surface due to the largest surface density of gold atoms. Therefore, in the case of evaporated or annealed gold, the surface is principally Au(111). A film of this kind can be grown on mica wherein the surface will be atomically flat. An atomic force microscopic image of octadecanethiolate monolayer grown on this Au(111) film is presented in Fig. 5.4. The image scale is 3.02 × 3.02 nm. The nearest neighbor is located at a distance of 0.52 ± 0.03 nm (a) while the next nearest neighbor is located at a distance of 0.90 ± 0.04 nm (b) (Ref. 11).

Two binding modes of alkanethiol on a hollow site have been observed—one with the Au-S-C bond angle of 180° called the sp mode, and the other with Au-S-C bond angle 104° ($sp^3$ mode) (see Fig. 5.5). The energy difference between the two modes is 2.5 $\text{kcal mol}^{-1}$. Thus the thiolate can change from one mode to the other without much difficulty.

The overlayer structure of thiols on Ag(111) shows different types of lattice as shown in Fig. 5.6. The overlayer is of $(\sqrt{7} \times \sqrt{7})$ $R10.9°$ structure. The tilt angle in the case of thiols on Ag(111) surface is small as compared to gold. The observed value is about 5°. In some cases, the values were even close to zero

In XPS, X-ray is used to knock out the core electrons. Deep core electrons do not participate in bonding. Their energies are characteristic of the atoms from which they originate. Hence XPS has been used to find the elemental composition of the monolayer. At lower take-off angles, the ejection of photoelectrons from the atoms at the top layer will be much more as compared to those from the deeper layers. Hence angle-dependent XPS can be used to find the composition of the monolayer.

The capacitive charging current in an inert electrolyte can be used to measure the thickness of the monolayer by the equation $C_{ML} = \varepsilon_0 \varepsilon_r / d$, where $d$ is the thickness of the monolayer and $C_{ML}$ is the capacitance of the electrode covered with a monolayer. $\varepsilon_0$ is the permittivity of the free space and $\varepsilon_r$ is the dielectric constant of the separating material. By adding a redox couple, one can observe the Faradaic current. This gives the number of defects in the monolayer.

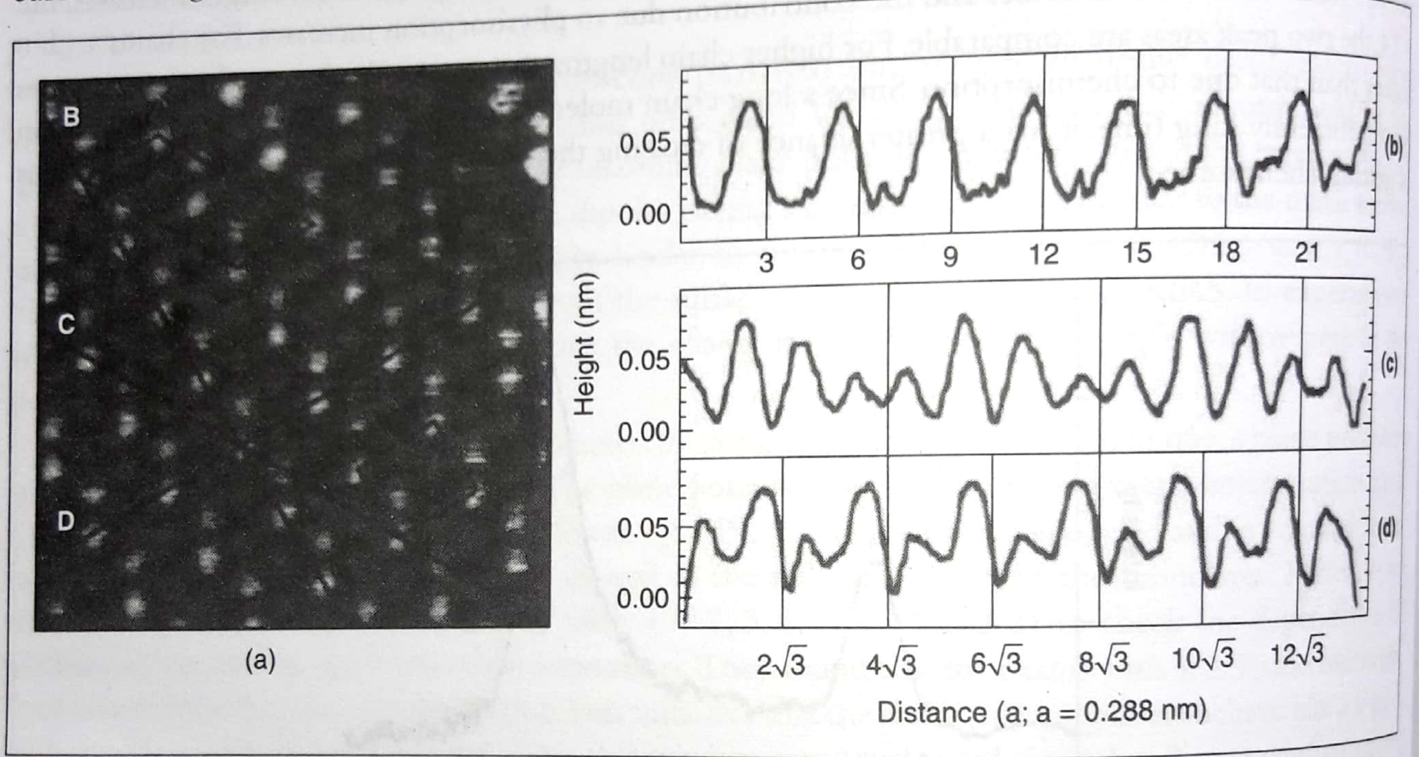


**Fig. 5.9:** *STM image of octanethiol on Au(111). Fig. 5.9(b) is the plot of the cross section labeled B in Fig. 5.9(a) running along the Au nearest neighbour direction. C and D are cross-sectional plots of Fig. 5.9(a) along the Au next-nearest-neighbour directions. Reprinted with permission from Poirier (Ref. 13). Copyright (1994) American Chemical Society.*

## 5.3 Growth Process

### 5.3.1 Growth from the Solution Phase

Various steps in the growth of monolayers are shown in Fig. 5.10.

The growth of the monolayer can be explained by using the Langmuir growth law. The rate of growth is proportional to the number of available sites given by the equation, $d\theta/dt = k(1-\theta)$, where $\theta$ is the

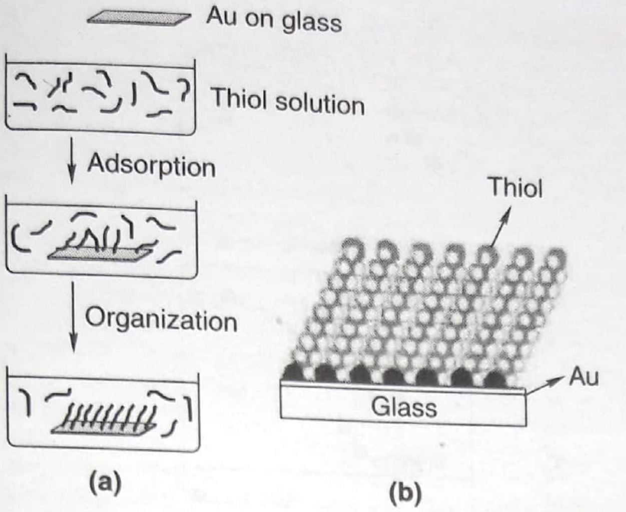


**Fig. 5.10:** *(a) Various steps during the formation of self-assembly. Gold coated glass slide is dipped in an ethanolic solution of thiol. The initial chemisorption process is very fast. This is followed by a slow step during which organization happens which takes several hours. (b) Structure of organized monolayer using a space filling model.*

fraction of sites occupied and *k* is the rate constant. Sum frequency generation (SFG) studies show three distinct steps during the growth of the monolayer. The first step corresponds to the chemisorption of the head group onto the metal surface and takes place very fast. Then the alkane chains start ordering into all-trans configuration, which is slower than the first process. During this straightening of the alkyl chain, the signal due to the $d_-$ mode (antisymmetric $CH_2$ vibration) decreases in intensity. The gradual reorientation of the terminal methyl group during the final step is indicated by the slow evolution of $r^+$ mode (symmetric $CH_3$). The evolution of different modes is shown in Fig. 5.11.

## 5.3.2 Growth from the Gas Phase

The growth of monolayer from the gas phase in UHV allows one to study the process by using various *in-situ* measurements. The study by low energy electron diffraction (LEED) shows that the first phase, occurring immediately after dosing with the adsorbent molecule, is the stripped phase. On continued deposition, the structure changes to the standing phase with C (4×2) lattice.

The growth of mercaptohexanol monolayer on a gold surface has been investigated by using STM (see Fig. 5.12). Exposing the surface to low concentration of mercaptohexanol gives strips as shown in Fig. 5.12 (pointing finger, Fig. 5.12(b)). In these strips, the sulphur atoms will be sitting in the next-nearest-neighbour three-fold hollow sites and the alkane chain will be parallel to the substrate. On increasing the dosing, this stripe starts growing and covers the whole surface (Fig. 5.12(c) and Fig. 5.12(d)). Towards the end of saturation, a new feature called 'islands' starts appearing (pointing finger, Fig. 5.12(e)). From this point onwards, the growth starts taking place in the perpendicular direction and the alkane chain will be

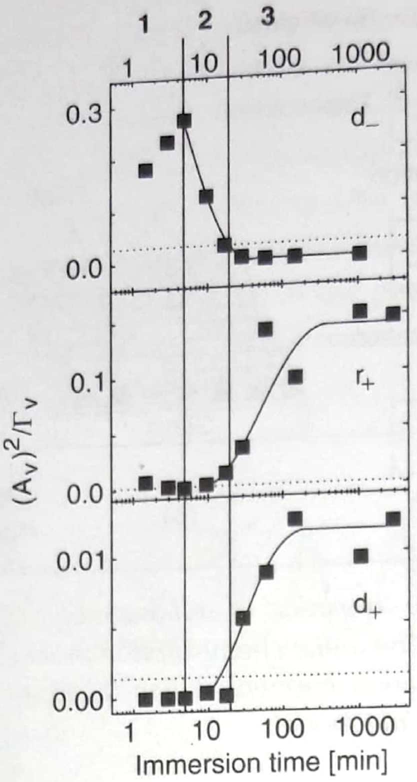


**Fig. 5.11:** *Intensities of the various modes upon the a adsorption of docosanethiol on Au(111). The three regions indicate the three steps during the growth process. Intensity of the features is plotted as a function of immersion time. Reprinted with permission from Schreiber F. (Ref. 14). Copyright (2000), with permission from Elsevier.*

perpendicular to the substrate in these islands. The Au vacancies will appear as deep pits after the island formation (Fig. 5.12(f)).

Even though the stripped phase with the alkane chain parallel to the surface, and the standing up phase with the alkane chain perpendicular to the surface, are the two important phases during the growth of the monolayer, metastable phases exist between the two extremes. This has been shown in Fig. 5.13.

### 5.3.3 Stability and Surface Dynamics

The thermal stability of SAMs depends on: (1) the strength of surface binding, and (2) the strength of lateral interaction. For alkanethiols on gold the thermal stability increases as a function of the chain length. While butanethiol monolayers desorb starting from a temperature of 75 °C, octadecane monolayers desorb at temperatures ranging from 170 to 230 °C (Ref. 15). Increasing the lateral $\pi$–$\pi$ interaction increases the thermal stability. Electrochemically the stability range of –0.1 to +0.1 V is very high, providing a large electrochemical window for most applications. This implies that a number of electrochemical processes can be conducted without monolayer desorption. The exposure of shorter chain thiols in solution can

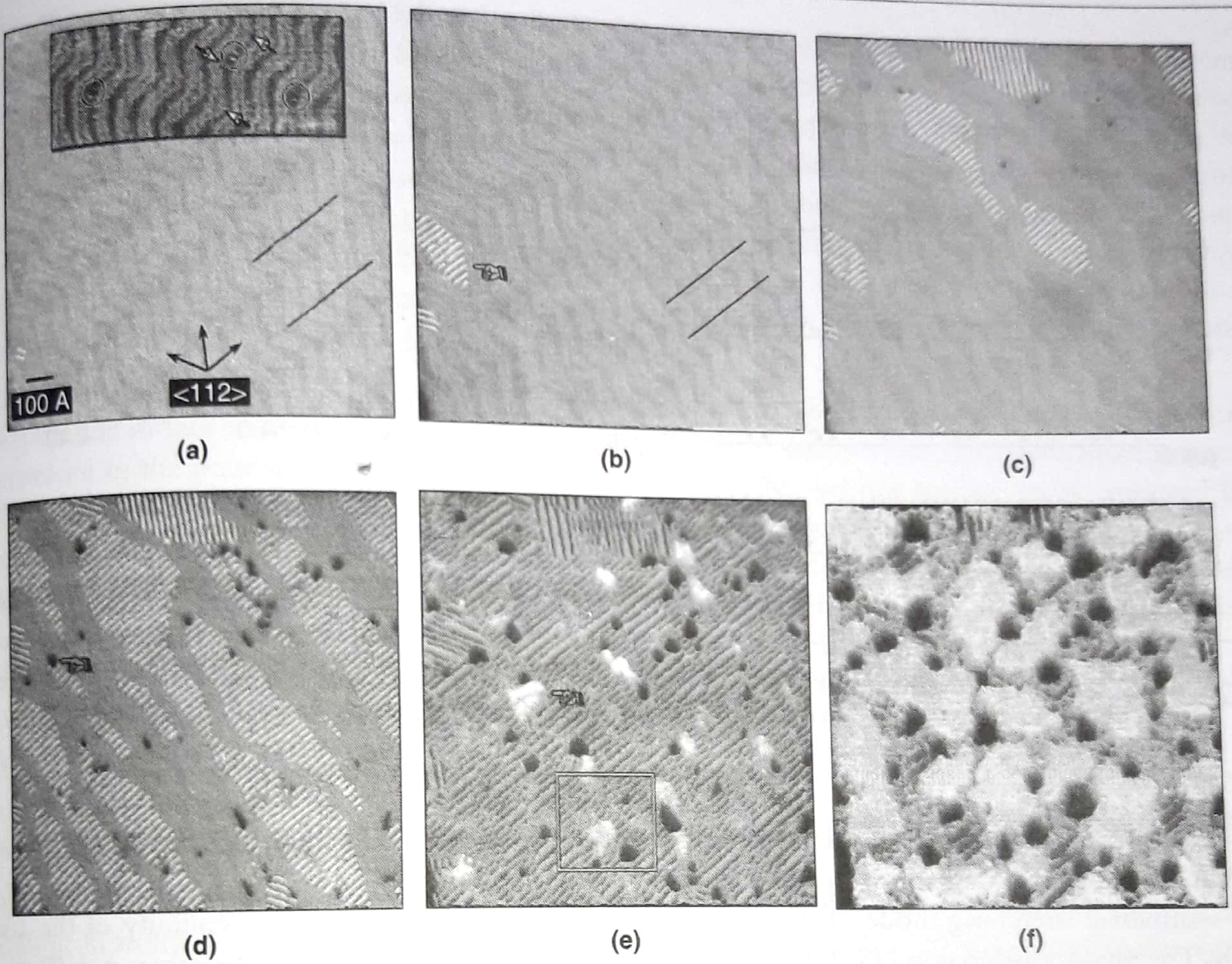


**Fig. 5.12:** *Constant current STM topographs showing the growth of mercaptohexanol monolayer from gas phase on Au (111) surface. (a) Clean Au (111) surface. (b) Stripped phase islands. (c) Striped phase growth. (d) Stripped phase growth showing Au vacancies. (e) Growth of standing up phase at the cost of the stripped phase. (f) Standing up phase growth at saturation limit. Reprinted with permission from Schreiber F. (Ref. 14). Copyright (2000) with permission from Elsevier.*

lead to the removal of defects on the SAM surface. This occurs by the exchange of monolayers at the grain boundaries, called 'ligand place exchange' and the diffusion of the monolayers, which occurs over a time window of several hours. The exposure of reactive gases such as ozone can affect the stability of the monolayer as the thiolate group can be oxidized (Ref. 16).

## 5.4 Phase Transitions

As a result of the van der Waals interaction, alkane thiol monolayers form crystalline phases on the metal surface. But as the temperature of the system increases, the orientational disorder increases. This weakens

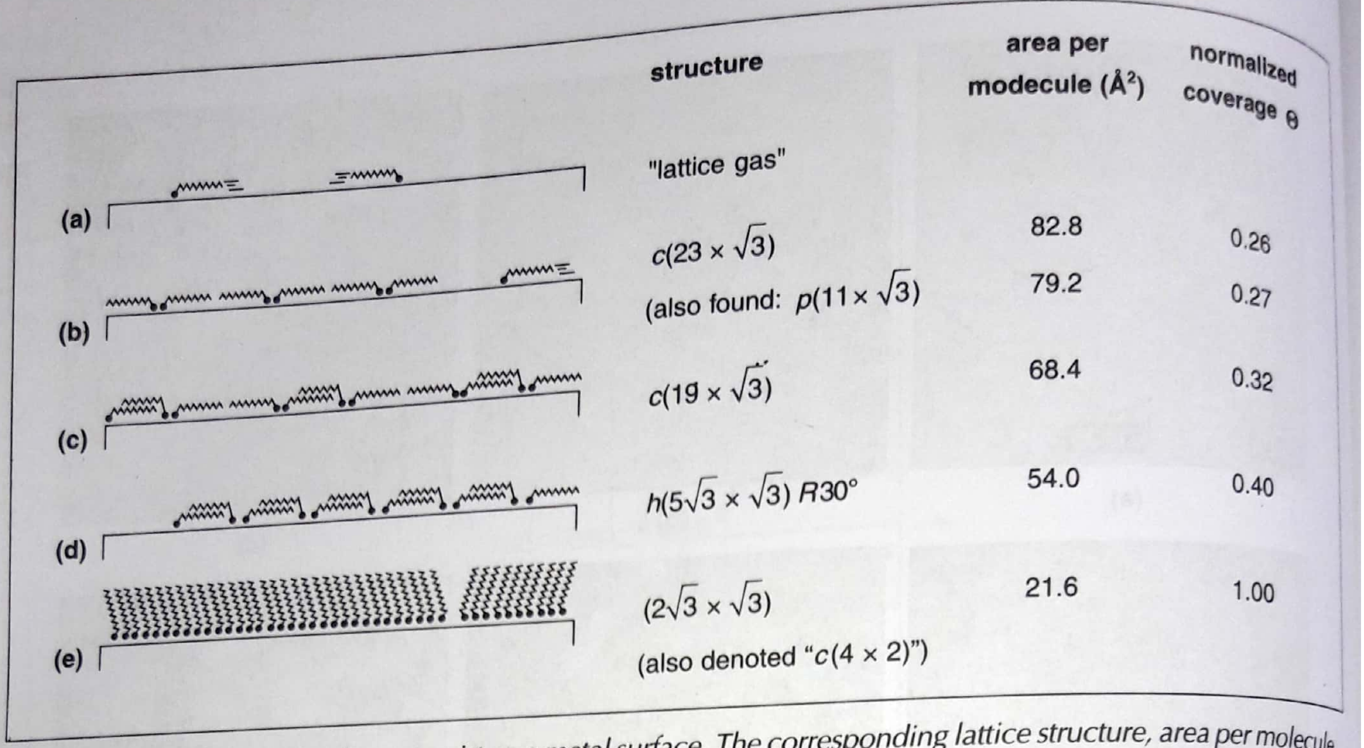


**Fig. 5.13:** *Various phases that can exist on a metal surface. The corresponding lattice structure, area per molecule and surface coverage have also been given. Reprinted with permission from Schreiber F. (Ref. 14). Copyright (2000) with permission from Elsevier.*

the van der Waals interactions, which give rise to liquid-like phases. Reflection absorption IR spectroscopy (RAIRS) has been used to study the phase transitions in planar SAMS. The position of the symmetric and anti-symmetric stretching mode of the methylene mode is indicative of the crystallinity of the alkane chains. The phase transitions in HS-$(CH_2)_{21}CH_3$/Au have been studied in detail by Bensebaa, *et al.* (Ref. 17). When the temperature was increased, the peak corresponding to $d_+$ showed broadening as well as a decrease in intensity. The same trend was shown by the $d_-$ mode also. The melting is complete at 411 K. The position of the $d_+$ and $d_-$ bands at this point exactly matches with that of the liquid alkanethiol confirming the liquid-like isotropic phase at this temperature.

## 5.5 Patterning Monolayers

SAMs are ideal templates for surface modifications. With appropriate modifications, patterned surfaces can be produced. Several methods are used for the patterning of monolayers. These belong to two kinds of routes: (1) decomposition, and (2) composition.

### 5.5.1 Decomposition

In this case, an already formed monolayer is given a desired pattern by decomposing a part of it. Patterning of the surface with a desired functionality in a specific area is important for molecular recognition. Among the several applications, one of particular importance is biorecognition wherein a biologically important material is anchored to the surface. This can be used for DNA recognition, as for instance, the binding of a DNA strand on the surface can be used to recognize the complementary strand in the solution. A change in the property of the monolayer or the substrate can be used to identify the presence of the analyte. In one of the approaches used, a mixed monolayer with mercaptopropionic acid (MPA) and mercaptohexanoic acid (MHA) was prepared first. The resultant monolayer formed segregated regions. The electrochemical potential for reductive desorption for MPA is lower than that of MHA and as a result, MPA can be selectively desorbed from the surface. By exposing a thiolated DNA, it can be bound to the region vacated by MPA (Ref. 18).

Lithography is another means of achieving patterned monolayers. The traditional lithography pathway is to expose the surface to be patterned to ultraviolet (UV) light at specific locations. On a SAM surface, UV exposure in the presence of oxygen leads to an oxidized SAM and this region can be removed by washing, thus exposing the bare metal surface. The exposed areas can be deposited with a new monolayer or can be etched away by an etchant. This process has been demonstrated on SAMs with patterns as small as 100 nm (Ref. 19). However, the problem with such methods is that the wavelength of light and patterns cannot be drawn beyond the resolution of the light used. If one wants to go to lower limits, wavelength of light has to be reduced, but in the X-ray regime, it is difficult to obtain reliable optics for manipulating light. This problem also affects the semiconductor industry.

Another lithographic method involves the use of particle beams. In this method, neutral atoms, ions or electrons are used to remove part of the surface. Patterns as small as 100 nm have been drawn with neutral Cs and Ar beams (Ref. 20).

In another method called 'nanoshaving', the adsorbate is removed physically (Ref. 21). This is achieved by scanning an atomic force microscope (AFM) tip at a load that is higher than the displacement threshold. The features can be as small as 20 nm. By conducting the shaving in a solution of another thiol, the second thiol can be deposited in regions vacated by the first, and a pattern can be created. The process is called 'nanografting'. A similar methodology can be used with scanning tunneling microscopy (STM) where the tip potential is kept high to cause thiol desorption.

## 5.5.2 Composition

In this case, a monolayer is made in a controlled fashion. Two kinds of approaches are used in composition. In the first called 'microcontact printing' (Ref. 22), a mask is generated on a polymer from the master. The mask is then inked with a thiol. Upon contact with the surface, the mask transfers the ink to specific areas of the surface. The exposed metal surface can be deposited with another thiol or the exposed material can be etched away by an etchant. Unlike in the case of beam lithography methods, microcontact printing has been used to make patterns on non-planar surfaces. The principal problem in this case, however, appears to be one of finding ways to reduce the dimension of the patterns.

The second approach is called 'dip-pen lithography' (Ref. 23). Here an AFM tip coated with a surfactant (ink) is drawn over a wet surface. The water meniscus touching the tip travels with it and solubilizes some of the molecules. In this approach, the ink can be made of a variety of materials including nanoparticles. The approach need not necessarily make a monolayer.

If the substrate can be controlled in such a way that deposition occurs only in the selected areas, patterns can be drawn. In one such approach, the potential was controlled on an array of electrodes. If this is done on selected areas of an already coated electrode, a part of the monolayers can be desorbed and another monolayer can be coated on such locations. It is also possible to control the potential on specific areas of an uncoated electrode to accelerate or decelerate deposition. Both these approaches have been used to make patterned monolayers.

## 5.6 Mixed Monolayers

One can obtain a mixed monolayer by mixing two monolayer forming species in an appropriate ratio. If the chemical constitutions of the two monolayer-forming entities are similar in terms of the alkyl chain length and the functionality, the mixed monolayer is similar to a two-dimensional alloy (two-dimensional in the sense that the film is planar, while the thickness is molecular). However, chemical differences between the species can lead to the segregation of one entity. If the two chemical constituents are separated, it is possible to anchor two different kinds of materials at these locations by using selective molecular chemistry.

## 5.7 SAMS and Applications

### 5.7.1 Sensors

The interest generated by the study of SAMs has shifted from fundamental studies to technology. The potential applications of SAMs include molecular recognition and wetting control. The chemical properties of the monolayers can be used for sensing applications. There are two important elements in a sensor, of which the first is the chemically selective recognition layer, while the second is the signal transducer which provides a signal that can be monitored. A number of approaches have been used to make selective recognition layers, which depends on the species to be detected. The fact that several of these sensing elements can be located on a given area provides the capability to sense several species simultaneously (see Chapter 12).

A variety of metal ion sensors can be made by functionalizing the metal surface with a ligand with high specificity to a particular ion. Sensors selective to $Cu^{2+}$ were made by functionalizing the gold surface with 2,2´-thiobisethyl acetoacetate. The selective detection of perchloroethylene in the presence of other molecules such as trichloroethylene, tetrachloromethane, chloroform, and toluene was achieved by using modified resorcin[4]arene as the monolayer (see Fig. 5.14). The incorporation of perchloroethlelene into the receptor site results in mass changes in terms of nanograms, which are detected with the help of a quartz microbalance oscillator.

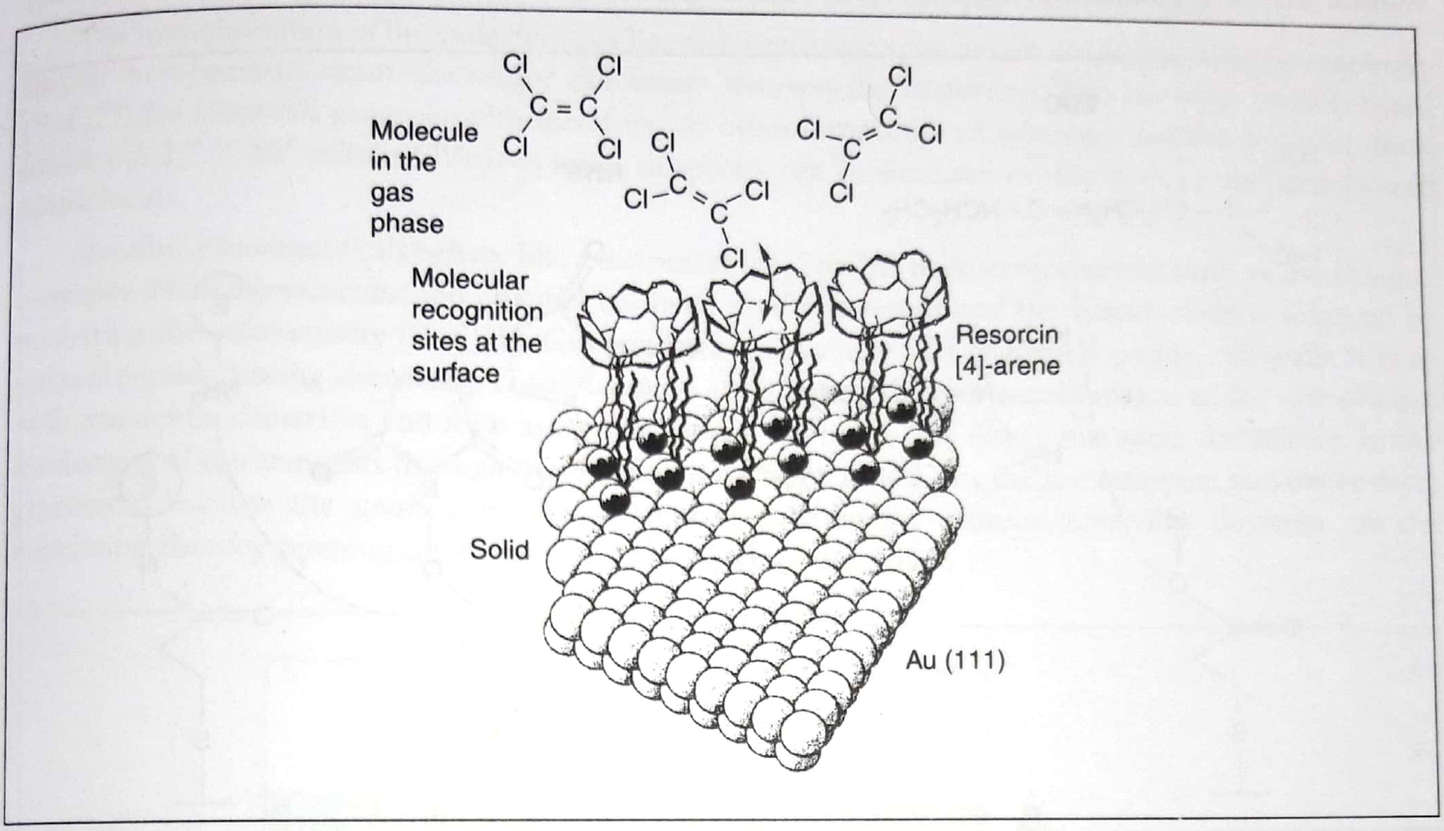


**Fig. 5.14:** *Molecular recognition by a monolayer of resorcinol on Au (111) surface. The receptor site showed high selectivity to perchloroethylene when dosed with a mixture of halocarbons. Reprinted with permission from Schierbaum, et al. (Ref. 24). Copyright (1994) AAAS.*

Among the most common examples of SAM-based sensors are enzyme biosensors. As enzymes are catalytic in action, they are also called catalytic biosensors. Here an enzyme acts as the recognition element. The signal is transduced by detecting either the molecule consumed or that generated. An example of this kind of sensor is the glucose biosensor which uses glucose oxidase (GOD), to oxidize glucose to gluconolactone. In this process, the enzyme is reduced and a mediator used in the process gets the enzyme back to the original state. In nature, $O_2$ is the oxidizer and $H_2O_2$ is produced in the process. The mediators used typically in experiments are ferrocene and ferricyanide, and their change is monitored electrochemically. The reduced form of the mediator gets oxidized at the electrochemical surface and the current generated is proportional to the amount of glucose oxidized. The immobilization of the enzyme is more controlled when it takes place on a SAM surface.

Enzyme immobilization on the monolayer surface can be achieved by several means. One method is to covalently modify the SAM by selected reactions. An approach used for this is described below. Here a mercaptopropionic acid monolayer is made on Au. The monolayer is activated by reacting with 1-ethyl-3(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS). This process makes a succinimide ester on the monolayer surface, helping amine groups of the enzyme to

## 5.7.3 Chemical Sensors

Depending on the kind of recognition element, a sensor may be biochemical or chemical. In the chemical category, the recognition element is non-biological in origin and is synthesized in the laboratory. There are several chemical sensors which use SAMs and utilize a variety of properties. Electrochemical, capacitance, plasmon resonance and mass are the most common properties utilized for transduction of the recognition event.

One of the most common sensing events is the quantitative detection of transition metal ions, especially in presence of other ions. The detection of Cu(II) in presence of Fe(III) is an example. The four-coordination preference of $Cu^{2+}$ can be provided by attaching a tetradentate ligand and the other end of the molecule can be anchored onto the gold surface. The sensor sites can be kept separated by preparing a mixed SAM. The presence of other ions does not influence the detection as they do not get attached to the electrode surface. A variety of ligands and metal ions can be used to implement this approach.

Molecular imprinting is another approach that has been developed for sensing. Here the shape of a molecule is imprinted on the monolayer surface and when the location is occupied by the analyte molecule, it is recognized as a sensing event. In one of the approaches demonstrated, a mould for the analyte barbituric acid, in the form of thiobarbituric acid, is made to bind the surface. The shape is imprinted on the surface by co-adsorbing another monolayer forming thiols. When the analyte molecule is exposed to the surface, it can bind to the cavities imprinted on the surface. This binding event changes the capacitance of the surface. Several molecules such as cholesterol, barburates, quinines, etc. have been detected in this way (Ref. 30).

## 5.7.4 pH Sensing is Ion Sensing

SAMs have been used for pH sensing by several investigators. The general approach is to have two electroactive species on the monolayer surface. While one is pH-sensitive, the other is insensitive and acts as a reference. This is seen in the case of quinine and ferrocene, both of which are immobilized on the monolayer surface. While in the first, the oxidation and reduction shift linearly with pH, the second does not show any response to pH. It is also possible to make the pH-independent electrochemistry of ferrocene pH-dependent by having a bifunctional molecule. In one of the approaches used, a ferrocene carboxylic acid is linked to the surface through a –S linkage. The oxidized state of ferrocene is stabilized by the deprotonation of the carboxylic acid group, which makes the redox chemistry of ferrocene pH-dependent.

## 5.7.5 Corrosion Prevention

When used as coatings, SAMs offer corrosion resistance. In this regard, several monolayers have been made on surfaces such as Au, Cu, Fe, etc. The chain length of the molecule has to be long enough to offer effective protection. The monolayer coating is inadequate in offering complete protection against ion penetration. The permeability of ions through the assembly poses a serious problem, thereby necessitating

an additional coating on the monolayer. An approach that has been tried to resolve this problem is to
a siloxane polymer of the SAM.

## 5.7.6 Other Areas

Self-assembled monolayers on a gold surface constitute an ideal system for practising fundamental
related to the electron transfer process. The electrode surface used for this purpose is modified
electoactive monolayers through self-assembly. The attachment of thiols with the active terminal
allows further derivatization through classical organic reactions. In one attempt, cycloaddition wa
used to derivatize a surface modified with thiol containing azide at the termini (Fig. 5.18).

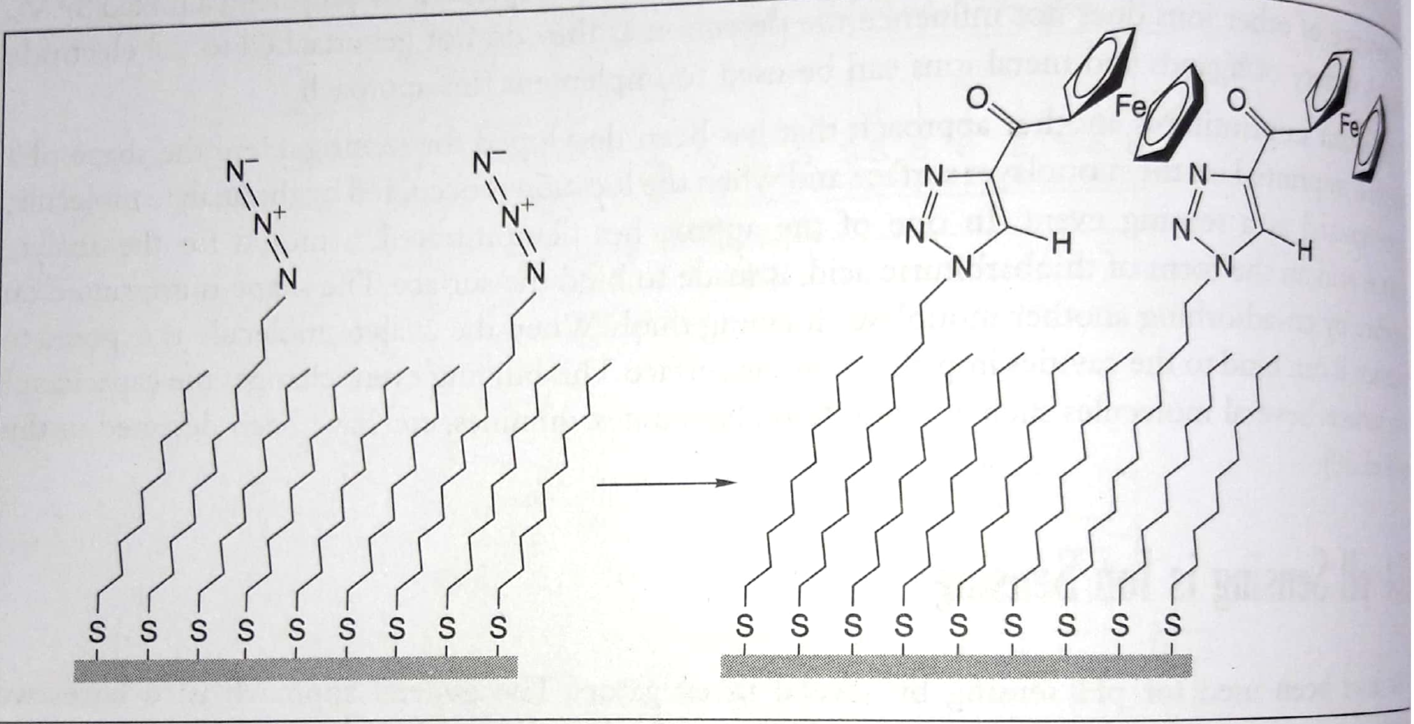


**Fig. 5.18:** *Electrode surface before and after cycloaddition. Reprinted with permission from Collman, et al. (Ref 31). Copyright (2004) American Chemical Society.*

Chemical force microscopy (CFM) combined with chiral discrimination by a molecule can be used to distinguish different chiral forms of the same molecule. In this technique, an AFM tip is functionalized with a chiral molecule. This chiral probe is then used to discriminate between the two chiral forms of the same molecule on a surface. The gold-coated AFM tip is functionalized with a chiral probe by using acylated phenyl glycine modified with alkanethiol. The changes in the friction or adhesion forces are used to distinguish between the two enantiomers of mandelic acid.

## 5.7.7 Wetting Control

The wetting properties of a surface can be modified, to a great extent, by coating it with a monolayer of molecules. This is one of the important applications of SAMs. A low coverage surface is made intentionally by the self-assembly of alkanethiol with a bulky end group on an Au(111) surface. The end group is then hydrolyzed to form a carboxy terminated monolayer with low surface coverage. The carboxylate groups generated by the hydrolysis can be attracted to the gold surface by applying an electric field. Thus the surface can now be made hydrophilic or hydrophobic by changing the electrochemical potential. The working of the sensor is schematically shown in Fig. 5.19 (Plate 4).

## 5.7.8 Molecular Electronics

SAMs are also used to make electrical contacts. By using a self-assembled monolayer of dithiol on gold, one can make a surface with pendent thiol groups and can also attach a gold nanoparticle. This attachment with a covalent linkage showed four orders of magnitude higher current than when the nanoparticle was physisorbed on the SAM surface at the same tip bias voltage. This showed that monolayer-based electrical contacts are feasible. In various studies, different kinds of interactions such as van der Waals, hydrogen bonding and covalent interactions have been made between monolayers attached to metallic surfaces such as gold and mercury. These studies have shown that the electron transfer rates increased in the order, van der Waals > hydrogen bonding < covalent.

In all these experiments, it is necessary to make a contact. This is done through monolayers. The experimental protocol is illustrated in Fig. 5.20. In the experiment, a nanoparticle solution is exposed to a monolayer making nanoparticles sit on the monolayer. The current flowing between the tip and the surface is measured at a bias voltage.

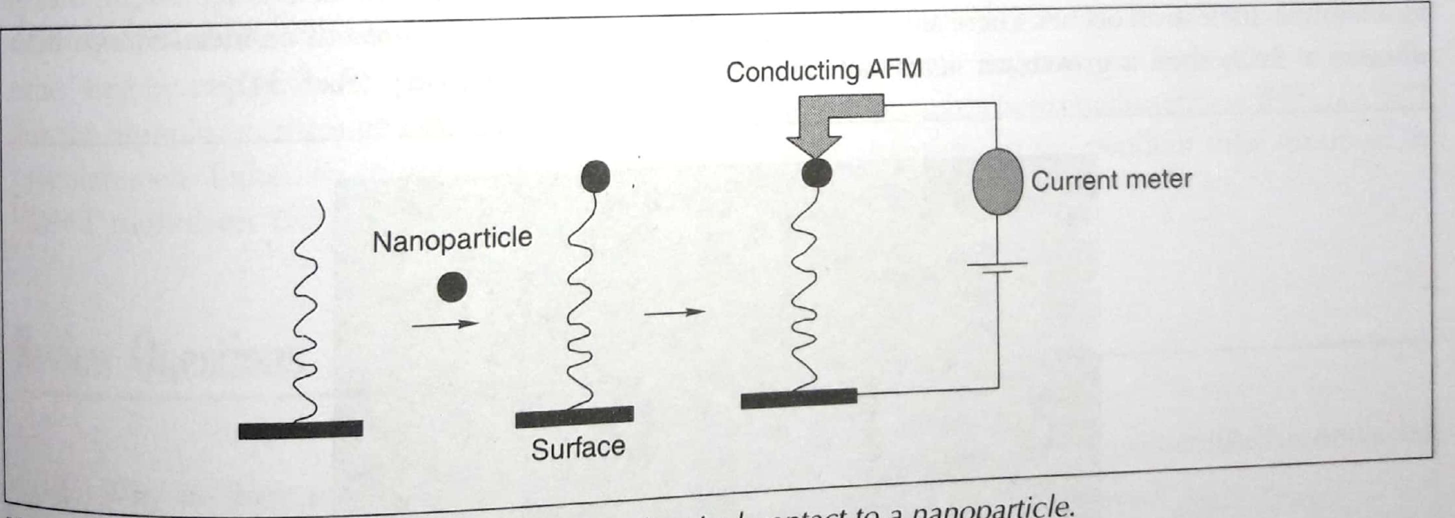


**Fig. 5.20:** *Experimental approach for making electrical contact to a nanoparticle.*

## 5.7.9 Templates

SAMS are excellent templates on which nanofabrication can be done. A given structure can be produced on the surface by using a number of methodologies. Various nanoscopic objects can be used for producing a structure. Several of these objects are detailed below.

In a scanning probe technique, a probe of nanometer dimensions is used to investigate a mate The investigation is on the surface of the material. This is done by holding the tip stationary and mov the sample or vice versa. The information, that is collected by moving the sample, can be of sev kinds, which differ from technique to technique. The collected data and its variation across the sam are used to create an image of the sample. The resolution of such an image depends on the sample, control one has on the movement on the tip/sample and the inherent nature of the data.

### 3.1.1 Scanning Tunneling Microscopy

STM was developed[1] in 1982 and the inventors were awarded the Nobel Prize for physics in 19 In STM, the phenomenon of electron tunneling is used to image the topography of the surface. T utilises the principle of vacuum tunneling. Here two surfaces, a tunneling probe and a surface, are brou near contact at a small bias voltage. If two conductors are held close together, their wavefunctions overlap. The electron wavefunctions at the Femi level have a characteristic exponential inverse de length $K$, which can be given as, $K=\sqrt{(4m\varphi)/\hbar}$, where $m$ is mass of electron, $\varphi$ is the local tunnel barrier height or the average work function of the tip and sample. When a small bias voltage $V$ is appl between the tip and the sample, the overlapped electron wavefunction permits quantum mechani tunneling and a current $I$ to flow through. The tunneling current $I$ decays exponentially with dista of separation as $I \propto Ve^{-\sqrt{(4m\varphi)d/h}}$ where $d$ is the distance between the tip and the sample and $\varphi$ is work function of the tip. The tunneling current is a result of the overlap of electronic wave functions the tip and the sample. By considering the actual values of electron work functions of most mater (typically about 4 eV), we find that tunneling current drops by an order of magnitude for every 1Å distance. The important aspect is that the tunneling current itself is very small, and in addition, i strongly distance dependent. As a result, direct measurement of vacuum tunneling was not obser till 1970s. Tunneling, however, was observed and was limited to tunneling through a barrier.

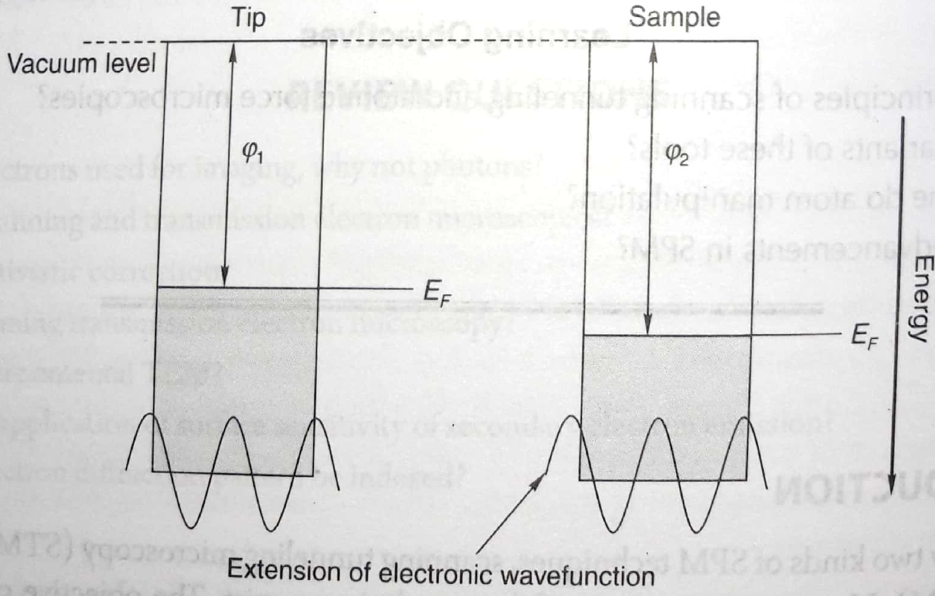


**Fig. 3.1** *Electron energy states of the sample and tip before the bias. When a sample and a tip ar held close together, there is a possibility of their electronic wave functions to overlap.*

Basic instrumental aspects in such a device are simple and is illustrated in Figs 3.1 and 3.2. In this, a tip is brought close to the sample so that electrons can tunnel through the vacuum barrier. The position of the tip is adjusted by two piezoelectric scanners, with x and y control. The z-axis position is continuously adjusted, taking feedback from the tunneling current, so that a constant tunneling current is maintained. The position of the z-axis piezo, therefore, reproduces the surface of the material. The position of the piezo is directly related to the voltage supplied to the piezoelectric drives. Scanning is possible in the constant height mode as well, but this is done only on extremely flat surfaces, so that the tip (distance modulation) does not crash by accident. The other mode of imaging is by modulating the tip at some frequency and measuring the resulting current variations. This is informative in understanding the compositional variation across the sample.

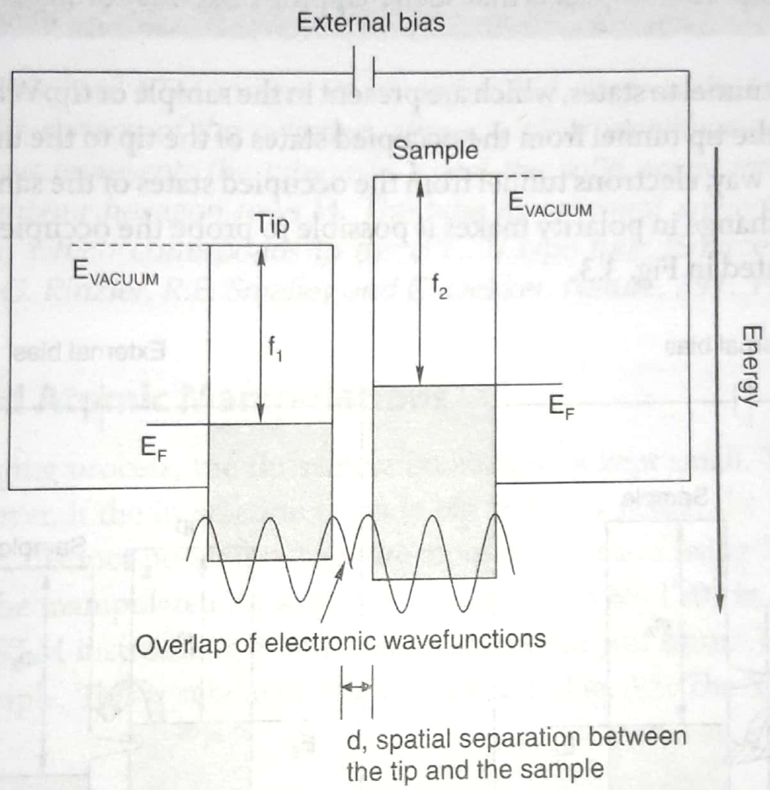


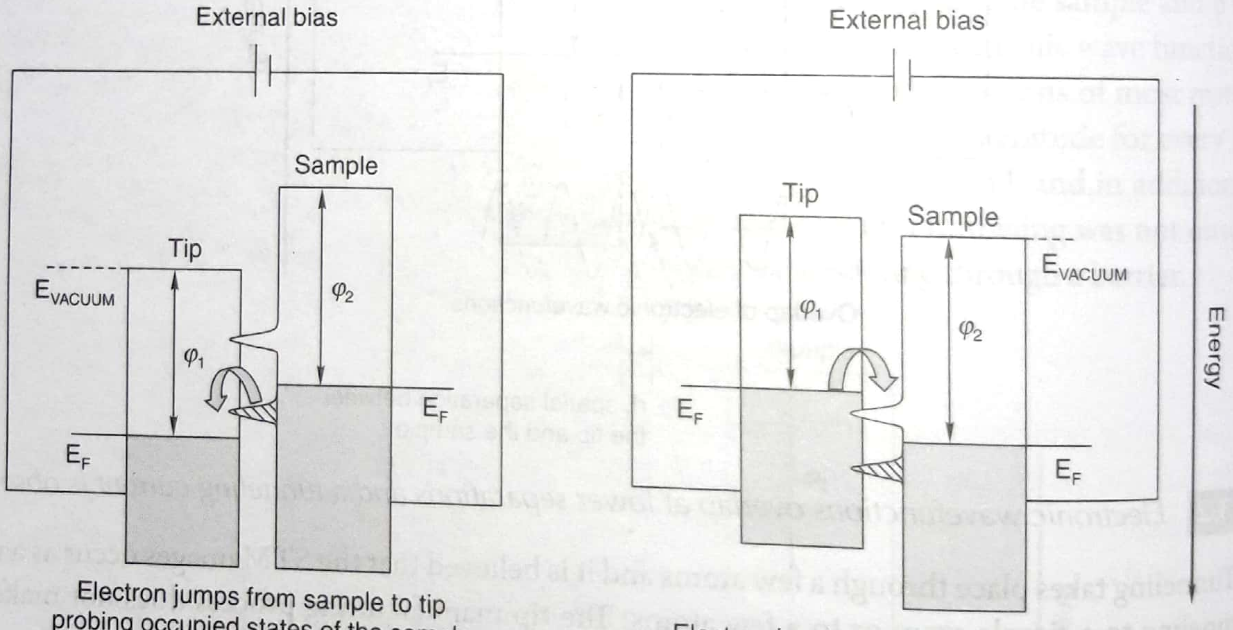
**Fig. 3.2** *Electronic wavefunctions overlap at lower separations and a tunneling current is observed.*

Tunneling takes place through a few atoms and it is believed that the STM images occur as a result of tunneling to a simple atom or to a few atoms. The tip manufacturing process does not make one atomically sharp tip alone. However, what appears to be happening is that electron tunneling takes place to whichever atomically sharp tip, which is closer to the surface.

STM has been used to understand numerous processes and a review of these is out of place here. Most of these studies relate to understanding various surface processes. The techniques available earlier for these studies before the arrival of STM, are low-energy electron diffraction (LEED), reflected high energy electron diffraction (RHEED), X-ray diffraction and variations of these techniques. Instead of probing the average structure of the surface as is possible with these techniques, STM allowed investigation of local structures. These studies focused on surface reconstruction, adsorption, chemical transformations, etc. at metal, semiconductor and even on insulating surfaces (under appropriate conditions to observe tunneling current). In the brief discussion below, we shall illustrate a few of the experiments of relevance to nanoscience and technology.

STM gives information on local density of states. Density of States (DOS) represents the quantity of electrons exist at specific values of energy in a material. Keeping the distance between the sample and the tip constant, a measure of the current change with respect to the bias voltage can probe the local DOS of the sample. A plot of $dI/dV$ as a function of V represents the LDOS. This is called scanning tunneling spectroscopy (STS). An average of the density of states mapped using STM is comparable to the results from ultraviolet photoelectron spectroscopy and inverse photoemission spectroscopy (see below). Such comparisons have been done in a few cases and the results indicate that the tip effects are unimportant. The important aspect is that such mapping of density of states is possible with spatial specificity.

Electrons can only tunnel to states, which are present in the sample or tip. When the tip is negatively biased, electrons from the tip tunnel from the occupied states of the tip to the unoccupied states of the sample. If it is the other way, electrons tunnel from the occupied states of the sample to the unoccupied states of the tip. Thus, change in polarity makes it possible to probe the occupied or unoccupied states of the sample as illustrated in Fig. 3.3.



Electron jumps from sample to tip probing occupied states of the sample

Electron jumps from tip to the sample probing unoccupied states of the sample

**Fig. 3.3** *Depending on the sample bias one can probe various kinds of states of the sample.*

STM has revolutionised a number of areas of fundamental science. The capability to analyse samples with atomic resolution, to see processes as they are occurring and to do all these while the sample is in atmospheric conditions are the advantages of STM. For nanoscience and technology, the use of STM are manifold. To give the reader a feel of those, we cite an example here. STM has been used in different ways to understand the electronic structure and properties of carbon nanotubes. An atomically resolved image[2] of a single-walled carbon nanotube is shown in the Fig. 3.4. The arrangement of the hexagons is seen. One has to remember that the graphitic sheet has been folded, so that the hexagons are not planar. From this, we can determine the tube axis and the chiral angle. This is 7° for this tube and the tube diameter is 1.3 nm. STS measurements determine the band gap and local electronic structure of the tubes.

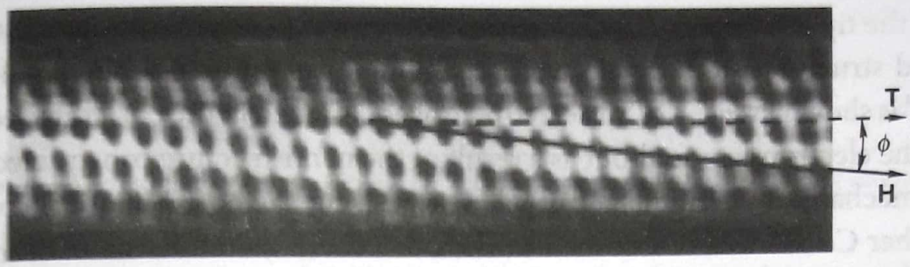


**Fig. 3.4** *Atomically resolved STM images of an individual single-walled carbon nanotube. The lattice on the surface of the cylinders allows a clear identification of the tube chirality. Dashed arrow represents the tube axis* **T** *and the solid arrow indicates the direction of nearest-neighbour hexagon rows* **H**. *The tube has a chiral angle* $\Phi = 7°$ *and a diameter d = 1.3 nm, which corresponds to the (11, 7) type tube (Source: J.W.G. Wildoer, L.C. Venema, A.G. Rinzler, R.E. Smalley and C. Dekker, Nature, 391, 1998, 59).*

### 3.1.2 STM Based Atomic Manipulations

In a normal STM imaging process, the tip-sample interaction is kept small. This makes the analysis non-destructive. However, if the interaction is made big and, as a result, the tip can move atoms on the substrate, there is a distinct possibility to write atomic structures using STM. This was done in 1990 by Eigler. When he manipulated Xe atoms on the surface of Ni(110) in a low temperature ultra high vacuum (UHV) STM instrument, a new branch of science was born.[3] Process of manipulating atoms is technically simple. This is schematically illustrated in Fig. 3.5. The STM scanning process is

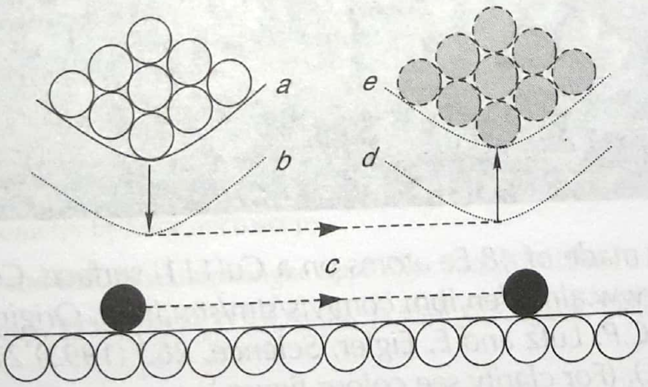


**Fig. 3.5** *Process of manipulating atoms on the surface. An STM tip at position a is brought to position b by vertical movement such that the tunneling current is large. Then the tip is slid over the surface to the desired location d, and subsequently, the tip is brought back to initial height e.*

stopped and the tip is brought just above the sample atom. The tip is lowered to increase the interaction between the tip and the atom. This is done by increasing the tunneling current (to the tune of ~30 nA). Note that typical tunneling current used for imaging is of the order of 1 nA. As a result of this, the tip-atom interaction is made strong and the tip can now be moved to the desired location. The interaction potential between the tip and the atom is strong to overcome the energy barrier, so that atom can slide on the surface. It is, however, not transferred to the tip from the substrate. After moving to the desired location, the tip is withdrawn by reducing the tunneling current. This process can be repeated to get the desired structure, atom by atom. A quantum corral built by arranging 48 Fe atoms on a Cu(111) surface[4] is shown in Fig. 3.6. The electron waves confined in the corral are seen in this picture. Confinement is the electrons come about as a result of the nanostructure constructed. At such length scales quantum mechanical phenomena can be observed. By having an elliptical corral of Co atoms and placing another Co atom at one of its foci, the other focus manifests some of the features of the atom, where no atom exists. When the atom is moved from the focus, the effect disappears.[5] This quantum mirage effect suggests transportation of data in the quantum mechanical size limit.

Numerous other manipulation strategies have been demonstrated. Tunneling current has been used to break chemical bonds. This has been shown in the case of oxygen and organic molecules. In the case of organic molecules, the detached fragments have been moved and further recombined in a desired fashion. Feynman's prediction of atomically constructed matter has come true.

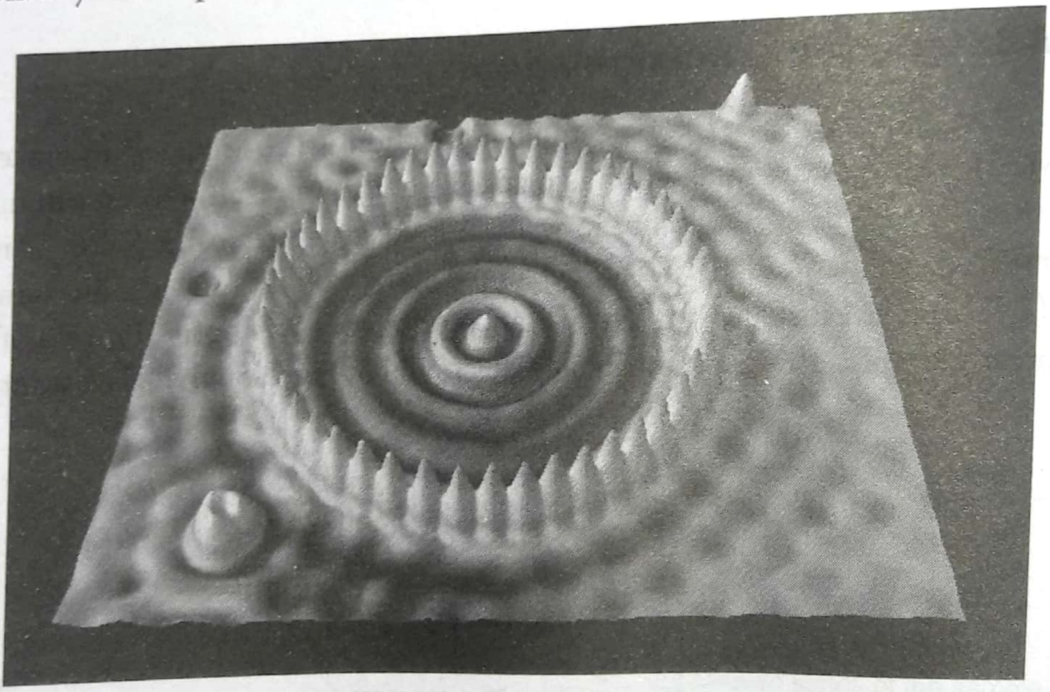


**Fig. 3.6** *Quantum corral made of 48 Fe atoms on a Cu(111) surface. Colour image taken from the website, http://www.almaden.ibm.com/vis/stm/stm.html. Original image was published in, M.F. Crommie, C.P. Lutz and E. Eigler, Science, 262 (1993) 218. (Copyright AAAS, Used with permission.). (For clarity see colour figure.)*

Numerous modifications of STM are available. We reproduce a list of variants in Table 3.1 reproduced from Reference 9. An interested reader may consult the references and additional reading material listed at the end of the chapter. The most current developments are in the areas of fast scanning STM, ultra low temperature STM and spin polarised STM. In the first, dynamical processes taking place at the surface, such as a chemical reaction, are monitored and the images are captured so as to construct a movie. This can be combined with a solution phase STM, so that reactions in solutions can be investigated. In spin polarised STM, a magnetic tip is used so that the tunneling current is sensitive to the spin. In ultra low temperature STM, the measurements are done at temperatures of the order of mK, so that phenomena at low temperatures can be probed.

**Table 3.1** *SXM techniques and capabilities (from reference 9)*

1. *Scanning Tunneling Microscope* (1981), G. Binnig, H. Rohrer, 'Surface studies by scanning tunneling microscopy'.
   G. Binning, H. Rohrer, Ch. Gerber and E. Weibel, *Phys. Rev. Lett.*, 49 (1982), 57–61.
2. *Scanning Near-Field Optical Microscope* (1982), D.W. Pohl, 'Optical stethoscopy: Image recording with resolution L/20.'
   D.W. Pohl, W. Denk and M. Lanz, *Appl. Phys. Lett.*, 44 (1984), 651.
   A. Harootunian, E. Betzig, A. Lewis and M. Isaacson, *Appl. Phys. Lett.*, 49 (1986), 674.
3. *Scanning Capacitance Microscope* (1984), J.R. Matey, J. Blanc, 'Scanning capacitance microscopy'.
   J.R. Matey and J. Blanc, *J. Appl. Phys.*, 57 (1984), 1437–44.
4. *Scanning Thermal Microscope* (1985), C.C. Williams, H.K. Wickramasinghe, 'Scanning thermal profiler'.
   C.C. Williams and H.K. Wickramasinghe, *Appl. Phys. Lett.*, 49 (1985), 1587–89.
5. *Atomic Force Microscope* (1986), G. Binnig, C.F. Quate, Ch. Gerber, 'Atomic force microscope'.
   G. Binnig, C.F. Quate, and Ch. Gerber, *Phys. Rev. Lett.*, 56 (1986), 930–33.
6. *Scanning Attractive Force Microscope* (1987), Y. Martin, C.C. Williams, H.K. Wickramasinghe, 'Atomic force microscope–force mapping and profiling on a sub 100 Å scale'.
   Y. Martin, C.C. Williams, H.K. Wickramasinghe, *J. Appl. Phys.*, 61 (1987), 4723–29.
7. *Magnetic Force Microscopy* (1987), Y. Martin, H.K. Wickramasinghe, 'Magnetic imaging by "force microscopy" with 1000 Å resolution'.
   Y. Martin and H.K. Wickramasinghe, *Appl. Phys. Lett.*, 50 (1987), 1455–57.
8. *"Frictional" Force Microscope* (1987), C.M. Mate, G.M. McClelland, S. Chiang, 'Atomic scale friction of a tungsten tip on a graphite surface'.
   C.M. Mate, G.M. McClelland, R. Erlandsson, and S. Chiang, *Phys. Rev. Lett.*, 59 (1987), 1942–45.
9. *Electrostatic Force Microscope* (1987), Y. Martin, D.W. Abraham, H.K. Wickramasinghe, 'High resolution capacitance measurement and potentiometry by force microscopy'.
   Y. Martin, D.W. Abraham, and H.K. Wickramasinghe *Appl. Phys. Lett.*, 52 (1988) 1103–1105.
10. *Inelastic Tunneling Spectroscopy STM* (1987), D.P.E. Smith, D. Kirk, C.F. Quate, 'Detection of phonons will scanning tunneling microscope'.
    D.P.E. Smith, G. Binnig, and C.F. Quate, *Appl. Phys. Lett.*, 49 (1987), 1641–43.

*(Contd...)*

### 3.1.3 Atomic Force Microscopy

In this technique, interactions between a sharp probe and a sample are used for imaging. The cantilever, which probes the surface, has an atomically sharp tip and this is brought in contact with the surface. The large-scale use of AFM today is because of the use of microfabricated tips of Si or $Si_3N_4$. The spring constant of the tip is of the order of 1 N/m, and the shortest vertical displacement $d$ measurable is $<1/2\, kd^2> \sim \frac{1}{2} k_B T$. With $k_B T$ of the order of $4 \times 10^{-21}$ J at 298 K, the smallest vertical displacement observable is 0.5 Å. The interaction between the tip and the sample is of the order of a nano Newton, which is not directly measured in AFM. The extend of interaction between them is measured by the displacement of the cantilever. The displacement of the cantilever is monitored by the reflection of a laser from the back of the cantilever, detected on a segmented photodetector. A 4-segment photodiode is used for this purpose. In the very first AFM, the interaction was measured by the difference in tunneling current, the tip being fixed on the back of the cantilever. This allows the detection of normal and lateral displacements of the cantilever. Optical detection is far superior to other forms of detection, although there are problems associated with the laser, such as the heating of the cantilever and the sample. The image is generated from the interaction force. In the scan, the interaction force is kept constant by a feed-back control. The increase in the interaction force, when the tip approaches an elevated part, is related to the vertical displacement of the scanner needed to eliminate this increase in signal. This is converted to height. Thus, the basic components of the microscope are the cantilever, the detection system, scanners and the electronics. These components are schematically represented in Fig. 3.7. This also suggests that depending on the kind of interactions between the cantilever and the

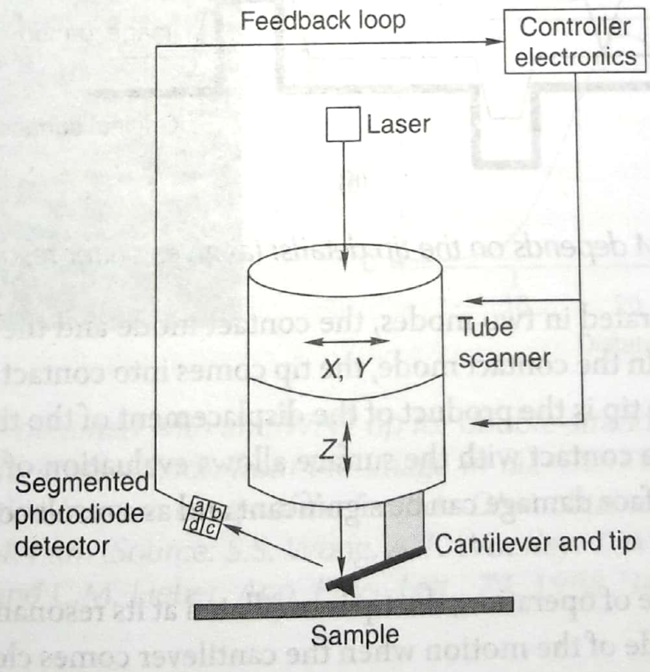


**Fig. 3.7** *Schematic representation of an atomic force microscope. The sample surface is scanned by the cantilever connected to a tubular scanner; the principal functional units in it are three piezoelectric scanners. The deflections of the cantilever are monitored by the segmented photodiode detector.*

surface, various kinds of microscopies are possible. The probe can be made magnetic to investigate the magnetic interactions with materials. This makes magnetic force microscopy. The tip can have specific temperature probes or the tip itself can be made of a thermocouple. This makes scanning thermal microscopy (SThM). The tip may be attached with molecules, which are designed to have specific molecular interactions with the surface. This makes chemical force microscopy. There are several such variations, some of which were listed before (Table 3.1).

Resolution in scanning probe microscopy cannot be defined similar to optical methods, where the diffraction limit determines the practically achievable resolution. SPM is a 3-D imaging technique and the resolution is affected by the tip geometry. As would be seen from Fig. 3.8, improved resolution can be obtained for sharper tips. In practical description of resolution, especially in the biological context, width of DNA measured is considered as a measure of resolution. DNA, in its β form, is known to have a diameter of 2 nm. Width alone is not enough to describe the resolution as SPM is a 3-D technique and height is important.

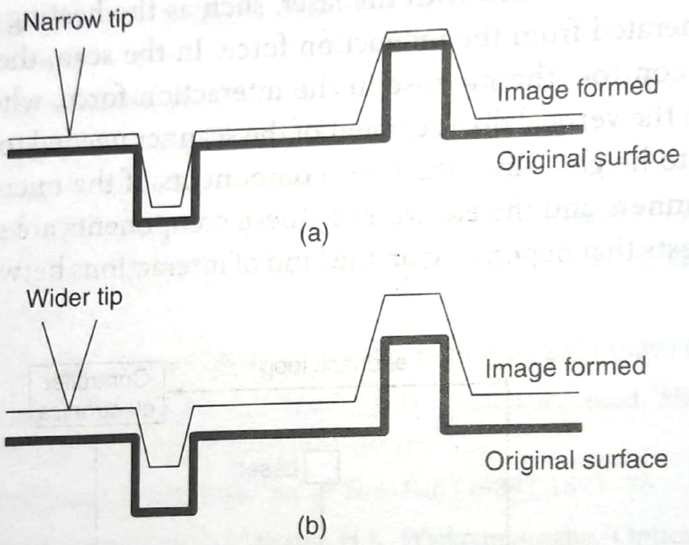


**Fig. 3.8** *Resolution in SPM depends on the tip details: (a) gives better resolution in comparison to (b).*

AFM is commonly operated in two modes, the contact mode and the non-contact or tapping or intermittent contact mode. In the contact mode, the tip comes into contact with the surface. The force between the sample and the tip is the product of the displacement of the tip and the force constant of the cantilever ($f = -kx$). The contact with the surface allows evaluation of surface friction. When the interaction is strong, the surface damage can be significant and as a result contact mode can be difficult to use for soft materials.

In the non-contact mode of operation, the tip is oscillated at its resonant frequency by an actuator. The decrease in the amplitude of the motion when the cantilever comes close to the sample is used to measure the tip-sample interaction. The drop in the amplitude is set to a pre-determined value. The intermittent contact the tip makes is gentle and does not damage the material, although the probes are generally harder. As a result of this gentle mode of scanning, this is the most often used scanning method, especially with materials, whose surfaces are important such as a polished silicon wafer.

Typical AFM images get resolution of the order of 5 nm. Atomic features have been observed, but this is not routine. With especially fabricated tips, 1 nm can be observed. True atomic features have been demonstrated in specific cases. The best known examples of nanoscale structures are DNA strands. Images of DNA spread on mica are shown in Fig. 3.8.[7] These images show variation in the shape and width of the curved structures depending on the type of imaging. The width of the molecule seen in AFM images need not be the actual width due to several factors. One corresponds to the relaxation of the molecule on the substrate, on which it is held for imaging. The other is to do with the tip induced deformation in the sample. The contour length of the macromolecule, on the contrary, is a measure of the molecular weight of the material.

Mechanical properties are measured using AFM. Correlation of these properties to the chemical composition and structure has to happen for a complete understanding of the material. This can be done by combining spectroscopy with imaging. Although a few such tools as confocal Raman microscopy and infrared microscopy, are available, the spatial resolution is of the order of microns or hundreds of nanometers. A combination of AFM with spectroscopy will be immensely useful. Scanning Near-field Optical Microscopy with Raman will be useful in this regard, but the current resolution of this is only of the order of 50 nm.

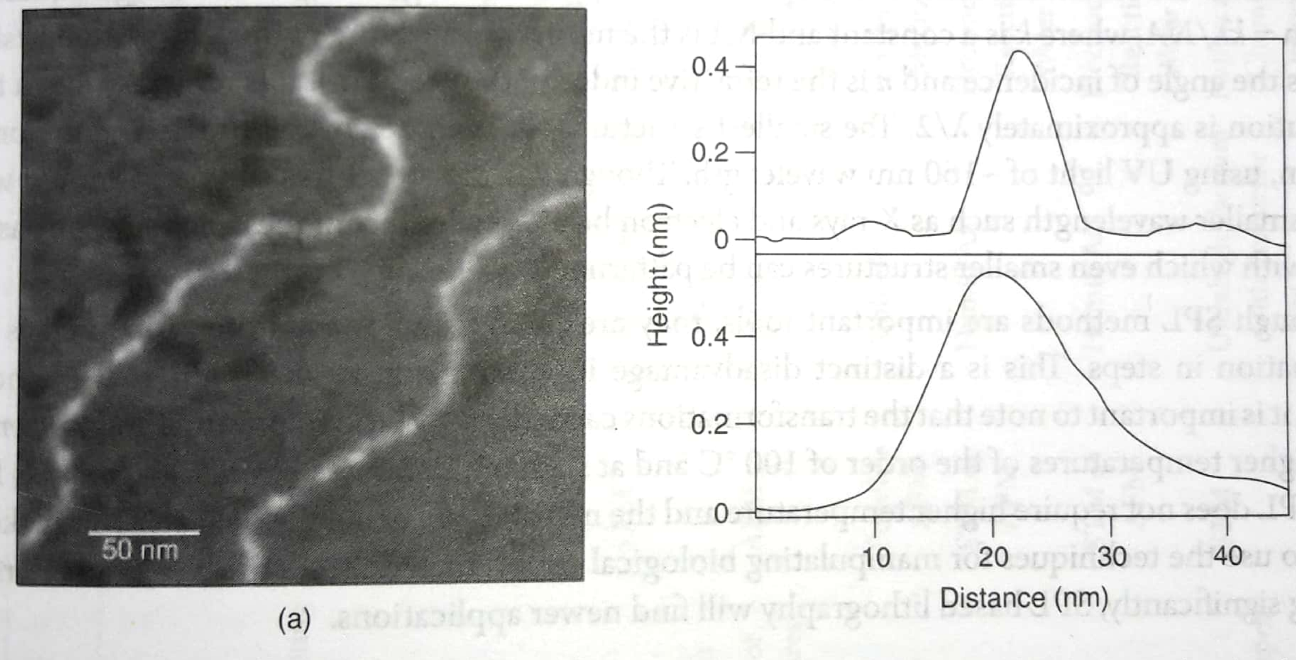


**Fig. 3.9** *(a) Height image obtained with an SWNT tip for double-stranded DNA adsorbed on mica. (b) Typical height cross-section from the image in (a). The FWHM is 5.6 nm. (c) Typical height cross-section from an image of the lambda-DNA obtained with a conventional Si tip. The FWHM is 14.4 nm (Source: S.S. Wong, A.T. Woolley, T.W. Odom, J-L. Huang, P. Kim, D.V. Vezenov, and C.M. Lieber, App. Phys. Lett., 73, 1998, 3465–67).*

# UNIT IV

# NANO SYSTEMS

## 4.1.QUANTUM DOT

### 4.1.1.AN ARTIFICIAL AND TUNABLE ATOM (QUANTUM DOT)

Quantum dots (QD) are very small semiconductor particles, only several nano metres in size, so small that their optical and electronic properties differ from those of larger LED particles. They are a central theme in nanotechnology. Many types of quantum dot will emit light of specific frequencies if electricity or light is applied to them, and these frequencies can be precisely tuned by changing the dots' size, shape and material, giving rise to many applications.

In the language of materials science, nanoscale semiconductor materials tightly confine either electrons or electron holes. Quantum dots are also sometimes referred to as artificial atoms, a term that emphasizes that a quantum dot is a single object with bound, discrete electronic states, as is the case with naturally occurring atoms or molecules.

Quantum dots exhibit properties that are intermediate between those of bulk semiconductors and those of discrete atoms or molecules. Their optoelectronic properties change as a function of both size and shape. Larger QDs (diameter of 5–6 nm, for example) emit longer wavelengths resulting in emission colors such as orange or red. Smaller QDs (diameter of 2–3 nm, for example) emit shorter wavelengths resulting in colors like blue and green, although the specific colors and sizes vary depending on the exact composition of the QD.

Because of their highly tunable properties, QDs are of wide interest. Potential applications include transistors, solar cells, LEDs, diode lasers and second-harmonic generation, quantum computing, and medical imaging. Additionally, their small size allows for QDs to be suspended in solution which leads to possible uses in inkjet printing and spin-coating. They have also been used in Langmuir-Blodgett thin-films processing techniques result in less expensive and less time-consuming methods of semiconductor fabrication.

### 4.1.2.NANO WIRE

A nanowire is an extremely thin wire with a diameter on the order of a few nanometer s (nm) or less, where 1 nm = $10^{-9}$ meters. Two processes in nanotechnology by which nanowires can be manufactured are suspension and deposition. A suspended nanowire is held up by the ends in an evacuated chamber, and then is chemically etched or bombarded with high-speed atom s or molecule s to reduce its diameter. Another method involves indenting the surface of a wire in the center of a suspended span, raising the temperature, and then stretching the wire while it is near its melting point. A deposited nanowire is fabricated on a surface consisting of some non-conducting substance such as plastic or glass. The process is similar to that by which semiconductor chips are grown, except that the result is a linear (one-dimensional) structure rather than a flat (two-dimensional) or solid (three-dimensional) structure.

Fields expected to benefit from nanotechnology include water purification, sanitation, agriculture, alternative energy (particularly photovoltaics), home and business construction, computer manufacturing, communications, and medicine.

### 4.1.3.APPLICATIONS

#### Electronic devices

Nanowires can be used for transistors. Transistors are used widely as fundamental building element in today's electronic circuits. As predicted by Moore's law, the dimension of transistors is shrinking smaller and smaller into nanoscale. One of the key challenges of building future nanoscale transistors is ensuring good gate control over the channel. Due to the high aspect ratio, if the gate dielectric is wrapped around the nanowire channel, we can get good control of channel electrostatic potential, thereby turning the transistor on and off efficiently.

Due to the unique one-dimensional structure with remarkable optical properties, the nanowire also opens new opportunities for realizing high efficiency photovoltaic devices. Compared with its bulk counterparts, the nanowire solar cells are less sensitive to impurities due to bulk recombination, and thus silicon wafers with lower purity can be used to achieve acceptable efficiency, leading to the a reduction on material consumption.

To create active electronic elements, the first key step was to chemically dope a semiconductor nanowire. This has already been done to individual nanowires to create p-type and n-type semiconductors.

The next step was to find a way to create a p–n junction, one of the simplest electronic devices. This was achieved in two ways. The first way was to physically cross a p-type wire over an n-type wire. The second method involved chemically doping a single wire with different dopants along the length. This method created a p-n junction with only one wire.

After p-n junctions were built with nanowires, the next logical step was to build logic gates. By connecting several p-n junctions together, researchers have been able to create the basis of all logic circuits: the AND, OR, and NOT gates have all been built from semiconductor nanowire crossings.

In August 2012, researchers reported constructing the first NAND gate from undoped silicon nanowires. This avoids the problem of how to achieve precision doping of complementary nanocircuits, which is unsolved. They were able to control the Schottky barrier to achieve low-resistance contacts by placing a silicide layer in the metal-silicon interface.

It is possible that semiconductor nanowire crossings will be important to the future of digital computing. Though there are other uses for nanowires beyond these, the only ones that actually take advantage of physics in the nanometer regime are electronic.

In addition, nanowires are also being studied for use as photon ballistic waveguides as interconnects in quantum dot/quantum effect well photon logic arrays. Photons travel inside the tube, electrons travel on the outside shell.

When two nanowires acting as photon waveguides cross each other the juncture acts as a quantum dot.

Conducting nanowires offer the possibility of connecting molecular-scale entities in a molecular computer. Dispersions of conducting nanowires in different polymers are being investigated for use as transparent electrodes for flexible flat-screen displays.

Because of their high Young's moduli, their use in mechanically enhancing composites is being investigated. Because nanowires appear in bundles, they may be used as tribological additives to improve friction characteristics and reliability of electronic transducers and actuators.

Because of their high aspect ratio, nanowires are also uniquely suited to dielectrophoretic manipulation, which offers a low-cost, bottom-up approach to integrating suspended dielectric metal oxide nanowires in electronic devices such as UV, water vapor, and ethanol sensors.

### 4.1.4.NANOWIRE LASERS

Nanowire lasers for ultrafast transmission of information in light pulsesNanowire lasers are nano-scaled lasers with potential as optical interconnects and optical data communication on chip. Nanowire lasers are built from III–V semiconductor hetero structures, the high refractive index allows for low optical loss in the nanowire core. Nanowire lasers are sub wavelength lasers of only a few hundred nanometers. Nanowire lasers are Fabry–Perot resonator cavities defined by the end facets of the wire with high-reflectivity, recent developments have demonstrated repetition rates greater than 200 GHz offering possibilities for optical chip level communications.

Sensing of proteins and chemicals using semiconductor nanowires In an analogous way to FET devices in which the modulation of conductance (flow of electrons/holes) in the semiconductor, between the input (source) and the output (drain) terminals, is controlled by electrostatic potential variation (gate-electrode) of the charge carriers in the device conduction channel, the methodology of a Bio/Chem-FET is based on the detection of the local change in charge density, or so-called "field effect", that characterizes the recognition event between a target molecule and the surface receptor.

This change in the surface potential influences the Chem-FET device exactly as a 'gate' voltage does, leading to a detectable and measurable change in the device conduction. When these devices are fabricated using semiconductor nanowires as the transistor element the binding of a chemical or biological species to the surface of the sensor can lead to the depletion or accumulation of charge carriers in the "bulk" of the nanometer diameter nanowire i.e. (small cross section available for conduction channels). Moreover, the wire, which serves as a tunable conducting channel, is in close contact with the sensing environment of the target, leading to a short response time, along with orders of magnitude increase in the sensitivity of the device as a result of the huge S/V ratio of the nanowires.

While several inorganic semiconducting materials such as Si, Ge, and metal oxides (e.g. In2O3, SnO2, ZnO, etc.) have been used for the preparation of nanowires, Si is usually the material of choice when fabricating nanowire FET-based chemo/biosensors.

Several examples of the use of silicon nanowire(SiNW) sensing devices include the ultra sensitive, real-time sensing of biomarker proteins for cancer, detection of single virus particles, and the detection of nitro-aromatic explosive materials such as 2,4,6 Tri-nitrotoluene (TNT) in sensitives superior to these of canines. Silicon nanowires could also be used in their twisted form, as electromechanical devices, to measure intermolecular forces with great precision.

### *4.1.5.*LIMITATIONS OF SENSING WITH SILICON NANOWIRE FET DEVICES

Generally, the charges on dissolved molecules and macromolecules are screened by dissolved counterions, since in most cases molecules bound to the devices are separated from the sensor surface by approximately 2–12 nm (the size of the receptor proteins or DNA linkers bound to the sensor surface). As a result of the screening, the electrostatic potential that arises from charges on the analyte molecule decays exponentially toward zero with distance. Thus, for optimal sensing, the Debye length must be carefully selected for nanowire FET measurements. One approach of overcoming this limitation employs fragmentation of the antibody-capturing units and control over surface receptor density, allowing more intimate binding to the nanowire of the target protein. This approach proved useful for dramatically enhancing the sensitivity of cardiac biomarkers (e.g. Troponin) detection directly from serum for the diagnosis of acute myocardial infarction

## 4.2.QUANTUM HALL EFFECT

The quantum Hall effect (or integer quantum Hall effect) is a quantum-mechanical version of the Hall effect, observed in two-dimensional electron systems subjected to low temperatures and strong magnetic fields, in which the Hall conductance$\sigma$ undergoes quantum Hall transitions to take on the quantized values

$$\sigma = \frac{\mathrm{Ichannel}}{\mathrm{VHall}} = v\frac{e2}{h}$$

where $I_{channel}$ is the channel current, $V_{Hall}$ is the Hall voltage, e is the elementary charge and h is Planck's constant. The prefactor v is known as the filling factor, and can take on either integer (v = 1, 2, 3,…) or fractional (v = 1/3, 2/5 3/7 2/3 3/5 1/5 2/9 3/13,5/2 12/5…) values. The quantum Hall effect is referred to as the integer or fractional quantum Hall effect depending on whether v is an integer or fraction, respectively.

The striking feature of the integer quantum Hall effect is the persistence of the quantization (i.e. the Hall plateau) as the electron density is varied. Since the electron density remains constant when the Fermi level is in a clean spectral gap, this situation corresponds to one where the Fermi level is an energy with a finite density of states, though these states are localized (see Anderson localization).

The fractional quantum Hall effect is more complicated, as its existence relies fundamentally on electron–electron interactions. The fractional quantum Hall effect is also understood as an integer quantum Hall effect, although not of electrons but of charge-flux composites known as composite fermions. In 1988, it was proposed that there was quantum Hall effect without Landau levels.[1] This quantum Hall effect is referred to as the quantum anomalous Hall (QAH) effect. There is also a new concept of the quantum spin Hall effect which is an analogue of the quantum Hall effect, where spin currents flow instead of charge currents.

## 4.3.CARBON NANOTUBES

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nano structure. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. Owing to the material's exceptional strength and stiffness, nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1, significantly larger than for any other material.

In addition, owing to their extraordinary thermal conductivity, mechanical, and electrical properties, carbon nanotubes find applications as additives to various structural materials. For instance, nanotubes form a tiny portion of the material(s) in some (primarily carbon fiber) baseball bats, golf clubs, car parts or damascus steel.

Nanotubes are members of the fullerene structural family. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called graphene. These sheets are rolled at specific and discrete ("chiral") angles, and the combination of the rolling angle and radius decides the nanotube properties; for example, whether the individual nanotube shell is a metal or semiconductor. Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Individual nanotubes naturally align themselves into "ropes" held together by van der Waals forces, more specifically, pi-stacking.

Applied quantum chemistry, specifically, orbital hybridization best describes chemical bonding in nanotubes. The chemical bonding of nanotubes involves entirely $sp^2$-hybrid carbon atoms. These bonds, which are similar to those of graphite and stronger than those found in alkanes and diamond (which employ $sp^3$-hybrid carbon atoms), provide nanotubes with their unique strength.

### 4.3.1.TYPES OF CNT'S

There is no consensus on some terms describing carbon nanotubes in scientific literature: both "-wall" and "-walled" are being used in combination with "single", "double", "triple" or "multi", and the letter C is often omitted in the abbreviation; for example, multi-walled carbon nanotube (MWNT)

## Properties

### 4.3.2.MECHANICAL

Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulusrespectively. 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.[38] Since carbon nanotubes have a low density for a solid of 1.3 to 1.4 $g/cm^3$,[39] its specific strength of up to 48,000 $kN \cdot m \cdot kg^{-1}$ is the best of known materials, compared to high-carbon steel's 154 $kN \cdot m \cdot kg^{-1}$.

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.[40] 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.

### 4.3.3.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 ≠ m and nm ≠ 0, then the nanotube is quasi-metallic with a very small band gap, otherwise the nanotube is a moderate semiconductor. 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 π [bonding] band meets the π* [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 σ* and π* 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 π-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 π-electron system of the nanotube. By contrast, π-electron acceptors such as $FeCl_3$or electron-deficient metallocenes function as p-type dopants since they draw π-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.

### 4.3.4.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

### 4.3.5.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 ·m$^{-1}$ ·K$^{-1}$;[57] compare this to copper, a metal well known for its good thermal conductivity, which transmits 385 W ·m$^{-1}$ ·K$^{-1}$. An individual SWNT has a room-temperature thermal conductivity across its axis (in the radial direction) of about 1.52 W ·m$^{-1}$ ·K$^{-1}$,[58] which is about as thermally conductive as soil. Macroscopic assemblies of nanotubes such as films or fibres have reached up to 1500 W ·m$^{-1}$ ·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 defects cause phonon scattering over a wide range of frequencies, leading to a greater reduction in thermal conductivity.

## Applications

### 4.3.6.CURRENT

Current use and application of nanotubes has mostly been limited to the use of bulk nanotubes, which is a mass of rather unorganized fragments of nanotubes. Bulk nanotube materials may never achieve a tensile strength similar to that of individual tubes, but such composites may, nevertheless, yield strengths sufficient for many applications. Bulk carbon nanotubes have already been used as composite fibers in polymers to improve the mechanical, thermal and electrical properties of the bulk product.

- Easton-Bell Sports, Inc. have been in partnership with Zyvex Performance Materials, using CNT technology in a number of their bicycle components – including flat and riser handlebars, cranks, forks, seatposts, stems and aero bars.
- Zyvex Technologies has also built a 54' maritime vessel, the Piranha Unmanned Surface Vessel, as a technology demonstrator for what is possible using CNT technology. CNTs help improve the structural performance of the vessel, resulting in a lightweight 8,000 lb boat that can carry a payload of 15,000 lb over a range of 2,500 miles.
- Amroy Europe Oy manufactures Hybtonite carbon nanoepoxy resins where carbon nanotubes have been chemically activated to bond to epoxy, resulting in a

composite material that is 20% to 30% stronger than other composite materials. It has been used for wind turbines, marine paints and a variety of sports gear such as skis, ice hockey sticks, baseball bats, hunting arrows, and surfboards.

- The Boeing Company has patented the use of carbon nanotubes for structural health monitoring of composites used in aircraft structures. This technology will greatly reduce the risk of an in-flight failure caused by structural degradation of aircraft.

Other current applications include:

- tips for atomic force microscope probes[86]
- in tissue engineering, carbon nanotubes can act as scaffolding for bone growth

Current research for modern applications include:

- using carbon nanotubes as a scaffold for diverse microfabrication techniques.
- energy dissipation in self-organized nanostructures under influence of an electric field.
- using carbon nanotubes for environmental monitoring due to their active surface area and their ability to absorb gases.[90]

### 4.3.7.POTENTIAL

The strength and flexibility of carbon nanotubes makes them of potential use in controlling other nanoscale structures, which suggests they will have an important role in nanotechnology engineering. The highest tensile strength of an individual multi-walled carbon nanotube has been tested to be 63 GPa.[37] Carbon nanotubes were found in Damascus steel from the 17th century, possibly helping to account for the legendary strength of the swords made of it.

Recently, several studies have highlighted the prospect of using carbon nanotubes as building blocks to fabricate three-dimensional macroscopic (>1mm in all three dimensions) all-carbon devices. Lalwani et al. have reported a novel radical initiated thermal crosslinking method to fabricated macroscopic, free-standing, porous, all-carbon scaffolds using single- and multi-walled carbon nanotubes as building blocks.

These scaffolds possess macro-, micro-, and nano- structured pores and the porosity can be tailored for specific applications. These 3D all-carbon scaffolds/architectures may be used for the fabrication of the next generation of energy storage, supercapacitors, field emission transistors, high-performance catalysis, photovoltaics, and biomedical devices and implants.

CNTs are potential candidates for future via and wire material in nano-scale VLSI circuits. Eliminating electromigration reliability concerns that plague today's Cu interconnects, isolated (single and multi-wall) CNTs can carry current densities in excess of 1000 MA/sq-cm without electromigration damage.

Large quantities of pure CNTs can be made into a freestanding sheet or film by surface-engineered tape-casting (SETC) fabrication technique which is a scalable method to fabricate flexible and foldable sheets with superior properties. Another reported form factor is CNT fiber (a.k.a. filament) by wet spinning. The fiber is either directly spun from the synthesis pot or spun from pre-made dissolved CNTs.

Individual fibers can be turned into a yarn. Apart from its strength and flexibility, the main advantage is making an electrically conducting yarn. The electronic properties of individual CNT fibers (i.e. bundle of individual CNT) are governed by the two-dimensional structure of CNTs. The fibers were measured to have a resistivity only one order of magnitude higher than metallic conductors at 300K. By further optimizing the CNTs and CNT fibers, CNT fibers with improved electrical properties could be developed.

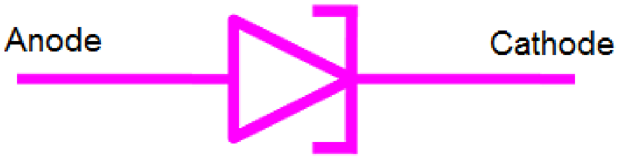
CNT-based yarns are suitable for applications in energy and electrochemical water treatment when coated with an ion-exchange membrane.[99] Also, CNT-based yarns could replace copper as a winding material. Pyrhönen et al. (2015) have built a motor using CNT winding

## 4.4.TUNNEL DIODE

A two-terminal semiconductor diode using tunneling electrons to perform high-speed switching operations.A Tunnel diode is a heavily doped p-n junction diode in which the electric current decreases as the voltage increases.In tunnel diode, electric current is caused by “Tunneling”. The tunnel diode is used as a very fast switching device in computers. It is also used in high-frequency oscillators and amplifiers.

### 4.4.1. SYMBOL OF TUNNEL DIODE

The circuit symbol of tunnel diode is shown in the below figure. In tunnel diode, the p-type semiconductor act as an anode and the n-type semiconductor act as a cathode.



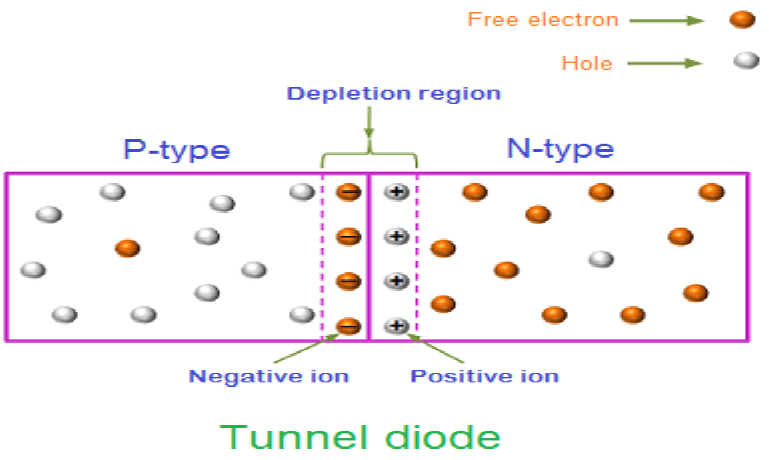
Tunnel diode symbol

We know that a anode is a positively charged electrode which attracts electrons whereas cathode is a negatively charged electrode which emits electrons. In tunnel diode, n-type semiconductor emits or produces electrons so it is referred to as the cathode. On the other hand, p-type semiconductor attracts electrons emitted from the n-type semiconductor so p-type semiconductor is referred to as the anode.

### 4.4.2.WHAT IS A TUNNEL DIODE?

Tunnel diodes are one of the most significant solid-state electronic devices which havemade their appearance in the last decade. Tunnel diode was invented in 1958 by Leo Esaki.Leo Esaki observed that if a semiconductor diode is heavily doped with impurities, it will exhibit negative resistance.

Negative resistance means the current across the tunnel diode decreases when the voltage increases. In 1973 Leo Esaki received the Nobel Prize in physics for discovering the electron tunneling effect used in these diodes.A tunnel diode is also known as Esaki diode which is named after Leo Esaki for his work on the tunneling effect. The operation of tunnel diode depends on the quantum mechanics principle known as "Tunneling". In electronics, tunneling means a direct flow of electrons across the small depletion region from n-side conduction band into the p-side valence band.



Physics and Radio-Electronics

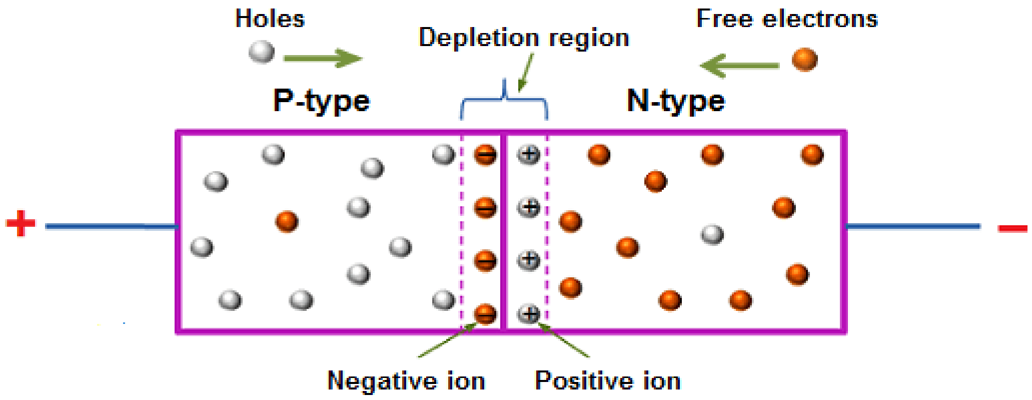
The germanium material is commonly used to make the tunnel diodes. They are also made from other types of materials such as gallium arsenide, gallium antimonide, and silicon.

### 4.4.3.WIDTH OF THE DEPLETION REGION IN TUNNEL DIODE

The depletion region is a region in a p-n junction diode where mobile charge carriers (free electrons and holes) are absent. Depletion region acts like a barrier that opposes the flow of electrons from the n-type semiconductor and holes from the p-type semiconductor.

The width of a depletion region depends on the number of impurities added. Impurities are the atoms introduced into the p-type and n-type semiconductor to increase electrical conductivity.

If a small number of impurities are added to the p-n junction diode (p-type and n-type semiconductor), a wide depletion region is formed. On the other hand, if large number of impurities are added to the p-n junction diode, a narrow depletion region is formed.



Forward bias tunnel diode

Physics and Radio-Electronics

In tunnel diode, the p-type and n-type semiconductor is heavily doped which means a large number of impurities are introduced into the p-type and n-type semiconductor. This heavy doping process produces an extremely narrow depletion region. The concentration of impurities in tunnel diode is 1000 times greater than the normal p-n junction diode.

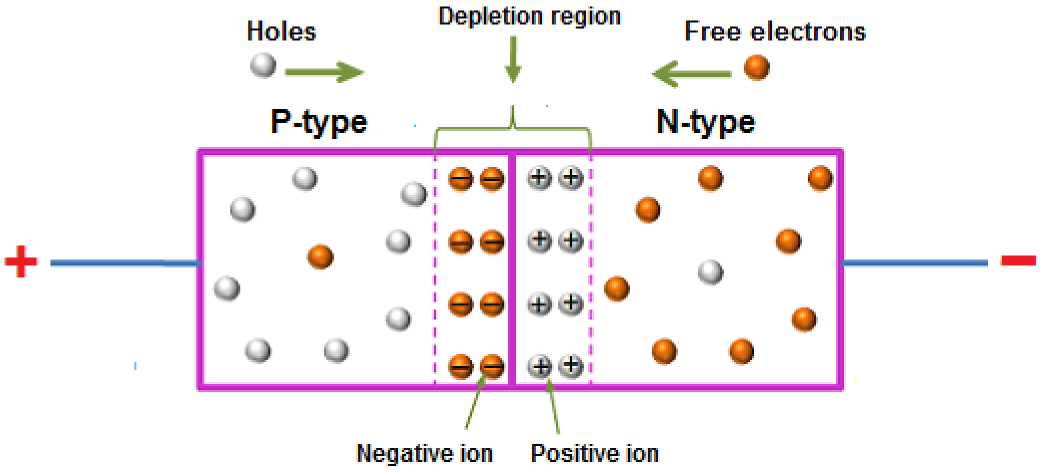
In normal p-n junction diode, the depletion width is large as compared to the tunnel diode. This wide depletion layer or depletion region in normal diode opposes the flow of current. Hence, depletion layer acts as a barrier. To overcome this barrier, we need to apply sufficient voltage. When sufficient voltage is applied, electric current starts flowing through the normal p-n junction diode.

Unlike the normal p-n junction diode, the width of a depletion layer in tunnel diode is extremely narrow. So applying a small voltage is enough to produce electric current in tunnel diode.Tunnel diodes are capable of remaining stable for a long duration of time than the ordinary p-n junction diodes. They are also capable of high-speed operations.

### 4.4.4.CONCEPT OF TUNNELING

The depletion region or depletion layer in a p-n junction diode is made up of positive ions and negative ions. Because of these positive and negative ions, there exists a built-in-potential or electric field in the depletion region. This electric field in the depletion region exerts electric force in a direction opposite to that of the external electric field (voltage).Another thing we need to remember is that the valence band and conduction band energy levels in the n-type semiconductor are slightly lower than the valence band and conduction band energy levels in the p-type semiconductor. This difference in energy levels is due to the differences in the energy levels of the dopant atoms (donor or acceptor atoms) used to form the n-type and p-type semiconductor.

Electric current in ordinary p-n junction diode When a forward bias voltage is applied to the ordinary p-n junction diode, the width of depletion region decreases and at the same time the barrier height also decreases. However, the electrons in the n-type semiconductor cannot penetrate through the depletion layer because the built-in voltage of depletion layer opposes the flow of electrons.



Forward bias p-n junction diode

If the applied voltage is greater than the built-in voltage of depletion layer, the electrons from n-side overcomes the opposing force from depletion layer and then enters into p-side. In simple words, the electrons can pass over the barrier (depletion layer) if the energy of the electrons is greater than the barrier height or barrier potential.

## 4.5.MOLECULAR TRANSISTOR

Molecular scale electronics, also called single-molecule electronics, is a branch of nanotechnology that uses single molecules, or nanoscale collections of single molecules, as electronic components. Because single molecules constitute the smallest stable structures imaginable, this miniaturization is the ultimate goal for shrinking electrical circuits.

The field is often termed simply as "molecular electronics", but this term is also used to refer to the distantly related field of conductive polymers and organic electronics, which uses the properties of molecules to affect the bulk properties of a material. A nomenclature distinction has been suggested so that molecular materials for electronics refers to this latter field of bulk applications, while molecular scale electronics refers to the nanoscale single-molecule applications treated here.[1][2]

### 4.5.1.TRANSISTORS

Single-molecule transistors are fundamentally different from the ones known from bulk electronics. The gate in a conventional (field-effect) transistor determines the conductance between the source and drain electrode by controlling the density of charge carriers between them, whereas the gate in a single-molecule transistor controls the possibility of a single electron to jump on and off the molecule by modifying the energy of the molecular orbitals. One of the effects of this difference is that the single-molecule transistor is almost binary: it is either on or off. This opposes its bulk counterparts, which have quadratic responses to gate voltage.

It is the quantization of charge into electrons that is responsible for the markedly different behavior compared to bulk electronics. Because of the size of a single molecule, the charging due to a single electron is significant and provides means to turn a transistor on or off (see Coulomb blockade). For this to work, the electronic orbitals on the transistor molecule cannot be too well integrated with the orbitals on the electrodes.

If they are, an electron cannot be said to be located on the molecule or the electrodes and the molecule will function as a wire.

A popular group of molecules, that can work as the semiconducting channel material in a molecular transistor, is the oligopolyphenylenevinylenes (OPVs) that works by the Coulomb blockade mechanism when placed between the source and drain electrode in an appropriate way.[4] Fullerenes work by the same mechanism and have also been commonly used.

Semiconducting carbon nanotubes have also been demonstrated to work as channel material but although molecular, these molecules are sufficiently large to behave almost as bulk semiconductors.

The size of the molecules, and the low temperature of the measurements being conducted, makes the quantum mechanical states well defined. Thus, it is being researched if the quantum mechanical properties can be used for more advanced purposes than simple transistors (e.g. spintronics

### 4.5.2.METHODS

One of the biggest problems with measuring on single molecules is to establish producible electrical contact with only one molecule and doing so without shortcutting the electrodes. Because the current photolithographic technology is unable to produce electrode gaps small enough to contact both ends of the molecules tested (on the order of nanometers), alternative strategies are applied.

### 4.5.3.MOLECULAR GAPS

One way to produce electrodes with a molecular sized gap between them is break junctions, in which a thin electrode is stretched until it breaks. Another is electro migration. Here a current is led through a thin wire until it melts and the atoms migrate to produce the gap. Further, the reach of conventional photolithography can be enhanced by chemically etching or depositing metal on the electrodes.

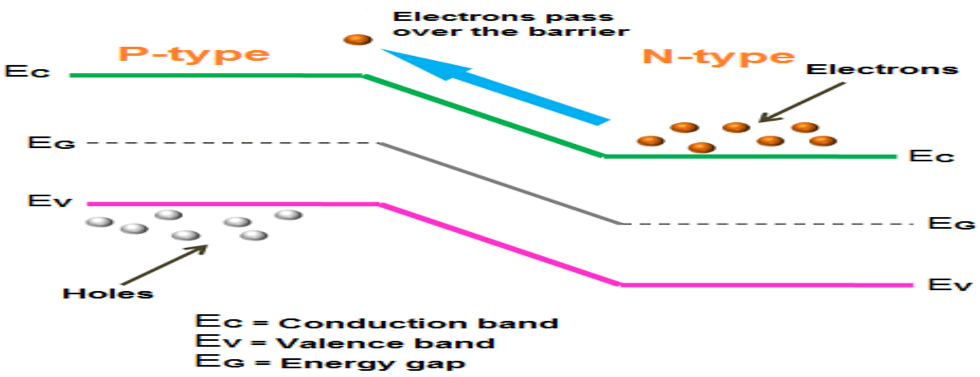
Probably the easiest way to conduct measurements on several molecules is to use the tip of a scanning tunneling microscope (STM) to contact molecules adhered at the other end to a metal substrate.

### Fullerene nano electronics

In polymers, classical organic molecules are composed of both carbon and hydrogen (and sometimes additional compounds such as nitrogen, chlorine or sulphur). They are obtained from petrol and can often be synthesized in large amounts. Most of these molecules are insulating when their length exceeds a few nanometers. However, naturally occurring carbon is conducting, especially graphite recovered from coal or encountered otherwise. From a theoretical viewpoint, graphite is a semi-metal, a category in between metals and semi-conductors. It has a layered structure, each sheet being one atom thick. Between each sheet, the interactions are weak enough to allow an easy manual cleavage.

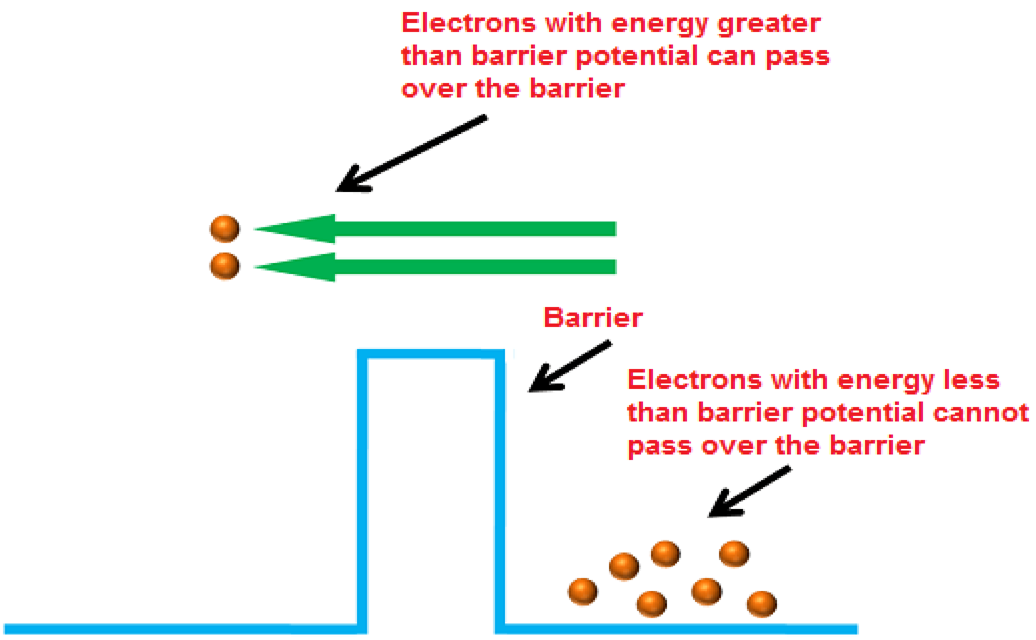
Tailoring the graphite sheet to obtain well defined nanometer-sized objects remains a challenge. However, by the close of the twentieth century, chemists were exploring methods to fabricate extremely small graphitic objects that could be considered single molecules. After studying the interstellar conditions under which carbon is known to form clusters, Richard Smalley's group (Rice University, Texas) set up an experiment in which graphite was vaporized via laser irradiation. Mass spectrometry revealed that clusters containing specific magic numbers of atoms were stable, especially those clusters of 60 atoms. Harry Kroto, an English chemist who assisted in the experiment, suggested a possible geometry for these clusters – atoms covalently bound with the exact symmetry of a soccer ball. Coined buck minsterfullerenes, buckyballs, or $C_{60}$, the clusters retained some properties of graphite, such as conductivity. These objects were rapidly envisioned as possible building blocks for molecular electronics.

Single E



Ec = Conduction band
Ev = Valence band
EG = Energy gap

Ordinary P-N junction diode



Electrons with energy greater than barrier potential can pass over the barrier

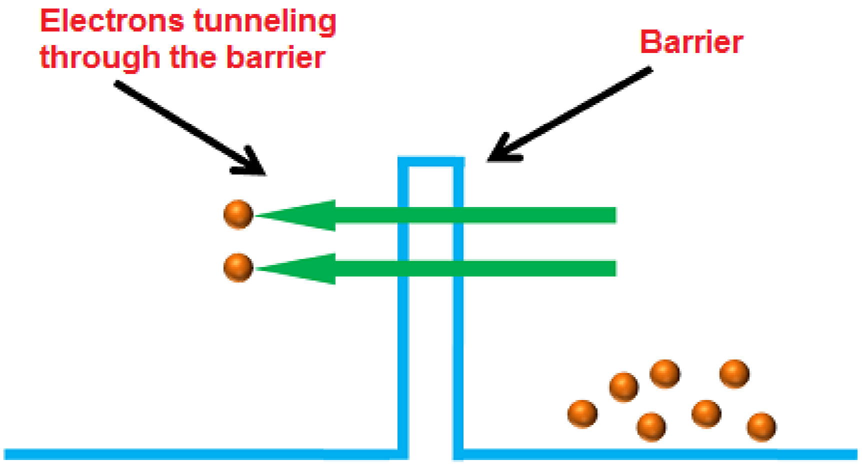
Electrons with energy less than barrier potential cannot pass over the barrier

Ordinary p-n junction diode

Therefore, an ordinary p-n junction diode produces electric current only if the applied voltage is greater than the built-in voltage of the depletion region.

### 4.5.4.ELECTRIC CURRENT IN TUNNEL DIODE

In tunnel diode, the valence band and conduction band energy levels in the n-type semiconductor are lower than the valence band and conduction band energy levels in the p-type semiconductor. Unlike the ordinary p-n junction diode, the difference in energy levels is very high in tunnel diode. Because of this high difference in energy levels, the conduction band of the n-type material overlaps with the valence band of the p-type material.



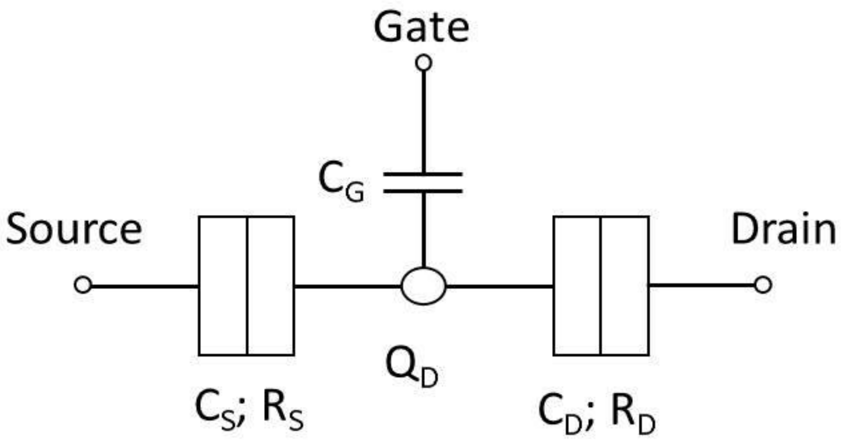
Tunnel diode

Quantum mechanics says that the electrons will directly penetrate through the depletion layer or barrier if the depletion width is very small.

The depletion layer of tunnel diode is very small. It is in nanometers. So the electrons can directly tunnel across the small depletion region from n-side conduction band into the p-side valence band.

## 4.6.SINGLE ELECTRON TRANSISTOR

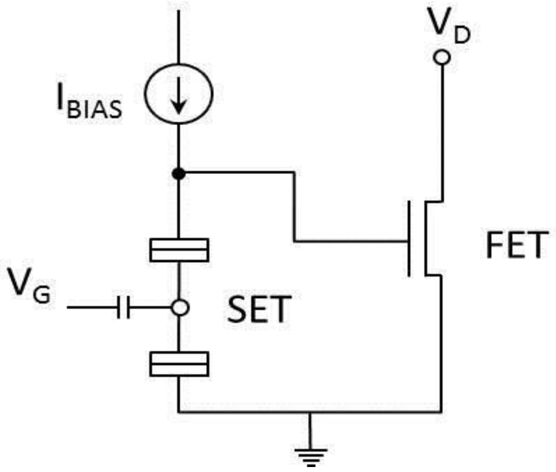
A single-electron transistor (SET) is a sensitive electronic device based on the Coulomb blockade effect. In this device the electron flows through a tunnel junction between source/drain to a quantum dot (conductive island). Moreover, the electrical potential of the island can be tuned by a third electrode, known as the gate, which is capacitively coupled to the island. Fig. 1 shows the basic schematic of a SET device. The conductive island is sandwiched between two tunnel junctions,[1] which are modeled by a capacitance ($C_D$ and $C_S$) and a resistor ($R_D$ and $R_S$) in parallel.



The increasing relevance of the Internet of things and the healthcare applications give more relevant impact to the electronic device power consumption. For this purpose, ultra-low-power consumption is one of the main research topics into the current electronics world. The amazing number of tiny computers used in the day-to-day world, e.g. mobile phones and home electronics; requires a significant power consumption level of the implemented devices.

In this scenario, the single-electron transistor has appeared as a suitable candidate to achieve this low power range with high level of device integration. The main technological difference between the well-established MOSFET device (metal-oxide-semiconductor field-effect transistor) and the SET lies on the device channel concept. Instead of having a conduction channel as in case of MOSFET, which is not allowing further reduction in its length; this channel is replaced by a small conducting "island" or quantum dot (QD).[2] By taking advantage of the Coulomb blockade phenomenon in controlling the transfer of individual electrons to the QD. Source and drain regions are separated from the QD by tunnel junctions. The research on SET is mainly supported on "orthodox theory" based on three assumptions:

1. The electron energy quantization inside the conductors is ignored, i.e. the electron energy spectrum is treated as continuous, what is valid only if ,  where $k_B$ is Boltzmann's constant and T is the temperature.
2. The time ($\tau_t$) of electron tunnelling through the barrier is assumed to be negligibly small in comparison with the other time scales. This assumption is valid for tunnel barriers used in single-electron devices of practical interest, where $\tau_t$~10-15s.
3. Coherent quantum processes consisting of several simultaneous tunnelling events, i.e. co-tunnelling, are ignored. This assumption is valid if the resistance of all the tunnel barriers of the system is much higher than the quantum resistance (~26 kΩ), to confine the electrons to the island.



The main benefits of the SET use are a high device integration level and ultra-low power consumption. Moreover, the SET fabrication process is CMOS-compatible (complementary metal–oxide–semiconductor), which increases the possibilities for integrating them into complex circuits. At this point some drawbacks appear to be overcome such as low current level and the low temperature operation. The current level of the SET can be amplified by manufacturing together with a field-effect transistor (FET), by generating a hybrid SET-FET circuit

Afterwards, the thermal fluctuations can suppress the Coulomb blockade; then, the electrostatic charging energy ($e^2/C_\Sigma$) must be greater than $k_BT$. This condition implies the maximum allowed island capacitance is inversely proportional to temperature. For these systems, to solve the drawback related to the SET operative only at cryogenic temperature it should be considered that an island capacitance below 1 aF is required to be room temperature operative. Note that the island capacitance is a function of their size. In this sense, to manufacture room temperature operative SETs the island size should be reduced towards 10 nm. Note that this level of device dimensions can jeopardize the SET manufacturability.

### 4.6.1.NEW MANUFACTURING PROPOSALS

In this context, the relevance of the SET-based circuits have been recently highlighted through the granting of a project by the European Union, IONS4SET (#688072). The project looks for the manufacturing feasibility of SET-FET circuits operative at room temperature. The main goal of this project is to design SET manufacturability process-flow for large-scale operations seeking to extend the use of the hybrid SET-CMOS architectures.

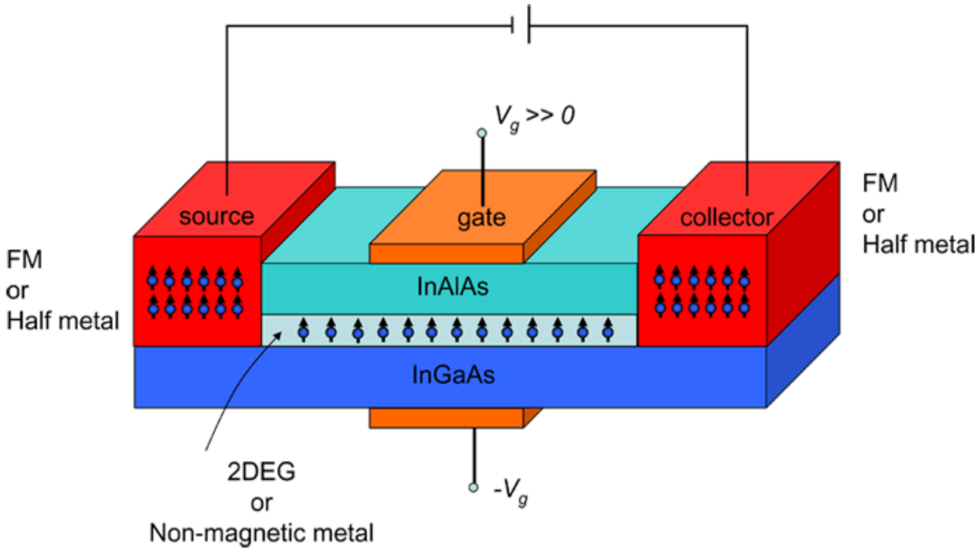
To assure room temperature operation, single dots of diameters below 5 nm have to be fabricated and located between source and drain with tunnel distances of a few nanometers. Up to now there is no reliable process-flow to manufacture a hybrid SET-FET circuit operative at room temperature. In this context, this EU project explores a more feasible way to manufacture the SET-FET circuit by using pillar dimensions of approximately 10 nm.

## 4.7.SPIN POLARIZED FIELD EFFECT TRANSISTOR (SPIN-FET)

Spin polarized field effect transistor (Spin FET) was proposed by Datta Das in 1990 . This has not been realized yet, but is regarded as one of the most advanced applications of spintoronics in the future.

In these devices a non magnetic layer which is used for transmitting and controlling the spin polarized electrons from source to drain plays a crucial role. For functioning of this device first the spins have to be injected from source into this non-magnetic layer and then transmitted to the collector. These non-magnetic layers are also called as semimetals, because they have very large spin diffusion lengths.

The injected spins which are transmitted through this layer start precessing as illustrated in Figure 1 before they reach the collector due to the spin-orbit coupling effect.



Spin polarized field effect transistor. Vg is the gate voltage. When Vg is zero the injected spins which are transmitted through the 2DEG layer starts precessing before they reach the collector, thereby reducing the net spin polarization. Vg is the gate voltage. When Vg >> 0 the precession of the electrons is controlled with electric filed thereby allowingthe spins to reach at the collector with the same polarization.

Hence the net spin polarization is reduced. In order to solve this problem an electric field is applied perpendicularly to the plane of the film by depositing a gate electrode on the top to reduce the spin-orbit coupling effect as illustrated in Figure 4. By controlling the gate voltage and polarity can the current in the collector can be modulated there by mimicking the MOSFET of the conventional electronics. Here again the problem of conductivity mismatch between the source and the transmitting layer is an important issue.

The interesting thing would be if a Heusler alloy is used as the spin source and a semimetallic Heusler alloy as the transmitting layer, the problem of conductivity mismatch may be solved. For example from the Slater-Pauling curve Mt = Zt - 24, Heusler alloys with Mt >>0 can act as spin sources and alloys with Mt ~ 0 can act as semimetals. Since both the constituents are of same structure the possibility of conductivity mismatch may be less.

### 4.8.THIN FILM

A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications.

A familiar example is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors, while more recently the metal layer is deposited using techniques such as sputtering. Advances in thin film deposition techniques during the 20th century have enabled a wide range of technological breakthroughs in areas such as magnetic recording media, electronic semiconductor devices, LEDs, optical coatings (such as antireflective coatings), hard coatings on cutting tools, and for both energy generation (e.g. thin-film solar cells) and storage (thin-film batteries). It is also being applied to pharmaceuticals, via thin-film drug delivery. A stack of thin films is called a multilayer.

In addition to their applied interest, thin films play an important role in the development and study of materials with new and unique properties. Examples include multiferroic materials, and superlattices that allow the study of quantum confinement by creating two-dimensional electron states.

### 4.8.1.DEPOSITION

The act of applying a thin film to a surface is thin-film deposition – any technique for depositing a thin film of material onto a substrate or onto previously deposited layers. "Thin" is a relative term, but most deposition techniques control layer thickness within a few tens of nanometres. Molecular beam epitaxy, Langmuir-Blodgett method and atomic layer depositionallow a single layer of atoms or molecules to be deposited at a time.

It is useful in the manufacture of optics (for reflective, anti-reflective coatings or self-cleaning glass, for instance), electronics(layers of insulators, semiconductors, and conductors form integrated circuits), packaging (i.e., aluminium-coated PET film), and in contemporary art (see the work of Larry Bell). Similar processes are sometimes used where thickness is not important: for instance, the purification of copper by electroplating, and the deposition of silicon and enriched uranium by a CVD-like process after gas-phase processing.

Deposition techniques fall into two broad categories, depending on whether the process is primarily chemical or physical.

### 4.8.2.CHEMICAL DEPOSITION

Here, a fluid precursor undergoes a chemical change at a solid surface, leaving a solid layer. An everyday example is the formation of soot on a cool object when it is placed inside a flame. Since the fluid surrounds the solid object, deposition happens on every surface, with little regard to direction; thin films from chemical deposition techniques tend to be conformal, rather than directional. Chemical deposition is further categorized by the phase of the precursor:

Plating relies on liquid precursors, often a solution of water with a salt of the metal to be deposited. Some plating processes are driven entirely by reagents in the solution (usually for noble metals), but by far the most commercially important process is electroplating. It was not commonly used in semiconductor processing for many years, but has seen a resurgence with more widespread use of chemical-mechanical polishing techniques.

Chemical solution deposition (CSD) or chemical bath deposition (CBD) uses a liquid precursor, usually a solution of organometallic powders dissolved in an organic solvent. This is a relatively inexpensive, simple thin-film process that produces stoichiometrically accurate crystalline phases. This technique is also known as the sol-gel method because the 'sol' (or solution) gradually evolves towards the formation of a gel-like diphasic system.

Langmuir-Blodgett method uses molecules floating on top of an aqueous subphase. The packing density of molecules is controlled, and the packed monolayer is transferred on a solid substrate by controlled withdrawal of the solid substrate from the subphase. This allows creating thin films of various molecules such as nanoparticles, polymers and lipids with controlled particle packing density and layer thickness.

Spin coating or spin casting, uses a liquid precursor, or sol-gel precursor deposited onto a smooth, flat substrate which is subsequently spun at a high velocity to centrifugally spread the solution over the substrate. The speed at which the solution is spun and the viscosity of the sol determine the ultimate thickness of the deposited film. Repeated depositions can be carried out to increase the thickness of films as desired.

Thermal treatment is often carried out in order to crystallize the amorphous spin coated film. Such crystalline films can exhibit certain preferred orientations after crystallization on single crystal substrates.

Dip coating is similar to spin coating in that a liquid precursor or sol-gel precursor is deposited on a substrate, but in this case the substrate is completely submerged in the solution and then withdrawn under controlled conditions. By controlling the withdrawal speed, the evaporation conditions (principally the humidity, temperature) and the volatility/viscosity of the solvent, the film thickness, homogeneity and nanoscopic morphology are controlled. There are two evaporation regimes: the capillary zone at very low withdrawal speeds, and the draining zone at faster evaporation speeds.

Chemical vapor deposition (CVD) generally uses a gas-phase precursor, often a halide or hydride of the element to be deposited. In the case of MOCVD, an organometallic gas is used. Commercial techniques often use very low pressures of precursor gas.

Plasma enhanced CVD (PECVD) uses an ionized vapor, or plasma, as a precursor. Unlike the soot example above, commercial PECVD relies on electromagnetic means (electric current, microwave excitation), rather than a chemical-reaction, to produce a plasma.

Atomic layer deposition (ALD) uses gaseous precursor to deposit conformal thin films one layer at a time. The process is split up into two half reactions, run in sequence and repeated for each layer, in order to ensure total layer saturation before beginning the next layer. Therefore, one reactant is deposited first, and then the second reactant is deposited, during which a chemical reaction occurs on the substrate, forming the desired composition. As a result of the stepwise, the process is slower than CVD, however it can be run at low temperatures, unlike CVD.

### 4.8.3.PHYSICAL DEPOSITION

Physical deposition uses mechanical, electromechanical or thermodynamic means to produce a thin film of solid. An everyday example is the formation of frost. Since most engineering materials are held together by relatively high energies, and chemical reactions are not used to store these energies, commercial physical deposition systems tend to require a low-pressure vapor environment to function properly; most can be classified as physical vapor deposition (PVD).

The material to be deposited is placed in an energetic, entropic environment, so that particles of material escape its surface. Facing this source is a cooler surface which draws energy from these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum deposition chamber, to allow the particles to travel as freely as possible. Since particles tend to follow a straight path, films deposited by physical means are commonly directional, rather than conformal.

Examples of physical deposition include: A thermal evaporator that uses an electric resistance heater to melt the material and raise its vapor pressure to a useful range. This is done in a high vacuum, both to allow the vapor to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber, and reduce the incorporation of impurities from the residual gas in the vacuum chamber. Obviously, only materials with a much higher vapor pressure than the heating element can be deposited without contamination of the film. Molecular beam epitaxy is a particularly sophisticated form of thermal evaporation.

An electron beam evaporator fires a high-energy beam from an electron gun to boil a small spot of material; since the heating is not uniform, lower vapor pressure materials can be deposited. The beam is usually bent through an angle of 270° in order to ensure that the gun filament is not directly exposed to the evaporant flux. Typical deposition rates for electron beam evaporation range from 1 to 10 nanometres per second.

In molecular beam epitaxy (MBE), slow streams of an element can be directed at the substrate, so that material deposits one atomic layer at a time. Compounds such as gallium arsenide are usually deposited by repeatedly applying a layer of one element (i.e., gallium), then a layer of the other (i.e., arsenic), so that the process is chemical, as well as physical; this is known also as atomic layer deposition. The beam of material can be generated by either physical means (that is, by a furnace) or by a chemical reaction (chemical beam epitaxy).

Sputtering relies on a plasma (usually a noble gas, such as argon) to knock material from a "target" a few atoms at a time. The target can be kept at a relatively low temperature, since the process is not one of evaporation, making this one of the most flexible deposition techniques. It is especially useful for compounds or mixtures, where different components would otherwise tend to evaporate at different rates. Note, sputtering's step coverage is more or less conformal. It is also widely used in the optical media. The manufacturing of all formats of CD, DVD, and BD are done with the help of this technique. It is a fast technique and also it provides a good thickness control. Presently, nitrogen and oxygen gases are also being used in sputtering.

Pulsed laser deposition systems work by an ablation process. Pulses of focused laser light vaporize the surface of the target material and convert it to plasma; this plasma usually reverts to a gas before it reaches the substrate.[5]

Cathodic arc deposition (arc-PVD) which is a kind of ion beam deposition where an electrical arc is created that literally blasts ions from the cathode. The arc has an extremely high power density resulting in a high level of ionization (30–100%), multiply charged ions, neutral particles, clusters and macro-particles (droplets). If a reactive gas is introduced during the evaporation process, dissociation, ionization and excitation can occur during interaction with the ion flux and a compound film will be deposited.

Electrohydrodynamic deposition (electrospray deposition) is a relatively new process of thin-film deposition. The liquid to be deposited, either in the form of nanoparticle solution or simply a solution, is fed to a small capillary nozzle (usually metallic) which is connected to a high voltage.

The substrate on which the film has to be deposited is connected to ground. Through the influence of electric field, the liquid coming out of the nozzle takes a conical shape (Taylor cone) and at the apex of the cone a thin jet emanates which disintegrates into very fine and small positively charged droplets under the influence of Rayleigh charge limit.

The droplets keep getting smaller and smaller and ultimately get deposited on the substrate as a uniform thin layer.

### .8.4.GROWTH MODES

In this growth mode the adsorbate-surface and adsorbate-adsorbate interactions are balanced. This type of growth requires lattice matching, and hence considered an "ideal" growth mechanism.

Stranski–Krastanov growth ("joint islands" or "layer-plus-island"). In this growth mode the adsorbate-surface interactions are stronger than adsorbate-adsorbate interactions.

Volmer-Weber ("isolated islands"). In this growth mode the adsorbate-adsorbate interactions are stronger than adsorbate-surface interactions, hence "islands" are formed right away.

### 4.8.5.EPITAXY

A subset of thin-film deposition processes and applications is focused on the so-called epitaxial growth of materials, the deposition of crystalline thin films that grow following the crystalline structure of the substrate. The term epitaxy comes from the Greek roots epi , meaning "above", and taxis , meaning "an ordered manner". It can be translated as "arranging upon".

The term homoepitaxy refers to the specific case in which a film of the same material is grown on a crystalline substrate. This technology is used, for instance, to grow a film which is more pure than the substrate, has a lower density of defects, and to fabricate layers having different doping levels. Heteroepitaxy refers to the case in which the film being deposited is different than the substrate.

Techniques used for epitaxial growth of thin films include molecular beam epitaxy, chemical vapor deposition, and pulsed laser deposition.[11]

### 4.8.6.APPLICATIONS

**Decorative coatings** The usage of thin films for decorative coatings probably represents their oldest application. This encompasses ca. 100 nm thin gold leafs that were already used in ancient India more than 5000 years ago. It may also be understood as any form of painting, although this kind of work is generally considered as an arts craft rather than an engineering or scientific discipline. Today, thin-film materials of variable thickness and high refractive index like titanium dioxide are often applied for decorative coatings on glass for instance, causing a rainbow-color appearance like oil on water. In addition, intransparent gold-colored surfaces may either be prepared by sputtering of gold or titanium nitride.

#### Optical coatings

Further information: Optical coating

These layers serve in both reflective and refractive systems. Large-area (reflective) mirrors became available during the 19th century and were produced by sputtering of metallic silver or aluminum on glass.

Refractive lenses for optical instruments like cameras and microscopes typically exhibit aberrations, i.e. non-ideal refractive behavior. While large sets of lenses had to be lined up along the optical path previously, nowadays, the coating of optical lenses with transparent multilayers of titanium dioxide, silicon nitride or silicon oxide etc. may correct these aberrations. A well-known example for the progress in optical systems by thin-film technology is represented by the only a few mm wide lens in smart phone cameras. Other examples are given by anti-reflection coatings on eyeglasses or solar panels.

#### Protective coatings

Thin films are often deposited to protect an underlying work piece from external influences. The protection may operate by minimizing the contact with the exterior medium in order to reduce the diffusion from the medium to the work piece or vice versa. For instance, plastic lemonade bottles are frequently coated by anti-diffusion layers to avoid the out-diffusion of $CO_2$, into which carbonic acid decomposes that was introduced into the beverage under high pressure. Another example is represented by thin TiN films in microelectronic chips separating electrically conducting aluminum lines from the embedding insulator $SiO_2$ in order to suppress the formation of $Al_2O_3$. Often, thin films serve as protection against abrasion between mechanically moving parts. Examples for the latter application are diamond-like carbon (DLC) layers used in car engines or thin films made of nanocomposites.

### Electrically operating coatings

Thin layers from elemental metals like copper, aluminum, gold or silver etc. and alloys have found numerous applications in electrical devices. Due to their high electrical conductivitythey are able to transport electrical currents or supply voltages. Thin metal layers serve in conventional electrical system, for instance, as Cu layers on printed circuit boards, as the outer ground conductor in coaxial cables and various other forms like sensors etc.[13] A major field of application became their use in integrated circuits, where the electrical network among active and passive devices like transistors and capacitors etc. is built up from thin Al or Cu layers. These layers dispose of thicknesses in the range of a few 100 nm up to a few µm, and they are often embedded into a few nm thin titanium nitride layers in order to block a chemical reaction with the surrounding dielectric like $SiO_2$. The figure shows a micrograph of a laterally structured TiN/Al/TiN metal stack in a microelectronic chip.

### Thin-film photovoltaic cells

Thin-film technologies are also being developed as a means of substantially reducing the cost of solar cells. The rationale for this is thin-film solar cells are cheaper to manufacture owing to their reduced material costs, energy costs, handling costs and capital costs. This is especially represented in the use of printed electronics (roll-to-roll) processes. Other thin-film technologies, that are still in an early stage of ongoing research or with limited commercial availability, are often classified as emerging or third generation photovoltaic cells and include, organic, dye-sensitized, and polymer solar cells, as well as quantum dot, copper zinc tin sulfide, nanocrystal and perovskite solar cells.

### Thin-film batteries

Thin-film printing technology is being used to apply solid-state lithium polymers to a variety of substrates to create unique batteries for specialized applications. Thin-film batteries can be deposited directly onto chips or chip packages in any shape or size. Flexible batteries can be made by printing onto plastic, thin metal foil, or paper.

# UNIT-V

## 5.1APPLICATIONS OF NANOTECHNOLOGY:

The driving force behind the fundamental research into nanocrystals is the perceived and demonstrated properties that can be exploited into applications. The application of these properties falls largely into two broad categories: improved properties and unique properties. The improved, or incremental, group covers those applications that have already been conceived but can benefit from the use of nanocrystals in terms of either particle size or surface area.

Many of these types of applications have found nearly instant commercial success and have opened the door to larger use. The ―unique‖ group of applications is a smaller set but holds the greatest potential. This group consists of properties that are exclusively attributed to nanostructuring and includes electronic and optical quantum confinement effects, super paramagnetism, and ceramic super plasticity, to name a few. To date, these have created niche commercial opportunities, but acceptance and interest are growing.

## HISTORICAL:

One might ask, whether nanocrystals are really new. The answer would have to be yes and no, with a qualification for each. For over a century the properties of small particles have been exploited in applications ranging from catalysis to the colors of stained glass. Some of the earliest recorded evidence came in 1856 when Michael Faraday discovered that nanometer-sized particles create the color variations of metal-particle colloids through surface charge effects.

He found that colloids of 6 nm gold particles are red and those of 12 nm particles are blue. There is even evidence that nature has made use of nanoparticles in areas of biomineralization that take place in bones and teeth. The reason we might say that nanostructuring is new is largely attributable to the developments of modern science as it has investigated the ever-shrinking world of matter.

Advances in theoretical and experimental tools and techniques have increased our understanding of matter in both the micro and the nano regimes, largely motivated by the development of applications and technology. Consider the development of atomic force and scanning tunneling microscopy that has led to sophisticated machines that change the landscape of surfaces atom byatom.

An obvious example of this revolution is in the world of semiconductor electronics, which is driven by the demand to reduce the size of circuits, pushing the envelope of both science and technology. This applies not only to materials, but to a host of areas including optics, manufacturing, chemicals, and electronic design.

## 5.2. OPTOELECTRONIC PROPERTIES OF MOLECULAR MATERIALS

Nano-technology, among which Nano-electronic is one of the most used branches, is a meeting point for different sciences in the future. Nanoelectronic is nanotechnology applied in the context of electronic circuits and systems.

Today's knowledge requires increasing the capacity of data restoration, data transition, advancements in sensor manufacturing technologies and making electronic components as small as possible; the electronic components' being smaller not only increases the speed of the process, but also reduces the amount of consumed energy, two important goals which are accessible through Nano-electronic technique. Today's electronic industry is based on silicon; this industry is 50 years old and has gradually matured technologically, industrially, and financially. Molecular electronic, which is supposed to replace silicon electronic in the future, is an incipient branch of Nanotechnology. Since minifying the size of electronic components on Nano-scale confronts various limitations, focusing on the molecular electronic is a considerable point which should attract attention. The molecular electronic is a branch of science based on Nanotechnology with multiple applications in electronic industry in which organic molecules are central. Aromatic hydrocarbon from the root of benzene can provide suitable environments for electron transition due to p orbitals, upper and lower electron clouds, and resonance phenomenon. Electronic circuits and logic gates are designed out of the joining of this hydrocarbons.

Circumacenes is a family of organic molecules with the chemical formula of $C_{(8n+16)/3}H_{(2n+22)/3}$ which is focused in molecular electronic. The size of Circumacenes is a few nanometers to several hundred nanometers, particularly for heavy circumacenes. Since recognizing and examining this family of Nanostructures needs huge time and money, an appropriate pattern to predict electronic features is very beneficial; Topological Indices Method (TIM), is a cheap and useful approach to gain this goal. A single number, representing a chemical structure in graph-theoretical terms via the molecular graph, is called a topological descriptor and if it, in addition, correlates with a molecular property it is called topological index; it is used to understand physicochemical properties of chemical compounds. Topological indices are interesting since they capture some of the properties of a molecule in a single number. Hundreds of topological indices have been introduced and studied, starting with the seminal work by Wiener in which he used the sum of all shortest-path distances of a (molecular) graph for modeling physical properties of alkanes.

## 5.3. NANOTECHNOLOGY DEVICES

### 5.3.1.NANODEVICES

Nano devices are critical enablers that will allow mankind to exploit the ultimate technological capabilities of electronic, magnetic, mechanical, and biological systems. While the best examples of nano devices at present are clearly associated with the semiconductor industry, the potential for such devices is much broader. Nano devices will ultimately have an enormous impact on our ability to enhance energy conversion, control pollution, produce food, and improve human health and longevity.

At the CUNY ASRC (City University of New York Advanced Science and Research Centre ), several faculty conduct research in Nanodevices. These efforts are based in the basic and applied sciences as well as technology aspects of electronics, photonics and biomedical devices. Much of this research focuses on the understanding of various physical phenomena that arise from novel material systems or novel device structures fabricated in our in-house NanoFabrication Facility.

Examples of research efforts underway at the ASRC and CUNY in NanoDevices research include: Photonic, plasmonic and metamaterial devices

- ✓ Bio/chemical/nano sensing devices
- ✓ Electron and nuclear spin devices
- ✓ Energy harvesting systems (photonic)
- ✓ Micro-electromechanical systems (MEMS)
- ✓ Microfluidics and Microsystems
- ✓ Low dimensional nanostructures
- ✓ Topological insulator electric and photonic systems

### 5.3.2.EVERYDAY APPLICATIONS OF NANOTECHNOLOGY

Though nanotechnology is a relatively new science, it already has numerous applications in everyday life, ranging from consumer goods to medicine to improving theenvironment.

### Medicine

One application of nanotechnology in medicine currently being developed involves employing nanoparticles to deliver drugs, heat, light or other substances to specific types of cells, such as cancer cells. Particles are engineered so that they are attracted to diseased cells, which allowdirect treatment of those cells. This technique reduces damage to healthy cells in the body and allows for earlier detection of disease. For example, nanoparticles that deliver chemotherapy drugs directly to cancer cells are under development.

**Electronics**

Nanoelectronics holds some answers on expanding the capabilities of electronics devices can be expanded while reducing their weight and power consumption. These include improving display screens on electronics devices and increasing the density of memory chips. Nanotechnology can also reduce the size of transistors used in integrated circuits. One researcher believes it may be possible to put the power of all of today's present computers in the palm of your hand.

**Environment**

Nanotechnology is being used in several applications to improve the environment. This includes cleaning up existing pollution, improving manufacturing methods to reduce the generation of new pollution, and making alternative energy sources more cost effective. Potential applications include: Cleaning up organic chemicals polluting groundwater. Researchers have shown that iron nanoparticles can be effective in cleaning up organic solvents that are polluting groundwater. The iron nanoparticles disperse throughout the body of water and decompose the organic solvent in place. This method can be more effective and cost significantly less than treatment methods that require the water to be pumped out of the ground.

Generating less pollution during the manufacture of materials. Researchers have demonstrated that the use of silver nanoclusters as catalysys can significantly reduce the polluting byproducts generated in the process used to manufacture propylene oxide. Propylene oxide is used to produce common materials such as plastics, paint, detergents and brake fluid.

Increasing the electricity generated by windmills. Epoxy containing carbon nanotubes is being used to make windmill blades. The resulting blades are stronger and lower weight and therefore the amount of electricity generated by each windmill is greater.

Producing solar cells that generate electricity at a competitive cost. Researchers have demonstrated that an array silicon nano wires embedded in a polymer results in low-cost but high-efficiency solar cells. This may result in solar cells that generate electricity as cost effectively as coal or oil.

**Consumer Products**

Nanotechnology has already found its way into numerous consumer products you use every day, from clothing to skin lotion. They include:Silver nano particles in fabric that kill bacteria making clothing odor-resistant.Skin care products that use nanoparticles to deliver vitamins deeper into the skinLithium ion batteries that use nano particle-based electrodes powering plug-in electric carsFlame retardant formed by coating the foam used in furniture with carbon nanofiers

## 5.4.ORGANIC LIGHT EMITTING DIODES (OLEDS)

An organic light-emitting diode (OLED) is a light-emitting diode (LED) in which the emissive electroluminescent layer is a film of organic compound that emits light in response to an electric current. This organic layer is situated between two electrodes; typically, at least one of these electrodes is transparent. OLEDs are used to create digital displays in devices such as television screens, computer monitors, portable systems such as smartphones, handheld game consoles and PDAs. A major area of research is the development of white OLED devices for use in solid-state lighting applications.

There are two main families of OLED: those based on small molecules and those employing polymers. Adding mobile ions to an OLED creates a light-emitting electrochemical cell (LEC) which has a slightly different mode of operation. An OLED display can be driven with a passive-matrix (PMOLED) or active-matrix (AMOLED) control scheme. In the PMOLED scheme, each row (and line) in the display is controlled sequentially, one by one,[4] whereas AMOLED control uses a thin-film transistor backplane to directly access and switch each individual pixel on or off, allowing for higher resolution and larger display sizes.

An OLED display works without a backlight because it emits visible light. Thus, it can display deep black levels and can be thinner and lighter than a liquid crystal display (LCD). In low ambient light conditions (such as a dark room), an OLED screen can achieve a higher contrast ratio than an LCD, regardless of whether the LCD uses cold cathode fluorescent lamps or an LED backlight.

## 5.5. ORGANIC THIN-FILM TRANSISTOR (OTFT)

Organic thin-film transistor (OTFT) technology involves the use of organic semiconducting compounds in electronic components, notably computer displays. Such displays are bright, the colors are vivid, they provide fast response times, and they are easy to read in most ambient lighting environments.

Several factors have motivated engineers to conduct and continue research in organic semiconductor technology. One of these factors is cost. Organic displays are relatively cheap, but until recently, they have proven slow in terms of carrier mobility (the ease with which an atom shares electron s and hole s with other atoms). Slow carrier mobility translates into sluggish response time, which limits the ability of a display to render motion such as is common in animated computer games and, increasingly, on the Web. Researchers at Lucent Technologies and Pennsylvania State University have, however, recently developed a process for growing organic crystals with carrier mobility rivaling that of traditional TFT materials. Further improvements are expected.

Another factor that motivates research in OTFT technology is application diversity. Organic substrates allow for displays to be fabricated on flexible surfaces, rather than on rigid materials as is necessary in traditional TFT displays. A piece of flexible plastic might be coated with OTFT material and made into a display that can be handled like a paper document. Sets of such displays might be bundled, producing magazines or newspapers whose page contents can be varied periodically, or even animated. This has far-reaching ramifications. For example, comic book characters might move around the pages and speak audible words. More likely, such displays will find use in portable computers and communications systems.

## 5.6.BIOELECTRONICS AND BIOSENSORS:

### 5.6.1.BIOSENSOR

A biosensor is an analytical device, used for the detection of a chemical substance, that combines a biological component with a physicochemical detector. The sensitive biological element, e.g. tissue, microorganisms, organelles, cell receptors, enzymes, antibodies, nucleic acids, etc., is a biologically derived material or biomimetic component that interacts, binds, or recognizes with the analyte under study. The biologically sensitive elements can also be created by biological engineering. The transducer or the detector element, which transforms one signal into another one, works in a physicochemical way: optical, piezoelectric, electrochemical, electro chemiluminescence etc., resulting from the interaction of the analyte with the biological element, to easily measure and quantify. The biosensor reader device with the associated electronics or signal processors that are primarily responsible for the display of the results in a user-friendly way. This sometimes accounts for the most expensive part of the sensor device, however it is possible to generate a user friendly display that includes transducer and sensitive element (holographic sensor). The readers are usually custom-designed and manufactured to suit the different working principles of biosensors.

### 5.6.2.BIOELECTRONICS

The branch of science concerned with the application of biological materials and processes in electronics, and the use of electronic devices in living systems.

Health issues have been a primary concern for humans since the early ages. As the years rolled by, there have been various improvements in the field of medicine. The introduction of various revolutionary techniques, approaches, and methods have seen great leaps in the field of medicine. Less pain in the approach to cure disease and other effects with better results has led to people having more faith in modern medical sciences. Now let us see how bioelectronics plays a vital role in the field of medicine and other areas.

Bioelectronics is the application of the principles of electronics to biology and medicine. Hollywood has expanded the horizons with its imagination, and movies like Star Wars, Star Trek, iRobot, Minority Report and many other sci-fi movies have shown us what modern technology is capable of. The potential of bioelectronics is also shown in these movies. Artificial limbs, humanoids, the various sensors that are attached to the body, etc. are the applications of bioelectronics.

### 5.6.3.DNA AND PROTEIN FUNCTIONAL SYSTEMS

Recent advances in nucleic acid recognition can enhance the power of DNA biosensors. For example, the introduction of peptide nucleic acid (PNA) has opened up exciting opportunities for DNA biosensors. PNA is a DNA mimic in which the sugar–phosphate backbone is replaced with a pseudopeptide one.

### 5.6.4. ELECTRONIC NOSES AND BIOSENSORS

An electronic nose is a device intended to detect odors or flavors.

Over the last decades, "electronic sensing" or "e-sensing" technologies have undergone important developments from a technical and commercial point of view. The expression "electronic sensing" refers to the capability of reproducing human senses using sensor arrays and pattern recognition systems. Since 1982, research has been conducted to develop technologies, commonly referred to as electronic noses, that could detect and recognize odors and flavors. The stages of the recognition process are similar to human olfaction and are performed for identification, comparison, quantification and other applications, including data storage and retrieval. However, hedonic evaluation is a specificity of the human nose given that it is related to subjective opinions. These devices have undergone much development and are now used to fulfill industrial needs

## Biosensors

A biosensor consists of an immobilised biologic molecule (enzymes, cellules or antibodies) next to a transducer, which transforms chemical signal into an electric signal or into other kind of output as optical, acoustic and heat signal when an analyte reaches to it. . Arnold and Meyerhoff defined biosensors as "a self contained analytical device that responds selectively and reversibly to the concentration or activity of chemical species in biological samples". Biosensors then consist of a biological sensing element and a transduction element.

Optical biosensors are based on optical changes while the biochemical reaction takes place. If a light beam is propagated through a waveguide, then the internally reflected light generates an electromagnetic "evanescent wave" that can be used to excite fluorescent molecules at the surface of the waveguide. The "evanescent wave" can couple with the electron plasma of a metal when the waveguide is coated with a metal thin layer. It causes the electrons to oscillate and thus generating a surface plasmon wave that is characterized by high sensitivity and specificity. The surface plasmon is an electromagnetic wave associated with the longitudinal oscillation of the free electron gas on the interface of the metal and the dielectric. Recently, surface plasmon resonance interferometry (SPRI) has been established as a novel method that gains in sensitivity and resolution for the detection of a multiplicity of analytes.

## THE ELECTRONIC NOSE

Recently, sensors with sensitivity to a wide range of volatiles compounds have been integrated in a system called electronic nose. The name of 'electronic nose' is due to the similarities between this instrument and the physiological system.

## 5.7. BIOMEDICAL APPLICATIONS:

A wealth of interest has developed for nanocrystals as applied to health and biological systems. In the area of medical diagnostics, colloidal or imbedded iron-based particles are being used to separate specific substances present in body fluid samples. Antibodies can be attached to magnetic colloidal particles, typically silica-coated iron oxides or polystyrene spheres with embedded iron oxides; when these are mixed with a blood sample the antibody reacts and binds with the target hormone.

Because the nanoparticle size creates both high surface area for reaction and a tendency to move rapidly in solution due to thermal Brownian motion, reactions can be quite rapid. The magnetic functionality of the particle permits detection of the antibody=hormone complex by separating and concentrating the reacted material from the blood sample. Even DNA detection through colorimetric techniques has been developed through the use of oligonucleotide-functionalized gold nanocrystals that can be assembled into periodic network materials.

Similar particles are also being developed for drug delivery. In this application, biochemical drugs can be bound to the magnetic nanocrystals and with applied magnetic fields can be steered into regions of the body where they are required. For example, malignant tumors can be attached with targeted drug delivery and concentration through the use of magnetic fields.

Rare, tumor-causing cells can also be targeted by nanocrystals with attached chemicals that bind to the cells and sweep them from the bloodstream before they have had a chance to degrade. Some previous examples showed that 100 tumor cells could be captured and removed from 50 million blood cells in less than one hour.

## 5.8 TYPES OF OPTO ELECTRONICS DEVICES ABD THEIR APPLICATIONS:

Optoelectronics is the communication between optics and electronics which includes the study, design and manufacture of a hardware device that converts electrical energy into light and light into energy through semiconductors. This device is made from solid crystalline materials which are lighter than metals and heavier than insulators. Optoelectronics device is basically an electronic device involving light. This device can be found in many optoelectronics applications like military services, telecommunications, automatic access control systems and medical equipments.

This academic field covers a wide range of devices including LEDs and elements, image pick up devices, information displays, optical communication systems, optical storages and remote sensing systems, etc. Examples of optoelectronic devices include telecommunication laser, blue laser, optical fiber, LED traffic lights, photo diodes and solar cells. Majority of the optoelectronic devices (direct conversion between electrons and photons) are LEDs, laser diodes, photo diodes and solar cells.

### Types of Optoelectronics Devices:

Optoelectronics are classified into different types such as

- ✓ Photodiode
- ✓ Solar Cells
- ✓ Light Emitting Diodes
- ✓ Optical Fiber
- ✓ Laser Diodes

### Photo Diode:

A photo diode is a semiconductor light sensor that generates a voltage or current when light falls on the junction. It consists of an active P-N junction, which is operated in reverse bias. When a photon with plenty of energy strikes the semiconductor, an electron or hole pair is created. The electrons diffuse to the junction to form an electric field.

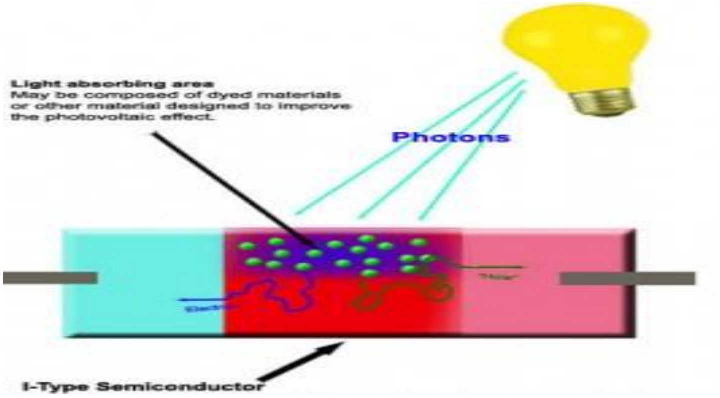


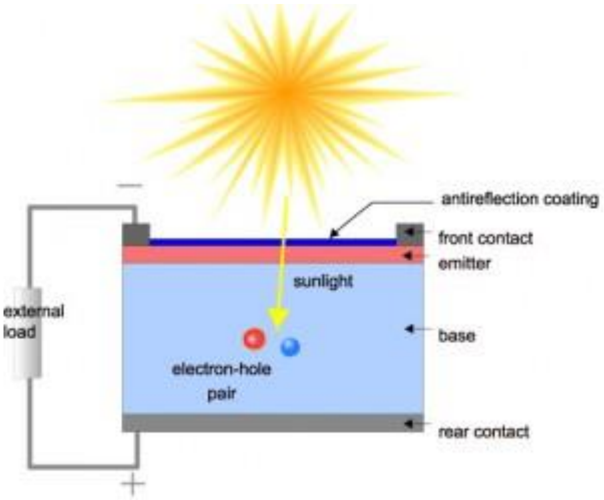
Photo Diode

This electric field across the depletion zone is equal to a negative voltage across the unbiased diode. This method is also known as the inner photoelectric effect. This device can be used in three modes: photovoltaic as a solar cell, forward biased as an LED and reverse biased as a photo detector.

Photodiodes are used in many types of circuits and different applications such as cameras, medical instruments, safety equipments, industries, communication devices and industrial equipments.

**Solar Cells:**

A solar cell or photo-voltaic cell is an electronic device that directly converts sun’s energy into electricity. When sunlight falls on a solar cell, it produces both a current and a voltage to produce electric power. Sunlight, which is composed of photons, radiates from the sun. When photons hit the silicon atoms of the solar cell, they transfer their energy to lose electrons; and then, these high-energy electron flow to an external circuit.



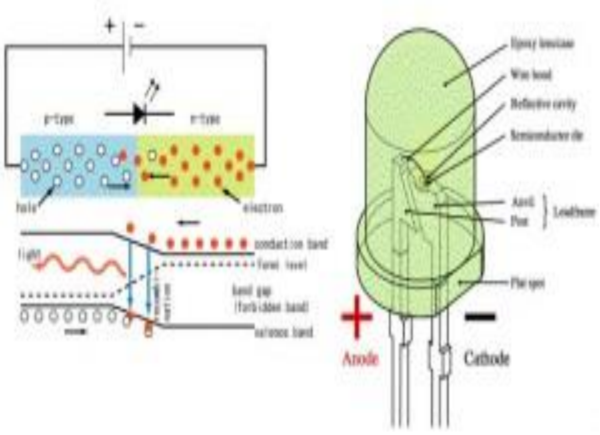
Solar Cells

The solar cell is composed of two layers which are struck together. The first layer is loaded with electrons, so these electrons are ready to jump from the first layer to the second layer. The second layer has some electrons taken away, and therefore, it is ready to take more electrons. The advantages of solar cells are that, there is no fuel supply and cost problem. These are very dependable and require little maintenance.

The solar cells are applicable in rural electrification, telecommunication systems, ocean navigation aids, electric power generation system in space and remote monitoring and control systems.

**Light-Emitting Diodes:**

Light-emitting diode is a P-N semiconductor diode in which the recombination of electrons and holes yields a photon. When the diode is electrically biased in the forward direction, it emits incoherent narrow spectrum light. When a voltage is applied to the leads of the LED, the electrons recombine with the holes within the device and release energy in the form of photons. This effect is called as electroluminescence. It is the conversion of electrical energy into light. The color of the light is decided by the energy band gap of the material.



Light Emitting Diode

The usage of LED is advantageous as it consumes less power and produces less heat. LEDs last longer than incandescent lamps. LEDs could become the next generation of lighting and used anywhere like in indication lights, computer components, medical devices, watches, instrument panels, switches, fiber-optic communication, consumer electronics, household appliances, etc.

**Applications of Optoelectronics Devices:**

1. LEDs could become the next generation of lighting and used anywhere like in indication lights, computer components, medical devices, watches, instrument panels, switches, fiber-optic communication, consumer electronics, household appliances, traffic signals, automobile brake lights, 7 segment displays and inactive displays, and also used in different electronic and electrical engineering projects such as

Propeller Display of Message by Virtual LEDs

LED Based Automatic Emergency Light

Mains Operated LED Light

Display of Dialed Telephone Numbers on Seven Segment Display

Solar Powered Led Street Light with Auto Intensity Control

**2.** The solar cells are applicable in rural electrification, telecommunication systems, ocean navigation aids, and electric power generation in space and remote monitoring and control systems and also used in different solar energy based projects such as

Solar Energy Measurement System

Arduino based Solar Street Light

Solar Powered Auto Irrigation System

Solar Power Charge Controller

Sun Tracking Solar Panel

Solar based Project from edgefxkits.com

**3**. Photodiodes are used in many types of circuits and different applications such as cameras, medical instruments, safety equipments, industries, communication devices and industrial equipments.

4. Optical fibers are used in telecommunications, sensors, fiber lasers, bio-medicals and in many other industries.

5. The laser diodes are used in fiber optic communication, optical memories, military applications, CD players, surgical procedures, Local Area Networks, long distance communications, optical memories, fiber optic communications and in electrical projects such as RF Controlled Robotic Vehicle with Laser Beam Arrangement and so on.

Thus, this is all about the optoelectronic devices which include laser diodes, photo diodes, solar cells, LEDs, optical fibers.These optoelectronic devices are used in different electronic project kits as well as in telecommunications, military services and in medical applications. For more information regarding the same, please post your queries by commenting below.

### 5.9. CNTs:

Many electronic applications of carbon nanotubes crucially rely on techniques of selectively producing either semiconducting or metallic CNTs, preferably of a certain chirality. Several methods of separating semiconducting and metallic CNTs are known, but most of them are not yet suitable for large-scale technological processes. The most efficient method relies on density-gradient ultracentrifugation, which separates surfactant-wrapped nanotubes by the minute difference in their density.

This density difference often translates into difference in the nanotube diameter and (semi)conducting properties. Another method of separation uses a sequence of freezing, thawing, and compression of SWNTs embedded in agarose gel. This process results in a solution containing 70% metallic SWNTs and leaves a gel containing 95% semiconducting SWNTs. The diluted solutions separated by this method show various colors. Moreover, SWNTs can be separated by the column chromatography method. Yield is 95% in semiconductor type SWNT and 90% in metallic type SWNT.

In addition to separation of semiconducting and metallic SWNTs, it is possible to sort SWNTs by length, diameter, and chirality. The highest resolution length sorting, with length variation of <10%, has thus far been achieved by size exclusion chromatography (SEC) of DNA-dispersed carbon nanotubes (DNA-SWNT). SWNT diameter separation has been achieved by density-gradient ultracentrifugation (DGU) using surfactant-dispersed SWNTs and by ion-exchange chromatography (IEC) for DNA-SWNT.

Purification of individual chiralities has also been demonstrated with IEC of DNA-SWNT: specific short DNA oligomers can be used to isolate individual SWNT chiralities. Thus far, 12 chiralities have been isolated at purities ranging from 70% for (8,3) and (9,5) SWNTs to 90% for (6,5), (7,5) and (10,5)SWNTs. There have been successful efforts to integrate these purified nanotubes into devices, e. g. FETs.

An alternative to separation is development of a selective growth of semiconducting or metallic CNTs. Recently, a new CVD recipe that involves a combination of ethanol and methanol gases and quartz substrates resulting in horizontally aligned arrays of 95–98% semiconducting nanotubes was announced.

Nanotubes are usually grown on nanoparticles of magnetic metal (Fe, Co), which facilitates production of electronic (spintronic) devices. In particular, control of current through a field-effect transistor by magnetic field has been demonstrated in such a single-tube nanostructure.

**Structural:**

Because of the carbon nanotube's superior mechanical properties, many structures have been proposed ranging from everyday items like clothes and sports gear to combat jackets and space elevators. However, the space elevator will require further efforts in refining carbon nanotube technology, as the practical tensile strength of carbon nanotubes can still be greatly improved.

For perspective, outstanding breakthroughs have already been made. Pioneering work led by Ray H. Baughman at the NanoTech Institute has shown that single and multi-walled nanotubes can produce materials with toughness unmatched in the man-made and natural worlds.

Carbon nanotubes are also a promising material as building blocks in bio-mimetic hierarchical composite materials given their exceptional mechanical properties (~1TPa in modulus, and ~100 GPa in strength). Initial attempts to incorporate CNTs into hierarchical structures led to mechanical properties that were significantly lower than these achievable limits. Windle et al. have used an *in situ* chemical vapor deposition (CVD) spinning method to produce continuous CNT yarns from CVD grown CNT aerogels.

With this technology, they fabricated CNT yarns with strengths as high as ~9 GPa at small gage lengths of ~1 mm, however, defects resulted in a reduction of specific strength to ~1 GPa at 20 mm gage length. Espinosa et al. developed high performance DWNT-polymer composite yarns by twisting and stretching ribbons of randomly oriented bundles of DWNTs thinly coated with polymeric organic compounds.

These DWNT-polymer yarns exhibited unusually high energy to failure of ~100 $J \cdot g^{-1}$ (comparable to one of the toughest natural materials – spider silk), and strength as high as ~1.4 GPa. Effort is ongoing to produce CNT composites that incorporate tougher matrix materials, such as Kevlar, to further improve on the mechanical properties toward those of individual CNTs.

Because of the high mechanical strength of carbon nanotubes, research is being made into weaving them into clothes to create stab-proof and bulletproof clothing. The nanotubes would effectively stop the bullet from penetrating the body, although the bullet's kinetic energy would likely cause broken bones and internal bleeding.

**In electrical circuits:**

Nanotube-based transistors, also known as carbon nanotube field-effect transistors (CNFETs), have been made that operate at room temperature and that are capable of digital switching using a single electron. However, one major obstacle to realization of nanotubes has been the lack of technology for mass production. In 2001 IBM researchers demonstrated how metallic nanotubes can be destroyed, leaving semiconducting ones behind for use as transistors. Their process is called "constructive destruction," which includes the automatic destruction of defective nanotubes on the wafer. This process, however, only gives control over the electrical properties on a statistical scale.

The potential of carbon nanotubes was demonstrated in 2003 when room-temperature ballistic transistors with ohmic metal contacts and high-k gate dielectric were reported, showing 20–30x higher ON current than state-of-the-art Si MOSFETs. This presented an important advance in the field as CNT was shown to potentially outperform Si. At the time, a major challenge was ohmic metal contact formation. In this regard, palladium, which is a high-work function metal was shown to exhibit Schottky barrier-free contacts to semiconducting nanotubes with diameters >1.7 nm.

The first nanotube integrated memory circuit was made in 2004. One of the main challenges has been regulating the conductivity of nanotubes. Depending on subtle surface features a nanotube may act as a plain conductor or as a semiconductor. A fully automated method has however been developed to remove non-semiconductor tubes.

Another way to make carbon nanotube transistors has been to use random networks of them. By doing so one averages all of their electrical differences and one can produce devices in large scale at the wafer level. This approach was first patented by Nanomix Inc. (date of original application June 2002). It was first published in the academic literature by the United States Naval Research Laboratory in 2003 through independent research work. This approach also enabled Nanomix to make the first transistor on a flexible and transparent substrate.

Large structures of carbon nanotubes can be used for thermal management of electronic circuits. An approximately 1 mm–thick carbon nanotube layer was used as a special material to fabricate coolers, this materials has very low density, ~20 times lower weight than a similar copper structure, while the cooling properties are similar for the two materials.

Overall, incorporating carbon nanotubes as transistors into logic-gate circuits with densities comparable to modern CMOS technology has not yet been demonstrated.

### As electrical cables and wires:

Wires for carrying electrical current may be fabricated from pure nanotubes and nanotube-polymer composites. Recently small wires have been fabricated with specific conductivity exceeding copper and aluminum; these cables are the highest conductivity carbon nanotube and also highest conductivity non-metal cables.

### As paper batteries:

A paper battery is a battery engineered to use a paper-thin sheet of cellulose (which is the major constituent of regular paper, among other things) infused with aligned carbon nanotubes. The nanotubes act as electrodes; allowing the storage devices to conduct electricity. The battery, which functions as both a lithium-ion battery and a supercapacitor, can provide a long, steady power output comparable to a conventional battery, as well as a supercapacitor's quick burst of high energy—and while a conventional battery contains a number of separate components, the paper battery integrates all of the battery components in a single structure, making it more energy efficient.

### Solar cells:

Solar cells developed at the New Jersey Institute of Technology use a carbon nanotube complex, formed by a mixture of carbon nanotubes and carbon buckyballs (known as fullerenes) to form snake-like structures. Buckyballs trap electrons, although they can't make electrons flow. Add sunlight to excite the polymers, and the buckyballs will grab the electrons. Nanotubes, behaving like copper wires, will then be able to make the electrons or current flow.

### Medical:

In the Kanzius cancer therapy, single-walled carbon nanotubes are inserted around cancerous cells, then excited with radio waves, which causes them to heat up and kill the surrounding cells.

Researchers at Rice University, Radboud University Nijmegen Medical Centre and University of California, Riverside have shown that carbon nanotubes and their polymer nanocomposites are suitable scaffold materials for bone cell proliferation and bone formation.

**Other applications:**

Carbon nanotubes have been implemented in nanoelectromechanical systems, including mechanical memory elements (NRAM being developed by Nantero Inc.) and nanoscale electric motors (see Nanomotor or Nanotube nanomotor).

In May 2005, Nanomix Inc. placed on the market a hydrogen sensor that integrated carbon nanotubes on a silicon platform. Since then, Nanomix has been patenting many such sensor applications, such as in the field of carbon dioxide, nitrous oxide, glucose, DNA detection, etc.

Eikos Inc of Franklin, Massachusetts and Unidym Inc. of Silicon Valley, California are developing transparent, electrically conductive films of carbon nanotubes to replace indium tin oxide (ITO). Carbon nanotube films are substantially more mechanically robust than ITO films, making them ideal for high-reliability touchscreens and flexible displays. Printable water-based inks of carbon nanotubes are desired to enable the production of these films to replace ITO Nanotube films show promise for use in displays for computers, cell phones, PDAs, and ATMs.

A nanoradio, a radio receiver consisting of a single nanotube, was demonstrated in 2007. In 2008 it was shown that a sheet of nanotubes can operate as a loudspeaker if an alternating current is applied. The sound is not produced through vibration but thermoacoustically.

A flywheel made of carbon nanotubes could be spun at extremely high velocity on a floating magnetic axis in a vacuum, and potentially store energy at a density approaching that of conventional fossil fuels. Since energy can be added to and removed from flywheels very efficiently in the form of electricity, this might offer a way of storing electricity, making the electrical grid more efficient and variable power suppliers (like wind turbines) more useful in meeting energy needs. The practicality of this depends heavily upon the cost of making massive, unbroken nanotube structures, and their failure rate under stress.

Carbon nanotube springs have the potential to indefinitely store elastic potential energy at ten times the density of lithium-ion batteries with flexible charge and discharge rates and extremely high cycling durability.

Ultra-short SWNTs (US-tubes) have been used as nanoscaled capsules for delivering MRI contrast agents in vivo.

Nitrogen-doped carbon nanotubes may replace platinum catalysts used to reduce oxygen in fuel cells. A forest of vertically-aligned nanotubes can reduce oxygen in alkaline solution more effectively than platinum, which has been used in such applications since the 1960s. The nanotubes have the added benefit of not being subject to carbon monoxide poisoning.

### 5.9.1.. NANOLITHOGRAPHY:

Nanolithography is a term used to describe a number of techniques for creating incredibly small structures. The sizes involved are on the order of tens of nanometers (nm). A nanometer is a billionth of a meter, much smaller than the width of a single human hair. The word lithography is used because the method of pattern generation is essentially the same as writing, only on a much smaller scale

One common method of nanolithography, used particularly in the creation of microchips, is known as photolithography. This technique is a parallel method of nanolithography in which the entire surface is drawn on in a single moment. Photolithography is limited in the size it can reduce to, however, because if the wavelength of light used is made too small the lens simply absorbs the light in its entirety. This means that photolithography cannot reach the super-fine sizes of some alternate technologies

A technology that allows for smaller sizes than photolithography is that of electron-beam lithography. Using an electron beam to draw a pattern nanometer by

Nanometer, incredibly small sizes (on the order of 20nm) may be achieved. Electron-beam lithography is much more expensive and time consuming than photolithography, however, making it a difficult sell for industry applications of nanolithography. Since electron-beam lithography functions more like a dot-matrix printer than a flash-photograph, a job that would take five minutes using photolithography will take upwards of five hours with electron-beam lithography.

New nanolithography technologies are constantly being researched and developed, leading to smaller and smaller possible sizes. Extreme ultraviolet lithography, for example, is capable of using light at wavelengths of 13.5nm. While hurdles still exist in this new field, it promises the possibility of sizes far below those produced by current industry standards. Other nanolithography techniques include dip-pen nanolithography, in which a small tip is used to deposit molecules on a surface. Dip-pen nanolithography can achieve very small sizes, but cannot currently go below 40nm.

Funding for nanolithography research comes from a number of places, including the private academic world, futurist companies with an eye towards next-generation nanotechnology, and established computer chip manufacturers looking to shrink their chips far below their current sizes. As interest in nanotechnology grows within industrial sectors, funding and research will no doubt expand in the field of nanolithography, leading to more adept technologies and even lower limits on size

## Optical lithography:

Optical lithography, which has been the predominant patterning technique since the advent of the semiconductor age, is capable of producing sub-100-nm patterns with the use of very short wavelengths (currently 193 nm). Optical lithography will require the use of liquid immersion and a host of resolution enhancement technologies (phase-shift masks (PSM), optical proximity correction (OPC)) at the 32 nm node. Most experts feel that traditional optical lithography techniques will not be cost effective below 22 nm. At that point, it may be replaced by a next-generation lithography (NGL) technique.

**Other nanolithography techniques:**

X-ray lithography can be extended to an optical resolution of 15 nm by using the short wavelengths of 1 nm for the illumination. This is implemented by the proximity printing approach. The technique is developed to the extent of batch processing. The extension of the method relies on Near Field X-rays in Fresnel diffraction: a clear mask feature is "demagnified" by proximity to a wafer that is set near to a "Critical Condition". This Condition determines the mask-to-wafer Gap and depends on both the size of the clear mask feature and on the wavelength. The method is simple because it requires no lenses.

A method of pitch resolution enhancement which is gaining acceptance is **double patterning**. This technique increases feature density by printing new features in between pre-printed features on the same layer. It is flexible because it can be adapted for any exposure or patterning technique. The feature size is reduced by non-lithographic techniques such as etching or sidewall spacers.

Work is in progress on an optical **maskless lithography** tool. This uses a digital micro-mirror array to directly manipulate reflected light without the need for an intervening mask. Throughput is inherently low, but the elimination of mask-related production costs - which are rising exponentially with every technology generation - means that such a system might be more cost effective in the case of small production runs of state of the art circuits, such as in a research lab, where tool throughput is not a concern.

The most common nanolithographic technique is Electron-Beam Direct-Write Lithography (EBDW), the use of a beam of electrons to produce a pattern — typically in a polymeric resist such as PMMA.

Extreme ultraviolet lithography (EUV) is a form of optical lithography using ultrashort wavelengths (13.5 nm). It is the most popularly considered NGL technique.

Charged-particle lithography, such as ion- or electron-projection lithographies (PREVAIL, SCALPEL, LEEPL), are also capable of very-high-resolution patterning.

Ion beam lithography uses a focused or broad beam of energetic lightweight ions (like $He^+$) for transferring pattern to a surface. Using Ion Beam Proximity Lithography (IBL) nano-scale features can be transferred on non-planar surfaces

**Neutral Particle Lithography:**

(NPL) uses a broad beam of energetic neutral particle for pattern transfer on a surface.

**Nanoimprint lithography:**

(NIL), and its variants, such as Step-and-Flash Imprint Lithography, LISA and LADI are promising nanopattern replication technologies. This technique can be combined with **contact printing**and **cold welding**.

**Scanning probe lithography:**

(SPL) is a promising tool for patterning at the deep nanometer-scale. For example, individual atoms may be manipulated using the tip of a scanning tunneling microscope (STM). Dip-Pen Nanolithography (DPN) is the first commercially available SPL technology based on atomic force microscopy.

**Atomic Force Microscopic Nanolithography:**

(AFM) is a chemomechanical surface patterning technique that uses an atomic force microscope.

**Magnetolithography:**

(ML) based on applying a magnetic field on the substrate using paramagnetic metal masks call "magnetic mask". Magnetic mask which is analog to photomask define the spatial distribution and shape of the applied magnetic field. The second component is ferromagnetic nanoparticles (analog to the photoresist) that are assembled onto the substrate according to the field induced by the magnetic mask.

**Bottom-up methods:**

Nanosphere lithography uses self-assembled monolayers of spheres (typically made of polystyrene) as evaporation masks. This method has been used to fabricate arrays of gold nanodots with precisely controlled spacings.

It is possible that molecular self-assembly methods will take over as the primary nanolithography approach, due to ever-increasing complexity of the top-down approaches listed above. Self-assembly of dense lines less than 20 nm wide in large pre-pattearned trenches has been demonstrated. The degree of dimension and orientation control as well as prevention of lamella merging still need to be addressed for this to be an effective patterning technique. The important issue of line edge roughness is also highlighted by this technique.

Self-assembled ripple patterns and dot arrays formed by low-energy ion-beam sputtering are another emerging form of bottom-up lithography. Aligned arrays of plasmatic and magnetic wires and nano particles are deposited on these templates via oblique evaporation. The templates are easily produced over large areas with periods down to 25 nm

**Photolithography:**

Photolithography (or "optical lithography") is a process used in microfabrication to selectively remove parts of a thin film or the bulk of a substrate. It uses light to transfer a geometric pattern from a photo mask to a light-sensitive chemical "photoresist", or simply "resist," on the substrate. A series of chemical treatments then either engraves the exposure pattern into, or enables deposition of a new material in the desired pattern upon, the material underneath the photo resist. For example, in complex integrated circuits, a modern CMOS wafer will go through the photolithographic cycle up to 50 times.

Photolithography shares some fundamental principles with photography in that the pattern in the etching resist is created by exposing it to light, either directly (without using a mask) or with a projected image using an optical mask. This procedure is comparable to a high precision version of the method used to make printed circuit boards. Subsequent stages in the process have more in common with etching than with lithographic printing. It is used because it can create extremely small patterns (down to a few tens of nanometers in size), it affords exact control over the shape and size of the objects it creates, and because it can create patterns over an entire surface cost-effectively. Its main disadvantages are that it requires a flat substrate to start with, it is not very effective at creating shapes that are not flat, and it can require extremely clean operating conditions.

A single iteration of photolithography combines several steps in sequence. Modern cleanrooms use automated, robotic wafer track systems to coordinate the process. The procedure described here omits some advanced treatments, such as thinning agents or edge-bead removal.

**Cleaning:**

If organic or inorganic contaminations are present on the wafer surface, they are usually removed by wet che

**Preparation:**

The wafer is initially heated to a temperature sufficient to drive off any moisture that may be present on the wafer surface. Wafers that have been in storage must be chemically cleaned to remove contamination. A liquid or gaseous "adhesion promoter", such as Bis(trimethylsilyl)amine ("hexamethyldisilazane", HMDS), is applied to promote adhesion of the photoresist to the wafer.

The surface layer of silicon dioxide on the wafer reacts with HMDS to form tri-methylated silicon-dioxide, a highly water repellent layer not unlike the layer of wax on a car's paint. This water repellent layer prevents the aqueous developer from penetrating between the photoresist layer and the wafer's surface, thus preventing so-called lifting of small photoresist structures in the (developing) pattern.

mical treatment, e.g. the RCA clean procedure based on solutions containing hydrogen peroxide.

**Photoresist application:**

The wafer is covered with photoresist by spin coating. A viscous, liquid solution of photoresist is dispensed onto the wafer, and the wafer is spun rapidly to produce a uniformly thick layer. The spin coating typically runs at 1200 to 4800 rpm for 30 to 60 seconds, and produces a layer between 0.5 and 2.5 micrometres thick. The spin coating process results in a uniform thin layer, usually with uniformity of within 5 to 10 nanometres. This uniformity can be explained by detailed fluid-mechanical modelling, which shows that the resist moves much faster at the top of the layer than at the bottom, where viscous forces bind the resist to the wafer surface.

Thus, the top layer of resist is quickly ejected from the wafer's edge while the bottom layer still creeps slowly radially along the wafer. In this way, any 'bump' or 'ridge' of resist is removed, leaving a very flat layer. Final thickness is also determined by the evaporation of liquid solvents from the resist. For very small, dense features (<125 or so nm), thinner resist thicknesses (<0.5 micrometres) are needed to overcome collapse effects at high aspect ratios; typical aspect ratios are <4:1.

The photo resist-coated wafer is then prebaked to drive off excess photoresist solvent, typically at 90 to 100 °C for 30 to 60 seconds on a hotplate

**Exposure and developing:**

After prebaking, the photoresist is exposed to a pattern of intense light. Optical lithography typically uses ultraviolet light (see below). Positive photoresist, the most common type, becomes soluble in the basic developer when exposed; exposed negative photoresist becomes insoluble in the (organic) developer. This chemical change allows some of the photoresist to be removed by a special solution, called "developer" by analogy with photographic developer. To learn more about the process of exposure and development of positive resist, see, for example: Ralph Dammel, "Diazonaphtoquinone-based resists", SPIE Optical Engineering Press, Vol TT11 (1993

A PEB (post-exposure bake) is performed before developing, typically to help reduce standing wave phenomena caused by the destructive and constructive interference patterns of the incident light. In DUV (deep ultraviolet, or shorter than 300 nm exposure wavelength) lithography, CAR (chemically amplified resist) chemistry is used. This process is much more sensitive to PEB time, temperature, and delay, as most of the "exposure" reaction (creating acid, making the polymer soluble in the basic developer) actually occurs in the PEB.

The develop chemistry is delivered on a spinner, much like photoresist. Developers originally often contained sodium hydroxide (NaOH). However, sodium is considered an extremely undesirable contaminant in MOSFET fabrication because it degrades the insulating properties of gate oxides (specifically, sodium ions can migrate in and out of the gate, changing the threshold voltage of the transistor and making it harder or easier to turn the transistor on over time). Metal-ion-free developers such as tetramethylammonium hydroxide (TMAH) are now used.

The resulting wafer is then "hard-baked" if a non-chemically amplified resist was used, typically at 120 to 180 °C for 20 to 30 minutes. The hard bake solidifies the remaining photoresist, to make a more durable protecting layer in future ion implantation, wet chemical etching, or plasma etching

**Etching:**

In etching, a liquid ("wet") or plasma ("dry") chemical agent removes the uppermost layer of the substrate in the areas that are not protected by photoresist. In semiconductor fabrication, dry etching techniques are generally used, as they can be made anisotropic, in order to avoid significant undercutting of the photoresist pattern. This is essential when the width of the features to be defined is similar to or less than the thickness of the material being etched (i.e. when the aspect ratio approaches unity). Wet etch processes are generally isotropic in nature, which is often indispensable for microelectromechanical systems, where suspended structures must be "released" from the underlying layer.

The development of low-defectivity anisotropic dry-etch process has enabled the ever-smaller features defined photolithographically in the resist to be transferred to the substrate material.

**Photoresist removal:**

After a photoresist is no longer needed, it must be removed from the substrate. This usually requires a liquid "resist stripper", which chemically alters the resist so that it no longer adheres to the substrate. Alternatively, photoresist may be removed by a plasma containing oxygen, which oxidizes it. This process is called ashing, and resembles dry etching.

**Exposure ("printing") systems:**

Exposure systems typically produce an image on the wafer using a photomask. The light shines through the photomask, which blocks it in some areas and lets it pass in others. (Maskless lithography projects a precise beam directly onto the wafer without using a mask, but it is not widely used in commercial processes.) Exposure systems may be classified by the optics that transfer the image from the mask to the wafer.

**Contact and proximity:**

A contact printer, the simplest exposure system, puts a photomask in direct contact with the wafer and exposes it to a uniform light. A proximity printer puts a small gap between the photomask and wafer. In both cases, the mask covers the entire wafer, and simultaneously patterns every die.

Contact printing is liable to damage both the mask and the wafer, and this was the primary reason it was abandoned for high volume production. Both contact and proximity lithography require the light intensity to be uniform across an entire wafer, and the mask to align precisely to features already on the wafer. As modern processes use increasingly large wafers, these conditions become increasingly difficult

Research and prototyping processes often use contact or proximity lithography, because it uses inexpensive hardware and can achieve high optical resolution. The resolution in proximity lithography is approximately the square root of the product of the wavelength and the gap distance. Hence, except for projection lithography (see below), contact printing offers the best resolution, because its gap distance is approximately zero (neglecting the thickness of the photoresist itself). In addition, nanoimprint lithography may revive interest in this familiar technique, especially since the cost of ownership is expected to be low; however, the shortcomings of contact printing discussed above remain as challenges

**Projection:**

Very-large-scale integration (VLSI) lithography uses projection systems. Unlike contact or proximity masks, which cover an entire wafer, projection masks (known as "reticles") show only one die or an array of die (known as a "field"). Projection exposure systems (steppers or scanners) project the mask onto the wafer many times to create the complete pattern

**Photomasks:**

The image for the mask originates from a computerized data file. This data file is converted to a series of polygons and written onto a square fused quartz substrate covered with a layer of chrome using a photolithographic process. A laser beam (laser writer) or a beam of electrons (e-beam writer) is used to expose the pattern defined by the data file and travels over the surface of the substrate in either a vector or raster scan manner. Where the photoresist on the mask is exposed, the chrome can be etched away, leaving a clear path for the illumination light in the stepper/scanner system to travel through.

**Resolution in projection systems:**

The ability to project a clear image of a small feature onto the wafer is limited by the wavelength of the light that is used, and the ability of the reduction lens system to capture enough diffraction orders from the illuminated mask. Current state-of-the-art photolithography tools use deep ultraviolet (DUV) light from excimer lasers with wavelengths of 248 and 193 nm (the dominant lithography technology today is thus also called "excimer laser lithography"), which allow minimum feature sizes down to 50 nm. Excimer laser lithography has thus played a critical role in the continued advance of the so-called Moore’s Law for the last 20 years (see below).

The minimum feature size that a projection system can print is given approximately by:

**CD=K1._λ__ NA**

Where

$CD$ is the **minimum feature size** (also called the **critical dimension**, *target design rule*). It is also common to write 2 *times* the *half-pitch*.

$k_1$ (commonly called *k1 factor*) is a coefficient that encapsulates process-related factors, and typically equals 0.4 for production. The minimum feature size can be reduced by decreasing this coefficient through Computational lithography.

$\lambda$ is the wavelength of light used

$NA$ is the numerical aperture of the lens as seen from the wafer

According to this equation, minimum feature sizes can be decreased by decreasing the wavelength, and increasing the numerical aperture (to achieve a tighter focused beam and a smaller spot size). However, this design method runs into a competing constraint. In modern systems, the depth of focus is also a concern.

$$D_F = k_2 \cdot \frac{\lambda}{NA^2}$$

Here, $k_2$is another process-related coefficient. The depth of focus restricts the thickness of the photoresist and the depth of the topography on the wafer. Chemical mechanical polishing is often used to flatten topography before high-resolution lithographic steps.

**Lithography:**

The process of imprinting patterns on semiconductor materials to be used as integrated circuits is defined as lithography. This new concept in nanolithography is based upon the transport of a chemically reactive material or ―ink‖ from the tip of a conventional silicon nitride Atomic Force Microscope (AFM) to the surface of interest or paper

Civilization has advanced as people discovered new ways of exploiting various physical resources such as materials, forces and energies. The history of computer technology has involved a sequence of changes from one type of physical realization to another --- from gears to relays to valves to transistors to integrated circuits and so on.

Today's advanced lithographic techniques can squeeze fraction of micron wide logic gates and wires onto the surface of silicon chips. However, when one wants to precisely position atoms or molecules on surfaces many problems occur some of which are due to the quantum nature of atoms. Nano materials used for the lithography includes carbon nano tubes, fullerenes etc.

### 5.9.2. DNA NANOTECHNOLOGY:

DNA nanotechnology is a branch of nanotechnology which uses the molecular recognition properties of DNA and other nucleic acids to create designed, artificial structures out of DNA for technological purposes. In this field, DNA is used as a structural material rather than as a carrier of genetic information, making it an example of bionanotechnology. DNA nanotechnology has applications in molecular self-assembly and in DNA computing.

Although DNA is usually considered in the context of molecular biology as the carrier of genetic information in living cells, DNA nanotechnology considers DNA solely as a chemical and as a material, and is usually pursued outside of any biological context. DNA nanotechnology makes use of the fact that, due to the specificity of Watson-Crick base pairing, only portions of the strands which are complementary to each other will bind to each other to form duplex DNA. DNA nanotechnology attempts to rationally design sets of DNA strands so that desired portions of each strand will assemble in the correct positions to for some desired target structure, a process called nucleic acid design.

Although the field is usually called DNA nanotechnology, its principles apply equally well to other nucleic acids such as RNA and PNA, and structures incorporating these have been made. For this reason the field is occasionally referred to as nucleic acid nanotechnology.

DNA nanotechnology creates complex structures out of nucleic acids by making use of the specificity of base pairing in nucleic acid molecules. The structure of a nucleic acid molecule consists of a sequence of nucleotides, distinguished by which nucleobase they contain. In DNA, the four bases used are adenine (A), cytosine (C), guanine (G), and thymine (T).

Nucleic acids have the property that two molecules will bind to each other to form a double helix only if the two sequences are complementary, meaning that they form matching sequences of base pairs, with A's only binding to T's, and C's only to G's. Because the formation of correctly matched base pairs is energetically favorable, nucleic acid strands are expected in most cases to bind to each other in the conformation that maximizes the number of correctly paired bases.

This property, that the sequence determines the pattern of binding and the overall structure, is used by the field of DNA nanotechnology in that sequences are artificially designed so that a desired structure is favored to form.

## Fundamental concepts:

These four strands associate into a DNA four-arm junction because this structure maximizes the number of correct base pairs, with A's matched to T's and C's matched to G's. See this image for a more realistic model of the four-arm junction showing its tertiary structure.

A double-crossover (DX) molecule. This molecule consists of five DNA single strands which form two double-helical domains, on the left and the right in this image. There are two crossover points where the strands cross from one domain into the other.

Nearly all structures in DNA nanotechnology make use of branched DNA structures containing junctions, as opposed to most biological DNA which exists in a linear double helix form.

One of the simplest branched structures, and the first made, is a four-arm junction which can be made using four individual DNA strands which are complementary to each other in the correct pattern. Unlike in natural Holliday junctions, in the artificial immobile four-arm junction shown below, the base sequence of each arm is different, meaning that the junction point is fixed in a certain position.

Junctions can be used in more complex molecules. One of the more widely-used of these is the "double-crossover" or DX motif. A DX molecule can be thought of as two DNA duplexes positioned parallel to each other, with two crossover points where strands cross from one duplex into the other.

Each junction point is itself topologically a four-arm junction. This molecule has the advantage that the junction points are now constrained to a single orientation as opposed to being flexible as in the four-arm junction. This makes the DX motif suitable as a structural building block for larger DNA complexes

**Design:**

DNA nanostructures must be rationally designed so that the individual nucleic acid strands will assemble into the desired structures. The design process of such nanostructures usually begins with the specification of a desired target structure and/or functionality. Then, the overall secondary structure of the target molecule is designed, meaning the arrangement of nucleic acid strands within the structure, and which portions of those strands should be bound to each other. The last step is the primary structure design, the specification of the actual base sequences of each nucleic acid strand.

**Structural design:**

The first step in designing a nucleic acid nanostructure is to decide how a given structure should be represented by a specific arrangement of nucleic acid strands. This design step thus determines the secondary structure, or the series of base pairs which hold the individual strands together in the desired shape. There are several approaches which have been demonstrated:

Tile-based structures. This approach breaks the target structure into smaller units with strong binding between the strands contained in each unit, and relatively weaker interactions between the units. It is often used to make periodic lattices, but can also be used to implement algorithmic self-assembly, making them one platform for DNA computing

Folding structures. An alternative to the tile-based approach, folding approaches make the nanostructure out of a single long strand. This long strand can either have a designed sequence which folds due to its interactions with itself, or it can be folded into the desired shape by using shorter, "staple" strands. This latter method is called DNA origami, which allows the creation of two- and three-dimensional shapes at the nanoscale using DNA (see #Arbitrary shapes below).

Kinetic assembly. Recently, there has been interest in controlling the kinetics of DNA self-assembly, so that transient dynamics can also be programmed into the assembly. Such a method also has the advantage of proceeding isothermally and thus not requiring a thermal annealing step required by solely thermodynamic approaches.

**Sequence design:**

After any of the above approaches are used to design the secondary structure of a target molecule, an actual sequence of nucleotides must be devised which will form into the desired structure. Nucleic acid design is the process of assigning a specific nucleic acid base sequence to each strand so that they will associate into a desired conformation. Nucleic acid design is central to the field of DNA nanotechnology.

Most methods seek to designing sequences so that the target structure is a thermodynamic minimum, and mis-assembled structures have higher energies and are thus disfavored. This is done either through heuristic methods such as sequence symmetry minimization and coding theory based approaches, or by explicitly using a full nearest-neighbor thermodynamic model. Geometric models are also used to examine tertiary structure of the nanostructures and ensure that the complexes are not overly strained.

Nucleic acid design has similar goals to protein design: in both, the sequence of monomers is designed to favor the desired folded or associated structure and to disfavor alternate structures. Nucleic acid design has the advantage of being a much computationally simpler problem, since the simplicity of Watson-Crick base pairing rules leads to simple heuristic methods which yield experimentally robust designs. However, nucleic acid structures are less versatile than proteins in their functionality

**Structural DNA nanotechnology:**

Structural DNA nanotechnology, sometimes abbreviated as SDN, focuses on synthesizing and characterizing nucleic acid complexes and materials with various nanoscale structures. Structural DNA nanotechnology is largely based on the fact that the three-dimensional structure of DNA—the nucleic acid double helix— has a robust, defined geometry which makes it possible to predict and design the structures of more complex DNA molecules. Many such structures have been created, including two- and three-dimensional structures; and periodic, aperiodic, and discrete structures.

**Periodic lattices:**

Smaller nucleic acid assemblies can be equipped with sticky ends in order to combine them into a two-dimensional periodic lattice. The earliest example of this was the array of DX, or double-crossover, molecules.

Each DX molecule can be designed with four sticky ends, one at each end of the two double-helical domains, and these sticky ends can be designed with sequences that cause the DX units to combine into a specific tessellated pattern. They thus form extended flat sheets which are essentially rigid two-dimensional crystals of DNA.

Two-dimensional arrays have been made out of other motifs as well, including the Holliday junction rhombus array as well as various DX-based arrays making use of a double-cohesion scheme

Creating three-dimensional lattices out of DNA was the earliest goal of DNA nanotechnology, but proved to be one of the most difficult to realize. Success in constructing three-dimensional DNA lattices was finally reported in 2009 using a motif based on the concept of tensegrity, a balance between tension and compression forces

### Nanotubes:

In addition to flat sheets, DX arrays have been made to form hollow nanotubes of 4–20 nm diameter. These DNA nanotubes are somewhat similar in size and shape to carbon nanotubes, but the carbon nanotubes are stronger and better conductors, whereas the DNA nanotubes are more easily modified and connected to other structures.

There have been multiple schemes for constructing DNA nanotubes, one of which uses the inherent curvature of DX tiles to form a DX lattice to curl around itself and close into a tube. An alternative design uses single-stranded "tiles" for which the rigidity of the tube is an emergent property. This method also has the benefit of being able to determine the circumference of the nanotube in a simple, modular fashion

**Polyhedra:**

A number of three-dimensional DNA molecules have been made which have the connectivity of a polyhedron such as an octahedron or cube. In other words, the DNA duplexes trace the edges of a polyhedron with a DNA junction at each vertex. The earliest demonstrations of DNA polyhedra involved multiple ligations and solid-phase synthesis

steps to create catenated polyhedra. More recent work has yielded polyhedra whose synthesis is much easier. These include a DNA octahedron made from a long single strand designed to fold into the correct conformation, as well as a tetrahedron which can be produced from four DNA strands in a single step, pictured at the top of this article.

**Arbitrary shapes:**

Nanostructures of arbitrary shapes are usually made using the DNA origami method. DNA origami makes use of a long natural virus strand as a "scaffold" strand, and computationally designs shorter "staple" strands which bind to portions of the scaffold strand and force it to fold into the desired shape. This method has the advantage of being easy to design, as the base sequence is predetermined by the scaffold strand sequence, and it also does not require high strand purity and accurate stoichiometry, as most other DNA nanotechnology methods do.

DNA origami was first demonstrated for two-dimensional shapes; demonstrated designs included the smiley face and a coarse map of North America. This was later extended to solid three-dimensional shapes.

In addition, structures have been constructed with two-dimensional faces which fold into an overall three-dimensional shape, akin to a cardboard box. These can be programmed to open and release their cargo in response to a stimulus, making them potentially useful as programmable molecular cages

**Functional nucleic acid nanostructures:**

DNA nanotechnology focuses on creating molecules with designed functionalities as well as structures. These include both dynamic functionality within the nucleic acid structure itself, for example with computation and mechanical motion, as well as by including other components such as small molecules or nanoparticles which have their own functionalities. Many classes of functional systems have been demonstrated.

**Nano architecture:**

The idea of using DNA arrays to template the assembly of other functional molecules was first suggested by Nadrian Seeman in 1987, but only recently has progress been made in reducing these kinds of schemes to practice. In 2006, researchers covalently attached gold nanoparticles to a DX-based tile and showed that self-assembly of the DNA structures also assembled the nanoparticles hosted on them. Also that year, Dwyer and LaBean demonstrated the letters "D" "N" and "A" created on a 4x4 DX array using streptavidin, and a hierarchical assembly based on this approach was also demonstrated that scales to larger arrays (8X8 and 8.96 MD). A non-covalent hosting scheme was shown in 2007, using Dervan polyamides on a DX array to arrange streptavidin proteins on specific kinds of tiles on the DNA array.

There has also been interest in using DNA nanotechnology to assemble molecular electronics devices. To this end, DNA has been used to assemble single walled carbon nanotubes into field-effect transistors.

**Algorithmic self-assembly:**

DNA nanotechnology has been applied to the related field of DNA computing. The DX tiles can have their sticky end sequences chosen so that they act as Wang tiles, allowing them to perform computation. A DX array has been demonstrated whose assembly encodes an XOR operation; this allows the DNA array to implement a cellular automaton which generates a fractal called the Sierpinski gasket. Another system has the function of a binary counter, displaying a representation of increasing binary numbers as it grows. These results show that computation can be incorporated into the assembly of DNA arrays, increasing its scope beyond simple periodic arrays.

Note that DNA computing overlaps with, but is distinct from, DNA nanotechnology. The latter uses the specificity of Watson-Crick basepairing to make novel structures out of DNA. These structures can be used for DNA computing, but they do not have to be. Additionally, DNA computing can be realized without using the types of molecules made possible by DNA nanotechnology

**Nano mechanical devices:**

DNA complexes have been made which change their conformation upon some stimulus. These are intended to have applications in nanorobotics. DNA machines have also been made which show a twisting motion. The first such device made use of the transition between the B-DNA and Z-DNA forms to respond to a change in buffer conditions. This reliance on buffer conditions, however, caused all devices to change state at the same time. A subsequent system, called "molecular tweezers," changes from an open to a closed state based upon the presence of control strands, allowing multiple devices to be individually operated in solution.

This was followed up by another system which relies on the presence of control strands to switch from a paranemic-crossover (PX) conformation to a double-junction (JX2) conformation.

Nucleic acid nanomachines have been made which exhibit directional motion along a linear track, called DNA walkers. A large number of schemes have been demonstrated. One strategy is to control the motion of the walker along the track using control strands which need to be manually added in sequence. Another approach is to make use of restriction enzymes or deoxyribozymes to cleave the strands and cause the walker to move forward, which has the advantage of running autonomously.

A later system extended the concept of DNA walkers to walk upon a two-dimensional surface rather than a linear track, and demonstrated the ability to selectively pick up and move molecular cargo. Additionally, a linear walker has been demonstrated which performs DNA-templated synthesis as the walker advances along the track, allowing autonomous multistep chemical synthesis directed by the walker.

### 5.9.3. DRUG DELIVERY SYSTEM:

Drug delivery is the method or process of administering a pharmaceutical compound to achieve a therapeutic effect in humans or animals. Drug delivery technologies modify drug release profile, absorption, distribution and elimination for the benefit of improving product efficacy and safety, as well as patient convenience and compliance. Drug release is from: diffusion, degradation, swelling, and affinity-based mechanisms. Most common routes of administration include the preferred non-invasive peroral (through the mouth), topical (skin), transmucosal (nasal, buccal/sublingual, vaginal, ocular and rectal) and inhalation routes.

Many medications such as peptide and protein, antibody, vaccine and gene based drugs, in general may not be delivered using these routes because they might be susceptible to enzymatic degradation or cannot be absorbed into the systemic circulation efficiently due to molecular size and charge issues to be therapeutically effective. For this reason many protein and peptide drugs have to be delivered by injection or a nanoneedle array. For example, many immunizations are based on the delivery of protein drugs and are often done by injection.

Current efforts in the area of drug delivery include the development of targeted delivery in which the drug is only active in the target area of the body (for example, in cancerous tissues) and sustained release formulations in which the drug is released over a period of time in a controlled manner from a formulation. Types of sustained release formulations include liposomes, drug loaded biodegradable microspheres and drug polymer conjugates.

## Drug delivery:

Nanomedical approaches to drug delivery center on developing nanoscale particles or molecules to improve drug bioavailability. Bioavailability refers to the presence of drug molecules where they are needed in the body and where they will do the most good. Drug delivery focuses on maximizing bioavailability both at specific places in the body and over a period of time. This can potentially be achieved by molecular targeting by nanoengineered devices.

It is all about targeting the molecules and delivering drugs with cell precision. More than $65 billion are wasted each year due to poor bioavailability. *In vivo* imaging is another area where tools and devices are being developed. Using nanoparticle contrast agents, images such as ultrasound and MRI have a favorable distribution and improved contrast.

The new methods of nano engineered materials that are being developed might be effective in treating illnesses and diseases such as cancer. What nano scientists will be able to achieve in the future is beyond current imagination. This might be accomplished by self assembled biocompatible nano devices that will detect, evaluate, treat and report to the clinical doctor automatically.

Drug delivery systems, lipid- or polymer-based nanoparticles, can be designed to improve the pharmacological and therapeutic properties of drugs. The strength of drug delivery systems is their ability to alter the pharmacokinetics and biodistribution of the drug. Nanoparticles have unusual properties that can be used to improve drug delivery. Where larger particles would have been cleared from the body, cells take up these nanoparticles because of their size.

Complex drug delivery mechanisms are being developed, including the ability to get drugs through cell membranes and into cell cytoplasm. Efficiency is important because many diseases depend upon processes within the cell and can only be impeded by drugs that make their way into the cell. Triggered response is one way for drug molecules to be used more efficiently. Drugs are placed in the body and only activate on encountering a particular signal.

For example, a drug with poor solubility will be replaced by a drug delivery system where both hydrophilic and hydrophobic environments exist, improving the solubility. Also, a drug may cause tissue damage, but with drug delivery, regulated drug release can eliminate the problem. If a drug is cleared too quickly from the body, this could force a patient to use high doses, but with drug delivery systems clearance can be reduced by altering the pharmacokinetics of the drug.

Poor biodistribution is a problem that can affect normal tissues through widespread distribution, but the particulates from drug delivery systems lower the volume of distribution and reduce the effect on non-target tissue. Potential nanodrugs will work by very specific and well-understood mechanisms; one of the major impacts of nanotechnology and nanoscience will be in leading development of completely new drugs with more useful behavior and less side effects.

### Protein and peptide delivery:

Protein and peptides exert multiple biological actions in human body and they have been identified as showing great promise for treatment of various diseases and disorders. These macromolecules are called biopharmaceuticals. Targeted and/or controlled delivery of these biopharmaceuticals using nanomaterials like nanoparticles and Dendrimers is an emerging field called nanobiopharmaceutics, and these products are called nanobiopharmaceuticals.

### Cancer:

The small size of nanoparticles endows them with properties that can be very useful in oncology, particularly in imaging. Quantum dots (nanoparticles with quantum confinement properties, such as size-tunable light emission), when used in conjunction with MRI (magnetic resonance imaging), can produce exceptional images of tumor sites. These nanoparticles are much brighter than organic dyes and only need one light source for excitation. This means that the use of fluorescent quantum dots could produce a higher contrast image and at a lower cost than today's organic dyes used as contrast media. The downside, however, is that quantum dots are usually made of quite toxic elements.

Another nanoproperty, high surface area to volume ratio, allows many functional groups to be attached to a nanoparticle, which can seek out and bind to certain tumor cells. Additionally, the small size of nanoparticles (10 to 100 nanometers), allows them to preferentially accumulate at tumor sites (because tumors lack an effective lymphatic drainage system). A very exciting research question is how to make these imaging nanoparticles do more things for cancer. For instance, is it possible to manufacture

multifunctional nanoparticles that would detect, image, and then proceed to treat a tumor? This question is under vigorous investigation; the answer to which could shape the future of cancer treatment. A promising new cancer treatment that may one day replace radiation and chemotherapy is edging closer to human trials. Kanzius RF therapy attaches microscopic nanoparticles to cancer cells and then "cooks" tumors inside the body with radio waves that heat only the nanoparticles and the adjacent (cancerous) cells.

Sensor test chips containing thousands of nanowires, able to detect proteins and other biomarkers left behind by cancer cells, could enable the detection and diagnosis of cancer in the early stages from a few drops of a patient's blood.

The basic point to use drug delivery is based upon three facts: a) efficient encapsulation of the drugs, b) successful delivery of said drugs to the targeted region of the body, and c) successful release of that drug there.

Researchers at Rice University under Prof. Jennifer West, have demonstrated the use of 120 nm diameter nanoshells coated with gold to kill cancer tumors in mice. The nano shells can be targeted to bond to cancerous cells by conjugating antibodies or peptides to the nanoshell surface.

By irradiating the area of the tumor with an infrared laser, which passes through flesh without heating it, the gold is heated sufficiently to cause death to the cancer cells.

Nanoparticles of cadmium selenide (quantum dots) glow when exposed to ultraviolet light. When injected, they seep into cancer tumors. The surgeon can see the glowing tumor, and use it as a guide for more accurate tumor removal.

In photodynamic therapy, a particle is placed within the body and is illuminated with light from the outside. The light gets absorbed by the particle and if the particle is metal, energy from the light will heat the particle and surrounding tissue. Light may also be used to produce high energy oxygen molecules which will chemically react with and destroy most organic molecules that are next to them (like tumors).

This therapy is appealing for many reasons. It does not leave a ―toxic trail‖ of reactive molecules throughout the body (chemotherapy) because it is directed where only the light is shined and the particles exist. Photodynamic therapy has potential for a noninvasive procedure for dealing with diseases, growth and tumors.

**Surgery:**

At Rice University, a flesh welder is used to fuse two pieces of chicken meat into a single piece. The two pieces of chicken are placed together touching. A greenish liquid containing gold-coated nanoshells is dribbled along the seam. An infrared laser is traced along the seam, causing the two sides to weld together. This could solve the difficulties and blood leaks caused when the surgeon tries to restitch the arteries that have been cut during a kidney or heart transplant. The flesh welder could weld the artery perfectly.

**Visualization:**

Tracking movement can help determine how well drugs are being distributed or how substances are metabolized. It is difficult to track a small group of cells throughout the body, so scientists used to dye the cells. These dyes needed to be excited by light of a certain wavelength in order for them to light up. While different color dyes absorb different frequencies of light, there was a need for as many light sources as cells. A way around this problem is with luminescent tags.

These tags are quantum dots attached to proteins that penetrate cell membranes. The dots can be random in size, can be made of bio-inert material, and they demonstrate the nanoscale property that color is size-dependent. As a result, sizes are selected so that the frequency of light used to make a group of quantum dots fluoresce is an even multiple of the frequency required to make another group incandesce. Then both groups can be lit with a single light source.

**Nanoparticle targeting:**

It is greatly observed that nanoparticles are promising tools for the advancement of drug delivery, medical imaging, and as diagnostic sensors. However, the biodistribution of these nanoparticles is mostly unknown due to the difficulty in targeting specific organs in the body. Current research in the excretory systems of mice, however, shows the ability of gold composites to selectively target certain organs based on their size and charge.

These composites are encapsulated by a dendrimer and assigned a specific charge and size. Positively-charged gold nanoparticles were found to enter the kidneys while negatively-charged gold nanoparticles remained in the liver and spleen. It is suggested that the positive surface charge of the nanoparticle decreases the rate of opsonization of nanoparticles in the liver, thus affecting the excretory pathway. Even at a relatively small size of 5 nm , though, these particles can become compartmentalized in the peripheral tissues, and will therefore accumulate in the body over time. While advancement of research proves that targeting and distribution can be augmented by nano particles, the dangers of nanotoxicity become an important next step in further understanding of their medical uses.

## Neuro-electronic interfaces

Neuro-electronic interfacing is a visionary goal dealing with the construction of nanodevices that will permit computers to be joined and linked to the nervous system This idea requires the building of a molecular structure that will permit control and detection of nerve impulses by an external computer. The computers will be able to interpret, register, and respond to signals the body gives off when it feels sensations. The demand for such structures is huge because many diseases involve the decay of the nervous system (ALS and multiple sclerosis).

Also, many injuries and accidents may impair the nervous system resulting in dysfunctional systems and paraplegia. If computers could control the nervous system through neuro-electronic interface, problems that impair the system could be controlled so that effects of diseases and injuries could be overcome. Two considerations must be made when selecting the power source for such applications.

They are refuelable and nonrefuelable strategies. A refuelable strategy implies energy is refilled continuously or periodically with external sonic, chemical, tethered, magnetic, or electrical sources. A nonrefuelable strategy implies that all power is drawn from internal energy storage which would stop when all energy is drained.

One limitation to this innovation is the fact that electrical interference is a possibility. Electric fields, electromagnetic pulses (EMP), and stray fields from other *in vivo* electrical devices can all cause interference.

Also, thick insulators are required to prevent electron leakage, and if high conductivity of the in vivo medium occurs there is a risk of sudden power loss and ―shorting out.‖ Finally, thick wires are also needed to conduct substantial power levels without overheating. Little practical progress has been made even though research is happening.

The wiring of the structure is extremely difficult because they must be positioned precisely in the nervous system so that it is able to monitor and respond to nervous signals. The structures that will provide the interface must also be compatible with the body's immune system so that they will remain unaffected in the body for a long time. In addition, the structures must also sense ionic currents and be able to cause currents to flow backward. While the potential for these structures is amazing, there is no timetable for when they will be available.

**Nano robots:**

The somewhat speculative claims about the possibility of using nanorobots in medicine, advocates say, would totally change the world of medicine once it is realized. Nanomedicine would make use of these nanorobots (e.g., Computational Genes), introduced into the body, to repair or detect damages and infections.

According to Robert Freitas of the Institute for Molecular Manufacturing, a typical blood borne medical nanorobot would be between 0.5-3 micrometres in size, because that is the maximum size possible due to capillary passage requirement. Carbon could be the primary element used to build these nanorobots due to the inherent strength and other characteristics of some forms of carbon (diamond/fullerene composites), and nanorobots would be fabricated in desktop nanofactories specialized for this purpose.

Nanodevices could be observed at work inside the body using MRI, especially if their components were manufactured using mostly $^{13}C$ atoms rather than the natural $^{12}C$ isotope of carbon, since $^{13}C$ has a nonzero nuclear magnetic moment. Medical nanodevices would first be injected into a human body, and would then go to work in a specific organ or tissue mass.

The doctor will monitor the progress, and make certain that the nanodevices have gotten to the correct target treatment region. The doctor will also be able to scan a section of the body, and actually see the nanodevices congregated neatly around their target (a tumor mass, etc.) so that he or she can be sure that the procedure was successful.

**Cell repair machines:**

Using drugs and surgery, doctors can only encourage tissues to repair themselves. With molecular machines, there will be more direct repairs. Cell repair will utilize the same tasks that living systems already prove possible. Access to cells is possible because biologists can insert needles into cells without killing them. Thus, molecular machines are capable of entering the cell.

Also, all specific biochemical interactions show that molecular systems can recognize other molecules by touch, build or rebuild every molecule in a cell, and can disassemble damaged molecules. Finally, cells that replicate prove that molecular systems can assemble every system found in a cell. Therefore, since nature has demonstrated the basic operations needed to perform molecular-level cell repair, in the future, nanomachine based systems will be built that are able to enter cells, sense differences from healthy ones and make modifications to the structure.

The healthcare possibilities of these cell repair machines are impressive. Comparable to the size of viruses or bacteria, their compact parts would allow them to be more complex. The early machines will be specialized. As they open and close cell membranes or travel through tissue and enter cells and viruses, machines will only be able to correct a single molecular disorder like DNA damage or enzyme deficiency. Later, cell repair machines will be programmed with more abilities with the help of advanced AI systems.

Nano computers will be needed to guide these machines. These computers will direct machines to examine, take apart, and rebuild damaged molecular structures.

Repair machines will be able to repair whole cells by working structure by structure. Then by working cell by cell and tissue by tissue, whole organs can be repaired. Finally, by working organ by organ, health is restored to the body. Cells damaged to the point of inactivity can be repaired because of the ability of molecular machines to build cells from scratch. Therefore, cell repair machines will free medicine from reliance on self repair alone.

## Nanonephrology:

Nanonephrology is a branch of nanomedicine and nanotechnology that seeks to use nano-materials and nano-devices for the diagnosis, therapy, and management of renal diseases.

It includes the following goals:

- ✓ The study of kidney protein structures at the atomic level
- ✓ Nano-imaging approaches to study cellular processes in kidney cells
- ✓ Nano medical treatments that utilize nanoparticles to treat various kidney diseases

Advances in Nanonephrology are expected to be based on discoveries in the above areas that can provide nano-scale information on the cellular molecular machinery involved in normal kidney processes and in pathological states. By understanding the physical and chemical properties of proteins and other macromolecules at the atomic level in various cells in the kidney, novel therapeutic approaches can be designed to combat major renal diseases. The nano-scale artificial kidney is a goal that many physicians dream of. Nano-scale engineering advances will permit programmable and controllable nano-scale robots to execute curative and reconstructive procedures in the human kidney at the cellular and molecular levels.

Designing nanostructures compatible with the kidney cells and that can safely operate in vivo is also a future goal. The ability to direct events in a controlled fashion at the cellular nano-level has the potential of significantly improving the lives of patients with kidney diseases.