

UNIT- I:

INTRODUCTION: History and Scope, Classification of Nano structured Materials, Fascinating Nanostructures, and applications of nano-materials, challenges and future prospects.

History of nanotechnology

Nanoscience and nanotechnology are the study and application of extremely small things and can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering.

How It Started

The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled "There's Plenty of Room at the Bottom" by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (CalTech) on December 29, 1959, long before the term nanotechnology was used. In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules. Over a decade later, in his explorations of ultraprecision machining, Professor Norio Taniguchi coined the term nanotechnology. It wasn't until 1981, with the development of the scanning tunneling microscope that could "see" individual atoms, that modern nanotechnology began.

Feynman's 1959 talk is often cited as a source of inspiration for Nanoscience, but it was virtually unknown outside of his small audience at the time and only published as a scientific paper in 1992.¹ Nanoscience really sprang into the public consciousness sometime after the invention of the scanning tunnelling microscope (STM) in 1981.² Here was an amazing tool that could image and manipulate atoms. Atomic scale imaging had been possible in the past with multimillion-dollar transmission electron microscopes, but the STM was a benchtop tool that a graduate student could assemble for a few hundred dollars.

The First International Conference on Scanning Tunneling Microscopy was held in Santiago De Compostela, Spain, July 14–18, 1986 (becoming a yearly fixture thereafter with an exponential growth in the number of papers presented). The impact of the STM on surface science was already so great at this time that the 1986 Nobel Prize in physics was awarded to Gerd Binnig and Heinrich Rohrer for their invention of the STM. (It was shared with Ernst Ruska, one of the inventors of the electron microscope.) Fueled by the low cost and ease of building atomic resolution microscopes, interest in Nanoscience spread like wildfire

Scanning Tunneling Microscopy, papers were presented that reported images of biological molecules. The invention of the atomic force microscope (AFM) in 1986⁵ greatly extended the reach of these tools. Now insulating materials could be imaged with atomic resolution and new types of direct measurement and manipulation on the atomic scale were made possible. The chemists could image directly some of the fantastic structures they had only dreamed of making, and a bright young biochemist in New York, Ned Seeman, was able to realize his dream⁶ of building nanoscale machines with self-assembly of DNA molecules.

Thus was born the field of DNA nanotechnology. Major government funding of Nanoscience as a separate discipline began in the 1990s, with considerable subsequent impact on inventions in the development of technology.⁸ Those of us who were swept up in this field found biologists, engineers, chemists, and materials scientists (and even geologists) knocking on the doors of our physics labs. The days of research within the narrow confines of one traditional discipline were over.

Nanoparticles and structures have been used by humans in fourth century AD, by the Roman, which demonstrated one of the most interesting examples of nanotechnology in the ancient world. The Lycurgus cup, from the British Museum collection, represents one of the most outstanding achievements in ancient glass industry. It is the oldest famous example of dichroic glass. Dichroic glass describes two different types of glass, which change color in certain lighting conditions. This means that the Cup have two different colors: the glass appears green in direct light, and red-purple when light shines through the glass

In 1990, the scientists analyzed the cup using a transmission electron microscopy (TEM) to explain the phenomenon of dichroism. The observed dichroism (two colors) is due to the presence of nanoparticles with 50–100 nm in diameter. X-ray analysis showed that these nanoparticles are silver-gold (Ag-Au) alloy, with a ratio of Ag:Au of about 7:3, containing in addition about 10% copper (Cu) dispersed in a glass matrix. The Au nanoparticles produce a red color as result of light absorption (~520 nm). The red-purple color is due to the absorption by the bigger particles while the green color is attributed to the light scattering by colloidal dispersions of Ag nanoparticles with a size > 40 nm. The Lycurgus cup is recognized as one of the oldest synthetic nanomaterials. A similar effect is seen in late medieval church windows, shining a luminous red and yellow colors due to the fusion of Au and Ag nanoparticles into the glass. shows an example of the effect of these nanoparticles with different sizes to the stained glass windows.

Scope of nanotechnology

It has a huge scope in the upcoming generations. It is the third highest booming field when compared with IT and Internet. In India, Bangalore and Chennai are the manufacturing hub for IT and Medicine. The Indian government has already started Nanoscience and Nanotechnology initiatives and various funding agencies like the Department of Science and Technology.

Nanotechnology opens up an almost unlimited field of research activity. Especially in medicine, nanotechnology offers exciting opportunities. Novel diagnostic procedures and therapies promise wide-ranging development potential. For example, novel drugs can be developed. Supported by the progressive miniaturization in the electronics industry, interdisciplinary research teams are researching so-called nanobots. Prototypes already available today should continue to shrink below the size of blood cells and be able to move in the human organism. These nanobots could then transport drugs and dose them specifically to the disease centers.

The development of long fibrous devices that can be introduced into the human organism would be the consequent continuation of minimally invasive surgery. Substances could be more specifically administered and, for example, tissue samples.

Classic mechanical and plant engineering also wants to benefit from innovative materials whose structures show improved properties during machining and in use. So today the rotors of wind turbines are designed with a special coating, which has a positive effect on efficiency.

The ever-focused area of power generation and storage is developing new systems to quench the hunger for energy from previously unused sources. Novel concepts for energy generation, for example from ambient temperature or air movement combined with the optimized capacity of the storage media, promise a more efficient use of the energy available in nature.

The food industry is researching foods that, for example, have a longer shelf life due to the nanoparticles or, depending on their temperature and duration, have different flavors

in the domestic oven. But also in agriculture, nanotechnology is used for developments in the field of biological crop protection.

According to the surveys conducted in Sweden and UK it came to know nanotechnology has been emerged as a promising technology in the construction industry. More importantly its influence is very much significant in concrete products. It was also identified that construction industry is one of the important sectors which will be influenced by nanotechnology. A lot of research and development initiations are being organized to bring out many more innovations in nanotechnology relevant to construction industry. A lot of investments were made by venture capitalist and industrial corporations to unleash the potential in construction sector by the applications of nanotechnology. By identifying those potential European commission in late 2002 allotted huge funds for initiating research by name GMA1-2002-72160 "NANOCONEX". Nanotechnology is identified as a vital application to the advancement of Civil Engineering field. Its applications are very much significant in the construction portfolio of Civil Engineering.

Nanotechnology in Concrete Compared to the other form of materials used in construction concrete is one of the most common and predominantly used constructional materials. Concrete is a heterogeneous, nano structured, multi phase, construction material consist of various sizes of small crystals. It is widely used in almost all construction activities. We can't assume any construction without concrete. It occupies nearly 70% of the volume of the structure. Cement is one of the vital components used in manufacturing of concrete, but cement has some disadvantages. A lot of research has been carried out in order to reduce the proportion of cement in the concrete. Nanotechnology has been emerged as a best tool to address many problems associated with ingredients of concrete.

Nanotechnology is used to study many properties of concrete like heat of hydration, alkali aggregate reaction particularly alkali silicate reaction. The presence of alkali and silica in cement and aggregates causes ASR. If the amount of cement content is replaced by the use of Pozzolona it reduces the occurring and severity of alkali silicate reaction. The properties of concrete may be altered in so many ways, one of the best ways is the incorporation of nano particles. Nano particles in terms of nano silica, nano clays, nano titanium Oxide (TiO_2), Nano Iron (Fe_2O_3), Nano alumina (Al_2O_3), CuO, ZnO_2 and ZrO_2 . Nanomaterials in concrete will improve the pore structure of concrete, speed up the C-S-H gel formation and improve the concrete mechanical and durability properties. More particularly fly ash improves durability and strength of the concrete to the maximum extent but due to the addition of fly ash the early strength of the concrete may be reduced. The problem of low strength at early stage may be overcome by the incorporation of Nano-Silica which improves the density and structure of the concrete.

The addition of Nano- Silica improves resistance to segregation and also augments the strength of hardened concrete and offers more repulsion towards water absorption and prevents calcium leaching. Nano iron imparts the ability of self sensing and also improves its compressive and Flexural strength. Nano titanium helps the concrete for self cleaning. It is experimentally proved that how nanotechnology enhanced the life span of bridges. As per the study conducted by National Institute of Standards and technology, US, in 2007,

Nanotechnology is found best suitable in making pavements. Pavements should be very strong, durable, resistant to weathering, wearing and skid resistant. The pavements with all these features were successfully possible with the applications of ZnO_2 nano silica particles. Water logging on roads causes weathering it can be avoided by means of proper drainage and quick run-off. Hydrophobic roads, made of nano particles facilitate fast run-off. Nanotechnology is also used for water purification. The quality and availability of water can also be improved by nanotechnology. By using advanced methods and materials water can be made fit for reuse.

The salinity of water can also be reduced. With the application of nanotechnology carbon fibre reinforced plastics are also made. As they are very light in weight they don't exhibit good electric properties. Plastic solar cells are also made to produce solar energy which is very cheaper than conventional silicon semi conductors. By using these cells energy can be saved and they are also eco friendly since they reduce emission of carbon particles. Almost all developed countries are trying to use LED lamps instead of conventional lamps. Many more smart materials are produced with the application of nanotechnology. Smart materials have the influence of external stimuli like temperature, moisture, electric and magnetic fields etc.

CLASSIFICATION OF NANOMATERIALS

The classification of nanomaterials is based on the number of dimensions as shown in Fig. 1. According to Siegel, nanostructured materials are classified as:

Zero dimensional (0D),

One dimensional (1D),

Two dimensional (2D)

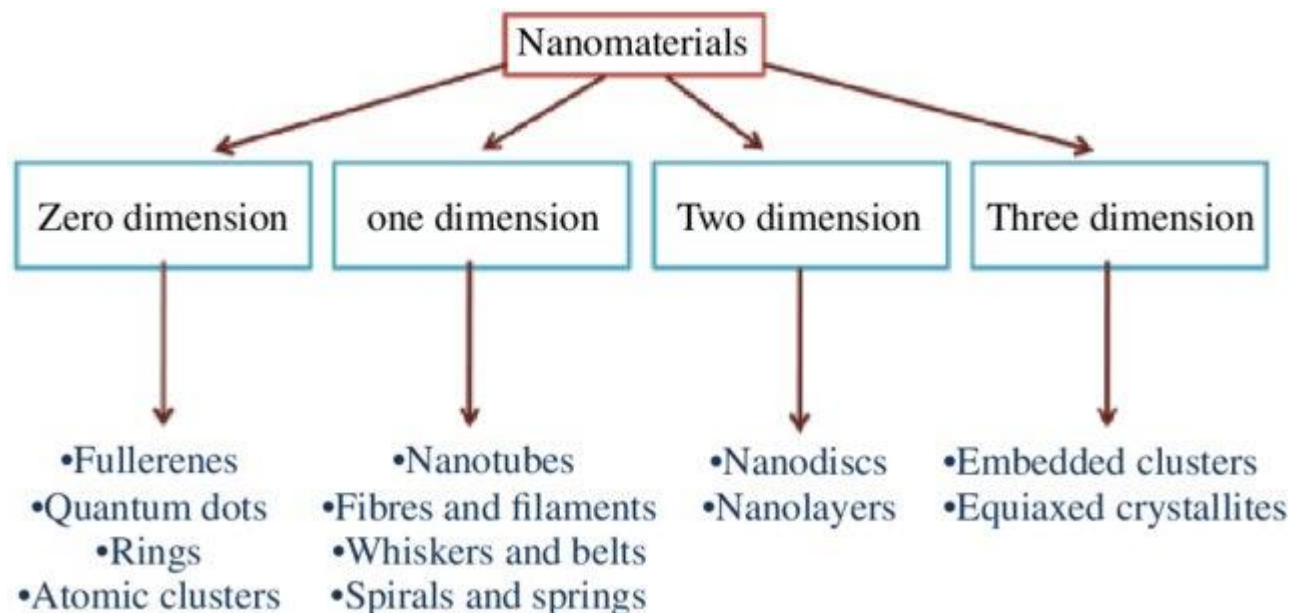
Three dimensional (3D)

(i) Zero-dimensional nanomaterials: Here, all dimensions (x, y, z) are at nanoscale, i.e., no dimensions are greater than 100 nm. It includes nanospheres and nanoclusters.

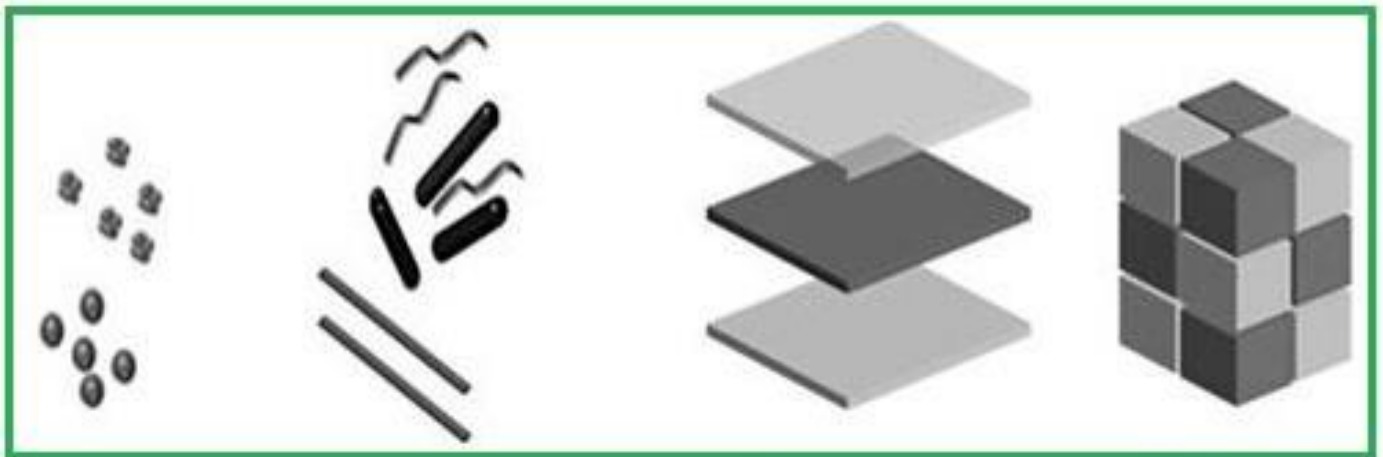
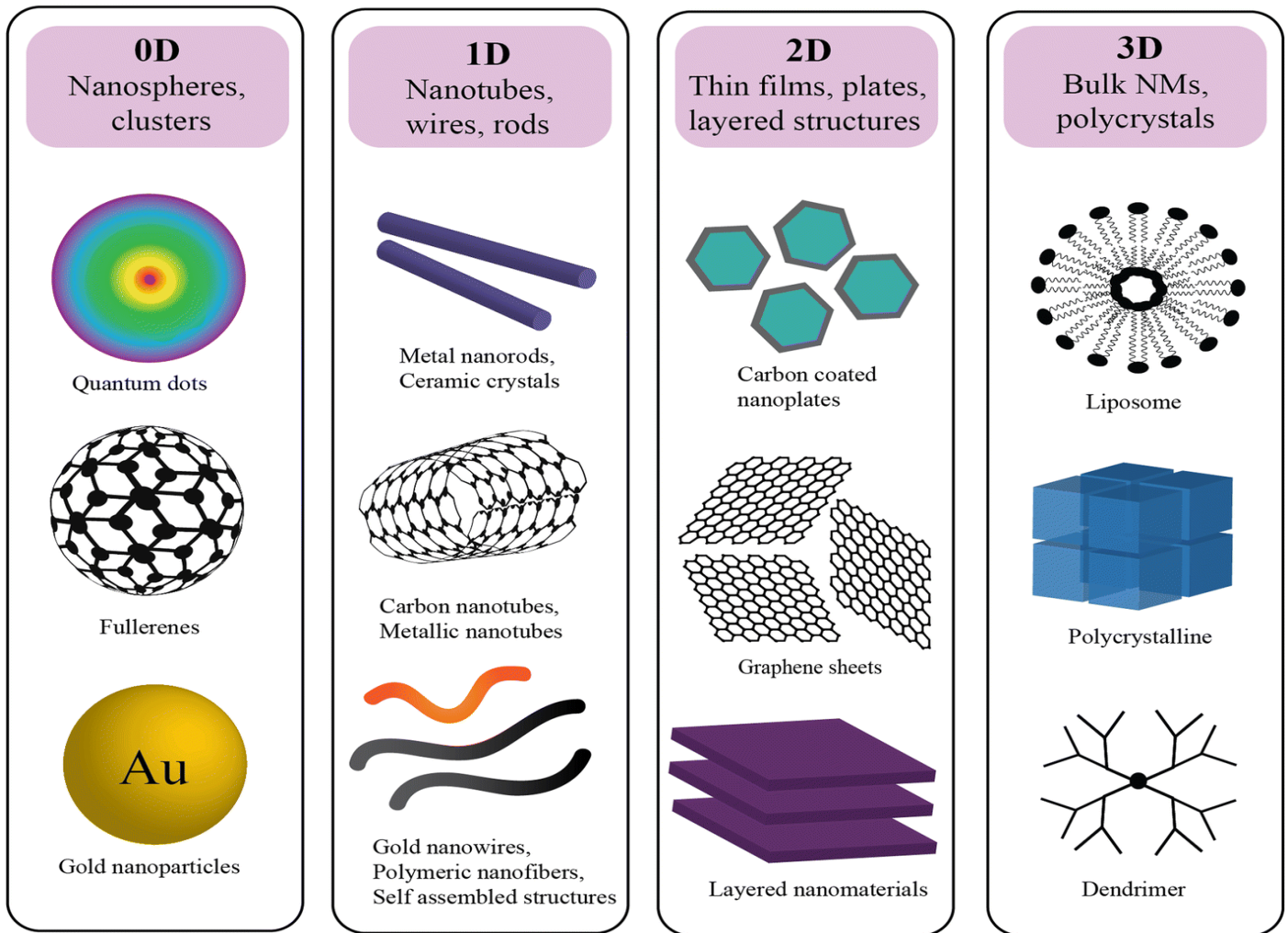
(ii) One-dimensional nanomaterials: Here, two dimensions (x, y) are at nanoscale and the other is outside the nanoscale. This leads to needle shaped nanomaterials. It includes nanofibres, nanotubes, nanorods, and nanowires.

(iii) Two-dimensional nanomaterials: Here, one dimension (x) is at nanoscale and the other two are outside the nanoscale. The 2D nanomaterials exhibit platelike shapes. It includes nanofilms, nanolayers and nanocoatings with nanometre thickness.

(iv) Three-dimensional nanomaterials: These are the nanomaterials that are not confined to the nanoscale in any dimension. These materials have three arbitrary dimensions above 100 nm. The bulk (3D) nanomaterials are composed of a multiple arrangement of nanosize crystals in different orientations. It includes dispersions of nanoparticles, bundles of nanowires and nanotubes as well as multilayers (polycrystals) in which the 0D, 1D and 2D structural elements are in close contact with each other and form interfaces.



NMs classification based on dimensionality



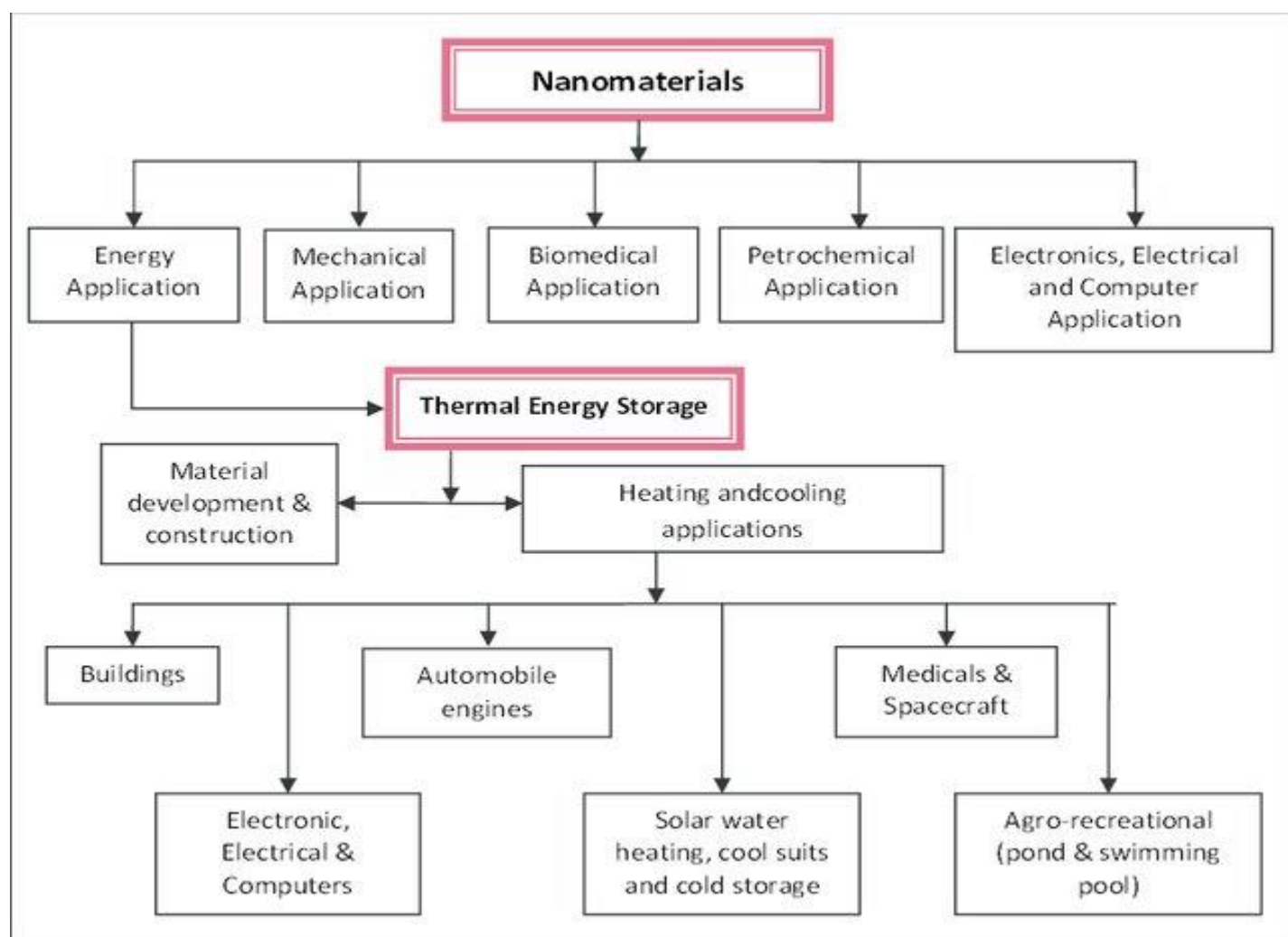
Fascinating nanostructures

Nanoparticle research is a fascinating branch of science. The strongly size-related properties of nanoparticles offer uncountable opportunities for surprising discoveries. The often unexpected and unprecedented behavior of nanoparticles bears great potential for innovative technological applications, but also poses great challenges to the scientists. They have to develop highly controllable synthesis approaches, more sensitive characterization tools and finally new models and theories to explain the experimental observations. In this review, we discuss a personal selection of papers dedicated to nanoparticle research, which we believe provide an illustrative overview of current research directions in this rapidly developing field. We have structured the text in five sections: introduction, nanoparticle synthesis, formation mechanisms, nanoparticle assembly, and applications. The chosen

examples within these sections are not directly related to each other, but reflect the remarkable broadness of nanoparticle research covering historical aspects, basic and applied science as well as commercial applications.

Applications of Nanomaterials

The efficient progress in nanotechnology has transformed many aspects of food science and the food industry with enhanced investment and market share. Recent advances in nanomaterials and nanodevices such as nanosensors, nano-emulsions, nanopesticides or nanocapsules are intended to bring about innovative applications in the food industry. In this review, the current applications of nanotechnology for packaging, processing, and the enhancement of the nutritional value and shelf life of foods are targeted. In addition, the functionality and applicability of food-related nanotechnologies are also highlighted and critically discussed in order to provide an insight into the development and evaluation of the safety of nanotechnology in the food industry



Nature the best of nanotechnologist

You wake up in the morning and put on your nature influenced clothes. You do not have to worry that it is raining outside today because water and dirt just roll off like drops on a lotus leaf. You do not have to worry that the electricity is out because your clothes can create its own light through firefly-inspired bioluminescence which can also keep your smart phone charged. No need for pockets. Anything you need to carry you can just stick to your clothes with the same Van der Waals forces that a gecko uses. Do you think this is all a dream? No, this is all possible and we have nanotechnology to thank along with some very important chemistry.

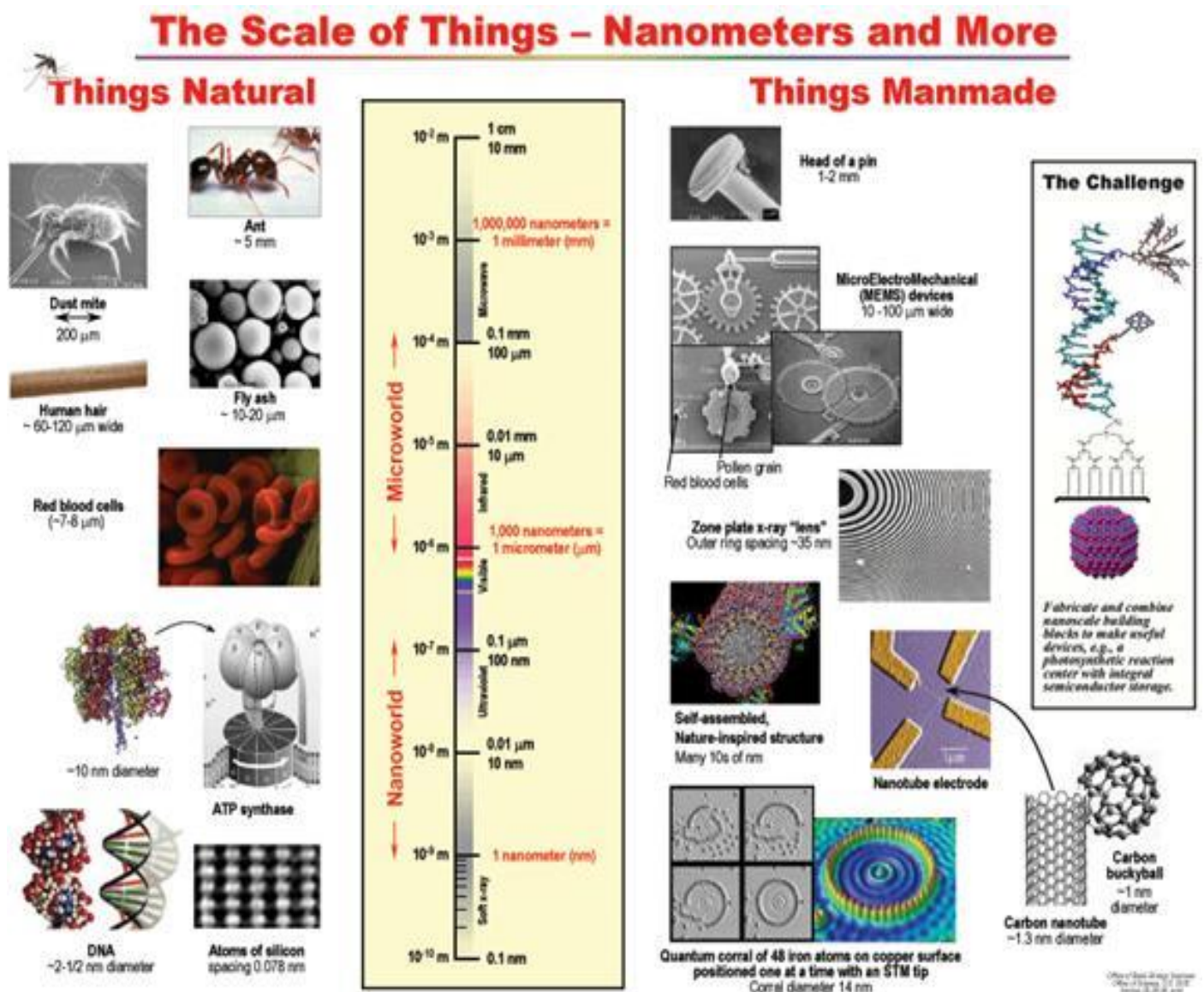
Nanomaterials abound in the living systems of nature and nanoscientists are examining the properties and potential uses of these natural nanostructures in an area of

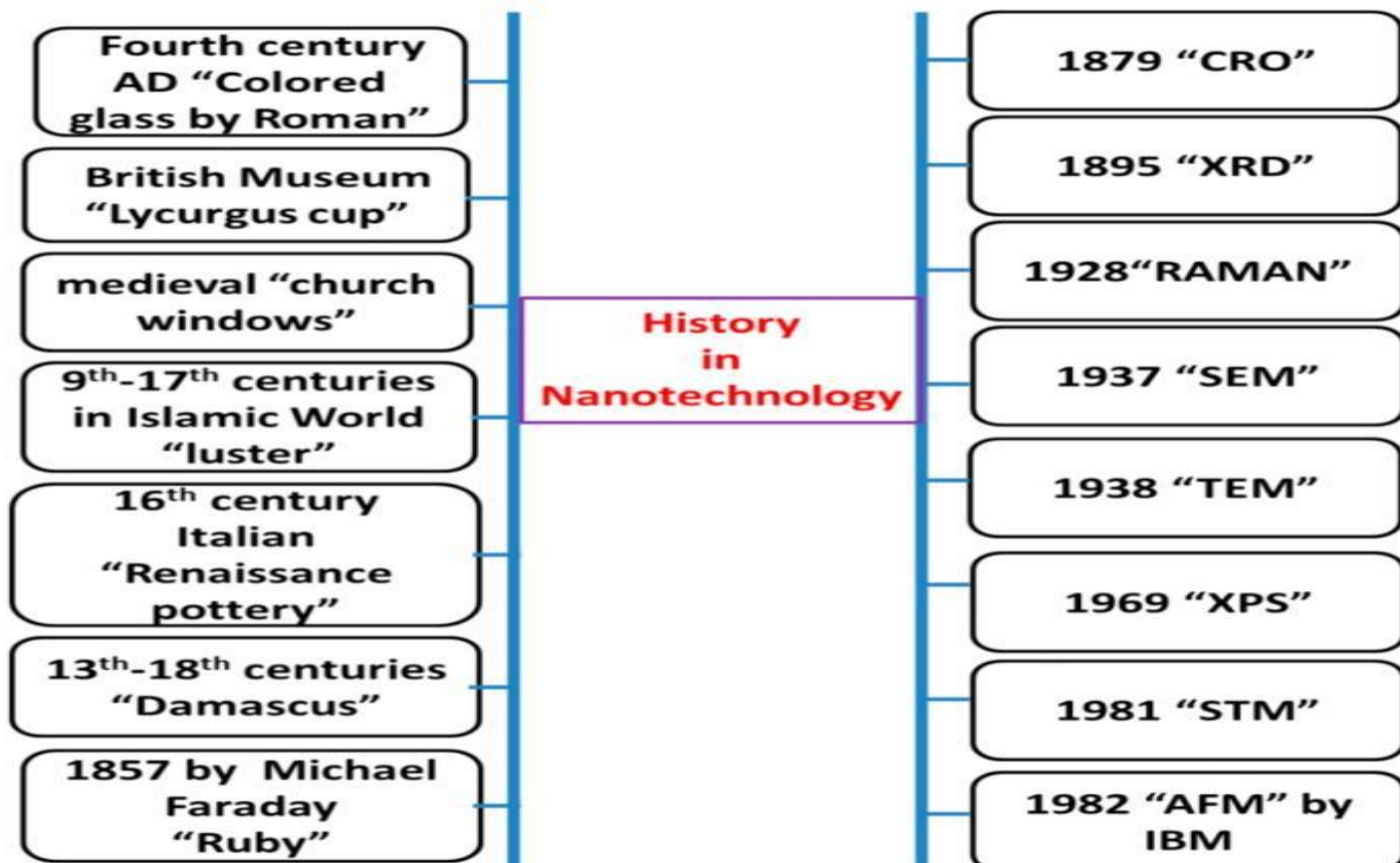
research called biomimicry. What types of nanostructures are found in nature? They include inorganic materials such as clays, carbonaceous soot (think carbon black), and natural inorganic thin films to a variety of organic nanostructures such as proteins and chitin (insect and crustacean shells) to organic structures such as wing ribs and epidermal projections. These structures lead to a variety of behaviors in nature including the wettability of surfaces, the iridescence of butterfly wings, and the adhesive properties of the gecko foot. Let's examine a few examples of these biomimetic structures.

Nanotechnology deals with the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications.

Challenges Future Prospects

Nanotechnology is an emerging and rapidly growing field whose dynamics and prospects pose many great challenges not only to scientists and engineers but also to society at large. This volume includes the state-of-the-art philosophical, ethical, and sociological reflection on nanotechnology, written by leading scholars from the humanities and social sciences in North America and Europe. It unravels the philosophical underpinnings of nanotechnology, its metaphysical and epistemological foundations, and its conceptual complexity. It explores the ethical issues of nanotechnology, its impact on human, environmental, and social conditions, and the options for reasonable risk management. It examines the public discourse on nanotechnology and its related visions and provides both lessons from the past and outlooks for the future.





Clusters
0D



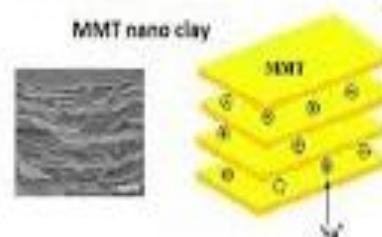
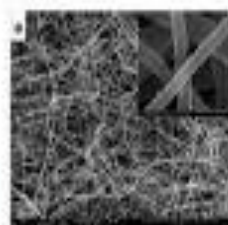
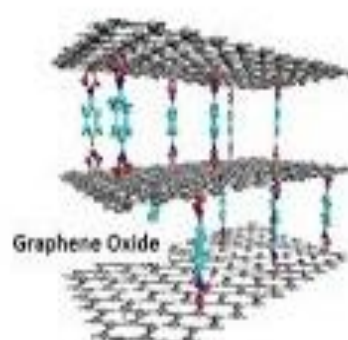
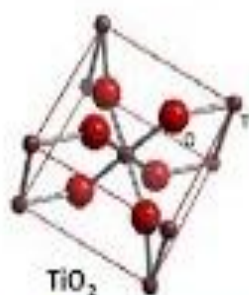
Nanotubes, fibers and rods
1D

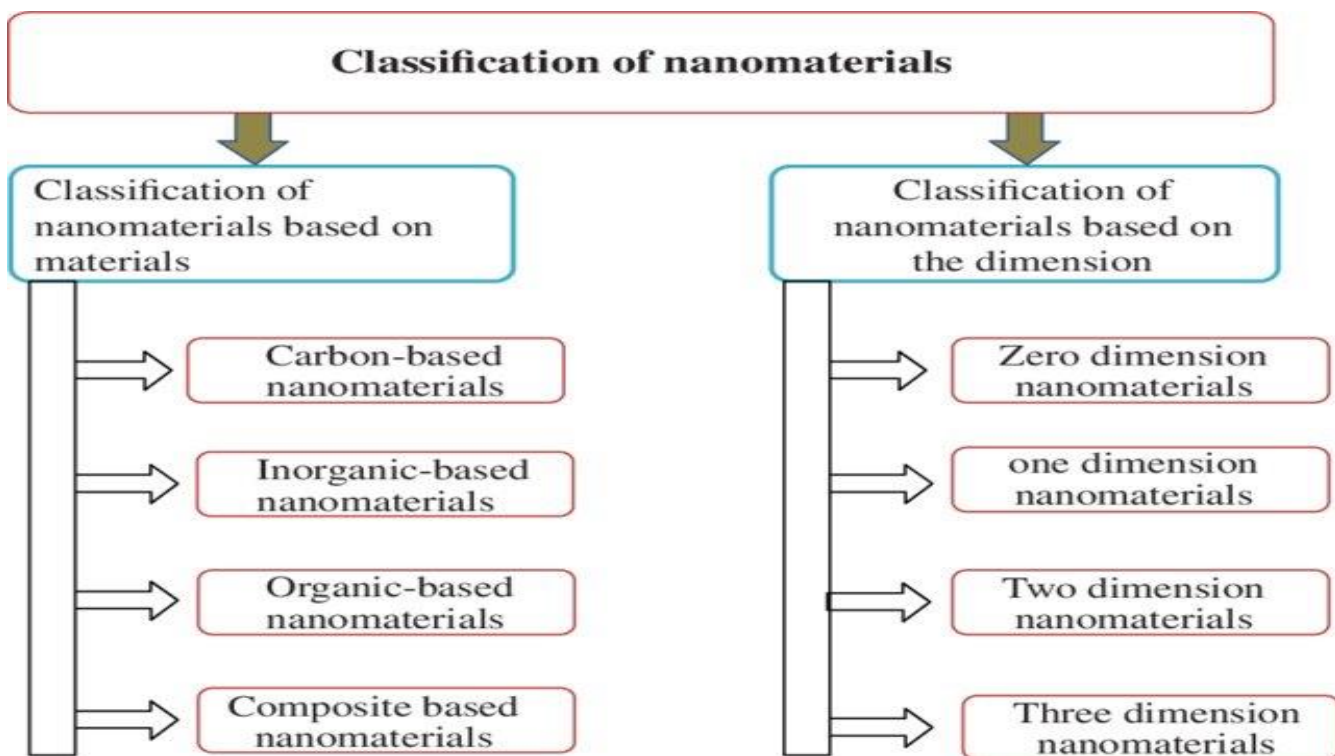
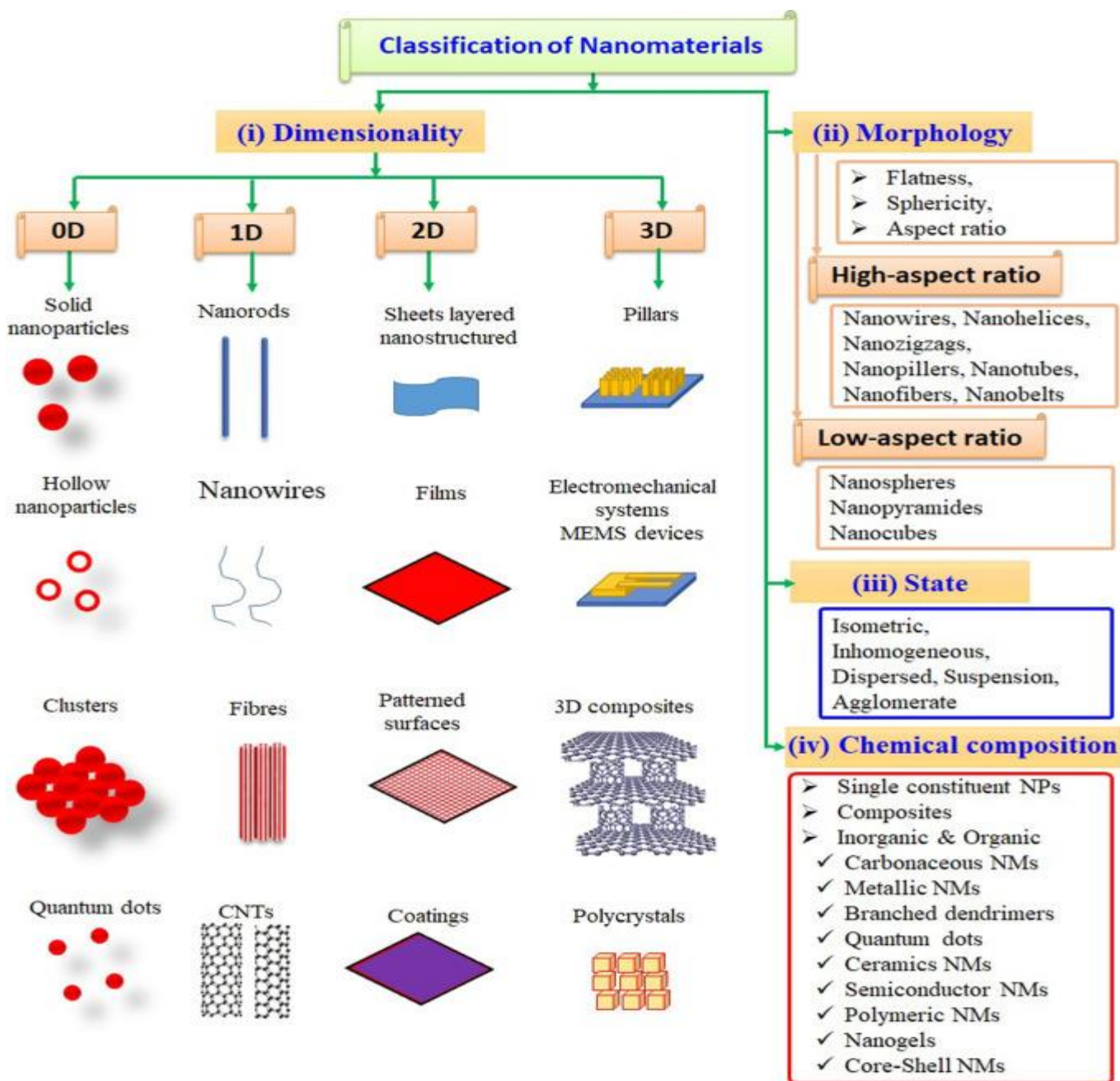


Films and coats
2D



Polycrystals
3D



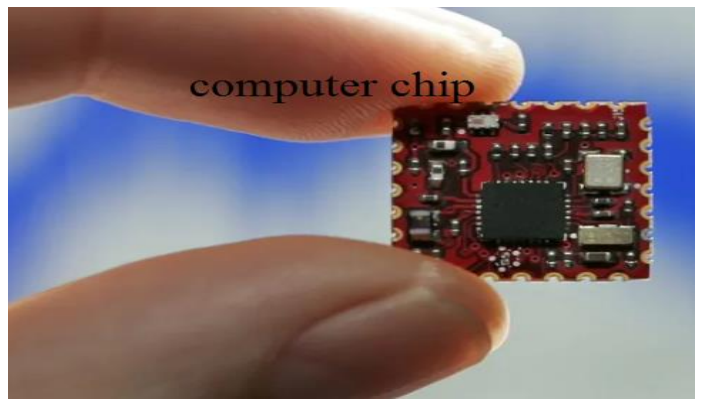
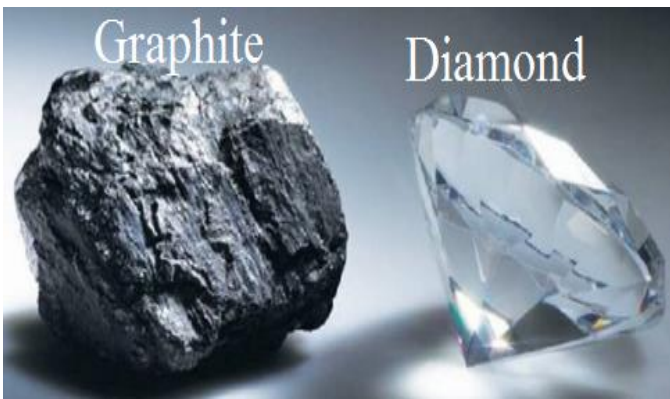


UNIT- II:

UNIQUE PROPERTIES OF NANO MATERIALS: Microstructure and Defects in Nano crystalline Materials: Dislocations, Twins, stacking faults and voids, Grain Boundaries, triple and declinations. Effect of Nano-dimensions on Materials Behavior: Elastic properties, Melting Point, Diffusivity, Grain growth characteristics, enhanced solid solubility. Magnetic Properties: Soft magnetic nanocrystalline alloy, Permanent magnetic nanocrystalline materials, Giant Magnetic Resonance, Electrical Properties, Optical Properties, Thermal Properties and Mechanical Properties.

Microstructure and Defects in Nano crystalline Materials

If we have the ability to construct matter, atom by atom, we would be able to perform wonders. For example, we know that both graphite and diamond are made of pure carbon. Thus, in belief, if we are able to rearrange the atoms (carbon) in graphite at our discretion, it would be possible to make diamond! Or, if we could rearrange the atoms (silicon and oxygen) in sand (and add a few other trace elements), it should be possible to make a computer chip.



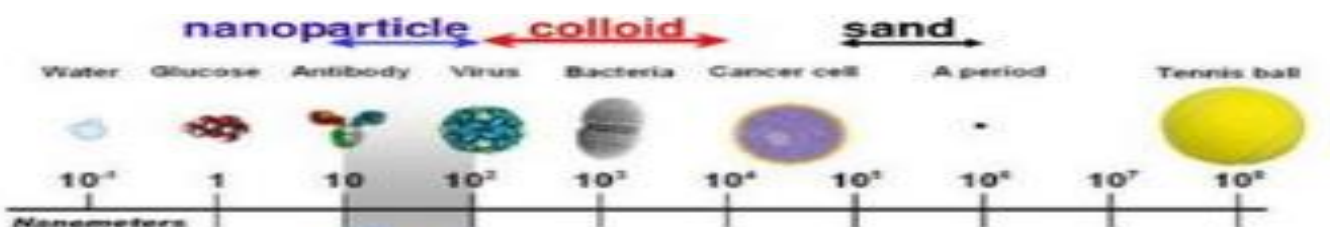
Engineering at the nano-level can bring about large changes in the properties of the products. Also, the high defect concentration in nanomaterials results in novel and unique physical, chemical and mechanical properties of this class of materials.

MICROSTRUCTURE AND DEFECTS IN NANOCRYSTALLINE MATERIALS

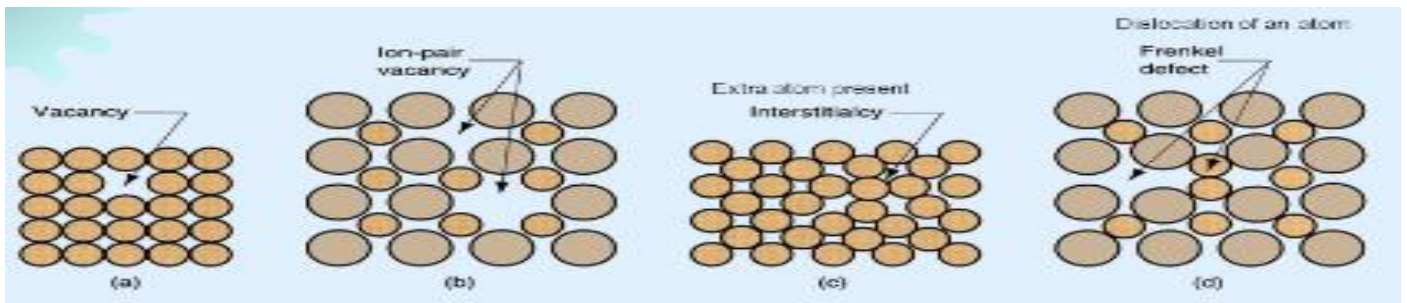
In order to understand the novel properties of nanostructured materials, we need to understand the structure and its inter-relationship with properties. The microstructural features of importance in nanomaterials include:

Grain size, distribution and morphology

- The nature of grain boundaries and interphase interfaces
- Nature of intra-grain defects
- Composition profiles across grains and interfaces
- Residual impurities from processing



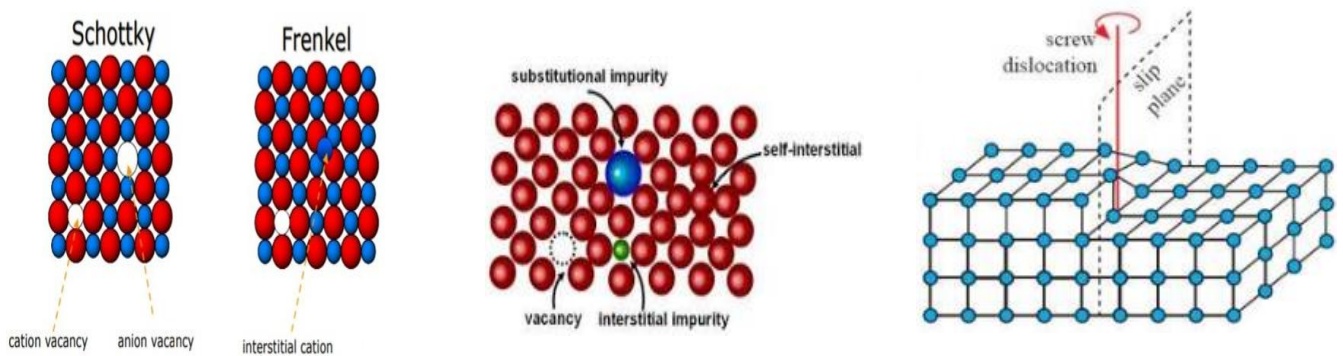
Crystal lattice imperfections, such as point, linear, planar and volume defects, lead to the structure-sensitive properties of materials. The atomic structure of nanostructured materials



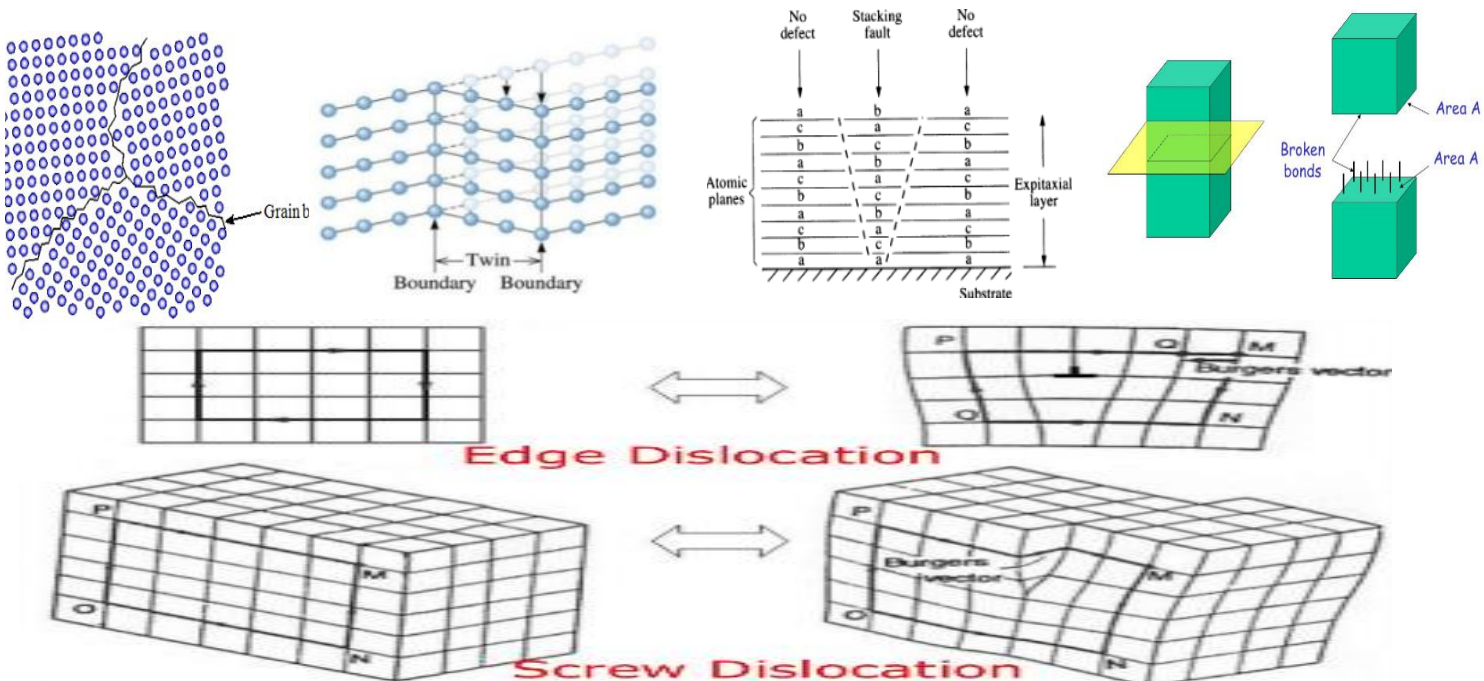
Crystals are three-dimensional, periodic arrangements of atoms/molecules in space.

Any imperfection leading to disruption of periodicity is referred to as a 'crystalline defect'. These defects are usually classified based on their dimensionality, namely, point defects (0D), line defects (1D), surface defects (2D) and volume defects (3D).

Vacancies, substitutional and interstitial solutes are the common point defects observed in metals and alloys. In case of ionic solids, Schottky (anion-cation vacancy pairs) and Frenkel (vacancy-interstitial pairs of the same ions) defects may also be observed. Dislocations are the most observed line defects and refer to a missing plane of atoms. Among the surface defects, grain boundaries, twins, stacking faults and free surfaces



Among the surface defects, grain boundaries, twins, stacking faults and free surfaces are the most common. Inclusions, voids and micro cracks constitute the volume defects.



Missing rows of atoms in a crystal are regions of high energy and stress due to disruption of the atomic bonds in the plane. This provides a heavy force for dislocations to be done at surfaces or grain boundaries to minimize the strain energy of the crystal.

In effect, this may be treated as equivalent to an attractive force applied by the surface on dislocations in the crystal. This force is inversely proportional to the distance of separation and hence becomes negligible for dislocations farther than a critical distance. However, for dislocations close to the surface or grain boundary, the attractive force can be large enough to result in applying the dislocations. Hence, for a small distance from the surface and grain boundaries, one would not expect to find any dislocations.

Dislocations

Dislocations are, in general, stable in conventional microcrystalline materials, though not thermodynamically stable defects. However, when the magnitude of the critical distance becomes comparable with that of the grain size, as in nanomaterials, the stability of dislocations is changed significantly. Hence, with decreasing grain size of nanograined materials, dislocation stability is reduced, due to the large grain boundary area.

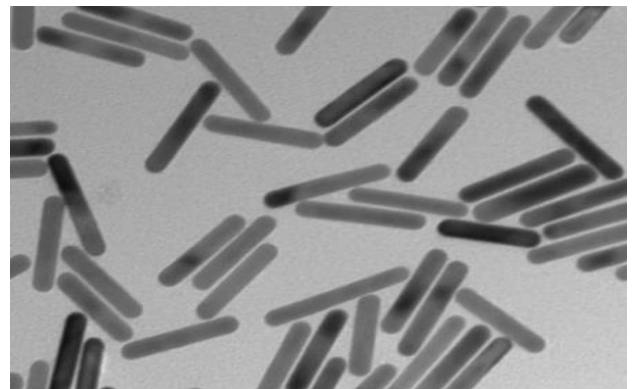
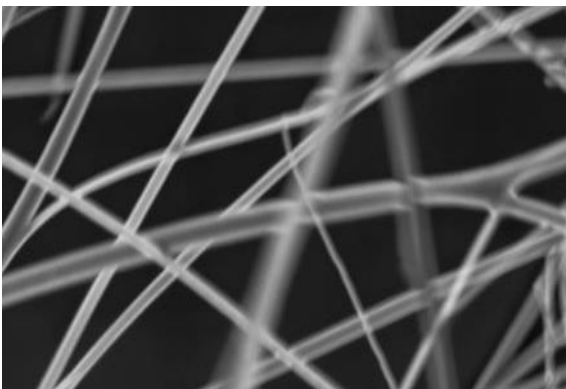
It is well known that dislocation mobility and interactions play a large role in determining the deformation and plastic flow behaviour of conventional crystalline materials. Hence, it is expected that the deformation behaviour of nanocrystalline materials is significantly different from that of conventional microcrystalline materials.

The typical dislocation density in annealed (hardened) crystalline materials is about $10^{10}/\text{cm}$. As the grain size is reduced to about 10 nm, the dislocation density can reduce by 2–3 orders or more and finally, below a critical grain size, dislocations are no longer stable, i.e., there will be no dislocations in the nanocrystalline materials below the critical grain size.

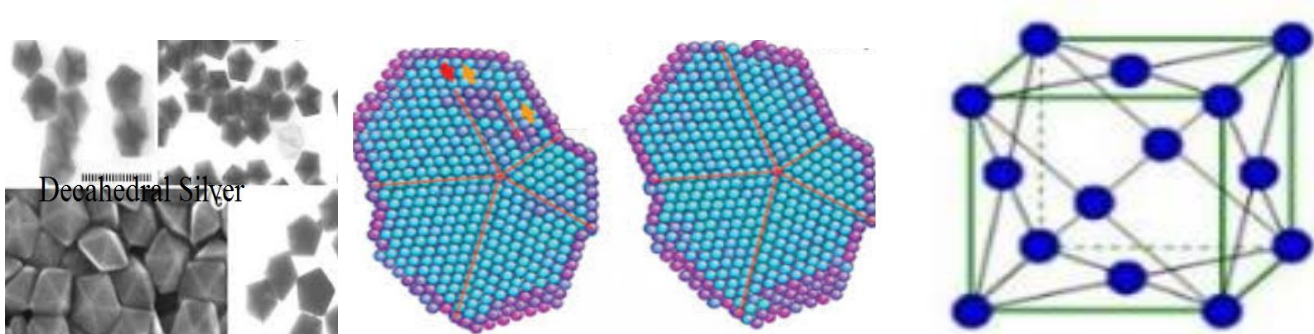
In contrast to whiskers (single crystals without dislocations), nanomaterials have a large number of grain boundaries as defects. Hence, the plastic deformation behaviour of the material cannot be governed by dislocation mechanisms. This can result in significantly different mechanical properties in nanomaterials below the critical sizes. The effect of decreasing dislocation density on the deformation mechanism is an area of significant scientific curiosity.

Twins, stacking faults and voids

planar defects are often observed, even after annealing, in many faceted nanomaterials, including nano rods and nanowires. These planar defects include twins and stacking faults (intrinsic or extrinsic), and are usually neglected by most analytical models.



For example, many bulk metals have the face-centred cubic structure, but nanocrystals and nanorods of the same material often exhibit various structural modifications such as single or multiple symmetric twinning, as well as five-fold cyclic twinning, resulting in decahedral and truncated decahedral nanostructures below critical sizes.



Twins are generally observed in crystals subjected to deformation under high strain rate or at low temperatures. During crystallization of liquid metal, it is expected that volume misfit strains can be easily accommodated in the liquid phase, and hence one does not expect the formation of twins in the nucleating crystals.

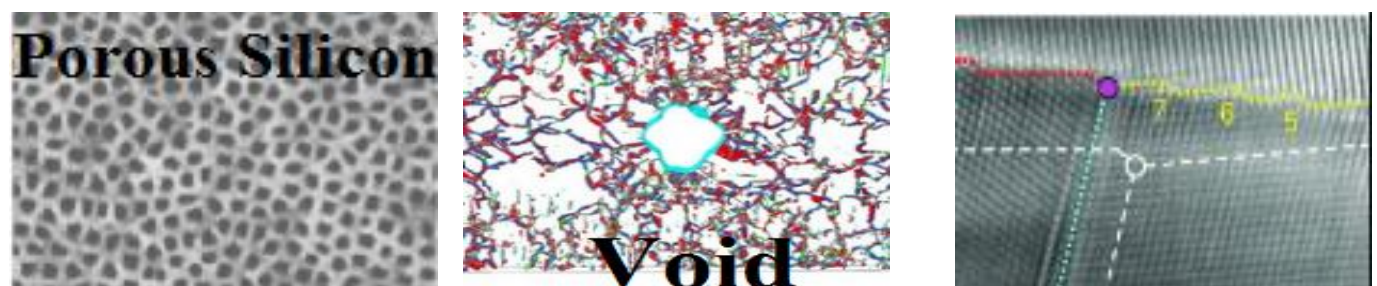


Voids in nanocrystallites may be located at either

Triple junctions

Large porosities

Due to insufficient compaction and sintering of nanocrystallites synthesized from the powder method. Although both types of voids influence the behaviour of the nanocrystallites, the first is structurally more important. It is suggested that triple junction voids arise as a result of relaxation of nanocrystalline grain boundaries.



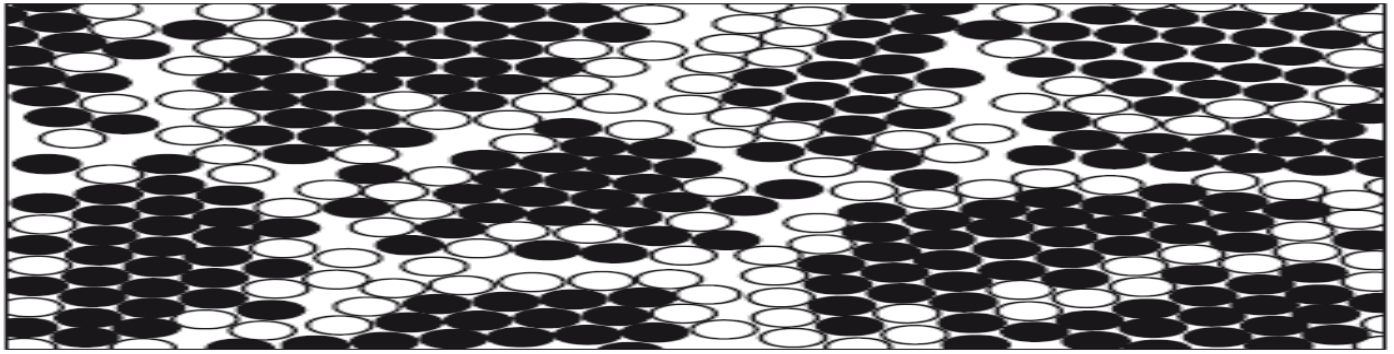
Grain boundaries, triple junctions and disclinations

A schematic representation of a hard-sphere model of an equiaxed nanocrystalline metal as shown in Figure.

Two types of atoms can be distinguished:

Crystal atoms with nearest-neighbour configurations corresponding to the lattice (black circles) .

Boundary atoms with a variety of interatomic spacings (white circles). Nanocrystalline materials typically contain a high number of interfaces with random orientation relationships, so, a substantial fraction of atoms lies in the interfaces.



The hypothetical structure of a nanomaterial. The black circles indicate atoms in the grain, while the white circles indicate atoms at the grain boundaries.

Assuming that the grains have the shape of spheres or cubes, the volume fraction of nanocrystalline materials associated with the boundaries (V_i) is estimated to be:

$$V_i = \frac{3\delta}{d}$$

where δ is the average interface thickness and d is the average grain diameter. Thus, the volume fraction of interfaces can be as much as 60% for 5 nm grains, 30% for 10 nm grains, and about 3% for 100 nm grains, for a grain boundary thickness of 1 nm.

According to the phase mixture model, many properties of nanocrystalline materials can be estimated by a simple rule of mixtures,

$$X = V_{cr} X_{cr} + V_{ic} X_{ic}$$

where subscripts cr and ic refer to the crystalline and intercrystallite components of nanocrystalline materials, and X and V denote the property and volume fraction of the respective components. Intercrystallite components include the grain boundaries, triple lines and quadruple nodes. Taking a cubic unit cell or a regular polyhedron unit cell of nanocrystalline materials, the volume fraction of each component can be expressed as follows:

$$V_{cr} = \frac{(d - \delta)^3}{d^3}$$

$$V_{gb} = \frac{6(d - \delta)^2(\delta/2)}{d^3}$$

$$V_{ij} = \frac{12(d - \delta)(\delta/2)^2}{d^3}$$

$$V_{qn} = \frac{\delta^3}{d^3}$$

Where the subscribes cr , gb , tj and qn refer to crystallite, grain boundary, triple lines and quadruple nodes, respectively; d and δ represent the grain size and grain boundary thickness.

When the grain size is smaller than about 20 nm, the total volume of the intercrystallite region (grain boundary and triple junctions) becomes significant. The density of grain boundaries in nanocrystals is very large ($\sim 10^{19} \text{ cm}^{-3}$) and there is wide distribution of interatomic spacing at these grain boundaries.

It has been suggested that the triple junctions can be described based on the disclination defect model.

Disclinations (as Figure) are line defects characterised by a rotation vector ω in contrast to the translational vector b for dislocations.



A schematic showing disclination.

The triple junctions may be considered to form a network of disclinations. Theoretical calculations have shown that triple junction energies are comparable to dislocation energies, and that compensating disclinations play a significant role in the properties of nanocrystalline metals with grain size less than about 10 nm. These triple junctions are linear defects that play a significant role in the mechanical, thermodynamic and kinetic properties of polycrystals. This role may be particularly important in nanocrystalline materials, where the grain boundaries are short and contain a small number of structural units.

Effect of Nano-dimensions on Materials Behavior

As with decrease in size the surface area increases, so nanostructure have more surface area for reaction. Hence reactivity increases with decrease in particle size.

Effect of Nano-dimensions on Elastic properties:

Size effects decisively influence the properties of materials at small length scales. In the context of mechanical properties, the trend of 'smaller is stronger' has been well established. This statement refers to an almost universal trend of increased strength with decreasing size. A strong influence of size on the elastic properties has also been widely reported, albeit without a clear trend. However, the influence of nanostructure shape on the mechanical properties has been critically neglected.

Here, profound influence of shape and size on the elastic properties of materials on the example of gold nanowires. The elastic properties are determined using in-situ mechanical testing in scanning and transmission electron microscopy by means of resonance excitation and uniaxial tension. The combination of bending and tensile load types allows for an independent and correlative calculation of the Young's modulus. We find both cases of softening as well as stiffening, depending critically on the interplay between size and shape of the wires.

Effect of Nano-dimensions on Melting Point:

By considering the surface effects, the melting temperature of nanosolids (nanoparticles, nanowires and nanofilms) has been predicted based on size-dependent cohesive energy. It is shown that the melting temperature of free standing nanosolids decreases with decrease in the solid size, and the melting temperature variation for spherical nanoparticle, nanowire and nanofilm of a material in the same size is 3:2:1.

A model for size- and shape-dependent specific heat was introduced. The specific heat of nanosolids was found to increase with decrease of the particle size for spherical, nanowire and nanofilm shapes. Moreover, the model was applied to determine the shape

and size dependence of the melting entropy and enthalpy of nanosolids. The prediction of the present model for specific heat, melting entropy and enthalpy was found to be in good agreement with the molecular dynamics results and the available experimental data, indicating that our present model at nanoscale can be applied for a wide range of surface-related phenomena. The present model has the potential to be applied for calculation of the thermodynamical properties of nanomaterials.

Effect of Nano-dimensions on Diffusivity

Diffusion in nanostructures has many challenging features even if the role of structural defects (dislocations, phase- or grain-boundaries) can be neglected. This can be the case for diffusion in amorphous materials, in epitaxial, highly ideal thin films or multilayers, in dissolution of thin films or in kinetics of surface segregation, where diffusion along short circuits can be ignored and only fundamental difficulties, related to nanoscale effects, raise. Different examples for diffusion in such materials will be given with special emphasis on the validity limit of the continuum approach especially if the diffusion coefficient depends strongly on composition (non-linearity).

It was shown recently by us that even for ideal systems (like Cu/Ni) this non-linearity leads to linear shift of an originally sharp interface (instead of the parabolic behaviour) and to sharpening of an initially diffuse interface. The sharpening takes place, even if the effects of stresses (built in mismatch, thermal and diffusional stresses) are taken into account. Furthermore, deviations from the parabolic law are present in phase separating systems as well, but here the interplay of the strong composition dependence and the phase separation tendency results in a more complex behaviour. These deviations are typical nano effects i.e. they diminish with time; in the examples investigated here after dissolution of several hundred atomic planes the parabolic law already fulfils.

Effect of Nano-dimensions on Grain growth characteristics

The hardness measured by the nanosize indenter under atomic indentation is examined for the cases of nanocrystalline nickel by means of molecular dynamics (MD) simulations. The grain size effect observed is different from the one by uniform deformation or deep indentation. The results show that hardness can only show inverse Hall-Petch (H-P) effect, no H-P effect is observed with the grain size up to 40 nm. Grain boundary (GB) absorption of the localized strain is the main deformation mechanism when the indenter size and the depth both come to nano size. The area of plastic zone generated beneath the tip is strongly dependent on the GB density, sample with small grain size results in larger plastic area, which leads to the softer response of hardness.

In atomic depth indentation on nanocrystalline nickel with grain size from 5 nm to 40 nm using indenters with various sizes have revealed that only inverse H-P effect appears. Following can be concluded.

1. The inverse H-P effect could be explained by the strain contributions from GBs and grain interior. The larger grain size results in large portion of strain in grain interior, producing higher hardness under ultra shallow indentation. The H-P relation does not hold even the crystal size is above the conventional transition size. Our observation indicates the GB absorption and GB sliding comes to play an important role in the ultra shallow contact, few generated dislocations can be easily absorbed by GBs.

2. The area of plastic zone generated beneath the tip is size dependent; larger GB density induces larger plastic area from GB mediation, and thus causes softer response.

Effect of Nano-dimensions on enhanced solid solubility

The effects of particle size on their solubility, dissolution, and oral bioavailability were investigated. Solubility and dissolution testing were performed in three types of dissolution medium, and the studies demonstrated that the equilibrium solubilities of coenzyme Q10 nanocrystals and bulk drugs were not affected by the dissolution media but the kinetic solubilities were. Kinetic solubility curves and changes in particle size distribution were determined and well explained by the proposed solubilization model for the nanocrystals and bulk drugs.

The particle size effect on dissolution was clearly influenced by the diffusion coefficients of the various dissolution media, and the dissolution velocity of coenzyme Q10 increased as particle size decreased. The bioavailability of coenzyme Q10 after oral administration in beagle dogs was improved by reducing the particle size. For 700 nm nanocrystals, the AUC₀₋₄₈ was 4.4-fold greater than that for the coarse suspensions, but a further decrease in particle size from 700 nm to 120 nm did not contribute to improvement in bioavailability until the particle size was reduced to 80 nm, when bioavailability was increased by 7.3-fold.

Magnetic properties of nanoparticles

Magnetic properties of nanoparticles are used for drug delivery, therapeutic treatment, contrast agents for MRI imaging, bio separation, and in-vitro diagnostics. These nano meter-sized particles are superparamagnetic, a property resulting from their tiny size—only a few nanometers—a fraction of the width of a human hair (nanoparticles are approximately 1/1,000 thinner than human hair). Superparamagnetic nanoparticles are not magnetic when located in a zero magnetic field, but they quickly become magnetized when an external magnetic field is applied. When returned to a zero magnetic field they quickly revert to a non-magnetized state. Super para magnetism is one of the most important properties of nanoparticles used for bio magnetic separation.

Soft magnetic nanocrystalline alloy

Magnetic materials permeate numerous daily activities in our lives.¹ They are essential components of a diversity of products including hard drives that reliably store information on our computers, decorative magnets that keep the shopping list attached to the refrigerator door, electric bicycles that speed our commute to work, as well as wind turbines for conversion of wind energy to electrical power. While permanent magnets require materials that maintain their magnetization even under the influence of external stimuli, soft magnetic materials can easily change their magnetization when external conditions require it.

Permanent magnets require the magnetization vs. field hysteresis loop, $M(H)$, to be broad, with a large coercive field in order to allow energy to be stored in the material. In contrast, soft magnetic materials require a narrow hysteresis loop, which implies the use of small amounts of energy to magnetize the material. As the area of the loop is related to energy losses during the cyclic magnetization of the material, a low coercive field implies better energy efficiency of the final application in which the soft magnetic material is used.

As indicated in the previous section, obtaining materials in which the exchange correlation length is much larger than the structural correlation length will lead to effective

magnetic anisotropies that are negligible when compared to the magneto crystalline anisotropy of the bulk material. In practice, this can be achieved by controlled crystallization of a precursor amorphous alloy.

Soft magnetic nanocrystalline alloys have been used to study the super para magnetism of nanocrystals embedded in the matrix in order to develop models of the dipolar interactions between superparamagnetic nanoparticle or to propose procedures for the determination of critical exponents of multiphase magnetic systems.

Nanocrystalline alloys are among the softest magnetic materials known to science, and different alloy families have been optimized for unique applications and operating conditions. In addition to compositional effects that will affect intrinsic magnetic properties, the use of different processing methods enables the optimization of extrinsic properties such as coercivity.

The physical reason for the extremely low values of magnetic anisotropy and coercive field can be explained using the random anisotropy model: the two characteristic length scales of nanocrystalline alloys (grain size and magnetic correlation length) are very different, and anisotropy cannot be detected macroscopically, even if each nanocrystal is anisotropic.

Soft magnets are currently used in a variety of applications, ranging from energy conversion to sensors. Remaining challenges in the development of soft magnetic nanocrystalline alloys include the optimization of material properties for specific applications and the enhancement of their usability by decreasing brittleness and increasing thermal stability of the metastable phases. These goals can be achieved by a combination of compositional changes and appropriate processing of the alloys.

Tuning the hysteresis loops by processing the materials under the simultaneous influence of magnetic field, stress, and temperature is a promising route to broadening the applications of nanocrystalline soft magnets. In addition, the design of exchange-coupled hard-soft magnetic nanocomposites is an area of significant interest in which ultrasoft nanocrystalline alloys may play a role. Moreover, the interest in soft nanocrystalline alloys is not limited to technological applications as these materials are also a good testing ground for developing fundamental models of multiphase magnetic materials.

Permanent magnetic nanocrystalline materials

Recent developments in nanocrystalline rare earth-transition metal magnets are reviewed and emphasis is placed on research work at IFW Dresden. Principal synthesis methods include high energy ball milling, melt spinning and hydrogen assisted methods such as reactive milling and hydrogenation-disproportionation-desorption-recombination. These techniques are applied to NdFeB-, PrFeB- and SmCo-type systems with the aim to produce high remanence magnets with high coercivity. Concepts of maximizing the energy density in nanostructured magnets by either inducing a texture via anisotropic HDDR or hot deformation or enhancing the remanence via magnetic exchange coupling are evaluated

In recent developments in research in nanostructured permanent magnets (hard magnetic materials) with emphasis on bottom-up approaches to fabrication of hard/soft nanocomposite bulk magnets. Theoretical and experimental findings on the effects of soft phase and interface conditions on interphase exchange interactions are given. Synthesis techniques for hard magnetic nanoparticles, including chemical solution methods,

surfactant-assisted ball milling and other physical deposition methods are reviewed. Processing and magnetic properties of warm compacted and plastically deformed bulk magnets with nanocrystalline morphology are discussed. Prospects of producing bulk anisotropic hard/soft nanocomposite magnets are presented.

Giant Magnetic Resonance of nano materials

The discovery of giant magnetoresistance (GMR) occurred in the late 1980s,^{1,2} at the dawn of the age of the modern computing. This discovery, and its fortuitous timing, resulted in the rapid commercial deployment of GMR-based devices in the read heads of hard disk drives, accelerating the miniaturization of data storage and driving the digital revolution. The immediate impact of GMR won Albert Fert and Peter Grünberg, the discoverers of this phenomenon, the Nobel Prize in Physics. Today, giant (GMR), tunnelling (TMR), and anisotropic (AMR) magnetoresistance are still instrumental in spin valve devices for reading and writing data. Of further interest is that within emerging areas of research there is tremendous promise for application of MR devices in areas requiring sensitive magnetic field sensors, including navigation,³ biomedical sensing,⁴ and more complex applications in spintronics.⁵ Creating new magneto resistive materials is vitally important to developing these new areas.

Despite the overwhelming need for new materials, the vast phase space of magnetic materials remains unexplored for MR applications. Reporting in *ACS Central Science*, Zhou and Rinehart demonstrate a novel approach to the creation of magneto resistive materials with an intriguing report of tunnelling magnetoresistance (TMR) in colloidally prepared CoFe_2O_4 nanoparticles.⁶ Leveraging advances in nanoparticle preparation techniques, Rinehart and co-workers demonstrate how commonly held assumptions about the nature and limitations of nanoparticle-based magnetoresistance need to be questioned. Chief among these assumptions are the defining importance of (1) highly crystalline interfaces and (2) magnetically ordered materials.

TMR arises within conductive ferro- or ferrimagnetic materials at the interface between different magnetic domains. If the magnetization vectors of adjacent magnetic domains are aligned, then electrons can move between them relatively unimpeded. If the domains' magnetization vectors are oppositely aligned, then electron flow between those domains is impeded, resulting in decreased conductivity across the interface. This phenomenon underpins spin valve magnetic field sensors used in many different devices. An extension of this phenomenon arises in granular solids which are composed of many independent ferro- or ferrimagnetic single-domain particles which align upon exposure to an external magnetic field.

PROPERTIES OF MATERIALS

The mechanical and physical properties of materials are determined by their chemical composition and their internal structure, like grain size or crystal structure. Mechanical properties may be greatly affected by processing due to the rearrangement of the internal structure. Metalworking processes or heat treatment might play a role in affecting some physical properties like density and electrical conductivity, but those effects are usually insignificant.

Mechanical and physical properties are a key determinant for which alloy is considered suitable for a given application when multiple alloys satisfy the service conditions. In almost every instance, the engineer designs the part to perform within a given range of properties. Many of the mechanical properties are interdependent – high performance in one category may be coupled with lower performance in another. Higher-

strength, as an example, maybe achieved at the expense of lower ductility. So a broad understanding of the product's environment will lead to the selection of the best material for the application.

Electrical properties of nanomaterials

The electrical properties of the nanomaterials or nanoparticles. The properties like conductivity or resistivity are come under category of electrical properties. These properties are observed to change at nanoscale level like optical properties. The examples of the change in electrical properties in nanomaterials are:

1. Conductivity of a bulk or large material does not depend upon dimensions like diameter or area of cross section and twist in the conducting wire etc. However it is found that in case of carbon nanotubes conductivity changes with change in area of cross section.
2. It is also observed that conductivity also changes when some shear force (in simple terms twist) is given to nanotube.
3. Conductivity of a multiwalled carbon nanotube is different than that of single nanotube of same dimensions.
4. The carbon nanotubes can act as conductor or semiconductor in behaviour but we all know that large carbon (graphite) is good conductor of electricity.

Dielectric properties of nanomaterials

The small grain size of nanomaterials has significant effect due to drastic change in the physical properties of the materials used for their interconnects and components. The issue of the dielectric property for nanomaterials is very important and attractive for their potential applications as capacitor, memory device and sensor. The dielectric property of nanomaterials interestingly exhibits unusual property which will give rise to develop new materials². The frequency behaviour of dielectric materials gives the valuable information about the conduction phenomena of nanostructures materials with their capping. It is to be noted that the dielectric properties in nanomaterials have some interesting aspects especially for metal nanoparticles in which the capping are basically insulating and the core is metallic. However, when they form such complex system of nanoparticles, the basically insulating capping would change their insulating state into more conductive phase, due their ionic form, while those of the metal turning into insulating phase as the particle size is reduced to that of a few atoms big (~1 nm), due to quantum size effect. How this situation influences their overall dielectric properties is of fundamental importance.

Optical properties of nanomaterial

Optical properties of nanomaterial such as absorption, transmission, reflection, and light emission are dynamic and may differ significantly from properties exhibited by the same bulk material. A wide range of optical effects may be produced for a variety of applications by simply manipulating its shape, size, and surface functionality. This manipulation may be achieved via different means, depending on the composition, size, and orientation. The optical property of nanomaterial is very important in a variety of ways. They are capable of confining their electrical properties to produce quantum effect with the possibility of the variation in shape, size, or type having effect on the color they produce. For example, spherical gold nanomaterial of 25-nm diameter appears green while those in the range of 100 nm appear orange. In the same vein, spherical gold nanomaterial of 100-nm diameter appears orange while a similar size of spherical silver nanomaterial appears yellow.

The optical properties of nanomaterials are some of the most important, and can be identified using various spectroscopic techniques. In small nanoclusters, reduced dimensionality in their electronic structure has the most profound effect on the energies of the highest occupied molecular orbital, which is a valence band, and the lowest unoccupied molecular orbital, which is essentially the conduction band. Optical properties such as emission and adsorption occur when electron transition occurs between these two states. Semiconductors and many metals show large changes in optical properties as a function of particle size. A simple example is the color of various nanoparticle solutions. As the size increases, the color of the colloidal suspension of gold changes its color from red to yellow.

Nanoparticles' color is due to the surface plasmon resonance effect, which is a resonance of the outer electron bands of the particles with light wavelengths. When light photons excite the outer electrons of the particles, the outer electrons on the metal particles jiggle at certain wavelengths and absorb light corresponding to that resonance. The relationship of particle size to color is well known and is mathematically quantified by the Mie and Rayleigh scattering theories. Properties like photocatalysis, photoconductivity, photoemission, electroluminescence, etc., are also affected by reduced dimensionality of nanoparticles.

Optoelectronic properties of nanomaterials

Electronic and optoelectronic devices, from computers and smart cell phones to solar cells, have become a part of our life. Currently, devices with featured circuits of 45 nm in size can be fabricated for commercial use. However, further development based on traditional semiconductor is hindered by the increasing thermal issues and the manufacturing cost. During the last decade, nanocrystals have been widely adopted in various electronic and optoelectronic applications. They provide alternative options in terms of ease of processing, low cost, better flexibility, and superior electronic/optoelectronic properties. By taking advantage of solution-processing, self-assembly, and surface engineering, nanocrystals could serve as new building blocks for low-cost manufacturing of flexible and large area devices.

Tunable electronic structures combined with small exciton binding energy, high luminescence efficiency, and low thermal conductivity make nanocrystals extremely attractive for FET, memory device, solar cell, solid-state lighting/display, photodetector, and lasing applications. Efforts to harness the nanocrystal quantum tunability have led to the successful demonstration of many prototype devices, raising the public awareness to the wide range of solutions that nanotechnology can provide for an efficient energy economy. This special issue aims to provide the readers with the latest achievements of nanocrystals in electronic and optoelectronic applications, including the synthesis and engineering of nanocrystals towards the applications and the corresponding device fabrication, characterization and computer modeling.

Thermal properties of nanomaterials

The recent advances of nanotechnologies in the past decades have resulted in the burst of promising synthesis, processing and characterization technologies, which enables the routine production of a variety of nanomaterials with highly controlled structures and related properties. By controlling the structures of nanomaterials at nano scale dimensions, the properties of the nanostructures can be controlled and tailored in a very predictable manner to meet the needs for a variety of applications. Examples of the

engineered nanostructures include metallic and non-metallic nanoparticles, nanotubes, quantum dots and superlattices, thin films, nano composites and nano electronic and optoelectronic devices which utilize the superior properties of the nanomaterials to fulfill the applications.

Mechanical properties of nanomaterials

The special mechanical properties of nanoparticles allow for novel applications in many fields, e.g., surface engineering, tribology and nanomanufacturing/nanofabrication. In this review, the basic physics of the relevant interfacial forces to nanoparticles and the main measuring techniques are briefly introduced first. Then, the theories and important results of the mechanical properties between nanoparticles or the nanoparticles acting on a surface, e.g., hardness, elastic modulus, adhesion and friction, as well as movement laws are surveyed. Afterwards, several of the main applications of nanoparticles as a result of their special mechanical properties, including lubricant additives, nanoparticles in nanomanufacturing and nanoparticle reinforced composite coating, are introduced. A brief summary and the future outlook are also given in the final part.

Magnetic properties of nanomaterials

Interstellar space, lunar samples, and meteorites have inclusive magnetic nanoparticles. The geomagnetic navigational aids in all migratory birds, fishes and other animals contain magnetic nanoparticles. The most common iron storage protein ferritin ($[\text{FeOOH}]_n$ containing magnetic nanoparticle) is present in almost every cell of plants and animals including humans. The human brain contains over 10^8 magnetic nanoparticles of magnetite–maghemite per gram of tissue. Denis G. Rancourt has written a nice survey of magnetism of Earth, planetary and environmental nanomaterials.

Effect of size reduction on properties

Size-dependent effects in nanostructured (nanocrystalline, nanophase or nanocomposite) materials are of great importance both for fundamental considerations and modern technology. The effect of the nanoparticle/nano crystallite size on surface energy, melting point, phase transformations, and phase equilibriums is considered as applied to nanostructured materials. The role of size-dependent effects in phonon, electronic, superconducting, magnetic, and partly mechanical properties is also analyzed in detail. Special attention is paid to the contribution of other factors such as the grain boundary segregations, interface structure, residual stresses and pores, non-uniform distribution of grain sizes, and so on.

UNIT- III:

SYNTHESIS ROUTES: Bottom up approaches: Physical Vapor Deposition, Inert Gas Condensation, Laser Ablation, Chemical Vapor Deposition, Molecular Beam Epitaxy, Sol-gel method, Self-assembly. Top down approaches: Mechanical alloying, Nano-lithography. Consolidation of Nano powders: Shock wave consolidation, Hot iso-static pressing and Cold iso-static pressing, Spark plasma sintering.

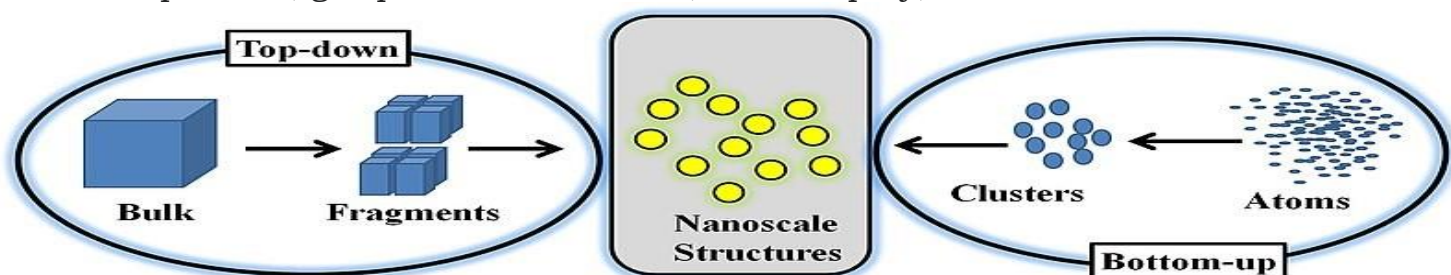
SYNTHESIS ROUTES BOTTOM-UP APPROACH

Synthesis of nanomaterials and nanostructures are the important aspect of nanoscience and nanotechnology. New physical properties and applications of nanomaterials are only possible when nanostructured materials are made available with desired size, shape, morphology, crystal structure and chemical composition. These notes provide a clear and concise understanding on Top-down and Bottom-up approaches for synthesis of nanomaterials.

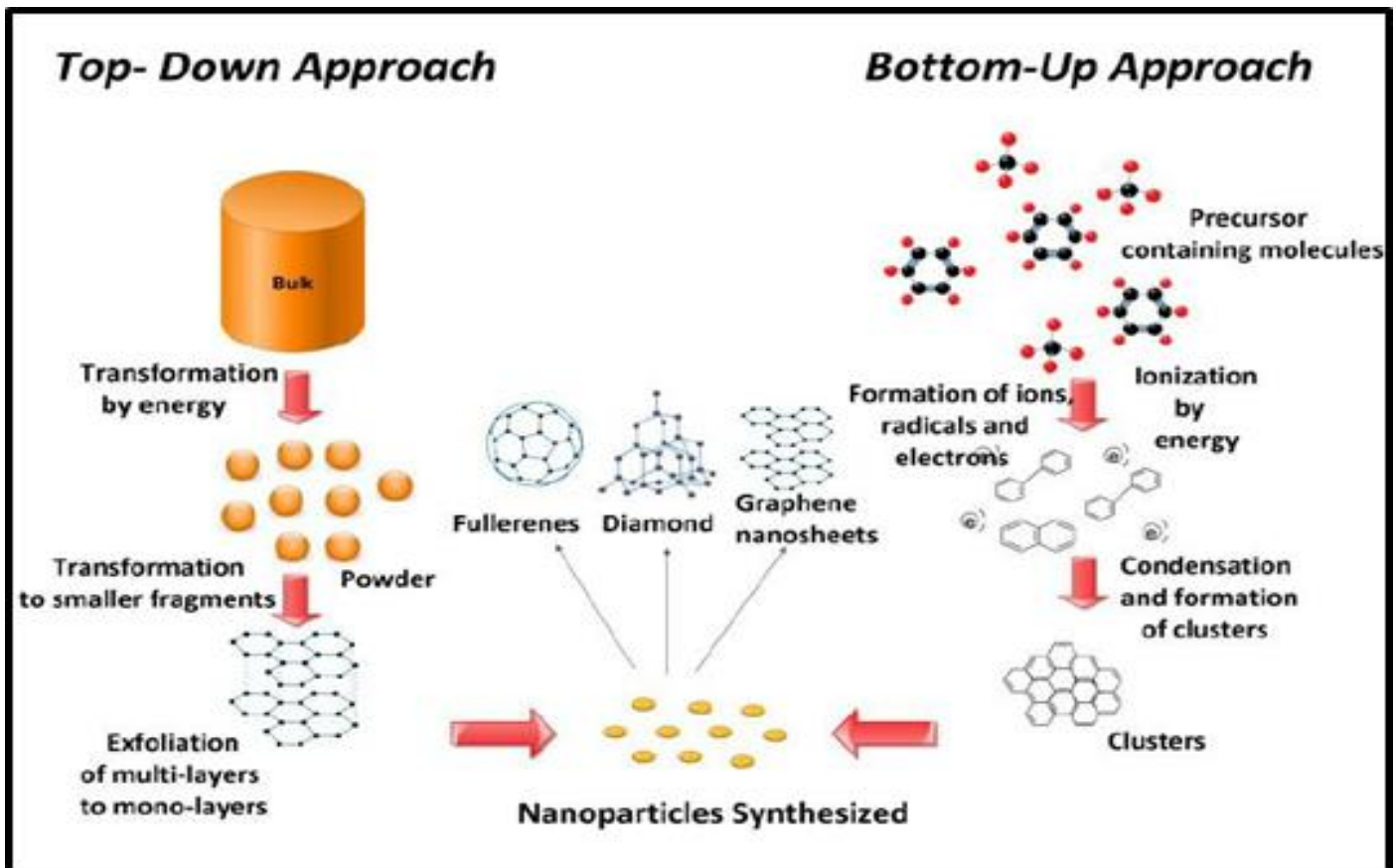
Nanostructure materials have attracted a great deal of attention because their physical, chemical, electronic and magnetic properties show dramatic change from higher dimensional counterparts and depend on their shape and size. Many techniques have been developed to synthesize and fabricate nanostructure materials with controlled shape, size, dimensionality and structure. The performance of materials depends on their properties. The properties in turn depend on the atomic structure, composition, microstructure, defects and interfaces which are controlled by thermodynamics and kinetics of the synthesis.

Classification of Techniques for synthesis of Nanomaterials There are two general approaches for the synthesis of nanomaterials Top- down approach, Bottom-up approach.

Top-down approach Top-down approach involves the breaking down of the bulk material into nanosized structures or particles. Top-down synthesis techniques are extension of those that have been used for producing micron sized particles. Top-down approaches are inherently simpler and depend either on removal or division of bulk material or on miniaturization of bulk fabrication processes to produce the desired structure with appropriate properties. The biggest problem with the top-down approach is the imperfection of surface structure. For example, nanowires made by lithography are not smooth and may contain a lot of impurities and structural defects on its surface. Examples of such techniques are high-energy wet ball milling, electron beam lithography, atomic force manipulation, gas-phase condensation, aerosol spray, etc.



Bottom-up approach The alternative approach, which has the potential of creating less waste and hence the more economical, is the 'bottom- up'. Bottom-up approach refers to the build up of a material from the bottom: atom-by-atom, molecule-by-molecule, or cluster-by cluster. Many of these techniques are still under development or are just beginning to be used for commercial production of nanopowders. Organometallic chemical route, reverse-micelle route, sol-gel synthesis, colloidal precipitation, hydrothermal synthesis, template assisted sol-gel, electrodeposition etc, are some of the well- known bottom-up techniques reported for the preparation of luminescent nanoparticles.



PHYSICAL VAPOR DEPOSITION

Evaporation technique

Thermal deposition inside a vacuum chamber where the material, usually in a boat is heated typically to its melting point and the substrate to be deposited on is positioned facing the source. A high current flowing through the boat heats it up and causes evaporation. A crystal monitor is mounted close to the substrate, which provides an estimate of how much and how fast the material is being deposited.

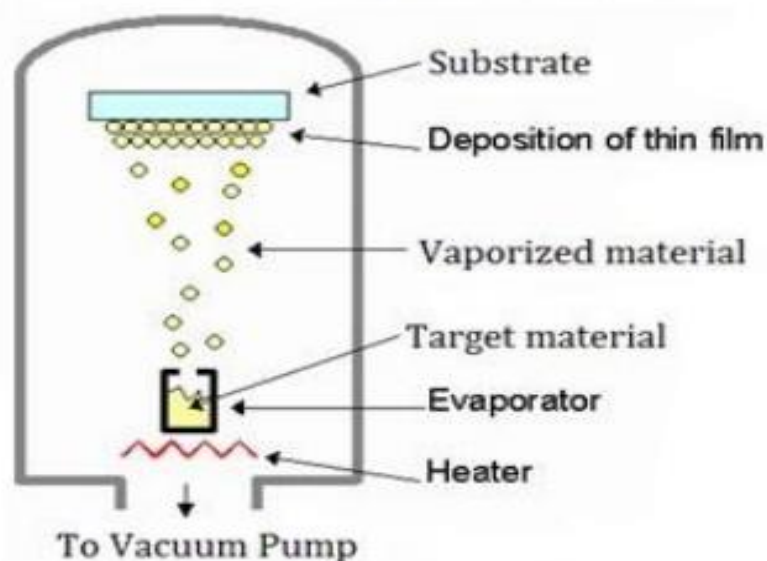
Limitations-

High temperature process (500-1200oC)

Ultra high vacuum(10^{-6} torr)

High cost

Resistance heating evaporation

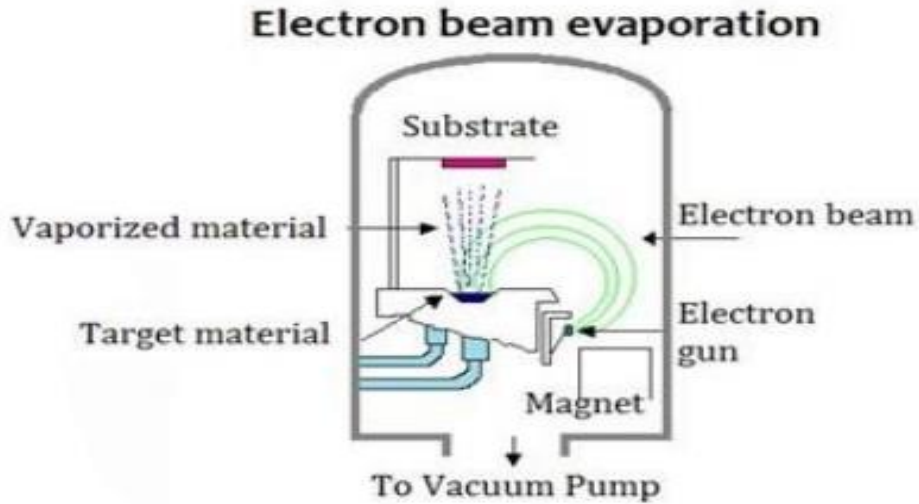


ELECTRON-BEAM EVAPORATION

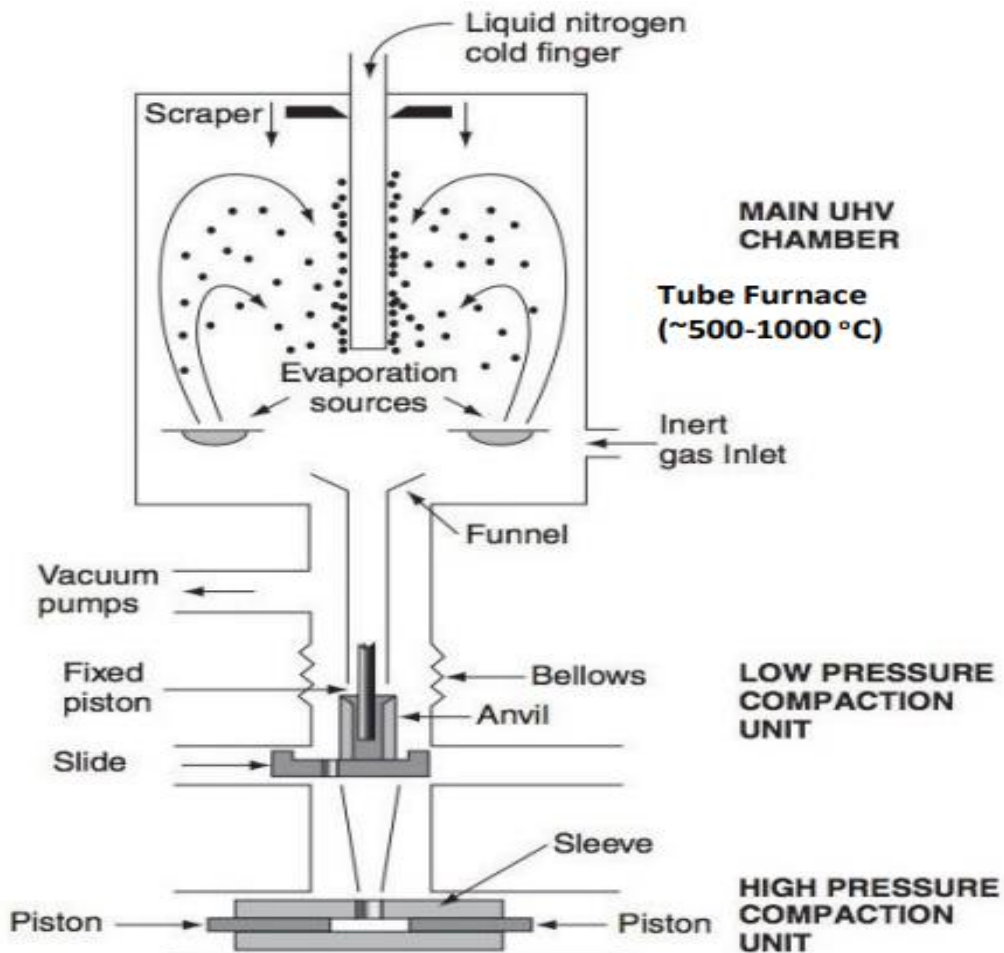
This technique is based in the heat produced by high energy electron beam bombardment on the material to be deposited. A high dc voltage is applied to a tungsten filament that causes electrons to be emitted out. These emitted electrons are accelerated to excites the target solid and produces vapors, which travels to the substrate. As they reach the surface, they condense and form a thin film coating.

Used for depositing materials with high melting point (W, Ta, C, etc.)

As electrons can be focalized, it is possible to obtain a very localized heating on the material to evaporate, with a high density of evaporation power (several kW)



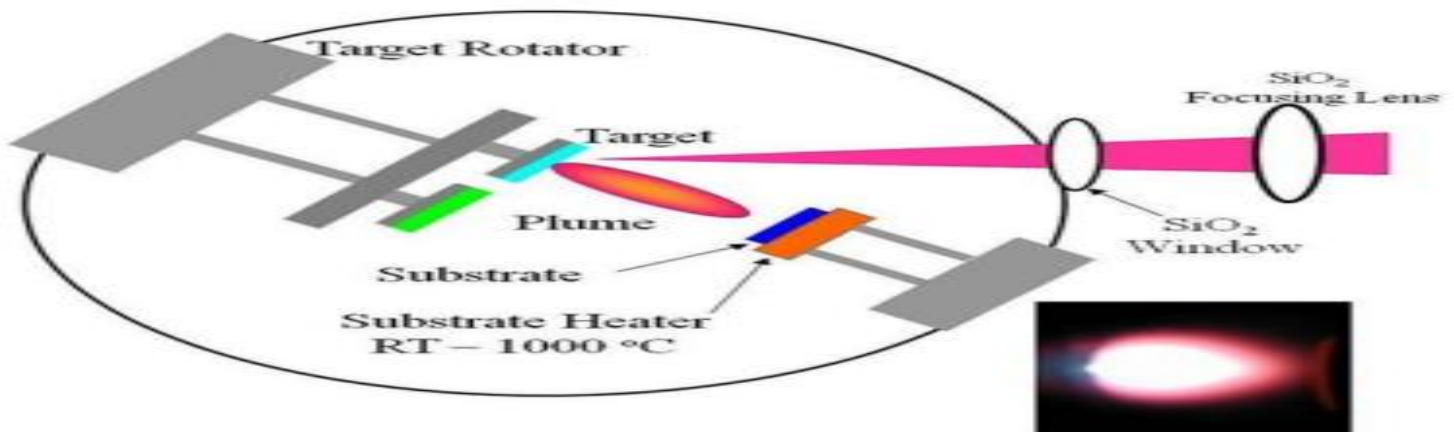
INERT GAS CONDENSATION



Inert-gas condensation: The inert gas evaporation–condensation (IGC) technique, in which nanoparticles are formed via the evaporation of a metallic source in an inert gas, has been widely used in the synthesis of ultrafine metal particles. In this process, a metal is evaporated inside an ultrahigh vacuum (UHV) chamber filled with inert gas (He). The vaporized species collide with Helium molecules thus losing kinetic energy. As collisions limit the mean free path, supersaturation can be achieved above the vapors source. At high supersaturation, the vapors rapidly form no. of clusters that grow via coalescence and agglomeration. These clusters get condensed on liquid nitrogen-cooled surfaces to form nanoparticles. The size, morphology, and yield of the NPs should be controlled.

LASER ABLATION

Laser ablation pulsed laser deposition system. This method is applicable for high melting point elements and transition metal



In this method, a solid metal rod is ablated using a Nd:YAG laser (high Power) in a chamber containing Ar gas. In the plasma that results from the laser ablation, metal atoms are evaporated and condensed on water cooled substrate. Later the substrate is heated to remove the impurities. NPs of Iron, gold, palladium, and compounds of sulphide are prepared by this method.

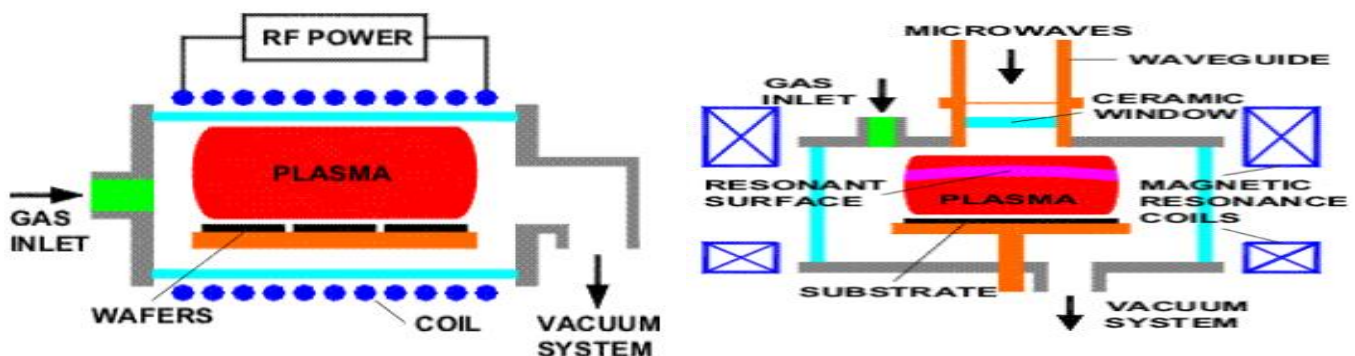
Advantage: capable of High deposition rate of 2-3 g/min

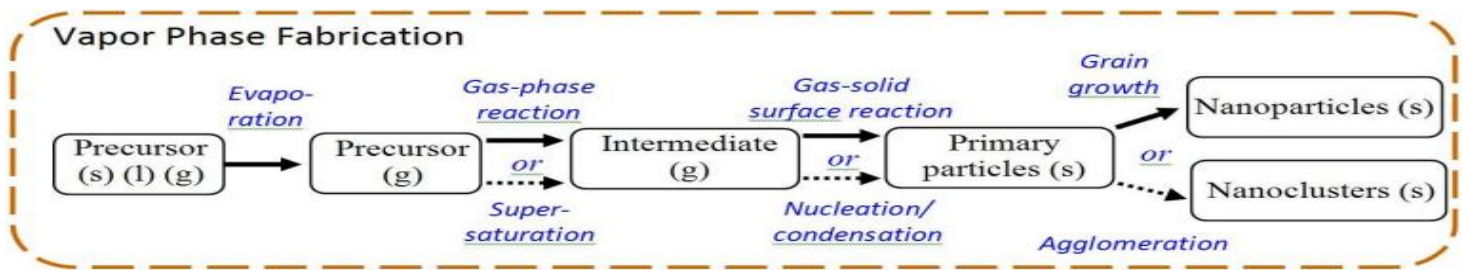
Disadvantage: High temperature method

low quality of material deposited

CHEMICAL VAPOR DEPOSITION

Chemical vapor Deposition: Bottom-Up approach Chemical vapour deposition (CVD) is a chemical process used to produce high-purity, highperformance solid materials. The process is often used in the semiconductor industry to produce thin films. In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Plasma Enhanced CVD- • RF-plasma enhanced CVD • Microwave Plasma Enhanced CVD The energy source (RF/ Microwave power) is intended to generate a plasma in which the gases are broken down to form reaction species.





- (i) precursor vaporization (typically involves a catalyst)
- (ii) nucleation, and
- (iii) growth stage

SPUTTERING

Sputter deposition are methods of depositing thin films by sputtering. They involve ejecting material from a “target” that is a source onto a “substrate” such as a silicon wafer. Atoms of Target (source) materials are ejected or sputtered by high energy ion bombardment of high-energy noble gas atoms, commonly Argon, produced by a high voltage DC or RF glow discharge. These ejected sputtered atoms (due to momentum transfer) form a thin film coating after condensing on substrate kept as anode plate. Sputtered atoms ejected from the target have a wide energy distribution, typically up to tens of eV.

Advantages

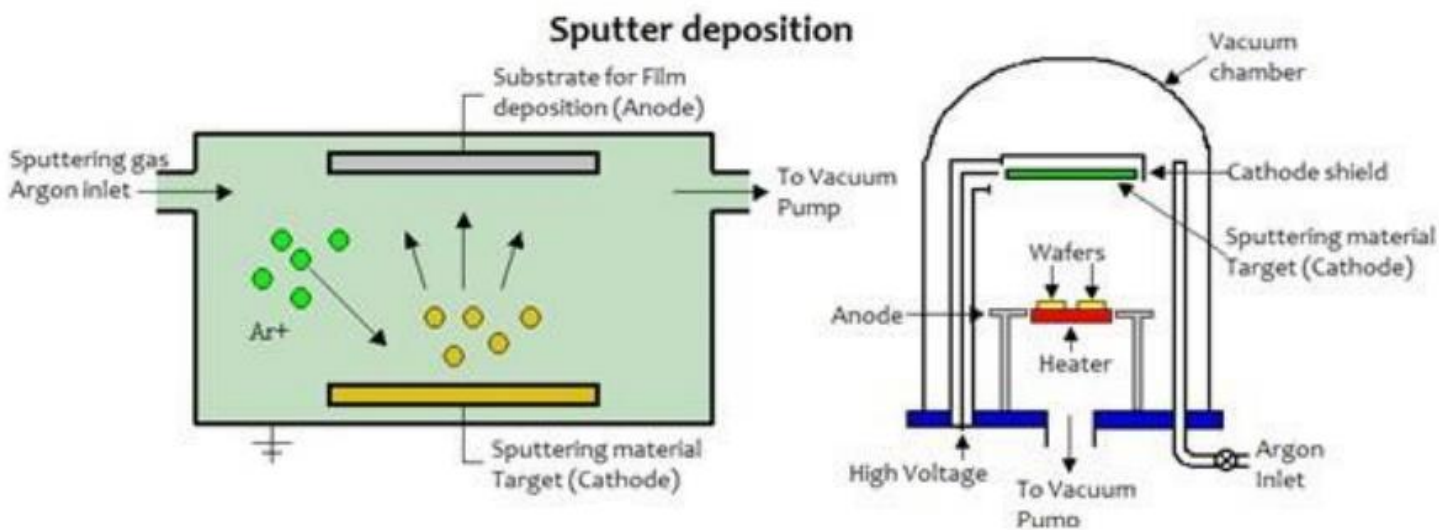
Non-thermal process, no heating reqd.

low vacuum(10⁻³ torr) is needed.

Limitations-

controlling Deposition parameters is difficult

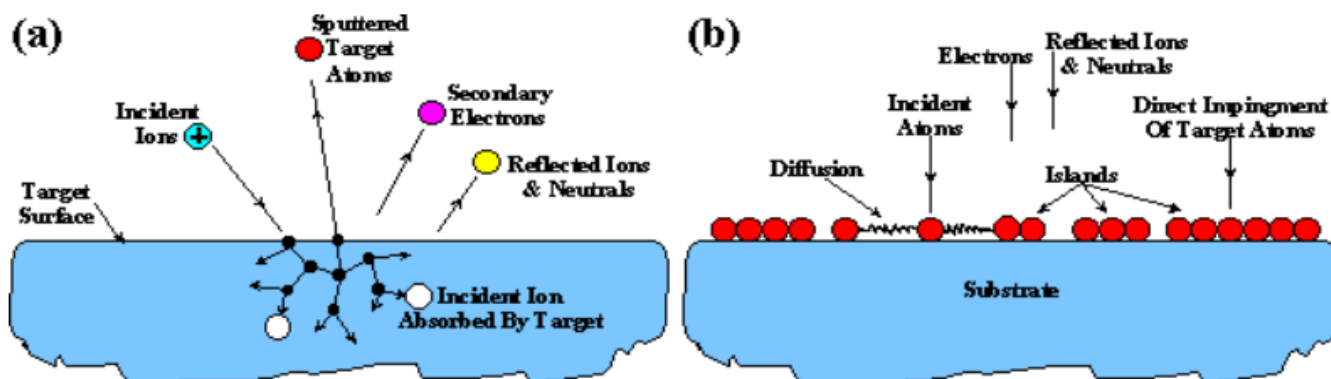
High cost



THIN FILM DEPOSITION BY SPUTTERING PROCESS

The sputtering process consists of the bombardment of the target material by fast moving, heavy, inert gas ions from a plasma. The bombarding ions cause atoms to be ejected from the target material by momentum transfer between the colliding ions and the target atoms. The process is schematically shown in Figure, where a number of processes are shown to occur when the ions collide with the target material. Some of the bombarding ions are reflected back and are neutralized, but may still be sufficiently energetic to reach the substrate where the film is being deposited. This can be a source of substrate bombardment (back scattering) which can effect the resulting properties of the film. The majority of the colliding ions tend to induce sputtering by ejecting atoms of the target material by momentum transfer. This is a secondary collision process, as shown schematically. The ejected atoms will have random directions but, as discussed, the sputtering process can induce texture in the resulting films due to the sputtering conditions. Secondary electrons which are emitted either join the oscillating plasma gas,

which cause the continuous ionization of the gas to sustain the incident ions needed for sputtering, or they liberate their energy in the form of heat on colliding with the substrate or other parts of the chamber. The sputtered target atoms which are deposited at the substrate form the resulting thin film. The basic processes occurring at the surface of the substrate are shown in Figure. The mobility of the incident atoms arriving at the substrate is highly dependent upon the sputtering parameters (pressure and power), the temperature of the substrate, the distance between target and substrate, and the surface.

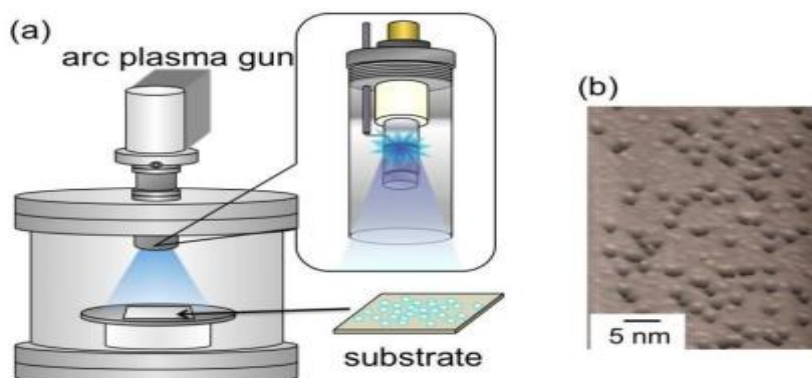
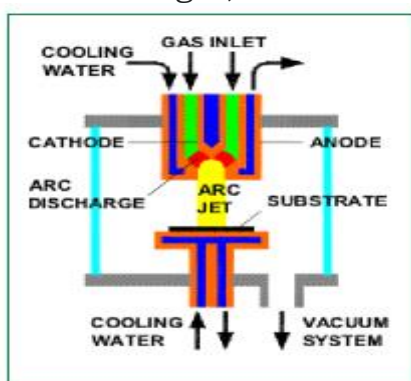


PLASMA PROCESSING METHODS

In general, plasma processing involves chemical and physical reactions between particles and solid surfaces in contact with the plasma. Some examples are plasma etching, thin film deposition, protective coating, surface hardening, ion implantation etc.

In this electric arc discharge method, material is vaporized between two electrodes by arc produced by applying very high voltage (50-100V) across the electrodes. This ionizes the inert gas and plasma is generated (temperature 6000oC), due to which metal atoms are evaporated and get condensed on water cooled substrate. Later the substrate is heated to remove the impurities. Carbon nanotubes are prepared by graphite as cathode. Nanotubes of dichalcogenides are prepared by such as MoS₂, WS₂ are prepared are prepared by starting with MoO₃ and WO₃.

Arc discharges technique: plasma of inert gases is produced by DC (direct current) glow or arc discharges,



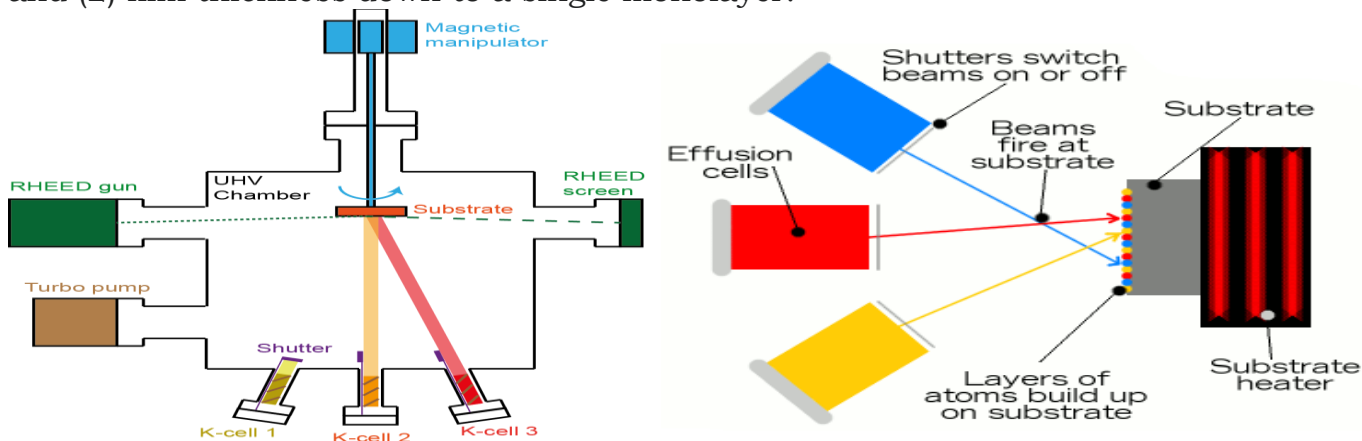
MOLECULAR BEAM EPITAXY

Molecular beam epitaxy (MBE) is an experimental technique utilized for layer-by-layer growth of thin films of various quantum materials. Out of the variety of thin film growth techniques available, MBE is considered to be one of the cleanest, but also one of the most technically challenging and demanding, as MBE growth takes place in ultra-high vacuum (UHV) environment.

Typical MBE experimental setup consists of two or more Knudsen effusion cells (K-cells), located at the bottom of a UHV chamber and aligned towards the center of the chamber where a sample holder with a substrate is located. Each individual K-cell contains a different element in ultra pure solid form (i.e. elemental 99.999% Selenium, Bismuth, etc.) which can be used in the thin film synthesis. The process of MBE growth starts by heating the K-cells to appropriate temperatures until the elements in each cell

reach a sublimation point. Then, the shutters are opened and physical vapor from each K-cell diffuses through the chamber until it reaches the substrate where it gets deposited, and the thin film gets formed. The final composition and stoichiometry of the film will depend on the temperature and surface atomic structure of the substrate, as well as the flux ratios of individual components reaching the substrate. For more uniform growth, substrate can be continuously rotated at low rotation speeds (~1-2 rotations per minute) by utilizing a stepper motor attached to the magnetic manipulator.

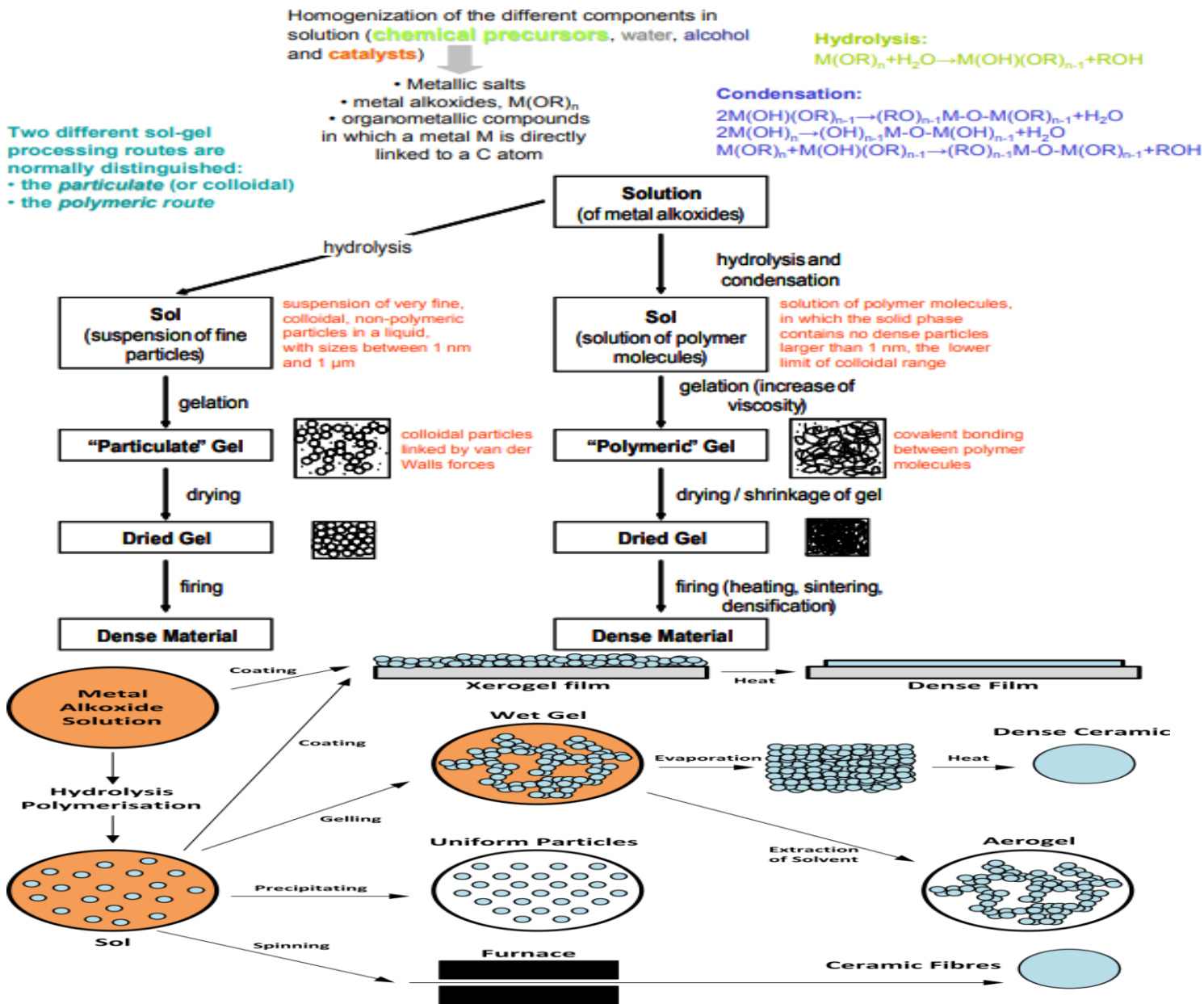
To characterize the samples in-situ during growth, we use reflection high-energy electron diffraction (RHEED). Electrons emitted from the RHEED gun incident at a very low angle with respect to the sample surface are diffracted, and the resulting diffraction pattern is observed on the screen. This pattern can reveal: (1) quality of the film surface, and (2) film thickness down to a single monolayer.



SOL-GEL METHOD

The sol-gel process may be described as: "Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid." A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid. A gel consists of a three dimensional continuous network, which encloses a liquid phase. In a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by van der Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. The gelation process may be reversible if other interactions are involved.

The idea behind sol-gel synthesis is to "dissolve" the compound in a liquid in order to bring it back as a solid in a controlled manner. Multi component compounds may be prepared with a controlled stoichiometry by mixing sols of different compounds. The sol-gel method prevents the problems with co-precipitation, which may be inhomogeneous, by a gelation reaction. Enables mixing at an atomic level. Results in small particles, which are easily sinterable. The sol-gel method was developed in the 1960s mainly due to the need of new synthesis methods in the nuclear industry. A method was needed where dust was reduced (compared to the ceramic method) and which needed a lower sintering temperature. In addition, it should be possible to do the synthesis by remote control. One of the well known examples of a sol-gel system often cited is quick clay. Clay may form a sol (quick clay) if it is washed sufficiently to remove the counter ions. Quick clay may be gelled if enough counter ions are added, so that the colloidal particles aggregate. (exfoliation/restacking may be involved) Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films. If the gel is dried by evaporation, then the capillary forces will result in shrinkage, the gel network will collapse, and a xerogel is formed. If drying is performed under supercritical conditions, the network structure may be retained and a gel with large pores may be formed. This is called an aerogel, and the density will be very low. A record is $< 0.005 \text{ g/cm}^3$.



SELF-ASSEMBLY

Nanoparticles are classified as having at least one of three dimensions be in the range of 1-100 nm. The small size of nanoparticles allows them to have unique characteristics which may not be possible on the macro-scale. Self-assembly is the spontaneous organization of smaller subunits to form larger, well-organized patterns. For nanoparticles, this spontaneous assembly is a consequence of interactions between the particles aimed at achieving a thermodynamic equilibrium and reducing the system's free energy. The thermodynamics definition of self-assembly was introduced by Nicholas A. Kotov. He describes self-assembly as a process where components of the system acquire non-random spatial distribution with respect to each other and the boundaries of the system. This definition allows one to account for mass and energy fluxes taking place in the self-assembly processes.

This process occurs at all size scales, in the form of either static or dynamic self-assembly. Static self-assembly utilizes interactions amongst the nano-particles to achieve a free-energy minimum. In solutions, it is an outcome of random motion of molecules and the affinity of their binding sites for one another. A dynamic system is forced to not reach equilibrium by supplying the system with a continuous, external source of energy to balance attractive and repulsive forces. Magnetic fields, electric fields, ultrasound fields, light fields, etc. have all been used as external energy sources to program robot swarms at small scales. Static self-assembly is significantly slower compared to dynamic self-assembly as it depends on the random chemical interactions between particles.

HYDROTHERMAL GROWTH

Hydrothermal synthesis is one of the most commonly used methods for preparation of nanomaterials. It is basically a solution reaction-based approach. In hydrothermal synthesis, the formation of nanomaterials can happen in a wide temperature range from room temperature to very high temperatures. To control the morphology of the materials to be prepared, either low-pressure or high-pressure conditions can be used depending on the vapor pressure of the main composition in the reaction. Many types of nanomaterials have been successfully synthesized by the use of this approach. There are significant advantages of hydrothermal synthesis method over others.

Hydrothermal synthesis can generate nanomaterials which are not stable at elevated temperatures. Nanomaterials with high vapor pressures can be produced by the hydrothermal method with minimum loss of materials. The compositions of nanomaterials to be synthesized can be well controlled in hydrothermal synthesis through liquid phase or multiphase chemical reactions. This special issue serves as a forum presenting the recent research results of hydrothermal synthesis of nanomaterials. Several papers on hydrothermal synthesis of nanoparticles, nanorods, nanotubes, hollow nanospheres, and graphene nanosheets have been published in this special issue. New synthesis methods, for example, microwave-assisted hydrothermal synthesis and template-free self-assembling catalytic synthesis, etc.

THIN-FILM GROWTH OF NANO MATERIALS

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, Integrated passive 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 phenomena.

TOP-DOWN APPROACH OF NANO MATERIALS

Top-down approach Top-down approach involves the breaking down of the bulk material into nanosized structures or particles. Top-down synthesis techniques are extension of those that have been used for producing micron sized particles. Top-down approaches are inherently simpler and depend either on removal or division of bulk material or on miniaturization of bulk fabrication processes to produce the desired structure with appropriate properties.

BALL MILLING

Ball milling is an economic and facile technique to produce nanosized materials. It is a top-down approach of nanoparticle synthesis which includes mechanical breakdown of large substances into smaller one. It is used in producing metallic as well as ceramic nanomaterials. In this module, the readers will learn the working principle and applications of Ball-mill technique in nanomaterials synthesis. The basic principle of a ball mill is very ancient. However, the machine itself could be produced only after the industrial revolution. Typically, ball mill is a grinder and is often employed blend materials by grinding/crushing them, for potential applications in mineral dressing processes, paints, pyrotechnics, ceramics as well as selective laser sintering.

The working of a ball mill is based on impact and attrition: the impact, caused by the balls dropping from top of the shell, breaks down the particles, thereby resulting in reduction in size. Ball mill includes a hollow cylindrical shell which is rotated about its own axis. The axis of the shell is either horizontal or slightly inclined, thereby making a small angle with the horizontal. The shell is partially filled with balls. The balls form the grinding medium of the ball mill. These balls are usually made up of steel, ceramic, flint pebbles, or hard rubber. The inner wall of the shell is generally contains a coating of abrasion resistant material, e.g., manganese steel or rubber. Rubber lined (or coated) ball mills cause less wear to the products. The mill is nearly equal in length and diameter.

In continuously operated mills, precursor material is fed from left side at an angle of 60° , and the end product is removed from right side at 30° . When the shell is rotated, the balls lift upwards on the rising side of the mill. After reaching near the top of the shell, the balls fall down, causing an impact on the particles trapped between these balls and the shell surface. This impact reduced the size of these particles.

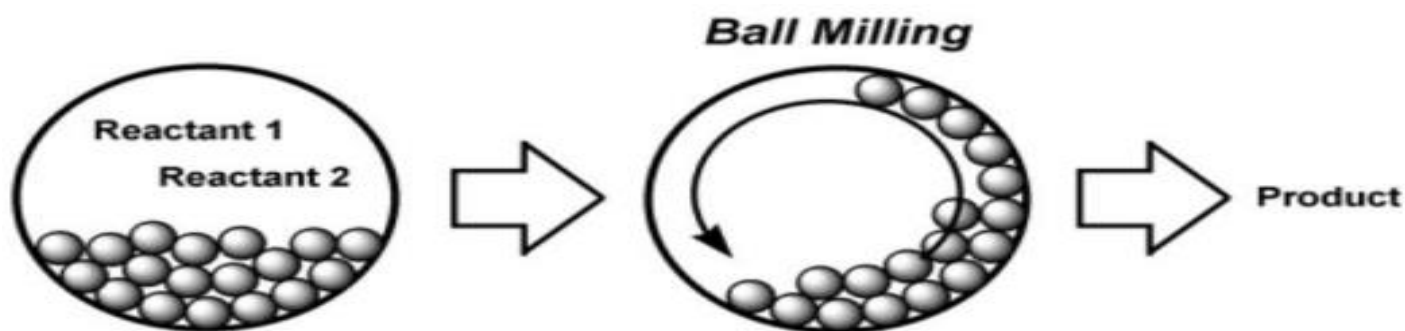
a. It consists of stainless steel chamber and several small iron, silicon carbide, hardened steel, or tungsten carbide balls to rotate inside the mill.

b. Powder of material is put in the steel chamber. The powder is reduced to nanosize using ball mill. A magnet is positioned outside the chamber to apply pulling force on the material. This force raises milling energy as the milling chamber or container rotates the metallic balls.

c. The ball and material - mass ratio is generally kept at 2:1.

d. These metallic balls impart very high energy to the powder resulting in crushing of the powder. The ball milling process generally takes 100 to 150 hrs to give uniformly crushed fine powder.

e. It is mechanical processing technique; consequently the structural as well as chemical changes are caused by the mechanical energy.



Schematics showing nanoparticle synthesis via ball milling method.

a. Initial Stage: Initially, compressive forces from collisions of balls flatten the powder particles. Micro-forging causes variations in the shapes of individual particles, or cluster of particles, owing to repeated impact of high energy (kinetic energy) milling balls. In spite of this, such deformations of the powder cause do not effectively change the mass.

b. Intermediate stage: In this stage, considerable variations occur in contrast to the first stage. Powders experience considerable cold welding. The fine blending of the constituents of powder reduces the diffusion distance to few microns. The dominating processes at this stage are fracturing and cold welding. Though dissolution may occur to a certain extent, yet the alloyed powder does not have homogeneous chemical composition.

c. Final stage: This stage exhibits marked refinement and size reduction. Microstructurally, particles appear more homogenous at this stage. This stage marks the formation of true alloys.

d. Completion stage: The structure of the powder particles is tremendously deformed and is metastable. The lamellae are not resolvable via optical microscope. Alloying beyond this stage does not cause any improvement in the constituents' distribution. True alloy is formed which has same composition as the precursor.

MICROFABRICATION

Microfabrication is the process of fabricating miniature structures of micrometre scales and smaller. Historically, the earliest microfabrication processes were used for integrated circuit fabrication, also known as "semiconductor manufacturing" or "semiconductor device fabrication". In the last two decades microelectromechanical systems (MEMS), microsystems (European usage), micromachines (Japanese terminology) and their subfields, microfluidics/lab-on-a-chip, optical MEMS (also called MOEMS), RF MEMS, Power MEMS, BioMEMS and their extension into nanoscale (for example NEMS, for nano electro mechanical systems) have re-used, adapted or extended microfabrication methods.

Flat-panel displays and solar cells are also using similar techniques. Miniaturization of various devices presents challenges in many areas of science and engineering: physics, chemistry, materials science, computer science, ultra-precision engineering, fabrication processes, and equipment design. It is also giving rise to various kinds of interdisciplinary research.[1] The major concepts and principles of microfabrication are microlithography, doping, thin films, etching, bonding, and polishing.

Microfabrication is actually a collection of technologies which are utilized in making microdevices. Some of them have very old origins, not connected to manufacturing, like lithography or etching. Polishing was borrowed from optics manufacturing, and many of the vacuum techniques come from 19th century physics research. Electroplating is also a 19th-century technique adapted to produce micrometre scale structures, as are various stamping and embossing techniques.

To fabricate a microdevice, many processes must be performed, one after the other, many times repeatedly. These processes typically include depositing a film, patterning the film with the desired micro features, and removing (or etching) portions of the film. Thin film metrology is used typically during each of these individual process steps, to ensure the film structure has the desired characteristics in terms of thickness (t), refractive index (n) and extinction coefficient (k), for suitable device behavior. For example, in memory chip fabrication there are some 30 lithography steps, 10 oxidation steps, 20 etching steps, 10 doping steps, and many others are performed. The complexity of microfabrication processes can be described by their mask count. This is the number of different pattern layers that constitute the final device. Modern microprocessors are made with 30 masks while a few masks suffice for a microfluidic device or a laser diode. Microfabrication resembles multiple exposure photography, with many patterns aligned to each other to create the final structure.

NANOLITHOGRAPHY

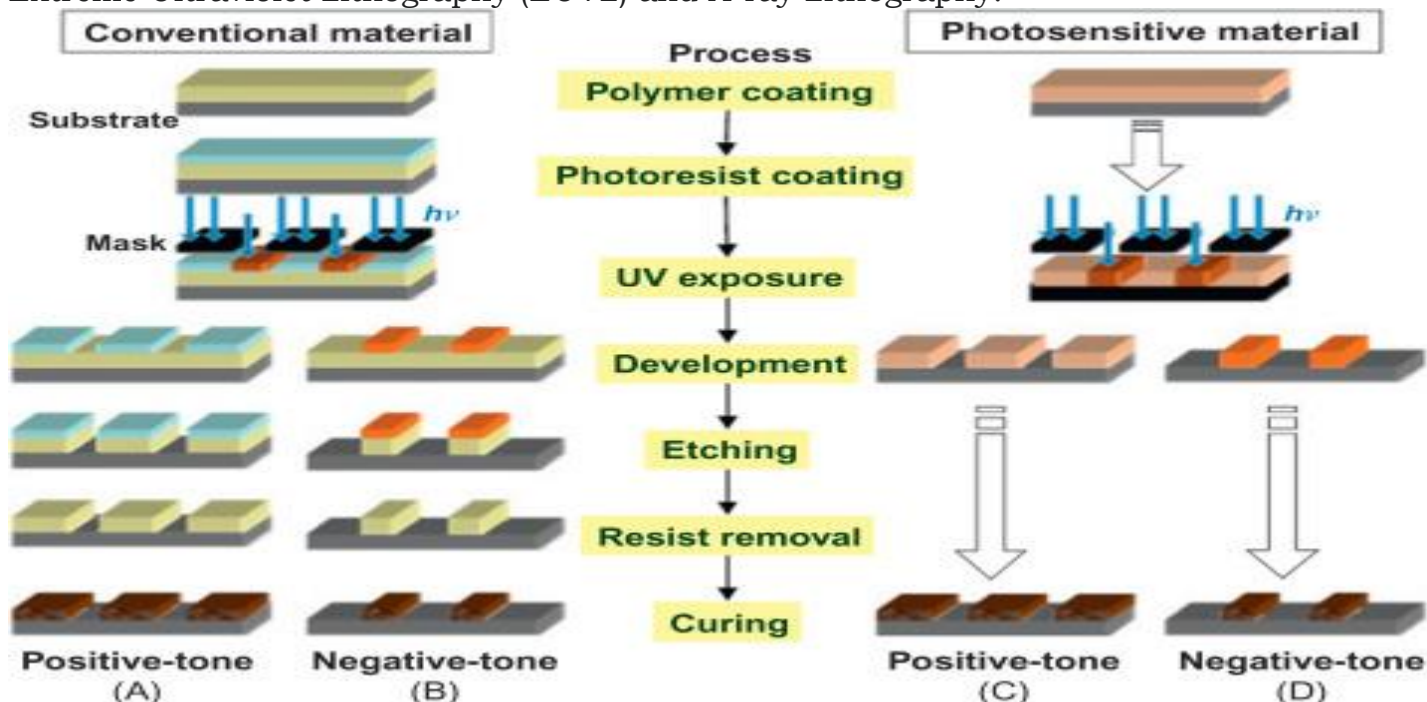
Nanolithography is the branch of nanotechnology concerned with the study and application of the nanofabrication of nanometer-scale structures, meaning nanopatterning with at least one lateral dimension between the size of an individual atom and approximately 100 nm. The term nanolithography is derived from the Greek words "nanos", meaning dwarf; "lithos", meaning rock or stone; and "graphein" meaning to write. Therefore the literal translation is "tiny writing on stone", however nowadays one understands something different whenever this term is associated with nanotechnology. Nanolithography is used e.g. during the nano-fabrication of leading-edge semiconductor integrated circuits (nanocircuitry), for nanoelectromechanical systems (NEMS) or for almost any other fundamental application across various scientific disciplines

Nanolithography is a powerful and versatile tool to fabricate nanoscale patterns. Nanolithography can be used to construct well-defined 2D metal arrays on substrates with fine controlled shape, size, and spacing through a multistep process. Electron beam lithography (EBL) is a branch of nanolithography that is widely used to fabricate metal nanostructures. The fabrication of metal nanostructures is carried out with scaling down of a predeposited parent layer with a focused electron beam [67,68]. The gold nanohole

and/or nanodisk arrays with controlled spacing and size can be obtained with the use of this technique.

The size-dependent surface-enhanced Raman spectroscopy (SERS) effect can be studied by varying the diameter and the distance between the holes. In this, the nanohole array plays a crucial role and acts as an excellent model to study the dimension-dependent SERS effect. Nanosphere lithography (NSL) technique is another typical example of nanolithography. This technique contains a multistep process developed by Van Duyn et al. to produce surface-confined nanostructure arrays. In NSL the two-dimensional nanostructures are deposited by using a monolayer self-assembly of polystyrene spheres with controlled diameter as a mask. With this approach, ordered arrays of triangular Cu, Ag, and Al nanocrystals have been prepared successfully. Another example of nanolithography in addition to EBL and NSL are nanoimprint lithography and hole-mask lithography, which are also beneficial tools for constructing two-dimensional metal nanostructures.

This technology can be suitable to use in nanofabrication of various semiconducting Integrated Circuits (ICs), NEMS and for various applications in research. The modification in semiconductor chips at the nano-scale (in the range of 10⁻⁹ meter) is also possible. This method is contrasting to various existing nanolithographic techniques like Photolithography (Venugopal, 2011), Nanoimprint lithography (NIL), Scanning Probe Lithography (SPL), Atomic Force Microscope (AFM) nanolithography, Extreme Ultraviolet Lithography (EUVL) and X-ray Lithography.



CONSOLIDATION OF NANO POWDERS

The driving force of nano powder consolidation during sintering is the reduction of the large surface area of nanoparticles. Additionally, the high sintering pressure also assists the consolidation by inducing large shear stresses at the contact points between particles that yield plastic deformation thereby contributing to the filling of pores. This mechanism is especially important in the case of metallic powders having good deformability. Although the high temperature during sintering facilitates the consolidation by increasing the atomic mobility, it may also cause grain coarsening that is an unwanted phenomenon in processing of nanomaterials.

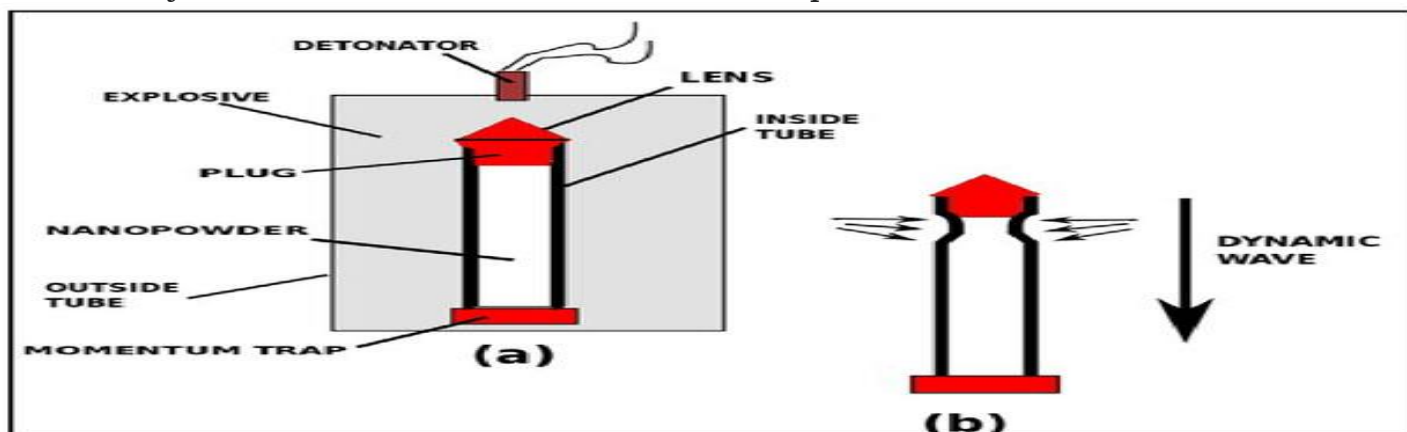
To minimize grain growth, usually the time and temperature of sintering are reduced together with a simultaneous increase of pressure for maintaining the low porosity level in the final product. In this section, some nano powder consolidation procedures are overviewed: shock wave consolidation, pressure less sintering, hot pressing, hot isostatic pressing, and spark plasma sintering. The reason of selection of these methods for review is that mainly they were used for the consolidation of the samples studied in the next

chapters. In *shock wave consolidation*, the high pressure and rapid loading rates applied on the powder result in interparticle bonding due to localized melting at the interfaces between the particles. In practice, the powder particles are enclosed in a steel block, which is covered by a plate on the top that drives the shock wave caused by the explosion toward the sample. The driver plate is usually made of a highly conductive, highly ductile material, such as copper.

Explosives and the detonator are packed on the top of the driver plate. Of late, gas guns are also widely used in performing shock wave consolidation. In the latter case, hydrogen gas activates the projectile, which travels all the way through the barrel and hits the powder sample. The duration and the pressure of the shock wave, which yields consolidation of the powder, are $\sim 10^{-6}$ s and 20–600 GPa, respectively. Shock wave consolidation technique is mainly used for metallic powders. As only the surfaces of the particles are heated up, the grain growth is suppressed.

SHOCK WAVE CONSOLIDATION

Nanotechnology based thermoelectric materials are considered attractive for developing highly efficient thermoelectric devices. Nano-structured thermoelectric materials are predicted to offer higher ZT over bulk materials by reducing thermal conductivity and increasing electrical conductivity. Consolidation of nano-structured powders into dense materials without losing nanostructure is essential towards practical device development. Using the gas atomization process, amorphous nano-structured powders were produced. Shockwave consolidation is accomplished by surrounding the nanopowder-containing tube with explosives and then detonated. The resulting shock wave causes rapid fusing of the powders without the melt and subsequent grain growth. We have been successful in generating consolidated nanostructured bismuth telluride alloy powders by using shockwave technique. Using these consolidated materials, several types of thermoelectric power generator devices have been developed. Shockwave consolidation is anticipated to generate large quantities of nanostructured materials expeditiously and cost effectively. In this paper, the technique of shockwave consolidation will be presented followed by Seebeck Coefficient and thermal conductivity measurements of consolidated materials. Preliminary results indicate a substantial increase in electrical conductivity due to shockwave consolidation technique.



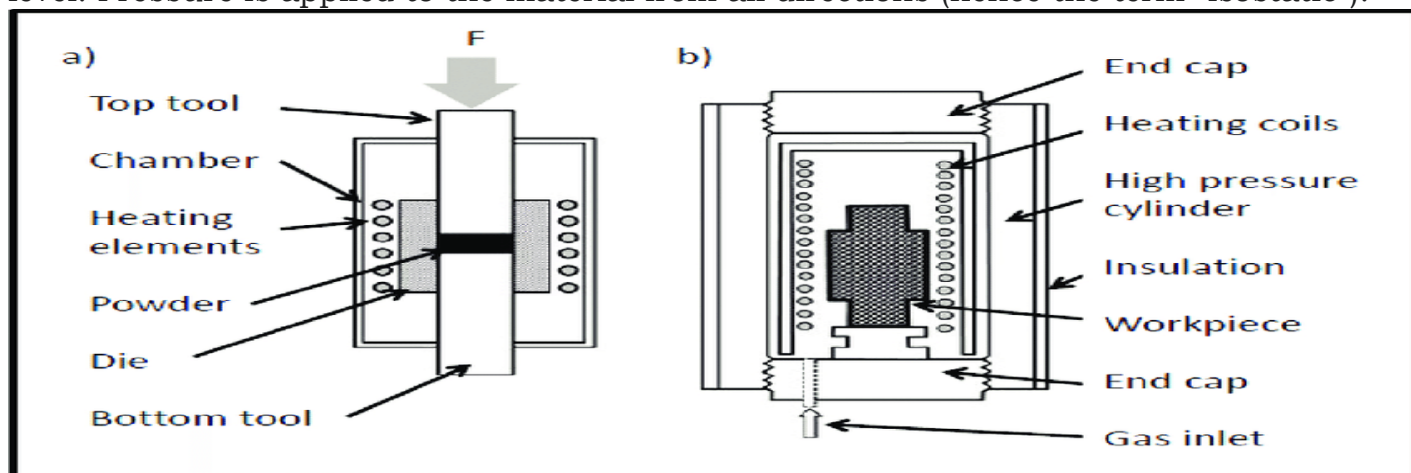
HOT ISOSTATIC PRESSING

Hot isostatic pressing (HIP) is a manufacturing process, used to reduce the porosity of metals and increase the density of many ceramic materials. This improves the material's mechanical properties and workability.

The process can be used to produce waste form classes. Calcined radioactive waste (waste with additives) is packed into a thin walled metal canister. The adsorbed gases are removed with high heat and the remaining material compressed to full density using argon gas during the heat cycle. This process can shrink steel canisters to minimize space in disposal containers and during transport. It was invented in the 1950s by the Battelle Company and has been used to prepare nuclear fuel for submarines since the 1960s. It is used to prepare inactive ceramics as well, and

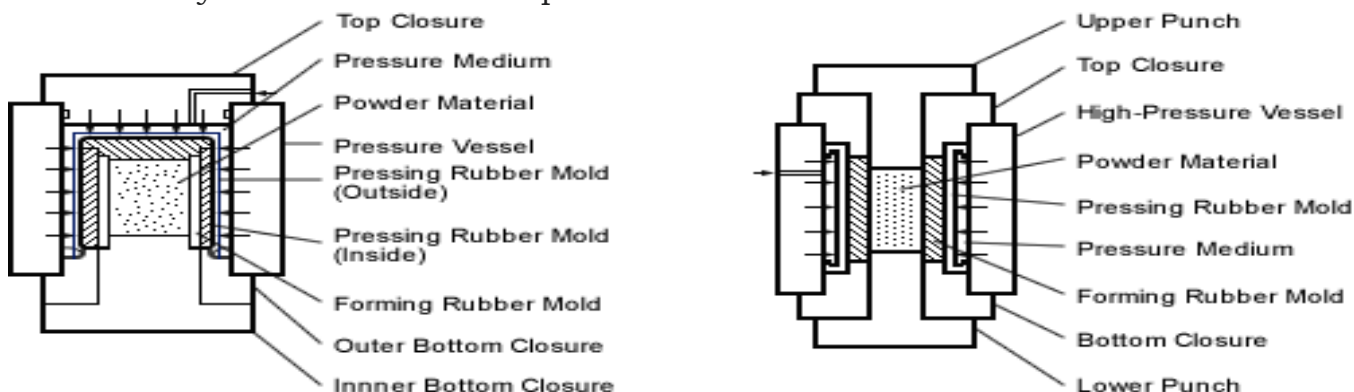
the Idaho National Laboratory has validated it for the consolidation of radioactive ceramic waste forms. ANSTO (Australia's Nuclear Science and Technology Organisation) is using HIP as part of a process to immobilize waste radionuclides from molybdenum-99 production.

The HIP process subjects a component to both elevated temperature and isostatic gas pressure in a high pressure containment vessel. The pressurizing gas most widely used is argon. An inert gas is used so that the material does not chemically react. The choice of metal can minimize negative effects of chemical reactions. Nickel, stainless or mild steel, or other metals can be chosen depending on the desired redox conditions. The chamber is heated, causing the pressure inside the vessel to increase. Many systems use associated gas pumping to achieve the necessary pressure level. Pressure is applied to the material from all directions (hence the term "isostatic").



COLD ISOSTATIC PRESSING

One of the biggest challenges for making dye-sensitised solar cells (DSCs) on plastic substrates is the difficulty in making good quality nanoporous TiO₂ films with both good mechanical stability and high electrical conductivity. Cold isostatic pressing (CIP) is a powder compaction technique that applies an isostatic pressure to a powder sample in all directions. It is particularly suitable for making thin films on plastic substrates, including non-flat surfaces. Cold isostatically pressed nanocrystalline TiO₂ electrodes with excellent mechanical robustness were prepared on indium tin oxide (ITO)-coated polyethylene naphthalate (PEN) substrates in the absence of organic binders and without heat treatment. The morphology and the physical properties of the TiO₂ films prepared by the CIP method were found to be very compatible with requirements for flexible DSCs on plastics. This room-temperature processing technique has led to an important technical breakthrough in producing high efficiency flexible DSCs. Devices fabricated on ITO/PEN films by this method using standard P-25 TiO₂ films with a Ru-complex sensitizer yielded a maximum incident photon-to-current conversion efficiency of 72% at the wavelength of 530 nm and showed high conversion efficiencies of 6.3% and 7.4% for incident light intensities of 100 and 15 mW cm⁻², respectively, which are the highest power conversion efficiencies achieved so far for any DSC on a polymer substrate using the widely used, commercially available P-25 TiO₂ powder.

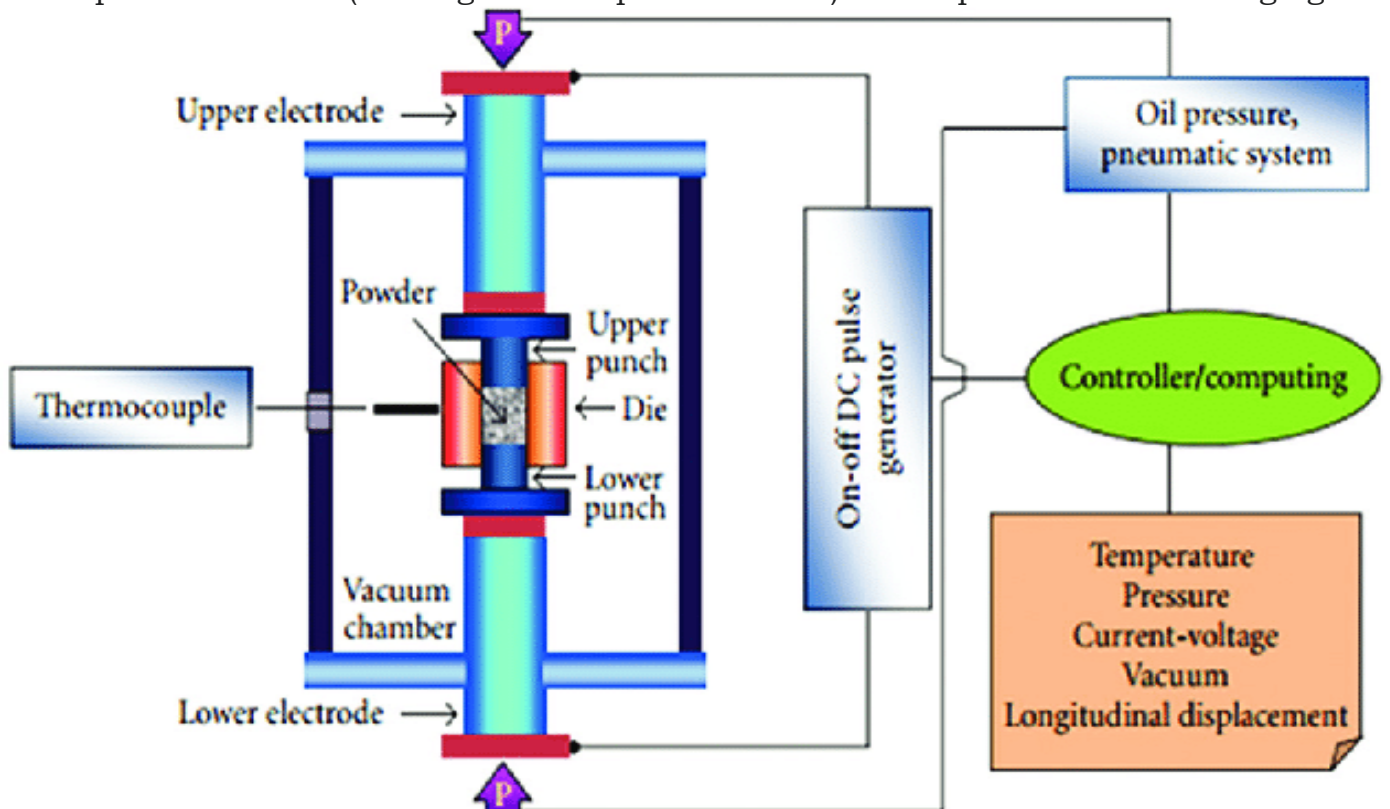


SPARK PLASMA SINTERING.

The main characteristic of SPS is that the pulsed or unpulsed DC or AC current directly passes through the graphite die, as well as the powder compact, in case of conductive samples. Joule heating has been found to play a dominant role in the densification of powder compacts, which results in achieving near theoretical density at lower sintering temperature compared to conventional sintering techniques. The heat generation is internal, in contrast to the conventional hot pressing, where the heat is provided by external heating elements. This facilitates a very high heating or cooling rate (up to 1000 K/min), hence the sintering process generally is very fast (within a few minutes).

The general speed of the process ensures it has the potential of densifying powders with nanosize or nanostructure while avoiding coarsening which accompanies standard densification routes. This has made SPS a good method for preparation of ceramics based on nanoparticles with enhanced magnetic, [magnetoelectric, piezoelectric, thermoelectric optical or biomedical properties. SPS is also used for sintering of Carbon Nanotubes for development of field electron emission electrodes. Functioning of SPS systems is schematically explained in a video link. While the term "spark plasma sintering" is commonly used, the term is misleading since neither a spark nor a plasma is present in the process. It has been experimentally verified that densification is facilitated by the use of a current.

The spark plasma sintering (SPS), a variant of field-assisted sintering (FAST) or pulsed electric current sintering (PECS), is a novel pressure assisted pulsed electric current sintering process, which utilizes ON-OFF DC pulse energizing. Due to the repeated application of an ON-OFF DC pulse voltage and current flow between powder particles, the spark discharges and the Joule heating (local high temperature state) are therefore dispersed to the overall specimen. The SPS process is based on the electrical spark discharge phenomenon and is a high efficient, energy saving technique with a high heating rate and a short holding time. The problem of rapid grain growth of nanomaterials during conventional sintering can be inhibited to a larger extent by using the SPS technique. The SPS can be used for diverse novel bulk material applications, but it is particularly suitable for the processing of nanomaterials. Despite such anticipated advantages, the optimization of the process window (heating rate-temperature-time) in SPS process is a challenging task



UNIT- IV:

TOOLS TO CHARACTERIZE NANOMATERIALS: X-Ray Diffraction (XRD), Small Angle X-ray scattering, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), Scanning Tunneling Microscope (STM), Field Ion Microscope (FEM), Three-dimensional Atom Probe (3DAP), Nano indentation

CHARACTERIZATION TECHNIQUES

Nanoscience and nanotechnology are considered to be the key technologies for the current century. Efforts are being made worldwide to create smart and intelligent textiles by incorporating various nanoparticles or creating nanostructured surfaces and nanofibres which lead to unprecedented level of performance, such as stain resistant, self-cleaning, antistatic, UV protective, etc. However, there are many challenges in the research and development of nanotechnology based products. The precise control of nanoparticle size, size distribution, dispersion at nanolevel and deposition needs sophisticated characterization techniques

X-RAY DIFFRACTION (XRD) AND SCHERRER METHOD

X-ray diffraction (XRD) relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. A primary use of the technique is the identification and characterization of compounds based on their diffraction pattern.

The dominant effect that occurs when an incident beam of monochromatic X-rays interacts with a target material is scattering of those X-rays from atoms within the target material. In materials with regular structure (i.e. crystalline), the scattered X-rays undergo constructive and destructive interference. This is the process of diffraction. The diffraction of X-rays by crystals is described by Bragg's Law, $n(\lambda) = 2d \sin(\theta)$. The directions of possible diffractions depend on the size and shape of the unit cell of the material.

The intensities of the diffracted waves depend on the kind and arrangement of atoms in the crystal structure. However, most materials are not single crystals, but are composed of many tiny crystallites in all possible orientations called a polycrystalline aggregate or powder. When a powder with randomly oriented crystallites is placed in an X-ray beam, the beam will see all possible interatomic planes. If the experimental angle is systematically changed, all possible diffraction peaks from the powder will be detected. The parafocusing (or Bragg-Brentano) diffractometer is the most common geometry for diffraction instruments.

This geometry offers the advantages of high resolution and high beam intensity analysis at the cost of very precise alignment requirements and carefully prepared samples. Additionally, this geometry requires that the source-to-sample distance be constant and equal to the sample-to-detector distance. Alignment errors often lead to difficulties in phase identification and improper quantification. A mis-positioned sample can lead to unacceptable specimen displacement errors. Sample flatness, roughness, and positioning constraints preclude in-line sample measurement. Additionally, traditional XRD systems are often based on bulky equipment with high power requirements as well as employing high powered X-ray sources to increase X-ray flux on the sample, therefore increasing the detected diffraction signals from the sample. These sources also have large excitation areas, which are often disadvantageous for the diffraction analysis of small samples or small sample features.

Polycapillary X-ray optics can be used to overcome many of these drawbacks and constraints to enhance XRD applications. Polycapillary collimating optics convert a highly divergent beam into a quasi-parallel beam with low divergence. They can be used to form a Parallel Beam XRD instrument geometry which greatly reduces and removes many sources of errors in peak position and intensity inherent to the parafocusing geometry, such as sample position, shape, roughness, flatness, and transparency. Polycapillary focusing optics collect X-rays from a divergent X-ray source and direct them to a small focused beam at the sample surface with diameters as small as tens of micrometers for micro X-ray diffraction applications of small samples or small specimen features. Both types of polycapillary optics direct very high X-ray intensities to the sample surface, such that XRD systems employing optics can use low power X-ray sources, reducing instrument size, cost, and power requirements.

X-ray diffraction using X-ray optics has been applied to many different types of applications including thin film analysis, sample texture evaluation, monitoring of crystalline phase and structure, and investigation of sample stress and strain.

Small Angle X-ray scattering (SAXS)

X-ray scattering is a nondestructive technique used to characterize the morphology of materials. A collimated beam of X-rays is transmitted through a specimen, and interactions with the matter within the sample cause some portion of the X-rays to be scattered away from the transmitted primary beam. When 2 photons having wavelength λ are scattered by features separated by a distance, d , the scattered photons are in phase only at a specific angle, 2θ . This relationship is described by Bragg's law.

Small-angle X-ray scattering (SAXS) is a small-angle scattering technique by which nanoscale density differences in a sample can be quantified. This means that it can determine nanoparticle size distributions, resolve the size and shape of (monodisperse) macromolecules, determine pore sizes, characteristic distances of partially ordered materials, and much more. This is achieved by analyzing the elastic scattering behaviour of X-rays when travelling through the material, recording their scattering at small angles (typically $0.1 - 10^\circ$, hence the "Small-angle" in its name). It belongs to the family of small-angle scattering (SAS) techniques along with small-angle neutron scattering, and is typically done using hard X-rays with a wavelength of $0.07 - 0.2$ nm.[clarification needed]. Depending on the angular range in which a clear scattering signal can be recorded, SAXS is capable of delivering structural information of dimensions between 1 and 100 nm, and of repeat distances in partially ordered systems of up to 150 nm. USAXS (ultra-small angle X-ray scattering) can resolve even larger dimensions, as the smaller the recorded angle, the larger the object dimensions that are probed.

SAXS and USAXS belong to a family of X-ray scattering techniques that are used in the characterization of materials. In the case of biological macromolecules such as proteins, the advantage of SAXS over crystallography is that a crystalline sample is not needed. Furthermore, the properties of SAXS allow investigation of conformational diversity in these molecules. Nuclear magnetic resonance spectroscopy methods encounter problems with macromolecules of higher molecular mass ($> 30-40$ kDa). However, owing to the random orientation of dissolved or partially ordered molecules, the spatial averaging leads to a loss of information in SAXS compared to crystallography.

SCANNING ELECTRON MICROSCOPY

Scanning Electron Microscope functions exactly as their optical counterparts except that they use a focused beam of electrons instead of light to “image” the specimen and gain information as to its structure and composition. Given sufficient light, the unaided human eye can distinguish two points 0.2 mm apart. If the points are closer together, they will appear as a single point. This distance is called the resolving power or resolution of the eye. Similarly, light microscopes use visible light (400- 700nm) and transparent lenses to see objects as small as about one micrometer (one millionth of a meter), such as a red blood cell (7 μm) or a human hair (100 μm). Light microscope has a magnification of about 1000x and enables the eye to resolve objects separated by 200 nm. Electron Microscopes were developed due to the limitations of light microscopes, which are limited by the physics of light. Electron Microscopes are capable of much higher magnifications and have a greater resolving power than a light microscope, allowing it to see much smaller objects at sub cellular, molecular and atomic level. The smallest the wavelength of the illuminating sources is the best resolution of the microscope

Working principles of SEM A beam of electrons is formed by the Electron Source and accelerated toward the specimen using a positive electrical potential. The electron beam is confined and focused using metal apertures and magnetic lenses into a thin, focused, monochromatic beam. Electrons in the beam interact with the atoms of the specimen, producing signals that contain information about its surface topography, composition and other electrical properties. These interactions and effects are detected and transformed into an image.

Components of SEM

Electron Column The electron column is where the electron beam is generated under vacuum, focused to a small diameter, and scanned across the surface of a specimen by electromagnetic deflection coils. The lower portion of the column is called the specimen chamber.

Electron gun: An electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB₆) cathodes, and field emission guns (FEG), which may be of the cold-cathode type using tungsten single crystal emitters or the thermally assisted Schottky type, using emitters of zirconium oxide.

Condenser Lenses: After the beam passes the anode it is influenced by two condenser lenses that cause the beam to converge and pass through a focal point. In conjunction with the selected accelerating voltage the condenser lenses are primarily responsible for determining the intensity of the electron beam when it strikes the specimen.

Apertures: The function of these apertures is to reduce and exclude extraneous electrons in the lenses. The final lens aperture located below the scanning coils determines the diameter or spot size of the beam at the specimen. The spot size on the specimen will in part determine the resolution and depth of field. Decreasing the spot size will allow for an increase in resolution and depth of field with a loss of brightness.

Scanning System: Images are formed by rastering the electron beam across the specimen using deflection coils inside the objective lens. The stigmator or astigmatism corrector is located in the objective lens and uses a magnetic field in order to reduce aberrations of the electron beam. The electron beam should have a circular cross section when it strikes the specimen however it is usually elliptical thus the stigmator acts to control this problem.

Specimen Chamber: The lower portion of the column is specimen stage and controls are located. Specimens are mounted and secured onto the stage which is controlled by a goniometer. The secondary electrons from the specimen are attracted to the detector by a positive charge. Manual stage controls are found on the front side of the specimen chamber for x-y-z movement.

Electron Detectors: Detectors collect the signal generated from interaction of beam with specimen. Electronic detectors convert the signal into digital images and most often collected signal are Secondary electrons by secondary electron detector (Everhart-Thornley) Backscattered electrons by backscattered electrons detector (Solid-State detector) and X-rays signal by Energy dispersive spectrometer (EDS) detector.

Vacuum System: Vacuum is produced by an oil diffusion pump backed by a mechanical pump. In the diffusion pump a stream of hot oil vapor strikes and pushes air molecules toward a mechanical pump that expels them from the system. A mechanical pump and valve system are used to preevacuate the system because a diffusion pump only operates after a vacuum is created. If the column is in a gas filled environment, electrons will be scattered collide with air molecules which would lead to reduction of the beam intensity and stability. Similarly, other gas molecules, which could come from the sample or the microscope itself, could form compounds and condense on the sample. This would lower the contrast and obscure detail in the image. The chemical and thermal stability is necessary for a well-functioning filament (gun pressure). The field emission gun, LaB6 and tungsten filament requires ~ 10⁻¹⁰, ~ 10⁻⁶ and 10⁻⁴ Torr, respectively. Hence, gun column of electron microscope require vacuum to facilitate the electrons signals from the sample to the detector for better imaging

How Scanning Electron Microscope (SEM) works Ernst Ruska and Max Knoll developed first electron microscope during 1931 with resolution of 100nm and later by addition of electromagnetic lenses, brought the resolution to 0.05nm. SEM is similar to the optical stereo-binocular microscope to observe the morphology and shape of the specimen. The electron gun produces an electron beam when tungsten wire is heated by current and accelerated by the anode. The beam travels in the vacuum column through electromagnetic fields and lenses, which focus the beam down toward the sample. A mechanism of deflection coils enables to guide the beam so that it scans the surface of the sample in a raster pattern.

When the incident beam touches the surface of the sample and produces signals viz., Secondary electrons (SE) Auger electrons Back scattered electrons (BSE) Characteristic X – Rays y Cathodoluminescence The emitted signals are trapped by electrical detectors, convert into digital images and displayed on a screen as digital image. Provides information sample's elemental composition, structural variation and morphology. In the SEM, use much lower accelerating voltages to prevent beam penetration into the sample since the requirement is generation of the secondary electrons from the true surface structure of a sample. Therefore, it is common to use low KV, in the range 1-5kV for biological samples, even though the SEMs are capable of up to 30 kV.

Interaction of Electron Beam with Specimen: When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to approximately 10 μm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy back scattered electrons by elastic scattering, emission of low energy secondary, auger electrons by inelastic

scattering and the emission of electromagnetic radiation (X-rays and cathodoluminescence), each of which can be detected by respective detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals, electronic detectors convert the signals into digital images and displayed on a computer monitor Backscattered electron: Those electrons, which are deflected, back in the direction of the beam. The special detector in scanning and transmission electron microscope traps these signals. These are used to discriminate areas of different atomic numbered elements. Higher atomic numbered elements gives off more backscattered electrons and appear brighter than lower numbered elements. It has the resolution to the level of 1000 nm. These electrons have high energy.

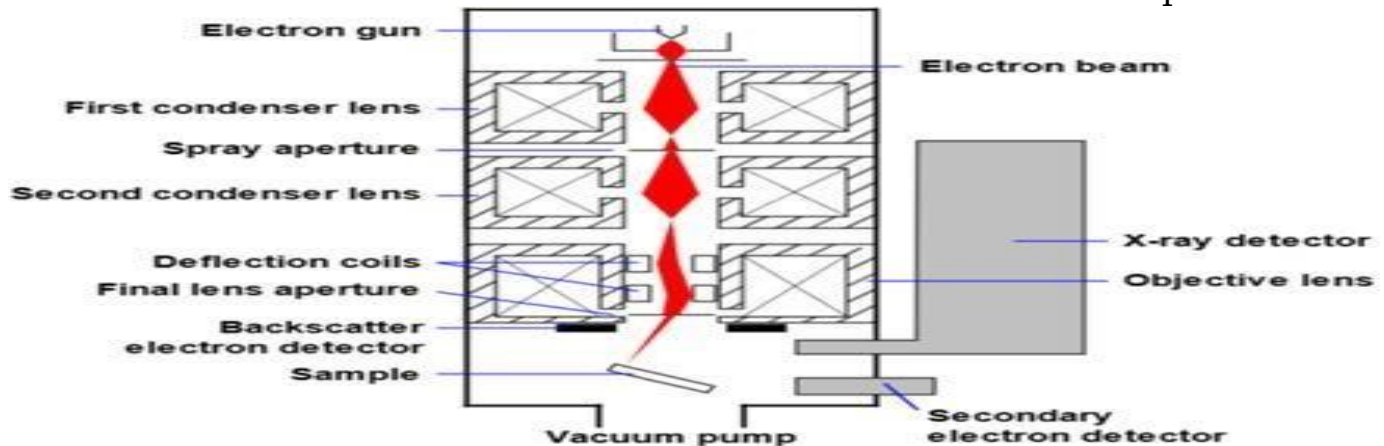
Secondary Electrons: These electrons are also collected with a special type of detector used in SEM and TEM. They are used primarily to reveal topographical feature of a specimen. It has the resolving power <10 nm. These electrons have low energy

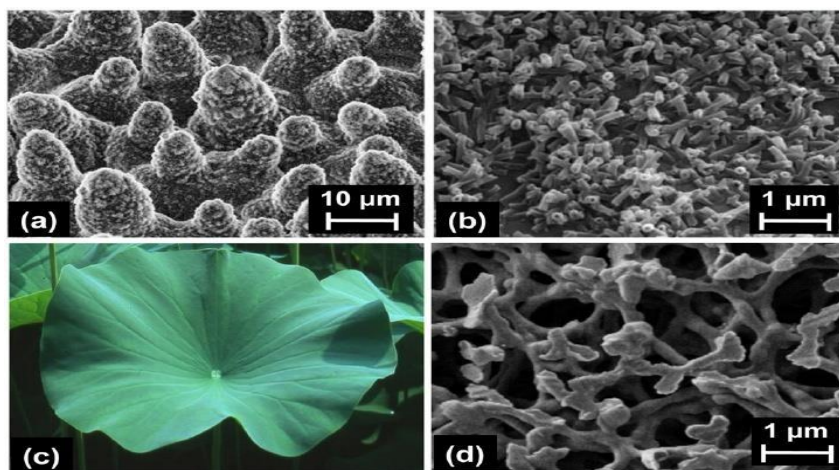
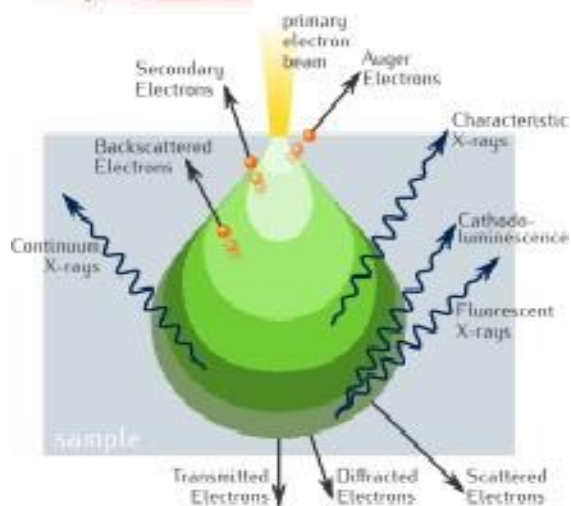
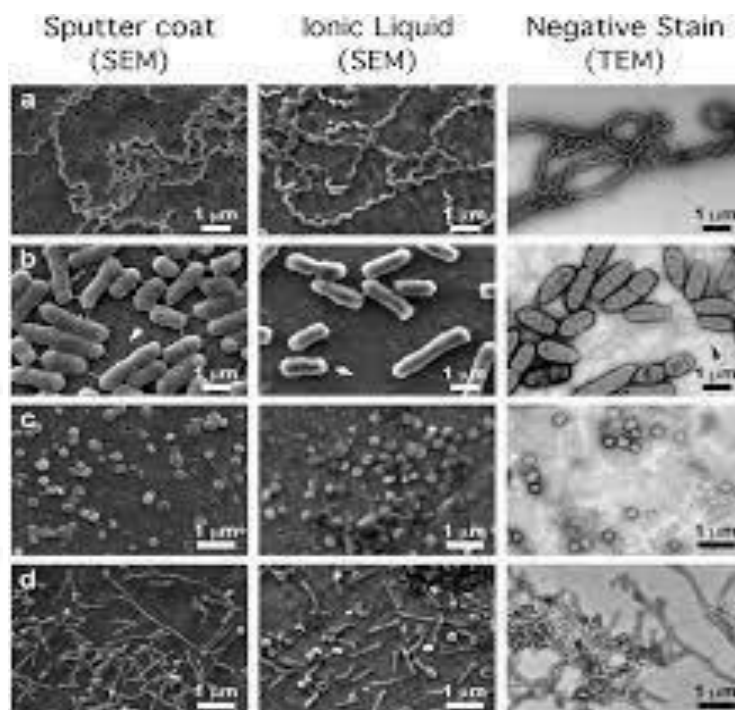
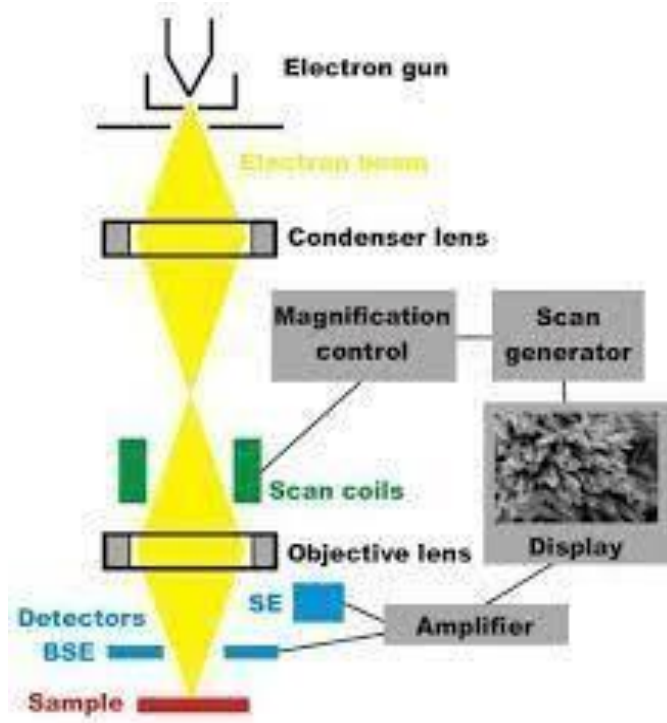
Auger Electrons: These are special types of low energy electrons that carry the information about the chemical nature (atomic composition) of the specimen. These are generated from the upper layer of specimen. It is a powerful tool in the material sciences for studying the distribution of the lighter numbered atomic elements on the surface of the specimen. It has limited application in biological sciences. It is specialized equipment known as scanning auger electron spectrometer.

Applications of Scanning Electron Microscopy Topography: The surface features of an object or “how it looks”, its texture; direct relation between these features and materials properties (hardness, reflectivity... etc.) **Morphology:** The shape and size of the particles making up the object; direct relation between these structures and materials properties (ductility, strength, reactivity...etc.) **Composition:** The elements and compounds that the object is composed of and the relative amounts of them; direct relationship between composition and materials properties (melting point, reactivity, hardness...etc.) **Crystallographic Information:** How the atoms are arranged in the object; direct relation between these arrangements and materials properties (conductivity, electrical properties, strength.etc.)

Advantages of SEM It gives detailed 3D and topographical imaging and the versatile information garnered from different detectors. This instrument works very fast. Modern SEMs allow for the generation of data in digital form. Most SEM samples require minimal preparation actions

Disadvantages of SEM SEMs are expensive and large. Special training is required to operate an SEM. The preparation of samples can result in artifacts. SEMs are limited to solid samples. SEMs carry a small risk of radiation exposure associated with the electrons that scatter from beneath the sample surface.





SCANNING TUNNELING MICROSCOPE (STM)

Scanning tunneling microscopy (STM) has been proven to be an extremely powerful tool for studying the electronic structures of solid-state systems. The STM topographic images, assisted by other surface analysis techniques with chemical specificity, lead to the structural determination of clean and adsorbate-covered surfaces. For example, the first atomically resolved STM image in history confirmed the Si(111) 7×7 surface reconstruction and identified Takayanagi's dimer-adatom-stacking-fault model as the correct Si(111) 7×7 surface structure. Combining scanning tunneling microscopy with spectroscopy, a number of beautiful experiments were carried out, e.g., to visualize the standing wave pattern of the two-dimensional surface state electrons in an artificial quantum corral, to provide the first direct spectroscopic signature of the Kondo resonance of an isolated magnetic impurity in a non-magnetic host, and to map out the electronic density of states inside a single vortex core of the Abrikosov flux lattice for a conventional type II superconductor.

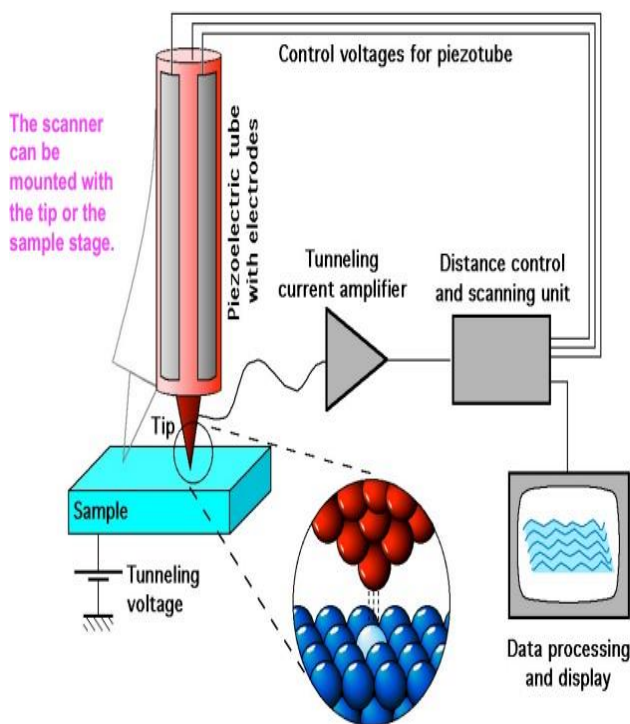
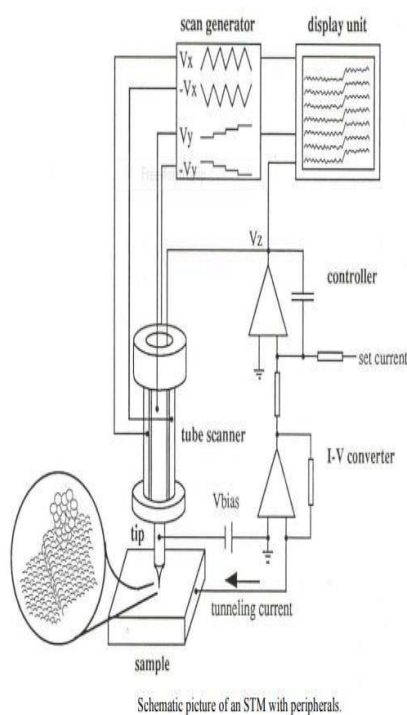
Furthermore, spatially resolved tunneling spectroscopy gave invaluable insights into open questions in the physics of strongly correlated electronic systems, such as the correlation between charge ordering and the metal-insulator transition in magnetic manganites and the various ordering phases in high-temperature cuprate superconductors. In this chapter, we summarize the operating principles of scanning tunneling microscopy/spectroscopy and then

present our development of a magnetic-field-compatible, cryogenic, variable-temperature STM for the study of cuprate superconductors.

OPERATION PRINCIPLES OF THE STM The central part of the STM is a sharp conductive tip which is moved in a very precise and controlled manner in three dimensions across the surface of the sample. A small voltage is applied between tip and sample (typically a few mV to a few V,

depending on the sample material) and when the tip is brought close enough to the sample (5-10 Å) a tunneling current flows (10 pA-10 nA). This is purely quantum mechanical phenomenon (classically there would be no current, since the region between tip and sample is insulating) as, as will be shown below, the current is exponentially dependent on the distance between tip and sample, varying approximately one order of magnitude per Ångström. By keeping the current constant, the distance to the sample is held constant and if the tip is scanned over the surface and its movement perpendicular to the sample required to keep the current constant is registered, the result is a topographical image of the sample surface.

Alternatively, the tip is scanned across the sample surface at a constant average height and the current variations are registered (this requires a surface that does not contain large protrusion into which the tip would crash). As will be discussed below, the constant-current image is actually not a true topographical image but an image of the surface electron density that, for certain sample materials like metals, agrees fairly well with the true topography. The vertical resolution is limited by the mechanical stability of the instrument and the capability of the electronics to keep the current constant, something that is facilitated by the exponential dependence on the distance between tip and sample. Vertical resolution in the 0.01 Å range are readily accomplished. Horizontally, the resolution is limited by the sharpness of the tip, and 10 Å resolution is routinely achieved. Under favourable conditions a lateral resolution as high as 1 Å may be achieved, such that individual atoms can be resolved.



Five basic components:

1. Metal tip,
2. Piezoelectric scanner,
3. Current amplifier (nA),
4. Bipotentiostat (bias),
5. Feedback loop (current)

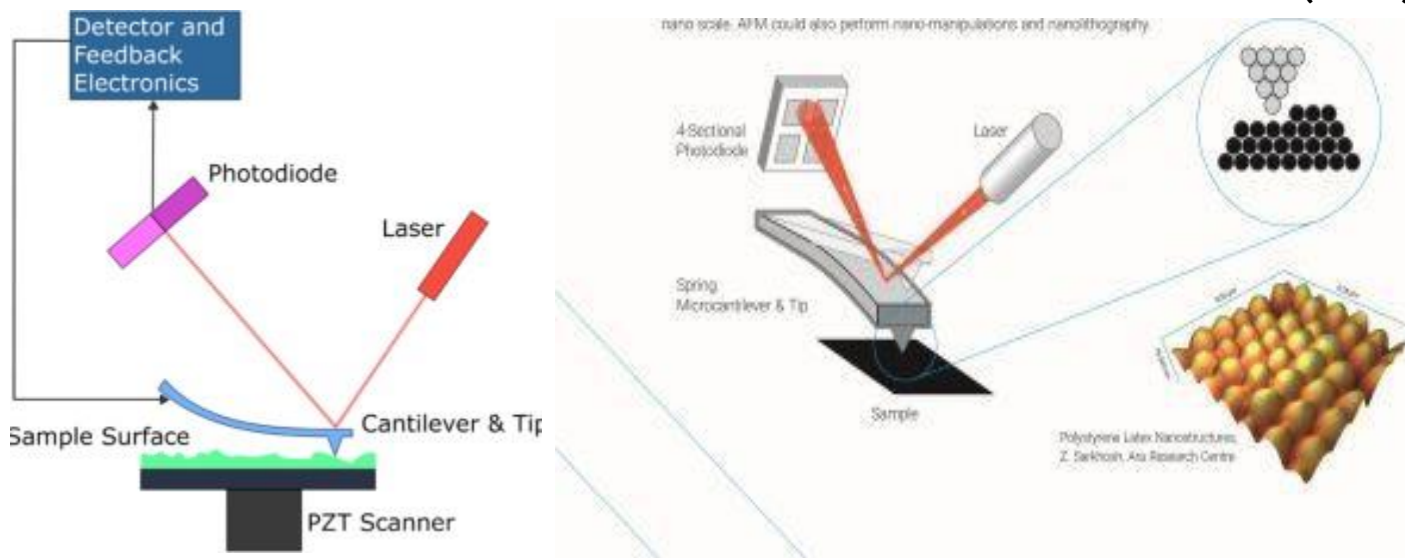
One of the advantages of STM is the possibility to use most kinds of sample materials, the only criterion being that the sample has to be conductive. STM has been used for determination of the surface structure of metals and

semiconductors as well as for studies of nucleation and growth of thin films in vacuum. Other applications include studies of biological materials and in situ studies of electrochemical reactions. There are applications of the STM other than pure topographical measurements, e.g. tunneling spectroscopy where different electronic states of the surface may be mapped with very high spatial resolution. Also emission of secondary particles such as electrons and photons induced by electrons from the tunneling tip have been studied with high spatial resolution using STM. Since the invention of the STM new exciting scanning probe techniques using different probe-sample interactions to control the separation have appeared. The most notable is the atomic force microscope (AFM) where the force between the tip and the sample is used in the same manner as the tunneling current in the STM. The resolution of the AFM is almost in the range of the STM and the sample materials do not have to be conductive.

Mechanical considerations Due to the extremely small distances involved, the mechanical rigidity and vibration isolation are of utmost importance. From the first comparably voluminous STMs which required several stages of vibration isolation, the development has gone towards small and rigid microscopes with little or no vibration isolation at all. It has even been possible to fabricate working miniature STMs on silicon wafers.

Tip The performance of the STM is much dependent on the condition of the tip as it determines the resolution of the instrument. The tip consists of a mechanically or electro-chemically sharpened wire of e.g. tungsten, gold, or platinum. Ideally it has a mono atomic point, but the apex continuously rearranges and sample atoms adsorb during operation. Since the image actually is a convolution of the tip and the sample, the symmetry of the tip is reflected in the recorded image and several different tips must be used for a given sample before conclusions can be drawn about the surface structure. Sometimes tunneling current flows simultaneously from several parts of the tip and the resulting image is a superposition of more than one image. The problem with a blunt, double tip is illustrated, where it can be seen that scanning the single protrusion on the sample with the double tip results in an image showing two “bumps”. When scanning with the sharp tip, the only distortion of the image is a slight broadening of the “bump”.

SCANNING PROBE MICROSCOPY or ATOMIC FORCE MICROSCOPY (AFM)



Scanning probe microscopes (SPMs) are a family of tools used to make images of nanoscale surfaces and structures, including atoms. They use a physical probe to scan back and forth over the surface of a sample. During this scanning process, a computer gathers data that are used to generate an image of

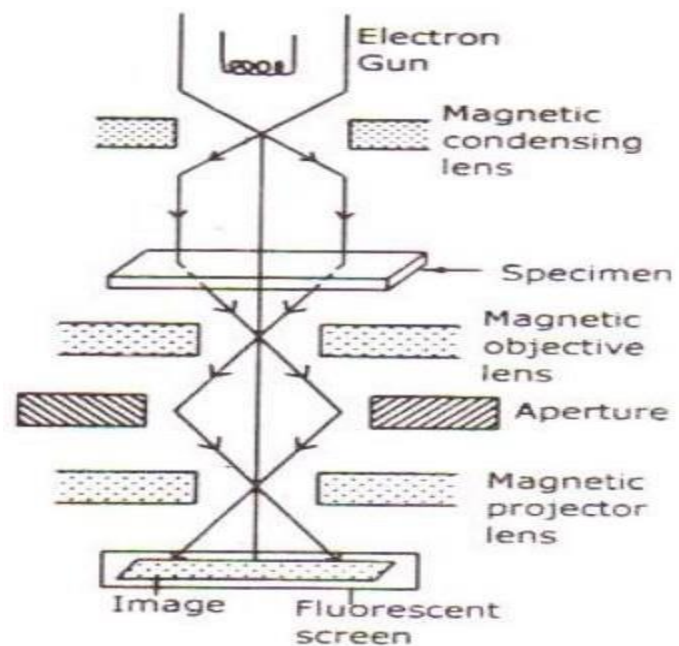
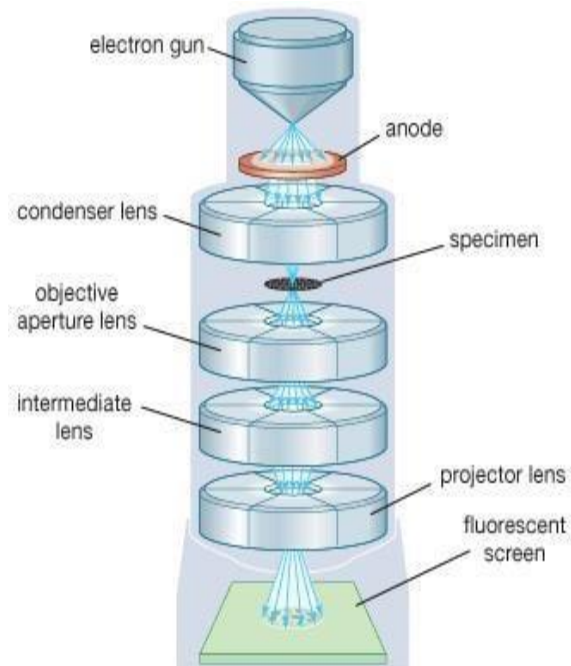
the surface. In addition to visualizing nanoscale structures, some kinds of SPMs can be used to manipulate individual atoms and move them to make specific patterns. SPMs are different from optical microscopes because the user doesn't "see" the surface directly. Instead, the tool "feels" the surface and creates an image to represent it.

SPMs are a very powerful family of microscopes, sometimes with a resolution of less than a nanometer. (A nanometer is a billionth of a meter.) An SPM has a probe tip mounted on the end of a cantilever. The tip can be as sharp as a single atom. It can be moved precisely and accurately back and forth across the surface, even atom by atom. When the tip is near the sample surface, the cantilever is deflected by a force. SPMs can measure deflections caused by many kinds of forces, including mechanical contact, electrostatic forces, magnetic forces, chemical bonding, van der Waals forces, and capillary forces. The distance of the deflection is measured by a laser that is reflected off the top of the cantilever and into an array of photodiodes (similar to the devices used in digital cameras). SPMs can detect differences in height that are a fraction of a nanometer, about the diameter of a single atom. Scanning probe microscope The tip is moved across the sample many times. This is why these are called "scanning" microscopes. A computer combines the data to create an image. The images are inherently colorless because they are measuring properties other than the reflection of light.

However, the images are often colorized, with different colors representing different properties (for example, height) along the surface. Scientists use SPMs in a number of different ways, depending on the information they're trying to gather from a sample. The two primary modes are contact mode and tapping mode. In contact mode, the force between the tip and the surface is kept constant. This allows a scientist to quickly image a surface. In tapping mode, the cantilever

oscillates, intermittently touching the surface. Tapping mode is especially useful when a scientist is imaging a soft surface. There are several types of SPMs. Atomic force microscopes (AFMs) measure the electrostatic forces between the cantilever tip and the sample. Magnetic force microscopes (MFMs) measure magnetic forces. And scanning tunneling microscopes (STMs) measure the electrical current flowing between the cantilever tip and the sample.

TRANSMISSION ELECTRON MICROSCOPY



Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting

with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. The first TEM was built by Max Kroll and Ernst Ruska in 1931, with this group developing the first TEM with resolution power greater than that of light in 1933 and the first commercial TEM in 1939.

The spatial resolution of the SEM depends on the size of the electron spot, which in turn depends on both the wavelength of the electrons and the electron-optical system which produces the scanning beam. The resolution is also limited by the size of the interaction volume, or the extent to which the material interacts with the electron beam. The spot size and the interaction volume are both large compared to the distances between atoms, so the resolution of the SEM is not high enough to image individual atoms, as is possible in the shorter wavelength (i.e. higher energy) (TEM). Depending on the instrument, the resolution can fall somewhere between less than 1 nm and 20 nm. By 2009, The world's highest SEM resolution at high beam energies (0.4 nm at 30 kV) is obtained with the Hitachi S-5500. In a TEM, a monochromatic beam of electrons is accelerated through a potential of 40 to 100 kilovolts (kV) and passed through a strong magnetic field that acts as a lens.

The resolution of a modern TEM is about 0.2 nm. This is the typical separation between two atoms in a solid. This resolution is 1,000 times greater than a light microscope and about 500,000 times greater than that of a human eye. More recently, advances in aberration corrector design have been able to reduce spherical aberrations and to achieve resolution below 0.5 Ångströms at magnifications above 50 million times. Improved resolution allows for the imaging of lighter atoms that scatter electrons less efficiently, such as lithium atoms in lithium battery materials. The ability to determine the position of atoms within materials has made the HRTEM an indispensable tool for nanotechnology research and development in many fields, including heterogeneous catalysis and the development of semiconductor devices for electronics and photonics.

The working principle of the Transmission Electron Microscope (TEM) is similar to the light microscope. The major difference is that light microscopes use light rays to focus and produce an image while the TEM uses a beam of electrons to focus on the specimen, to produce an image. Electrons have a shorter wavelength in comparison to light which has a long wavelength. The mechanism of a light microscope is that an increase in resolution power decreases the wavelength of the light, but in the TEM, when the electron illuminates the specimen, the resolution power increases increasing the wavelength of the electron transmission.

The wavelength of the electrons is about 0.005nm which is 100,000X shorter than that of light, hence TEM has better resolution than that of the light microscope, of about 1000times. This can accurately be stated that the TEM can be used to detail the internal structures of the smallest particles like a virion particle. Their working mechanism is enabled by the high-resolution power they produce which allows it to be used in a wide variety of fields. It has three working parts which include:

Electron gun

Image producing system Image recording system Electron gun

This is the part of the Transmission Electron Microscope responsible for producing electron beams. Electrons are produced by a cathode that is a tungsten filament that is V-shaped and it is normally heated. The tungsten filament is covered by a control grid known as a Wehnelt cylinder made up of a central hole which lies columnar to the tube. The cathode lies on top of or below the cylindrical column

hole. The cathode and the control grid are negatively charged with an end of the anode which is disk-shaped that also has an axial hole.

When electrons are transmitted from the cathode, they pass through the columnar aperture (hole) to the anode at high voltage with constant energy, which is efficient for focusing the specimen to produce an accurately defined image.

It also has the condenser lens system which works to focus the electron beam on the specimen by controlling the energy intensity and the column hole of the electron gun. The TEM uses two condenser lenses to converge the beam of electrons to the specimen. The two condenser lens each function to produce an image i.e the first lens which has strong magnification, produces a smaller image of the specimen, to the second condenser lens, directing the image to the objectives.

Image- Producing system

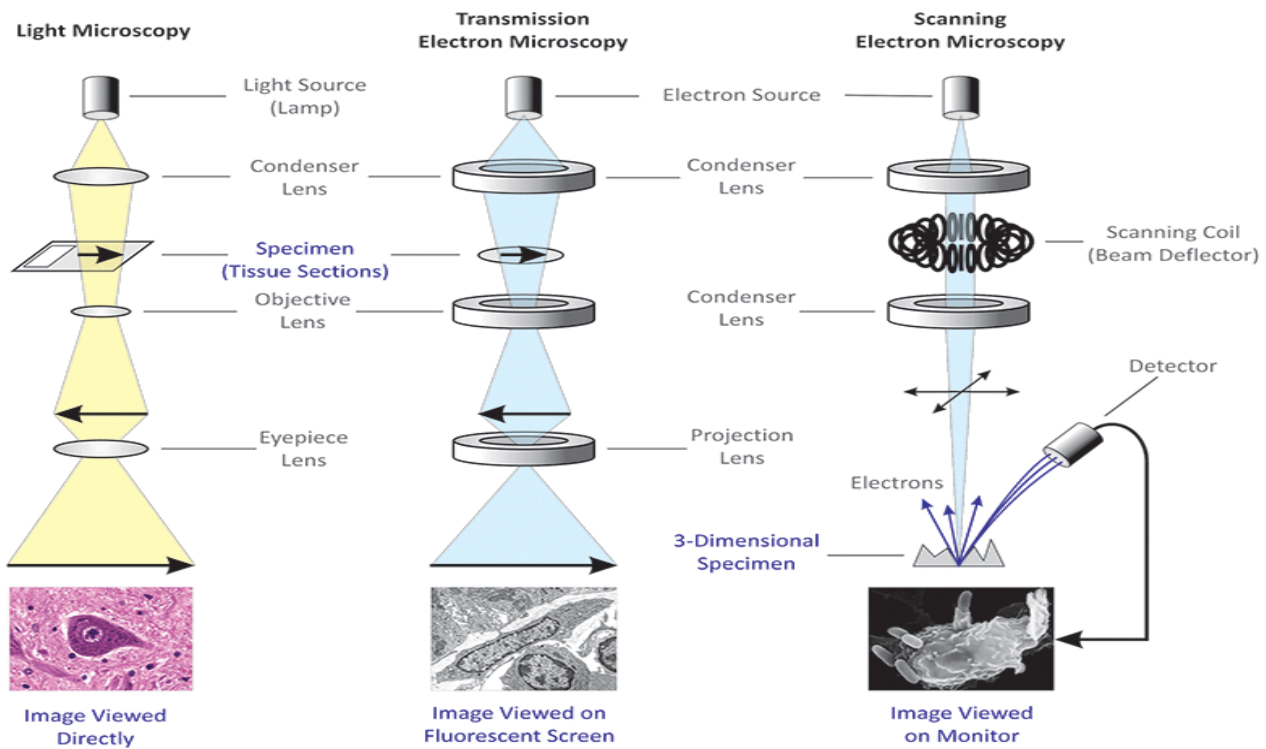
Its made up of the objective lens, a movable stage or holding the specimen, intermediate and projector lenses. They function by focusing the passing electrons through the specimen forming a highly magnified image. The objective has a short focal length of about 1-5mm and it produces an intermediate image from the condenser which are transmitted to the projector lenses for magnification. The projector lenses are of two types, i.e the intermediate lens which allows great magnification of the image and the projector lens which gives a generally greater magnification over the intermediate lens. To produce efficient high standard images, the objectives and the projector lenses need high power supplies with high stability for the highest standard of resolution.

Image-Recording System

Its made up of the fluorescent screen used to view and to focus on the image. They also have a digital camera that permanently records the images captured after viewing. They have a vacuum system that prevents the bombardment or collision of electrons with air molecules disrupting their movement and ability to focus. A vacuumed system facilitates the straight movement of electrons to the image. The vacuumed system is made up of a pump, gauge, valves and a power supply. The image that is formed is called a monochromatic image, which is greyish or black and white. The image must be visible to the human eye, and therefore, the electrons are allowed to pass through a fluorescent screen fixed at the base of the microscope. The image can also be captured digitally and displayed on a computer and stored in a JPEG or TIFF format. During the storage, the image can be manipulated from its monochromatic state to a colored image depending on the recording apparatus eg use of pixel cameras can store the image in color. The presence of colored images allows easy visualization, identification, and characterization of the images.

How does a Transmission Electron Microscope (TEM) work?

From the instrumentation described, the working mechanism is a sequential process of the parts of the TEM mentioned above. To mean: A heated tungsten filament in the electron gun produces electrons that get focus on the specimen by the condenser lenses. Magnetic lenses are used to focus the beam of electrons of the specimen. By the assistance offered by the column tube of the condenser lens into the vacuum creating a clear image, the vacuum allows electrons to produce a clear image without collision with any air molecules which may deflect them. On reaching the specimen, the specimen scatters the electrons focusing them on the magnetic lenses forming a large clear image, and if it passes through a fluorescent screen it forms a polychromatic image. The denser the specimen, the more the electrons are scattered forming a darker image because fewer



electron reaches the screen for visualization while thinner, more transparent specimens appear brighter.

Applications of Transmission Electron Microscope (TEM)

TEM is used in a wide variety of fields From Biology, Microbiology, Nanotechnology, forensic studies, etc. Some of these applications include:

To visualize and study cell structures of bacteria, viruses, and fungi
To view bacteria flagella and plasmids

To view the shapes and sizes of microbial cell organelles
To study and differentiate between plant and animal cells.

Its also used in nanotechnology to study nanoparticles such as ZnO nanoparticles
It is used to detect and identify fractures, damaged microparticles which further enable repair mechanisms of the particles.

Advantages of Transmission Electron Microscope (TEM)

It has a very powerful magnification of about 2 million times that of the Light microscope.

It can be used for a variety of applications ranging from basic Biology to Nanotechnology, to education and industrial uses.

It can be used to acquire vast information on compounds and their structures. It produces very efficient, high-quality images with high clarity.

It can produce permanent images.

It is easy to train and use the Transmission Electron Microscope
Limitations of Transmission Electron Microscope (TEM) Generally, the TEMs are very expensive to purchase

They are very big to handle.

The preparation of specimens to be viewed under the TEM is very tedious.

The use of chemical fixations, dehydrators, and embedments can cause the dangers of artifacts. They are laborious to maintain.

It requires a constant inflow of voltage to operate.

They are extremely sensitive to vibrations and electro-magnetic movements hence they are used in isolated areas, where they are not exposed.

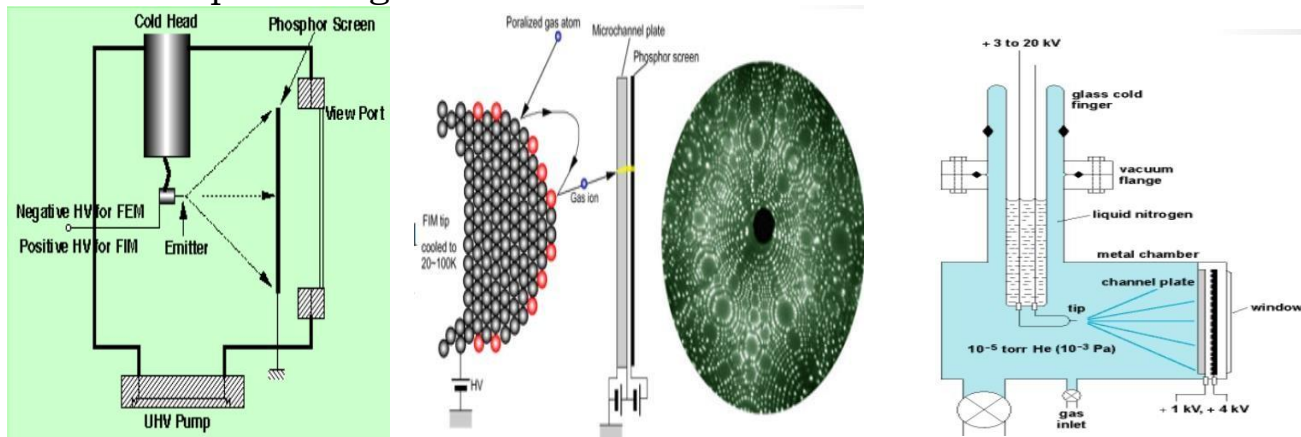
It produces monochromatic images, unless they use a fluorescent screen at the end of visualization.

FIELD ION MICROSCOPE (FIM)

The field ion microscope (FIM) can image the atomic structure of sharp metal tips with nanometer-sized radii and is notable as being the earliest technique to produce atomically resolved images of matter in real space. Using FIM, one can atomically characterize, and even engineer, the sharp tips used in scanning probe microscopy (SPM). In this chapter, we address the technical aspects of implementing these tips in SPM experiments and review their application to scanning tunneling microscopy (STM), atomic force microscopy (AFM), and SPM-based nanoindentation experiments.

Field emission microscopy (FEM) is an analytical technique used in materials science to investigate molecular surface structures and their electronic properties.

FEM was one of the first surface analysis instruments that approached near-atomic resolution. This instrument approached to view a surface on a scale of atomic dimensions and yet simultaneously allowed one to follow rapid changes at the surface.



In its simplest form, FEM consist of a sharp needle emitter and a fluorescent screen as shown by applying negative field to the emitter, electrons are emitted from the surface of the emitter to the direction of the screen. The image contrast appears due to the difference in current densities of electron, which originated from the difference in work functions and electric field on the emitter surface.

Requires a very good vacuum (ultra high vacuum) Emission is not due to the clean surface. No vibrations Tip materials can tolerate the high electrostatic fields and have high melting points

Surface Science (Electronic and Structural aspects) Field emission has been extensively used in the characterization of surface structures and electronic properties. The field ion microscope is a type of microscope that can be used to image the arrangement of atoms at the surface of a sharp metal tip. It was the first technique by which individual atoms could be spatially resolved. The imaging gas atoms (He, Ne) near the tip are polarized by the field and since the field is nonuniform the polarized atoms are attracted towards the tip surface. The imaging atoms then lose their kinetic energy performing a series of hops and accommodate to the tip temperature. Eventually, the imaging atoms are ionized by tunneling electrons into the surface and the resulting positive ions are accelerated along the field lines to the screen to form a highly magnified image of the sample tip. FIM like Field Emission Microscopy (FEM) . Both have same working conditions. However, there are some essential differences as follows: The tip potential is positive. The chamber is filled with a imaging gas (typically, He or Ne at 10^{-5} to 10^{-3} Torr). The tip is cooled to low temperatures ($\sim 20-80$ K).

Applications FIM has been used to study dynamical behavior of

surfaces and the behavior of adatoms on surfaces. The problems studied include: Surface diffusion of adatoms , Adatom-adatom interactions, Step motion, Equilibrium crystal shape, etc.

THREE-DIMENSIONAL ATOM PROBE (3DAP)

The development of three-dimensional (3-D), characterization techniques with high spatial and mass resolution is crucial for understanding and developing advanced materials for many engineering applications as well as for understanding natural materials. In recent decades, atom probe tomography (APT), which combines a point projection microscope and time-offlight mass spectrometer, has evolved to be an excellent characterization technique capable of providing 3-D nanoscale characterization of materials with sub-nanometer scale spatial resolution, with equal sensitivity for all elements. This review discusses the current state, as of APT instrumentation, new developments in sample preparation methods, experimental procedures for

different material classes, reconstruction of APT results, the current status of correlative microscopy, and application of APT for micro structural characterization in established scientific areas like structural materials as well as new applications in semiconducting nanowires, semiconductor devices, battery materials, catalyst materials, geological materials, and biological materials.

NANOINDENTATION

Nanoindentation is called as The depth sensing indentation The instrumented indentation Nanoindentation method gained popularity with the development of, Machines that can record small load and displacement with high accuracy and precision Analytical models by which the load-displacement data can be used to determine modulus, hardness and other mechanical properties.

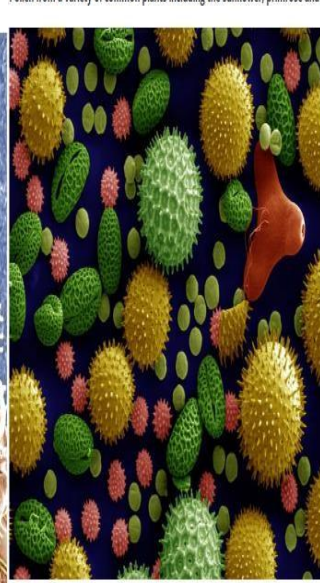
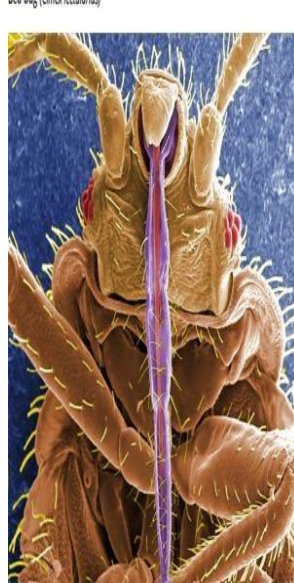
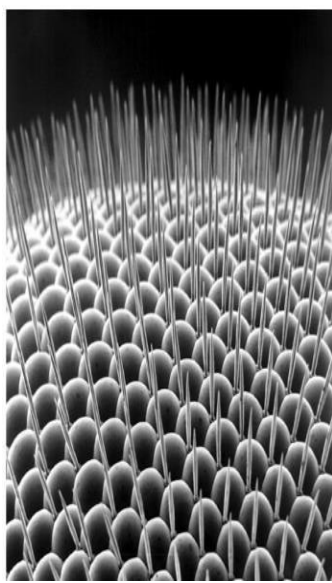
Microindentation A prescribed load applied to an indenter in contact with a specimen and the load is then removed and the area of the residual impression is measured. The load divided by the by the area is called the hardness. Nanoindentation A prescribed load is applied to an indenter in contact with a specimen. As the load is applied, the depth of penetration is measured. The area of contact at full load is determined by the depth of the impression and the known angle or radius of the indenter. The hardness is found by dividing the load by the area of contact. Shape of the unloading curve provides a measure of elastic modulus.

Head and mouth of a leaf beetle (Chrysomelidae family).

The eye of the fruit fly (Drosophila).

Bed bug (Cimex lectularius)

Pollen from a variety of common plants including the sunflower, primrose and lily.



UNIT- V:

APPLICATIONS OF NANO MATERIALS: Nano-electronics, Micro- and Nano-electromechanical systems (MEMS/NEMS), Nano sensors, Nano catalysts, Food and Agricultural Industry, Cosmetic and Consumer Goods, Structure and Engineering, Automotive Industry, Water- Treatment and the environment, Nano-medical applications, Textiles, Paints, Energy, Defense and Space Applications, Concerns and challenges of Nanotechnology.

Applications of Nano Materials: Nano-electronics

The term nanoelectronics refers to the use of nanotechnology in electronic components. These components are often only a few nanometers in size. However, the tinier electronic components become, the harder they are to manufacture.

Nanoelectronics covers a diverse set of devices and materials, with the common characteristic that they are so small that physical effects alter the materials 'properties on a nanoscale – inter-atomic interactions and quantum mechanical properties play a significant role in the workings of these devices. At the nanoscale, new phenomena take precedence over those that hold sway in the macro-world. Quantum effects such as tunnelling and atomistic disorder dominate the characteristics of these nanoscale devices

The first transistors built in 1947 were over 1 centimetre in size; the smallest working transistor today is 7 nanometers long – over 1.4 million times smaller (1 cm equals 10 million nanometers). The result of these efforts are billion-transistor processors where, once industry embraces 7nm manufacturing techniques, 20 billion transistor-based circuits are integrated into a single chip.

Nanoelectronics Devices Spintronics

Besides transistors, nanoelectronics devices play a role in data storage (memory). Here, spintronics – the study and exploitation in solid-state devices of electron spin and its associated magnetic moment, along with electric charge – is already an established technology. Read more: "Graphene spintronics - from science to technology".

Spintronics also plays a role in new technologies that exploit quantum behaviours for computing (read more: "Quantum computing moves forward with spintronics progress" and "The birth of topological spintronics").

Optoelectronics

Electronic devices that source, detect and control light – i.e. optoelectronic devices – come in many shapes and forms. Highly energy-efficient (less heat generation and power consumption) optical communications are increasingly important because they have the potential to solve one of the biggest problems of our information age: energy consumption.

In the field of nanotechnology, materials like nanofibers (see for instance: "Light-emitting nanofibers shine the way for optoelectronic textiles") and carbon nanotubes have been used and especially graphene has shown exciting potential for optoelectronic devices.

Displays

Display technologies can be grouped into three broad technology areas; Organic LEDs, electronic paper and other devices intended to show still images, and Field Emission Displays. For more, read our special section on Nanotechnology in Displays.

Wearable, flexible electronics

The age of wearable electronics is upon us as witnessed by the fast growing array of smart watches, fitness bands and other advanced, next-generation health monitoring devices such as electronic stick-on tattoos.

If current research is an indicator, wearable electronics will go far beyond just very small electronic devices or wearable, flexible computers. Not only will these devices be embedded in textile substrates but an electronics device or system could ultimately become the fabric itself. Electronic textiles (e-textiles) will allow the design and production of a new generation of garments with distributed sensors and electronic functions. Such e-textiles will have the revolutionary ability to sense, act, store, emit, and move – think biomedical monitoring functions or new man-machine interfaces – while ideally leveraging an existing low-cost textile manufacturing infrastructure (see for instance "wearing single-walled carbon nanotube electronics on your skin", a "temporary tattoo to monitor glucose levels" or "graphene Nanosensors tattoo on teeth monitors bacteria in your mouth").

Nanoelectronics in Energy

Solar cells and supercapacitors are examples of areas where nanoelectronics is playing a major role in energy generation and storage. To learn more read our detailed sections on Nanotechnology in Energy and Graphene Nanotechnology in Energy.

Molecular Electronics

Distinct from nanoelectronics, where devices are scaled down to nanoscale levels, molecular electronics deals with electronic processes that occur in molecular structures such as those found in nature, from photosynthesis to signal transduction.

Molecular electronics aims at the fundamental understanding of charge transport through molecules and is motivated by the vision of molecular circuits to enable miniscule, powerful and energy efficient computers (see for instance: "Adding an optoelectronic component to molecular electronics").

Applications of Nano-electromechanical systems

Nanoelectromechanical systems (NEMS) have advanced the technologies in a wide spectrum of fields, including nonlinear dynamics, sensors for force detection, mass spectrometry, inertial imaging, calorimetry, and charge sensing. Due to their low power consumption, fast response time, large dynamic range, high quality factor, and low mass, NEMS have achieved unprecedented measurement sensitivity. For optimized system functionalization and design, precise characterization of material properties at the nanoscale is essential. In this thesis, we will discuss three applications of NEMS: mechanical switches, using anharmonic nonlinearity to measure device and material properties, and mass spectrometry and inertial imaging.

The first application of NEMS is NEMS switches, switches with physical moving parts. Conventional electronics, based largely on silicon transistors, is reaching a physical limit in both size and power consumption. Mechanical switches provide a promising solution to surpass this limit by forcing a jump between the on and off states. Graphene, which is a single sheet of carbon atoms arranged in a hexagonal structure, has high mechanical strength and strong planar bonding, making it an ideal candidate for nanoelectromechanical switches. In addition, graphene is conductive, which decreases resistive heating at the contact area, therefore reducing bonding issues and subsequently

reducing degradation. We demonstrate using exfoliated graphene to fabricate suspended graphene NEMS switches with successful switching.

The second application of NEMS is the use of mechanical nonlinearity to measure device and material properties. While the nonlinear dynamics of NEMS have been used previously to investigate the longitudinal speed of sound of materials at nano- and micro-scales, we correct a previously attempted method that employs the anharmonicity of NEMS arising from deflection-dependent stress to interrogate the transport of RF acoustic phonons at nanometre scales. In contrast to existing approaches, this decouples intrinsic material properties, such as longitudinal speed of sound, from properties associated with linear dynamics, such as tension, of the structure. We demonstrate this approach through measurements of the longitudinal speed of sound in several NEMS devices composed of single crystal silicon along different crystal orientations. Good agreement with literature values is reported.

The third application of NEMS is mass spectrometry and inertial imaging. Currently, only doubly clamped beams and cantilevers have been experimentally demonstrated for mass spectrometry. We extend the one-dimension model for mass spectrometry to a novel method for inertial imaging. We further extend the theory of mass spectrometry and inertial imaging to two dimensions by using a plate geometry. We show that the mode shape is critical in performing NEMS mass spectrometry and inertial imaging, and that the mode shapes in plates deviate from the ideal scenario with isotropic stress. We experiment with various non-ideal conditions to match non-ideal mode shape observed.

Applications of micro-electromechanical systems:

Microelectromechanical system (MEMS) are used in a wide range of sensors, actuators, generators, energy sources, biochemical and biomedical systems and oscillators. Some examples of MEMS applications in engineering product design include:

MEMS microphone

Sensors such as MEMS accelerometers, MEMS gyroscopes, MEMS pressure sensors, MEMS tilt sensors and other types of MEMS resonant sensors. Actuators such as MEMS switches, micro-pumps, micro-levers and micro-grippers. Generators and energy sources such as MEMS vibration energy harvesters, MEMS fuel cells and MEMS radioisotope power generators. Biochemical and biomedical systems such as MEMS biosensors, lab-on-chips, and MEMS air microfluidic and particulate sensors. MEMS oscillators for accurate timekeeping and frequency control applications.

MEMS optical switch

At an even smaller nanometre scale, the fabrication technology morphs into a nanoelectromechanical system (NEMS). Furthermore, where MEMS is integrated with other technologies, various combinatory embodiments can take form, such as, biomes where biochemical and biomedical systems are realised on microfabricated devices, micro-opto-electro-mechanical system (MOEMS) or Opto MEMS where optical systems such as micro-mirrors are integrated to manipulate or sense light at the microscopic scale, radio frequency microelectromechanical system (RFMEMS) typically involves close integration with semiconductor microelectronics to provide RF transduction and switching capabilities.

Applications of Nano Sensors

Nanosensors can be chemical sensors or mechanical sensors. They are used:

Related Stories Study Reports Many Nanotechnology Companies Do What They Always Have, Now They Just Call it Nanotech Scientists Review Impact of Nanosensors for Cardiovascular Diseases Diagnosis Atomic Force Microscopes (AFM) What They Are, How They Work and What They Are Used For To detect various chemicals in gases for pollution monitoring For medical diagnostic purposes either as bloodborne sensors or in lab-on-a-chip type devices

To monitor physical parameters such as temperature, displacement and flow As accelerometers in MEMS devices like airbag sensors To monitor plant signalling and metabolism to understand plant biology To study neurotransmitters in brain for understanding neurophysiology Nanosensors aid in the progression of fields such as medical technology; precision agriculture; urban farming; plant nanoionics; prognostics and diagnostics; SERS-based sensors; and many industrial applications.

Nanosensors include:

Carbon Nanotube-Based Fluorescent Nanosensors, Quantum Dot-Based Fluorescent Nanosensors, DNA-Based Fluorescent Nanosensors, Peptide-Based Fluorescent Nanosensors, Plasmon Coupling-Based Nanosensors, Plasmonic Enhancing-/Quenching-Based Nanosensors, magnetic Resonance Imaging-Based Nanosensors, Photoacoustic-Based Nanosensors, Multimodal Nanosensors (synergistic Nanosensors with multiple modalities to overcome individual challenges), How Nanosensors Work

An analyte, sensor, transducer, and detector are the components of a sensor system, with feedback from the detector to the sensor. Sensitivity, specificity and ease of execution are the main goals in designing a sensor. Nanosensors typically work by monitoring electrical changes in the sensor materials. For example, carbon nanotube-based sensors work in this way. When a molecule of nitrogen dioxide (NO₂) is present, it will strip an electron from the nanotube, which in turn causes the nanotube to be less conductive.

If ammonia (NO₃) is present, it reacts with water vapor and donates an electron to the carbon nanotube, making it more conductive. By treating the nanotubes with various coating materials, they can be made sensitive to certain molecules and immune to others.

Like chemical Nanosensors, mechanical Nanosensors also tend to measure electrical changes. The Nanosensors used in the MEMS systems that car airbags depend upon are monitoring changes in capacitance. These systems have a miniscule, weighted shaft attached to a capacitor. The shaft bends with changes in acceleration and this is measured as changes in capacitance. Nanosensors have been developed to the point of measurement at the single-molecule level.

Applications of Nano catalysts

Nano catalysis is a rapidly growing field which involves the use of nanomaterials as catalysts for a variety of homogeneous and heterogeneous catalysis applications. Heterogeneous catalysis represents one of the oldest commercial practices of nanoscience; nanoparticles of metals, semiconductors, oxides, and other compounds have been widely used for important chemical reactions.

Although surface science studies have contributed significantly to our fundamental understanding of catalysis, most commercial catalysts, are still produced by "mixing,

shaking and baking" mixtures of multi-components; their nanoscale structures are not well controlled and the synthesis-structure-performance relationships are poorly understood. Due to their complex physico-chemical properties at the nanometre scale, even characterization of the various active sites of most commercial catalysts proves to be elusive.

A key objective of nano catalysis research is to produce catalysts with 100% selectivity, extremely high activity, low energy consumption, and long lifetime. This can be achieved only by precisely controlling the size, shape, spatial distribution, surface composition and electronic structure, and thermal and chemical stability of the individual nanocomponents. In this article, the exciting opportunities of nano catalysis in chemical and refining processes, as well as the challenges in developing nanostructured catalysts for industrial applications, are discussed.

The field of nano catalysis (the use of nanoparticles to catalyse reactions) has undergone an explosive growth during the past decade, both in homogeneous and heterogeneous catalysis. Since nanoparticles have a large surface-to-volume ratio compared to bulk materials, they are attractive candidates for use as catalysts.

In homogeneous catalysis, transition metal nanoparticles in colloidal solutions are used as catalysts. In this type of catalysis, the colloidal transition metal nanoparticles are finely dispersed in an organic or aqueous solution, or a solvent mixture.

Common Synthesis Methods for Colloidal Nanoparticles

The colloidal nanoparticle solutions must be stabilized in order to prevent aggregation of the nanoparticles and also to be good potential recyclable catalysts. Metal colloids are very efficient catalysts because a large number of atoms are present on the surface of the nanoparticles. The method that is used in synthesizing transition metal nanoparticles in colloidal solutions is very important for catalytic applications. The reduction method employed controls the size and the shape of the transition metal nanoparticles that are formed, which are very important in catalytic applications.

Applications of Nanotechnology in food industry

Nanomaterials are well designed as colour or flavour additives, preservatives, or carriers for food supplement (i.e. nanoencapsulation and nano emulsion), including animal feed products. The unique properties of engineered nanomaterials offer great advantages for food processing as ingredients or supplement. Additionally, inorganic oxide chemicals such as SiO₂ (E551), MgO (E530), and TiO₂ (E171) are permitted by the U.S. FDA as anti-caking agent, food flavour carrier, and food colour additives. For instance, TiO₂ is widely used as additive in foods such as gum, white sauces, cake icing, candy and puddings [19]. Current authorizations on the chemicals for food processing are all based on conventional particle size, except carbon black (authorized by EC 10/2011 but no longer authorized by the U.S. FDA) and titanium nitride. However, it is common to detect those chemicals used in foods in nanometre scale.

In addition to food products directly serving human beings, animal feeds play a significant role in the global food industry, ensuring economic and safe production of animal products throughout the world. Copper oxide, iron oxide, and zinc oxide now have been categorized as "generally recognized as safe" (GRAS) by the U.S. FDA as nutritional dietary supplement in animal feeds. The European Food Safety Authority (EFSA) Panel on Additives and Products or Substances used in Animal Feed (FEEDAP Panel) also concludes

the use of decapper oxide (Cu_2O or copper(I) oxide) as nutritional supply for all animal species is of no concern for consumer safety .

Food packaging

Food contact materials are intended to directly contact food products during manufacturing, transportation, and storage. Nanotechnology as novel solution now has been widely studied and developed for food packaging in food industry . Nanomaterials designed for food packaging possess many advantages when compared to conventional packaging materials. Among many novel nanomaterials, nano clay is one of the most widely used and studied for food packaging due to their mechanical, thermal, and barrier properties, and low cost. For instance, 1 wt % bentonite clay/poly (vinyl alcohol) loaded nanocomposite membrane significantly enhanced permeance with a water permeance of 6500 gpu and a selectivity value of 46.

Another study from showed 3% nano clay loaded woven carbon fibre /compatibilized polypropylene nanocomposites significantly improved interlaminar fracture toughness and elevated glass transition temperature increased by about 6 °C [24]. Additionally, significant enhancement of corrosion resistance was reported for epoxy/clay nanocomposites Nano clays are developed into several subclasses including montmorillonite, bentonite, kaolinite, hectorite, and halloysite, depending on the physiochemical properties of the nanomaterials. Montmorillonite and bentonite are now listed as GRAS and in Effective Food Contact Substance (FCS) notifications by the U.S. FDA. FCS acts as the U.S. FDA effective premarket notifications for food contact substances that have been demonstrated to be safe for their intended use. However, recent reports indicate potential migration risks associated with nano clay packaging

Applications of Nanotechnology in food industry

In agriculture, nanotechnology is employed to increase food production, with equivalent or even higher nutritional value, quality and safety. Efficient use of fertilizers, pesticides, herbicides and plant growth factors/regulators are the most important ways to improve crop production. Controlled release of pesticides, herbicides and plant growth regulators can be achieved via the usage of nanocarriers. For instance, poly (epsilon-caprolactone) Nano capsules have been recently developed as herbicide carrier for atrazine.

The treatment of mustard plants (*Brassica juncea*) with atrazine loaded poly (epsilon-caprolactone) Nano capsules enhanced the herbicidal activity compared to commercial atrazine, showing a drastic decrease in net photosynthetic rates and stomatal conductance, a significant increase of oxidative stresses, and ultimately weight loss and growth reduction of tested plants . Similarly, other nanocarriers like silica NPs [52] and polymeric NPs have also been developed as modified release system to deliver pesticides in a controlled manner. Nanoscale carriers can be utilized to perfectly achieve the delivery and slow release of these species. Such strategies are known as “precision farming” that improves crop yields but not damage soil and water.

Most importantly, application of nanoencapsulation can lower dosage of the herbicide, without any loss of efficiency, which benefits environment. In addition to nanocarriers, nanoparticle-mediated gene or DNA transfer in plants was used to develop insect-resistant varieties. More details can be found in previously published reviews]. Moreover, certain nanomaterials per se can act as pesticides with enhanced toxicity and sensitivity. Metal oxide nanomaterials like ZnO , TiO_2 , and CuO are widely studied to protect plant from pathogen infections owing to their intrinsic toxicity. We take ZnO NPs

as an example. It has been demonstrated that ZnO NPs can effectively inhibit growth of microbes such as *Fusarium graminearum*, *Aspergillus flavus* [58], *Aspergillus niger* [58], *Aspergillus fumigatus*.

Applications of Nanotechnology in cosmetics

Nanotechnology incorporation in cosmetic formulation is considered as the hottest and emerging technology available. Cosmetic manufacturers use nanoscale size ingredients to provide better UV protection, deeper skin penetration, long-lasting effects, increased color, finish quality, and many more. Micellar nanoparticles is one of the latest field applied in cosmetic products that becoming trending and widely commercialized in local and international markets. The ability of nano emulsion system to form small micellar nanoparticles size with high surface area allowing to effectiveness of bioactive component transport onto the skin. Oil in water nano emulsion is playing a major role as effective formulation in cosmetics such as make-up remover, facial cleanser, anti-aging lotion, sun-screens, and other water-based cosmetic formulations. The objective of this review is to critically discuss the properties, advantageous, and mechanism of micellar nanoparticles formation in nano emulsion system. Therefore, present article introduce and discuss the specific benefits of nano emulsion system in forming micellar nanoparticles for cosmetic formulation which become major factors for further development of micellar-based cosmetic segments.

Applications of Nanotechnology in consumer goods

Nanoparticles are now being used in the manufacture of scratchproof eyeglasses, crack-resistant paints, anti-graffiti coatings for walls, transparent sunscreens, stain-repellent fabrics, self-cleaning windows and ceramic coatings for solar cells. Nanoparticles can contribute to stronger, lighter, cleaner and “smarter” surfaces and systems. At the nanoscale, the properties of particles may change in unpredictable ways. Nanoparticles of titanium oxide used in sunscreens, for example, have the same chemical composition as the larger white titanium oxide particles used in conventional products for decades, but nanoscale titanium oxide is transparent. Antimony - tin oxide provides another example since nanoparticles of this oxide are incorporated into a coating to provide scratch-resistance and offer transparent protection from ultra-violet radiation, not seen with larger size particles.

There are several safety concerns in the automotive sector relating to nanotechnology. Nanoparticles as fillers in tyres can improve adhesion to the road, reducing the stopping distance in wet conditions. The stiffness of the car body can be improved by use of nanoparticle-strengthened steels. New sol-gel deposition methods make it possible to apply, economically, nanometre thick antireflection layers of silicon dioxide or other materials onto displays or panes. Ultra-thin transparent layers on a silver base can be used for eatable, and therefore mist and ice-free, window panes. Transparent and light materials could substitute car body parts that reduce all-round vision at the moment.

Applications of Nanotechnology in Structure and Engineering

Nanotechnology has the potential to make construction faster, safer, cheaper and more varied, resulting in smart construction. Automation of nanotechnology construction can allow for the creation of structures from advanced homes to gigantic skyscrapers much more quickly and at much lower cost and higher efficiency. In the near future, Nanotechnology can be used to sense cracks in foundations of structures and can send

nanobots to repair them. It can also provide self-powered failure prediction and prewarning mechanisms for high capital structures.

This paper explores the vision in making of smart and innovative infrastructure and leading a smart city with the help of application of nanotechnology in civil structures. The study of nanoscience and various nanoparticles and their implementation in construction field is illustrated in this paper. The article further emphasizes more on the futuristic demand and application of nanotechnology in constructing smart structures. The paper is managed to be written in simple language for easy grasping.

Development of structural engineering, daring structures with record spans or heights, meets two serious obstacles—the limitations of traditionally used materials and the need of continuous monitoring of new structures subjected to complex loads, including those of dynamic nature. Considering the responsibility for the life of people and the budget of new structures, the need of constant monitoring is inevitable. This is why structural engineers seek for new solutions; among them, smart structures based on self-monitoring materials seem to be one of the most attractive proposals.

It is still an unexplored area, but current research shows a high potential of the use of composites reinforced by carbon-based nanomaterials as self-sensing structural materials. Nanomaterials also influence other important features of structural materials, such as microstructure, mechanical, and transport-related properties. In this chapter, we present the state of art of the use of nanomaterials in structural engineering in various areas including mechanical and electrical properties as well as issues referring to durability.

Applications of Nanotechnology in Automotive Industry

Nanotechnology will play a major role in the car industry; but don't hold your breath to see anything like the Volkswagen Nano Spyder futuristic concept car anytime soon. This entrance to the 2006 Los Angeles Design challenge was supported by hydrogen fuel cells, solar power, wheel-mounted electric motors and inflatable organic body panels combine to form the unusual shape of the two-seater concept.

Nanotechnology – the creation and use of devices and machines on almost an atomic level – is likely to be the driving force behind the next great revolution to benefit humankind. The actual definition of nanotechnology can be quite broad, generally, in scientific and engineering terms, nanotechnology is the manipulation of matter with at least one dimension sized from 1 to 100 nanometers (0.000000001 m). That really does put it on an atomic scale, though the products that can be constructed in this way may be a little larger and can range from microscopic to anything under a millimetre.

While this kind of technology will have applications in many fields, there are likely to be huge advantages in the field of cars and motoring and in the near future, nanotechnology is likely to have a massive impact on the world of driving and vehicles.

It is a fact that nanotechnology can impact so many areas of motoring makes it one of the most important up and coming technologies, and it has attracted the attention of a great number of researchers. This has led to a growing number of breakthroughs in the field, and even more possibilities for this exciting and highly flexible area of science to push different fields of motoring forward. But where is nanotechnology having the greatest influence in car manufacture

We ask a lot of our internal combustion engines in terms of both increased performance and decreased size and weight. Those two elements together would usually mean disaster for a high-performance engine, but nano-engineering has allowed us to do both, and safely. Engine blocks, which house the fundamental moving parts of the mechanism, were traditionally made of cast iron, because it was the only practical material that could resist the high temperatures and pressures that were produced in the heart of an engine. But engineers soon found that certain grades of aluminium – which weighs around a third that of cast iron – were found to be suitable too.

But now, engineers have learned how to manipulate aluminium's on an atomic level – nanoengineering – to create materials that are both stronger while being more lightweight than even the current batch of strong aluminium alloys. This makes them even more fuel efficient while having an increased durability, even in the increasingly hostile conditions found in modern engines. It is a fact that an internal combustion engine performs better and is more efficient at higher temperatures, so this is always a goal for engine designers. We are now also experiencing methods of placing ultra-thin layers of engineering ceramics on metal substrates, creating a surface that is capable of withstanding higher temperatures and wear situations.

Manipulation of either the fundamental structure of the engine block material, or the surface architecture – or both, even – gives designers far greater scope in heat dissipation, wear characteristics, and strength at elevated temperatures. We have also seen advances in motor oils, particularly in respect to their ability to withstand the punishing environments of modern engines. Nano-manipulation has created a new breed of oils that are able to cling to internal surfaces for longer, meaning that it is in the right place when the engine starts, so that it offers protection right from the start. Nanotechnology oils are also able to put up with much greater use as the tolerances between engine parts decreases and they operate closer together.

Applications of nanotechnology in water treatment

The industrial contamination, along with domestic effluents, agricultural and urban runoff are contaminating rivers and making it difficult for conventional water treatment to remove all the pollutants. This contamination can impact in the quality of rivers, in the quality of life of aquatic animals and can impact in the human health through the consumption of water. In order to improve the water quality, nanotechnology has been studied as an alternative to better remove contaminants, such as, heavy metals, oily water separation and antimicrobial activity. Besides, with the increase in industrialization along with the contamination of rivers, seawater could be an interesting alternative for drinking water source after adequate treatment. Nanomaterials are being studied as a possibility to remove salt from seawater, making it possible to drink. However, there is a need to elucidate the potential risks to the environment that these nanomaterials can cause. Therefore, the aim of this review is to describe some applications of nanotechnology in water treatment regarding metals, oil removal from water, antimicrobial activity and desalination in order to improve water quality, as well, as discuss their potential risk to the environment.

Applications of Nanotechnology in environment

Nanotechnology has enormous potential for providing innovative solutions to a wide range of environmental issues. These include improved methods for reducing pollution, water treatment, environmental sensing, remediation, and making alternative energy sources more cost-effective. The unique properties of engineered nanomaterials enable these novel technologies for meeting the environmental challenges in a sustainable way. This review broadly focuses on the environmental applications of engineered nanomaterials in a sustainable approach and also emphasizes the future opportunities for their application in the natural environmental systems.

Generating less pollution during the manufacture of materials. One example of this is how researchers have demonstrated that the use of silver nanoclusters as catalysts can significantly reduce the polluting by-products 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.

Producing solar cells that generate electricity at a competitive cost. Researchers have demonstrated that an array of silicon nanowires embedded in a polymer results in low cost but high efficiency solar cells. This, or other efforts using nanotechnology to improve solar cells, may result in solar cells that generate electricity as cost effectively as coal or oil. 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.

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.

Cleaning up oil spills. Using photocatalytic copper tungsten oxide nanoparticles to break down oil into biodegradable compounds. The nanoparticles are in a grid that provides high surface area for the reaction, is activated by sunlight and can work in water, making them useful for cleaning up oil spills. Clearing volatile organic compounds (VOCs) from air. Researchers have demonstrated a catalyst that breaks down VOCs at room temperature. The catalyst is composed of porous manganese oxide in which gold nanoparticles have been embedded.

Reducing the cost of fuel cells. Changing the spacing of platinum atoms used in a fuel cell increases the catalytic ability of the platinum. This allows the fuel cell to function with about 80% less platinum, significantly reducing the cost of the fuel cell. Storing hydrogen for fuel cell powered cars. Using graphene layers to increase the binding energy of hydrogen to the graphene surface in a fuel tank results in a higher amount of hydrogen storage and a lighter weight fuel tank. This could help in the development of practical hydrogen-fuelled cars.

Applications of Nanotechnology in nano medical

The use of nanotechnology in medicine offers some exciting possibilities. Some techniques are only imagined, while others are at various stages of testing, or actually being used today. Nanotechnology in medicine involves applications of nanoparticles currently under development, as well as longer range research that involves the use of

manufactured nano-robots to make repairs at the cellular level (sometimes referred to as nanomedicine).

Whatever you call it, the use of nanotechnology in the field of medicine could revolutionize the way we detect and treat damage to the human body and disease in the future, and many techniques only imagined a few years ago are making remarkable progress towards becoming realities. [Nanotechnology in Medicine Application: Drug Delivery](#). 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 allows direct treatment of those cells. This technique reduces damage to healthy cells in the body and allows for earlier detection of disease.

For example researchers at North Carolina State University are developing a method to deliver cardiac stem cells to damaged heart tissue. They attach nanovesicles that are attracted to an injury to the stem cells to increase the amount of stem cells delivered to an injured tissue. [Read more about nanomedicine in drug delivery](#). [Nanotechnology in Medicine Application: Diagnostic Techniques](#) Researchers John Hopkins University are using nanoimprint lithography to manufacture a sensor that can detect covid-19 and other viruses that can be used with hand held testing device for quick results.

Researchers at Worcester Polytechnic Institute are using antibodies attached to carbon nanotubes in chips to detect cancer cells in the blood stream. The researchers believe this method could be used in simple lab tests that could provide early detection of cancer cells in the bloodstream. A test for early detection of kidney damage is being developed. The method uses gold nanorods functionalized to attach to the type of protein generated by damaged kidneys. When protein accumulates on the nanorod the colour of the nanorod shifts. The test is designed to be done quickly and inexpensively for early detection of a problem.

[Nanotechnology in Medicine Application: Antibacterial Treatments](#) Researchers at the University of Houston are developing a technique to kill bacteria using gold nanoparticles and infrared light. This method may lead to improved cleaning of instruments in hospital settings. Researchers at the University of Colorado Boulder are investigating the use of quantum dots to treat antibiotic resistant infections. [Nanotechnology in Medicine Application: Wound Treatment](#) Researchers at the University of Wisconsin have demonstrated a bandage that applies electrical pulses to a wound using electricity produced by nanogenerators worn by the patient.

For trauma patients with internal bleeding another way to reduce the blood loss is needed. Researchers at Chase Western Reserve University are developing polymer nanoparticles that act as synthetic platelets. Lab tests have shown that injection of these synthetic platelets significantly reduces blood loss. [Read more about nanomedicine wound treatments](#). [Nanotechnology in Medicine Application: Cell Repair](#) Nanorobots could actually be programmed to repair specific diseased cells, functioning in a similar way to antibodies in our natural healing processes. [Read about design analysis for one such cell repair nanorobot in this article: The Ideal Gene Delivery Vector: Chromalloy, Cell Repair Nanorobots for Chromosome Repair Therapy](#)

Applications of nanotechnology in textile industry

Nanotechnology is a growing interdisciplinary technology often seen as a new industrial revolution. Nanotechnology (NT) deals with materials 1 to 100 nm in length. The fundamentals of nanotechnology lie in the fact that the properties of materials drastically change when their dimensions are reduced to nanometre scale. Nowadays also the textile industry has discovered the possibilities of nanotechnology. So, we can define nanotechnology in textile as the understanding, manipulation, and control of matter at the above-stated length, such that the physical, chemical, and biological properties of the materials (individual atoms, molecules, and bulk matter) can be engineered, synthesized, and altered to develop the next generation of improved materials, devices, structures, and systems. It is used to develop desired textile characteristics, such as high tensile strength, unique surface structure, soft hand, durability, water repellence, fire retardancy, antimicrobial properties, and the like.

Modern Application of Nanotechnology in Textile Industry:

Nanotechnology is increasingly attracting worldwide attention because it is widely perceived as offering huge potential in a wide range of end uses. The unique and new properties of nano materials have attracted not only scientists and researchers but also businesses, due to their huge economical potential.

Nanotechnology also has real commercial potential for the textile industry. This is mainly due to the fact that conventional methods used to impart different properties to fabrics often do not lead to permanent effects, and will lose their functions after laundering or wearing. Nanotechnology can provide high durability for fabrics, because nano-particles have a large surface area-to-volume ratio and high surface energy, thus presenting better affinity for fabrics and leading to an increase in durability of the function. In addition, a coating of nano-particles on fabrics will not affect their breath ability or hand feel.

Applications of nanotechnology in paints industry

Nanomaterials are thought to improve these functionalities, i.e. water/dirt repellent “easy to clean”, UV-protection, antimicrobial resistance, scratch resistance or extending the paints’ lifespan. Nanomaterials in paints Nanomaterials are expected to improve the existing properties of paints due to their specific structural characteristics such as size, shape and greater surface area.

Currently, the most relevant nanomaterials for the paint industry are nanoscale titanium dioxide and silicon dioxide; but silver, zinc oxide, aluminium oxide, cerium dioxide, copper oxide, and magnesium oxide are also under investigation. The table provides an overview of potential functional benefits by integrating nanomaterials into the paints. Depending on the type of paint and the desired functionality, nanomaterials can be integrated as free powders, as stabilised particles in a suspension/dispersion or incorporated into master batches or granulate resulting in the nanomaterial being firmly embedded in the paint matrix.

There also exist paints or products that have a nanostructured surface, contain nano porous materials or temporarily contain nanostructured particles (e.g. produced from water glass during the drying of the paint). As these end products do not contain any nanomaterial, they are considered to pose no nano-specific risk to humans or the environment. Effects of nanomaterials in paints Nano titanium dioxide is used in paint to exploit two of its excellent properties: (i) photocatalytic activity and (ii) UV-protection. The combination of the photocatalytic effect, along with hydrophilic properties results in a

paints' self-cleaning effect. The surface will no longer need regular cleaning as the water and dirt will no longer stick on it. However, studies have shown that the use of photocatalytic nano titanium dioxide in organic paints leads to the degradation of the binder by UV irradiation. For this reason, the rutile type is preferred in organic facade coatings for UV-protection.

The addition of nano silicon dioxide to paints can improve the macro- and micro-hardness, abrasion, scratch and weather resistance. Adding nano silicon dioxide to polymeric resins creates paints with excellent abrasion properties. However, it decreases the elasticity of the paints, which is needed to resist the swelling and shrinking associated with temperature and humidity changes. Surfaces coated with nano silver containing paint provide excellent antimicrobial properties against bacteria and human pathogens. However, in contrast to indoor paint, the bactericidal efficiency of nano silver in paints for outdoor application seems to be insufficient due to the exposure to external conditions. Studies have shown that nano silver as well as nano titanium dioxide, are not able to fully prevent microbial and algal growth on test substrates in addition to being a poor deterrent from possible fungal colonisation.

Applications of nanotechnology in energy industry

Energy is of great importance in human life because of its benefits as the main resource for human activity. According to International Energy Agency (IEA), energy demands are expected to continue increasing until 2030. Because energy demand will never decrease, it is necessary to develop modern technology, such as nano based technology, in order to obtain a more effective and efficient process to produce more energy. The application of nano technology or nano material in the field of energy, which involves lithium-ion battery, fuel cell, light emitting diode (LED), ultra-capacitor, and solar cell (including Grätzel cell), is a hot topic in many scientific researches. Unfortunately, its current development is hampered by the expensive cost of production compared to conventional technologies. Therefore, priority should be given to nano technology in the energy sector order to obtain higher efficiency, lower production cost, and easier in its application.

Applications of nanotechnology in defence

Currently, most militaries of the advanced countries are utilizing nanotechnology in research, projects, and applications. Nanotechnology can provide the army with stronger and lighter ware, supports nanomedicines and bandages for wound healing, and stops bleeding, silver-packed foods as antibacterial and antiviral, gas and biological sensing. Despite this progress and improvement in nanotechnology, this technology has certain risks when manufactured or even when applied and disposed of. In this chapter, a comprehensive view of potential military applications of nanotechnology has been addressed. It also highlighted the potential applications of the cutting-edge developments of nanotechnology in defence. Protection armours, invisibility ware, fuel economy, lighter and stronger craft/ships/vehicles manufacturing, and radar undetected planes and submarines by electromagnetic camouflage are the most focused applications in nanotechnology to developed Marin, Air force, and even battlefield army.

Applications of nanotechnology in space

Nanotechnology may hold the key to making space flight more practical. Advancements in nanomaterials make lightweight solar sails and a cable for the space elevator possible. By significantly reducing the amount of rocket fuel required, these advances could lower the cost of reaching orbit and traveling in space. In addition, new

materials combined with Nanosensors and nanorobots could improve the performance of spaceships, spacesuits, and the equipment used to explore planets and moons, making nanotechnology an important part of the 'final frontier.' High-strength low-weight composites, advanced electronics, and screens with low power consumption, a range of physical sensors, multipurpose materials with embedded sensors, large surface materials, and modern air purification filters and membranes are among the aerospace applications for nanotechnology.

Concerns of Nanotechnology

Although most of the press coverage has been on the dangers of 'nano-goo' such as self-replicating particles that get out of control, or 'nano-robots', the real risks are much more simple, and real. The miniature size of nanomaterials and the way their surfaces are modified to increase the ease with which they can interact with biological systems - the very characteristics that make them attractive for applications in medicine and industry - makes nanomaterials potentially damaging for humans and the environment.

Nanoparticles are likely to be dangerous for three main reasons:

Nanoparticles may damage the lungs. We know that 'ultra fine' particles from diesel machines, power plants and incinerators can cause considerable damage to human lungs. This is both because of their size (as they can get deep into the lungs) and also because they carry other chemicals including metals and hydrocarbons in with them. Nanoparticles can get into the body through the skin, lungs and digestive system. This may help create 'free radicals' which can cause cell damage and damage to the DNA. There is also concern that once nanoparticles are in the bloodstream they will be able to cross the blood-brain barrier.

The human body has developed a tolerance to most naturally occurring elements and molecules that it has contact with. It has no natural immunity to new substances and is more likely to find them toxic. The danger of contact with nanoparticles is not just speculation. As more research is undertaken, concerns increase. Here are some of the recent findings: some nanoparticles cause lung damage in rats. Several studies have shown that carbon nanotubes, which are similar in shape to asbestos fibres, cause mesothelioma in the lungs of rats other nanoparticles have been shown to lead to brain damage in fish and dogs German study found clear evidence that if discrete nanometre diameter particles were deposited in the nasal region (in rodents in this case), they completely circumvented the blood/brain barrier, and travelled up the olfactory nerves straight into the brain inhaled carbon nanotubes can suppress the immune system by affecting the function of T cells, a type of white blood cell that organises the immune system to fight infections.

Challenges of Nanotechnology.

The most tremendous challenges in Nanotechnology are materials and properties about Nanoscale. At present, nanotechnology has been widely applied to the area of drug development. Some Nanoparticles could be toxic. The Nanoparticles are small, which will cross the blood-brain barrier, a membrane that protects the brain from poisonous chemicals in the bloodstream. It has 3D structures requires to design and manufacturing process to achieve a consistent product. Nanosized products like transistors and nanowires. Rapid DNA sequencing, Single-stranded genomic DNA or RNA, Organic and Inorganic Nano composites, Safety and Risk Assessment of Nanotechnology