UNIT -1

NANOTECHNOLOGY

1. Introduction

The prefix nano in the word nanotechnology means a billionth ($1x10^{-9}$). Nanotechnology deals with various structures of matter having dimensions of the order of billionth of a meter. While the word nanotechnology is relatively new, the existence of functional devices and structures of nanometer dimensions is not new, and in fact such structures have existed on Earth as long as life itself. The abalone, a mollusk, constructs very strong shells having irrridescent inner surface by organizing calcium carbonate into strong nanostrucutred bricks held together by a glue made of a carbohydrate-protein mix. Cracks initiated on the outside are unable to move through the shell because of the nanostructured bricks. The shells represent a natural demonstration that a structure fabricated from nanoparticle can be much stronger.

2. Historical Developments

- In the fourth-century A.D Roman glassmakers were fabricating glasses containing nanosized metals. An artifact from this period called the Lycurgus cup resides in the British Museum in London. The cup, which depicts the death of King Lycurgus, is made from soda lime glass containing silver and gold nanoparticles. The color of the cup changes from green to deep red when a light source is placed inside it. The great varieties of beautiful colors of the windows of medieval cathedrals are due to the presence of metal nanoparticles in the glass.

- Photography is an advanced and mature technology, developed in the eighteenth and nineteenth centuries, which depends on production of silver nanoparticles sensitive to light. Photographic films is an emulsion, a thin layer of gelatin containing silver halides, such as silver bromide, and a base of transparent cellulose acetate. The light decomposes the silver halides, producing nanoparticles of silver, which are the pixels of the image.

- In 1857, Michael Faraday published a paper in the Philosophical Transactions of the Royal Society, which attempted to explain how metal particles affect the color of church windows. Gustav Mie was the first to provide an explanation of the dependence of the color of the glasses on metal size and kind. His paper was published in the German Journal Annalen der Physik in 1908.

- Richard Feynman was awarded the Nobel Prize in physics in 1965 for his contributions to quantum electrodynamics. In 1960 he presented a visionary and prophetic lecture at a meeting of the American Physical Society, entitled “There is Plenty of Room at the Bottom”, where he speculated on the possibility and potential of nanosized materials. He envisioned etching lines a few atoms wide with beams of electrons, effectively predicting the existence of electron-beam lithography, which is used today to make silicon chips. He proposed manipulating individual atoms to make new small structures having very different properties. He envisioned building circuits on the scale of nanometers that can be used as elements in more powerful computers. He also recognized the existence of nanostructures in biological systems. Many of Feynman’s speculations have become reality. However, his thinking did not resonate with scientists at the time.

- There were other visionaries. Ralph Landauer, a theoretical physicist working or IBM in 1957, had idea on nanoscale electronics and realized the importance that quantum-mechanical effects would play in such devices. Uhlir reported the first observation of porous silicon in 1956, but it was not until 1990 when room temperature fluorescence was observed in this material that interest grew. Other work in this era involved making alkali metal nanoparticles by vaporizing sodium or potassium metal and then condensing them on cooler materials called substrates. Magnetic fluids called ferrofluids were developed in the 1960s. They consist of nanosized magnetic particles dispersed in liquids. The particles were made by ballmilling in the presence of a surface-active agent and liquid carrier. Another area of activity in the 1960s involved electron paramagnetic resonance (EPR) of conduction electrons in metal particles of nanodimensions referred to as colloids. Structural features o metal nanoparticles such as existence of magic numbers were revealed in the 1970s using mass spectroscopic studies of sodium metal beams. Group at Bell Laboratories and IBM fabricated the first two-dimensional quantum wells in the early 1970s. It was not until the 1980s with the emergence of appropriate methods of fabrication of nanostructures that a notable increase in research activity occurred, and a number of significant developments resulted.

- In 1981, a method was developed to make metal clusters using a high-powered focused laser to vaporize metals into a hot plasma. In 1985, this method was used to synthesize the fullerene (C60). In 1982, two Russian scientists, Ekimov and Omushchenko, reported the first observation of quantum confinement. The scanning tunneling microscope was developed during this decade by G.K. Bining and H. Roher of the IBM Research Laboratory in Zurich, and they were awarded Nobel Prize in 1986 for this. The invention of the scanning tunneling microscope (STM) and the atomic force microscope (AFM), provided new important tools for viewing, characterizing and atomic manipulation of nanostructures. This period was marked by development of methods of fabrication such as electron-beam lithography, which are capable of producing 10-nm structures. Also in this decade layered alternating metal magnetic and nonmagnetic materials, which displayed the fascinating property of giant magnetoresistance, were fabricated. The layers were a nanometer thick, and the materials have an important application in magnetic storage device in computers.

- In the 1990, Iijima made carbon nanotubes, and superconductivity and ferromagnetism were found in C60 structures. Efforts also began to make molecular switches and measure the electrical conductivity of molecules. A field-effect transistor based on carbon nanotubes was demonstrated. The study of self-assembly of molecules on metal surfaces intensified. Self-assembly refers to the spontaneous bonding of molecules to metal surfaces, forming an organized array of molecules on the surface. Self-assembly of thiol and disulfide compounds on gold has been most widely studied.

- In 1996, a number of government agencies led by National Science Foundation commissioned a study to assess the current worldwide status of trends, research and development in nanoscience and nanotechnology. Two general findings emerged from the study. The first observation was that materials have been and can be nanostructured for new properties and novel performance. The second observation of the U.S government study was a recognition of the broad range of disciplines that are contributing to developments in the field. These disciplines include physics, chemistry, biology and engineering (electrical, mechanical and chemical engineering). The interdisciplinary nature of the field makes it somewhat difficult for researchers in one field to understand and draw on developments in another area. To explore the potential of nanotechnology it is essential to know what are nanomaterials, how and why do they differ from other materials, how to synthesize/analyze the nanomaterials and organize them to apply in different areas.

3. Nanotechnology

- ***What is Nanotechnology?*** Broadly speaking however, nanotechnology is the act of purposefully manipulating matter at the atomic scale, otherwise known as the "nanoscale."

UNIT -1

Coined as "nano-technology" in a 1974 paper by Norio Taniguchi at the University of Tokyo, and encompassing a multitude of rapidly emerging technologies, based upon the scaling down of existing technologies to the next level of precision and miniaturization. Taniguchi approached nanotechnology from the 'top-down' standpoint, from the viewpoint of a precision engineer.

K. Eric Drexler introduced the term "nanotechnology" to the world in 1986, using it to describe a 'bottom-up' approach. Drexler approaches nanotechnology from the point-of-view of a physicist, and defines the term as "large-scale mechanosynthesis based on positional control of chemically reactive molecules."

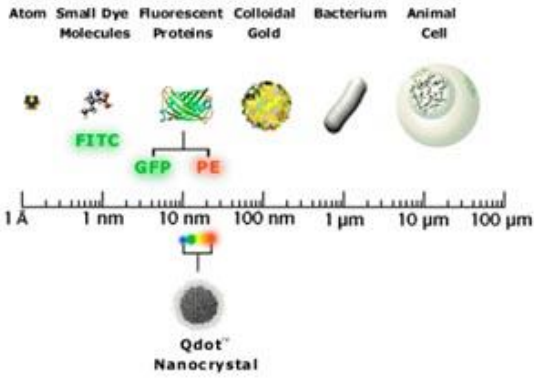
In the future, "nanotechnology" will likely include building machines and mechanisms with nanoscale dimensions, referred to these days as Molecular Nanotechnology (MNT). It uses a basic unit of measure called a "nanometer" (abbreviated ***nm***). Derived from the Greek word for midget, "nano" is a metric prefix and indicates a billionth part (10^{-9}).

There are one ***billion*** nm's to a meter. Each nm is only three to five ***atoms*** wide. They're small. Really small. ~40,000 times smaller than the width of an average human hair. (See How small is one-billionth of a meter?)

Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications. Encompassing nanoscale science, engineering and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale.

At the nanoscale, the physical, chemical, and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter. Nanotechnology R&D is directed toward understanding and creating improved materials, devices, and systems that exploit these new properties.

- **SIZE :** A *meter* is about the distance from the tip of your nose to the end of your hand (1 meter = 3.28 feet). One *thousandth* of that is a *millimeter*. Now take *one thousandth* of that, and you have a *micron*: a thousandth of a thousandth of a meter. Put another way: a *micron is a millionth of a meter*, which is the scale that is relevant to - for instance - building computers, computer memory, and logic devices. Now, let's go smaller, to the *nanometer*: A nanometer is one thousandth of a micron, and a thousandth of a millionth of a meter (a billionth of a meter). Imagine: *one billion nanometers in a meter*.



Another perspective: a **nanometer** is about the width of **six bonded carbon atoms**, and approximately 40,000 are needed to equal the width of an average human hair.

Another way to visualize a **nanometer**:

1 inch = 25,400,000 nanometers.

Red blood cells are ~7,000 nm in diameter, and ~2000 nm in height
White blood cells are ~10,000 nm in diameter
A virus is ~100 nm
A hydrogen atom is .1 nm
Nanoparticles range from 1 to 100 nm
Fullerenes (C60 / Buckyballs) are 1 nm
Quantum Dots (of CdSe) are 8 nm
Dendrimers are ~10 nm
DNA (width) is 2 nm
Proteins range from 5 to 50 nm
Viruses range from 75 to 100 nm
Bacteria range from 1,000 to 10,000 nm

- **Nanoscale features:** Nanomaterials are characterised at the nanometre scale in one, two or three dimensions, leading to quantum wells (e.g., thin films, layers, surface coatings), quantum wires (e.g., nanotubes, nanowires) or quantum dots (qdots), respectively. Nanoparticles with a diameter of less <100 nm are for example fullerenes, dendrimers and semiconductor quantum dots. The word quantum is associated with these three structures because profound changes in material properties emanate from the quantum mechanical nature of physics that rules the world in the ultra-small and where material properties no longer obey the classical macroscopic laws of physics. Materials can be scaled down many orders of magnitude from macroscopic to microscopic without any or little change in expected properties occurring. However, when the nanoworld is entered, characteristic changes are observed. For the time being no strict dimensional limits can be defined for this phenomenon. At the nanoscale, physics, chemistry, biology, material science, and engineering converge toward the same principles and tools. As a result, progress in nanoscience will have very far-reaching impact. The nanoscale is not just another step toward miniaturisation, but a qualitatively new scale. The change in behaviour is dominated in the first place by quantum mechanics, as mentioned above and is additionally attributable to material confinement in small structures, and the increase in surface area per volume (or mass unit). At the larger end of the nanometre scale other phenomena are crucial, such as surface tension and Brownian motion. Nanoscience is concerned with understanding these effects and their influence on material properties. Nanotechnology aims to exploit these effects to create structures, devices, and systems with novel properties and functions due to their size (The Royal Society & The Royal Academy of Engineering, 2004). In contrast to other key technologies, such as biotechnology, information and communication technology, nanotechnology is much less well-defined and well-structured. In fact, nanotechnology is immensely complex and covers multiple disciplines ranging from physics, chemistry, and biology to engineering disciplines.

  The Royal Society & The Royal Academy of Engineering (2004) definitions were given for nanoscience and nanotechnology:

  Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at larger scale.

  Nanotechnology is the design, characterisation, production and applications of structures, devices and systems by controlling shape and size at the nanometre scale.

UNIT -1

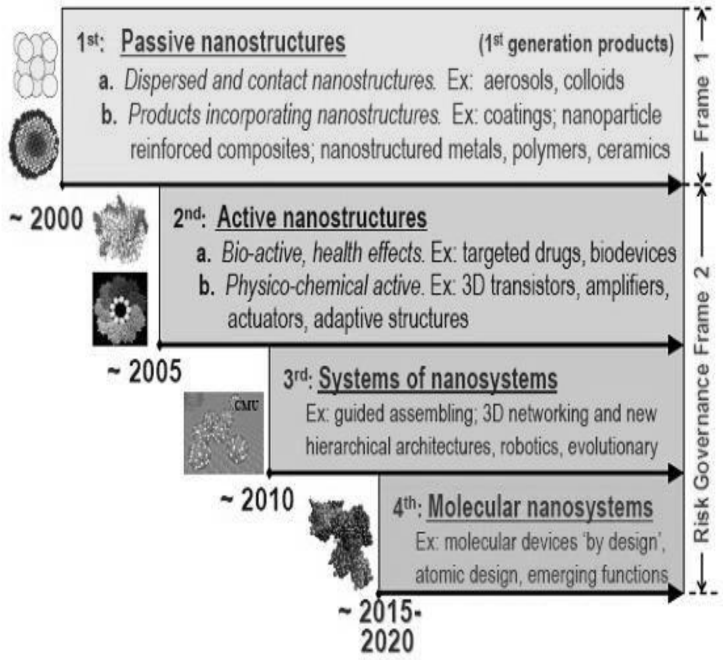
Nanobiotechnology is the unification of biotechnology and nanotechnology. This hybrid discipline can also mean making atomic-scale machines by imitating or incorporating biological systems at the molecular level, or building tiny tools to study or change natural structure properties atom by atom. Nanobiotechnology can have a combination of the classical micro-technology with a molecular biological approach. Biotechnology uses the knowledge and techniques of biology to manipulate molecular, genetic, and cellular processes to develop products and services, and is used in diverse fields from medicine to agriculture. Convergence, is an activity or trend that occurs based on common materials and capabilities-in this case the discipline that enables convergence is nanotechnology. The potential opportunities offered by this interface is truly outstanding; the overlap of biotech, nanotech and information technology is bringing to fruition many important applications in life sciences.

- Despite the apparent simplicity of definition, nanotechnology actually encompasses diverse lines of inquiry. Nanotechnology cuts across many disciplines, including colloidal science, chemistry, applied physics, materials science, and even mechanical and electrical engineering. It could variously be seen as an extension of existing sciences into the nanoscale, or as a recasting of existing sciences using a newer, more modern term.

  Related and interwoven fields include, but are not limited to: Nanomaterials, Nanomedicine, Nanobiotechnology, Nanolithography, Nanoelectronics, Nanomagnetics, Nanorobots, Biodevices (biomolecular machinery), AI, MEMS (MicroElectroMechanical Systems), NEMS (NanoElectroMechanical Systems), Biomimetic Materials, Microencapsulation, and many others.

- Two main approaches are used in nanotechnology: one is a "bottom-up" approach where materials and devices are built from molecular components which assemble themselves chemically using principles of molecular recognition; the other being a "top-down" approach where nano-objects are constructed from larger entities without atomic-level control. (i) Bottom-up approaches: These seek to arrange smaller components into more complex assemblies. DNA Nanotechnology utilises the specificity of Watson-Crick basepairing to construct well-defined structures out of DNA and other nucleic acids. More generally, molecular self-assembly seeks to use concepts of supramolecular chemistry, and molecular recognition in particular, to cause single-molecule components to automatically arrange themselves into some useful conformation. (ii)Top-down approaches: These seek to create smaller devices by using larger ones to direct their assembly. Many technologies descended from conventional **solid-state silicon methods** for fabricating microprocessors are now capable of creating features smaller than 100 nm, falling under the definition of nanotechnology. Giant magnetoresistance-based hard drives already on the market fit this description, as do atomic layer deposition (ALD) techniques. Solid-state techniques can also be used to create devices known as **nanoelectromechanical systems** or NEMS, which are related to microelectromechanical systems or MEMS. Atomic force microscope tips can be used as a nanoscale "write head" to deposit a chemical on a surface in a desired pattern in a process called **dip pen nanolithography**. This fits into the larger subfield of nanolithography. (iii) Functional approaches: These seek to develop components of a desired functionality without regard to how they might be assembled. **Molecular electronics** seeks to develop molecules with useful electronic properties. These could then be used as single-molecule components in a nanoelectronic device. For example rotaxane. Synthetic chemical methods can also be used to create **synthetic molecular motors**, such as in a so-called nanocar.

- **Four Generations:** Mihail (Mike) Roco of the U.S. National Nanotechnology Initiative has described *four generations* of nanotechnology development (see chart below). The current era, as Roco depicts it, is that of passive nanostructures, materials designed to perform one task. The second phase, which we are just entering, introduces active nanostructures for multitasking; for example, actuators, drug delivery devices, and sensors. The third generation is expected to begin emerging around 2010 and will feature nanosystems with thousands of interacting components. A few years after that, the first integrated nanosystems, functioning (according to Roco) much like a mammalian cell with hierarchical systems within systems, are expected to be developed



- Many scientists and technologists believe that nanoscience will provide the basis for an industrial revolution in the 21st century that will have an impact on the health, wealth, and security of the world's people as significant as the combined influence of antibiotics, integrated circuits, and human made polymers. Already, impressive examples demonstrate the potential impact of nanotechnology:
    - Carbon nanotubes have been shown to be ten times as strong as steel with one sixth of the weight and to exhibit semiconducting properties similar to silicon on the nanometer scale.
    - Nanoparticle-reinforced polymers, with lightweight and strong mechanical strength, improve fuel efficiencies and increase safety for transportation vehicles.
    - Molecular switches that could potentially improve computer storage capacity by a million times have been demonstrated.
    - Nanostructured silicates and polymers are used as effective contaminant scavengers for a cleaner environment.
    - New drugs made of nanoparticle powder have nearly ten times the bioavailability and faster response times compared with conventional drugs.

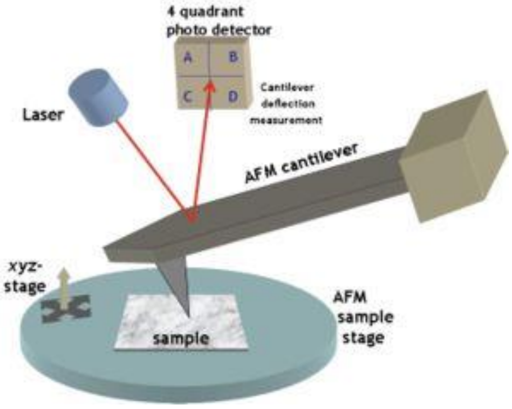
- Patterning of nanoporous surface texturing at the interface between medical implants and their biological substrates has provided a powerful new way to encourage tissue integration.

Examples of the impact on key industries include the following:

- Medical device industry with 300-500 large companies and small start-ups: to enable extreme miniaturization and the development of new types of products;
- High-tech materials and manufacturing industry: to enable the development of consumer and defense products based on new materials;
- Biotechnology industry: to enable the development of pharmaceutical products with highly controlled effects and the production of superior agricultural products;
- Data storage, information processing, and telecommunications industries: to produce highly advanced systems based on radically new technologies;
- Instrument and sensor industry: to enable the development of ultra-small sensors for process control and health diagnostics

4. Tools and techniques

Typical AFM setup. A microfabricated cantilever with a sharp tip is deflected by features on a sample surface, much like in a phonograph but on a much smaller scale. A laser beam reflects off the backside of the cantilever into a set of photodetectors, allowing the deflection to be measured and assembled into an image of the surface.



Another technique uses SPT™s (surface patterning tool) as the molecular “ink cartridge”. Each SPT is a microcantilever-based micro-fluidic handling device. SPTs contain either a single microcantilever print head or multiple microcantilevers for simultaneous printing of multiple molecular species. The integrated microfluidic network transports fluid samples from reservoirs located on the SPT through microchannels to the distal end of the cantilever. Thus SPTs can be used to print materials that include biological samples such as proteins, DNA, RNA, and whole viruses, as well as non-biological samples such as chemical solutions, colloids and particle suspensions. SPTs are most commonly used with molecular printers.

Nanotechnological techniques include those used for fabrication of nanowires, those used in semiconductor fabrication such as deep ultraviolet lithography, electron beam lithography, focused ion beam machining, nanoimprint lithography, atomic layer deposition, and molecular vapor deposition, and further including molecular self-assembly techniques such as those employing di-block copolymers.

However, all of these techniques preceded the nanotech era, and are extensions in the development of scientific advancements rather than techniques which were devised with the sole purpose of creating nanotechnology and which were results of nanotechnology research.

Nanoscience and nanotechnology only became possible in the 1910s with the development of the first tools to measure and make nanostructures. But the actual development started with the discovery of electrons and neutrons which showed scientists that matter can really exist on a much smaller scale than what we normally think of as small, and/or what they thought was possible at the time. It was at this time when curiosity for nanostructures had originated.

The atomic force microscope (AFM) and the Scanning Tunneling Microscope (STM) are two early versions of scanning probes that launched nanotechnology. There are other types of scanning probe microscopy, all flowing from the ideas of the scanning confocal microscope developed by Marvin Minsky in 1961 and the scanning acoustic microscope (SAM) developed by Calvin Quate and coworkers in the 1970s, that made it possible to see structures at the nanoscale. The tip of a scanning probe can also be used to manipulate nanostructures (a process called positional assembly). Feature-oriented scanning-positioning methodology suggested by Rostislav Lapshin appears to be a promising way to implement these nanomanipulations in automatic mode. However, this is still a slow process because of low scanning velocity of the microscope. Various techniques of nanolithography such as dip pen nanolithography, electron beam lithography or nanoimprint lithography were also developed. Lithography is a top-down fabrication technique where a bulk material is reduced in size to nanoscale pattern.

The top-down approach anticipates nanodevices that must be built piece by piece in stages, much as manufactured items are currently made. Scanning probe microscopy is an important technique both for characterization and synthesis of nanomaterials. Atomic force microscopes and scanning tunneling microscopes can be used to look at surfaces and to move atoms around. By designing different tips for these microscopes, they can be used for carving out structures on surfaces and to help guide self-assembling structures. By using, for example, feature-oriented scanning-positioning approach, atoms can be moved around on a surface with scanning probe microscopy techniques. At present, it is expensive and time-consuming for mass production but very suitable for laboratory experimentation.

In contrast, bottom-up techniques build or grow larger structures atom by atom or molecule by molecule. These techniques include chemical synthesis, self-assembly and positional assembly. Another variation of the bottom-up approach is molecular beam epitaxy or MBE. Researchers at Bell Telephone Laboratories like John R. Arthur. Alfred Y. Cho, and Art C. Gossard developed and implemented MBE as a research tool in the late 1960s and 1970s. Samples made by MBE were key to the discovery of the fractional quantum Hall effect for which the 1998 Nobel Prize in Physics was awarded. MBE allows scientists to lay down atomically-precise layers of atoms and, in the process, build up complex structures. Important for research on semiconductors, MBE is also widely used to make samples and devices for the newly emerging field of spintronics.

Newer techniques such as Dual Polarisation Interferometry are enabling scientists to measure quantitatively the molecular interactions that take place at the nano-scale.

5. Micro and Nanotechnologies

- Microtechnologies are related to micro manufacturing processes leading to miniaturized devices. It involves specific material and process technologies like micromachining or etching of layers staked for structuration with lithography techniques. First developed for automotive and IT applications, microsystems technologies are today a main miniaturisation approach for Life Science applications.

- Nanotechnologies are techniques allowing to synthesize, transform, measure, manipulate and assemble objects whose dimensions are less than or around 100 nanometers (nm) in order to work out special properties or functions like new mechanical, optical, electrical, magnetic, chemical and biological properties. Microtechnologies have first led to miniaturised solutions whose performances are today enhanced by nanotechnologies.
- Microtechnologies offer the advantages of miniaturisation to:
  - reduce cost by lowering sample volume and reagents used
  - enable faster analysis
  - enable high parallelisation
  - enable multiplex analysis
  - provide with higher accuracy
- While microtechnologies indeed bring the advantage of miniaturisation, nanotechnologies offer new physical, chemical and biological properties of materials at the nano scale:
  - Nanocoatings further expand microarrays applications by allowing the attachement of a broad range of probes
  - Nanotechnologies provide new surface to increase the biochips' sensitivity
  - Nanotechnologies make it possible to analyse interactions directly at the molecule level with sensors relying on conformational changes in biomolecules

4. Nanomachines and Nanodevices - MEMS/NEMS and BioMEMS/NEMS:

Nanotechnology research is aimed at developing tiny machines, devices having nanosized components, and nanosized molecules.

(a) Microelectromechanical systems (MEMSs): The extensive fabrication infrastructure developed for the manufacture of silicon integrated circuits has made possible development of machines and devices having components of micrometer dimensions. MEMS are also referred to as micro machines, or *Micro Systems Technology* (*MST*). MEMS generally range in size from a micrometer (a millionth of a meter) to a millimeter (thousandth of a meter). At these size scales, the standard constructs of classical physics do not always hold true. Due to MEMS' large surface area to volume ratio, surface effects such as electrostatics and wetting dominate volume effects such as inertia or thermal mass. Lithographic techniques combined with metal deposition processes, are used to make MEMS device. Microelectromechanical systems involve a mechanical response to an applied electrical signal, or an electrical response resulting from a mechanical deformation. The major advantages of MEMS devices are miniaturization, multiplicity, and the ability to directly integrate the devices into micoelectronics. Multiplicity refers to the large number of devices and designs that can be rapidly manufactured, lowering the price per unit item. Miniaturization has enabled the development of micrometer-sized devices The size of MEMS devices, which is comparable to electronic chips, allows their integration directly on the chip.

Microtechnologies or microsystems technologies (MST) are considered today as a main miniaturization and parallelization approach for Life Science applications.

• MST skills, associated materials and processes are indeed often of great interest to achieve new steps toward
– automation
– portability
– reduced cost by lowering sample volume and reagents use
– lower response delays
for many biological approaches.

(i) Fabrication:

MEMS can be defined as the combination of microsensors and/or microactuators and electronic devices integrated on a single chip. MEMS rely on the same technology that have given microelectronics devices. It consists in deposit and etch material layers to give them the shape and properties you need. The differences are that MEMS use a lot of different materials, and that due to the very large functions to be achieved, you can almost consider that there is one fabrication process per existing device.

Photolithography:

•The process of printing a given 2D pattern onto a thin film layer

•This is a photographic process that requires a photosensitive material “photoresist”, and a “mask”that permits exposure of only defined regions to the incident radiation

•After exposure, the PR can be then developed in a “developer” like the standard photographic process;

•3 main steps

1.Spin PR

2.Expose PR

3.Develop PR

•Positive or Negative Tone

1.PositivePR: This type of PR is removed (etched away) in the developer solution only in areas that have been exposed to UV radiation

2.NegativePR: This type of PR is hardened (and therefore cannot be removed) in the developer solution in areas that have been exposed to UV radiation.

Photoresist:

A polymer whose chemical properties change when it is exposed toincident radiation, typically UV light. Note that PR cannot be exposed to temperatures above about 200°C because it burns (note that this is a polymer like plastic).

•PR is typically in liquid form that can be spun onto a silicon wafer at speeds of a few thousand RPM’s. This spinning process creates a uniform film thickness in the range of 1-10’s of microns.

•After application, the PR is baked at 90-100°C to remove the solvents

•The PR is now ready to be exposed and developed.

(ii) Applications: Common applications of MEMS include:

- inkjet printers, which use piezoelectrics or bubble ejection to deposit ink on paper.
- accelerometers in modern cars for a large number of purposes including airbag deployment in collisions.
- MEMS gyroscopes used in modern cars and other applications to detect yaw; e.g. to deploy a roll over bar or trigger dynamic stability control.
- pressure sensors e.g. car tire pressure sensors, and disposable blood pressure sensors.
- Displays e.g the DMD chip in a projector based on DLP technology has on its surface several hundred thousand micromirrors.
- Optical switching technology which is used for switching technology and alignment for data communications, and is part of the emerging technology of smartdust. The motion-sensing controller in the Nintendo Wii video game system represents a popular consumer application of MEMS technology.

- Bio-MEMS applications in medical and health related technologies from Lab-On-Chip to MicroTotalAnalysis

- Microtechnology has made great strides in developing devices potentially useful for life science applications. Miniaturization of common biological techniques such as PCR and electrophoresis can result in more efficient processing. For example miniaturization improves electrophoretic analysis by reducing material usage, analysis space, and analysis time. Due to high surface to volume ratios at the microscale, Joule heating and temperature gradients are less problematic. This allows for higher voltages in shorter distances providing higher electric fields strengths resulting in faster separation time. Microtechnology has combined biological methods onto a single chip allowing for complete processing with minimal user interaction. This is particularly useful in "Lab-On-A-Chip" or point of care situations where resources are limited or the testing environment is less than ideal for sterile biological techniques. However despite the usefulness of these devices, few life science researchers are taking advantage of tools that have been developed. Microanalysis devices may be more efficient, but they can be cost prohibitive. One reason for this is virtually no commercial source exists for micro devices. Traditionally fabricated chips also require expensive MEMS (micro-electromechanical systems) cleanroom facilities or specialized equipment not available to most biological researchers. In addition, most chips do not contain a convenient method for sample collection, which may further discourage researchers from using the technology, as sample analysis after processing is often needed. Many devices developed also require complex or specialized equipment (specialized fittings, syringe pumps, etc) to operate and interface with the chip providing another barrier to life science researchers.

- **The impact of micro and nanotechnologies on drug discovery:** Microtechnologies have shown their high added value in supporting pharmaceutical R&D efforts, in improving the drug discovery process results, in proposing new and faster analysis possibilities while notably reducing the analysis cost. Micro and nanotechnologies will support pharmaceutical companies in their development strategy by providing solutions to:

    - Discover new drug candidates and therapeutic pathways
    - Reduce new therapies development time
    - Facilitate drugs launching with adapted delivery systems
    - Provide better treatment performances
    - Extend pharmaceutical products lifecycle thanks to innovative delivery systems.

  Miniaturised microtiter plate up to 1536 wells in combination with microdispensing systems (nl range up to pl) are examples of solutions provided in such objectives. Other good examples are microarrays, microsystems with tailored surface properties. They offer a high parallelization of analysis, leading to higher throughput and enhanced efficiency. They are the key solution to manage the high complexity level linked to molecular biology. This first microarray based on microtechnologies has successfully reached the market and is now becoming a gold standard in drug discovery both in academic and industrial research labs. It is produced by Affymetrix (US) with a process allowing the synthesis of nucleic acid probes on a glass wafer substrate. Some limits still remain especially in terms of sensitivity and reproducibility. Going a level forward, nanotechnologies are now entering the field to provide solutions for new biochips generation.

- **Microfluidic technology also improves drug discovery and development:** LabChip 3000 from Caliper Life Sciences (US) is a good example of microfluidics device. Recently Caliper Life Science announced that 12 of the top 15 pharmaceutical companies actively use Caliper systems in their discovery efforts, including AstraZeneca, Novartis and Vertex

Pharmaceuticals. Microtechnologies thus help scientists better predict which compounds will be successful drug candidates.

- **Micro and nanotechnologies in drug delivery**
  Micro and nanotechnologies are also showing a very high potential in drug delivery. Areas of high value addition are:
  • Facilitate drug launching with an adapted delivery system
  • Provides better treatment performances
  • Work in a non-invasive way
  • Be as small and compact as possible to be easily implanted in the body or portable for emergency tools
  • Extend pharmaceutical products lifecycle thanks to innovative delivery systems.

  Those miniaturization techniques have thus proven their added value in therapy through new generation medical devices. The commercialised product Respimat® Soft Mist™ Inhaler of Boehringer Ingelheim microParts for asthma or chronic obstructive pulmonary disease (COPD) treatment is a good example. Such device increases lung deposition by reducing side effects. Many developments are running in this field especially for implantable intelligent delivery systems with an actuation mode, allowing drug dispense with a specific dosing. For example ChipRX Inc (US) is working on the development of a Self Regulating Responsive Therapeutic System (figure 3). Future nanoparticles will act as the most suitable drug targeting system by providing treatment at the molecular level. They provide controlled drug release, reduce side effects, and make possible to deliver new drugs candidates not adapted to conventional delivery solutions.

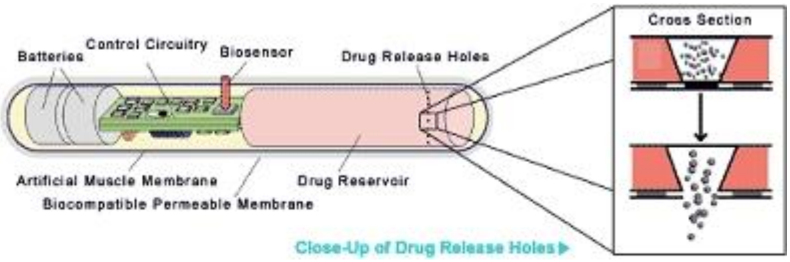


Figure - 3: ChipRX Self Regulating Respective Therapeutic System

(b) Bio-MEMS: After the commercialisation of MEMS (Micro Electro Mechanical Systems) in general, the fields of biology and medical care are about to create a new big market for micro systems. Biomedical applications mean both biotechnology and medical applications. The combination with micro system technologies is called BioMEMS, micro systems for biomedical applications. **(i) *In Vivo* applications:** Some essential requirements like small device dimensions, high reliability and durability, a high level of integration, and special durable biocompatible packages for *in vivo* MEMS devices can be derived. Despite of the last one, all these points would be fulfilled by classical silicon based micro systems or other established technologies (like microelectronics). For example implantable pressure sensors are being developed. Potential applications for such sensor implants will be the continuous monitoring of the pressure of blood, eyes or bladder. Other sensor developments with high impact are implantable glucose sensors for diabetes patients. These sensors would be able to monitor the glucose concentration in the blood in real-time, hence making self-testing several times a day unnecessary. This would bring a new standard of living for the increasing number of diabetes patients. However, a challenge for the usage of micro systems in these applications is that sensors as well as actuators have to have direct contact with the human body. Thus, “encapsulation” of the sensor by cells or degradation of the sensing surface layer is one of the biggest problems to be solved. At present, subcutaneous implantation of the glucose sensors seems to be the most promising alternative. From this simple example it can be seen, that biocompatible packaging issues are one of the most challenging problems for the *in vivo* application of micro systems. Solving these problems can be the necessary impulse needed for commercialization of a great variety of micro systems for *in vivo* applications. Therefore,strong interdisciplinary research in the area of biocompatible packaging is necessary. Once these problems have been overcome, future developments will combine these sensor technologies with micro scaled actuators like drug delivery systems. Larger implantable systems, especially for insulin dosage are already available on the market.

(ii) ***In Vitro*** **applications:** The same kinds of sensors as for the above mentioned prostheses are applicable. These sensors could be pressure, acceleration, angular rate, vibration and inclination sensors that monitor the current “state” of patients or of elder persons. The bigger share of in vitro applications is diagnostics, mainly *point-of-care* diagnostics and novel analytical systems for in-lab use. For both a high need for disposable systems is recognized. Disposable systems in general should be cheap thus material selection and their processing has to be cost-effective. In general, *point-of-care* sensor systems have to be easy to use, while for in-lab systems high throughput analysis is important. However, in both cases sensors have to interact with biological samples. Due to the reasons outlined above, the following general properties and requirements for disposable micro systems in biotechnological applications (mainly sensor systems) could be derived:
- larger sensing area or parallel analysis necessary to overcome statistical uncertainty , to improve cross sensitivity or to enable the device for parallelisation
- low material price, since batch processing is limited due to minimal possible sensor size
- low technological processing costs
- sterilization is still critical for these applications (which is one of the reasons for the devices to be disposable)
- Chemical and biological compatibility with conventional systems and reagents Most of these points can be better fulfilled by other materials than silicon. Especially polymers play a major role for disposable devices, but their processing in micro scale is not that far developed yet as for silicon based devices. Another advantage of polymers is their lower price compared to silicon, and the possibility to precisely replicate polymer devices using technologies like hot embossing, microinjection moulding and UV casting. First developments therefore concentrated on applications for simple micro structured polymer substrates. Due to the ease of polymer structuring and their optical transparency, it is comparably easy to integrate passive optical parts like waveguides, gratings or lenses. Since optical detection methods play a major role in biotechnology integrated optics can bring a new quality to micro structured devices for applications in biotechnology. The evolution of polymer electronics, polymer based electro-optical components and electrically deformable polymers could bring up a new generation of disposable polymer based sensor systems for biomedical applications. Such sensor systems would include also active optical sensing components and fluid actuation components for sample preparation and sample transport. Especially in the point of care fields, where accuracy is not as important as in laboratories, these sensors developments could have a high potential due to their combination of comparative price for high volumes and high functionality.

(b) Nanoelectromechnical systems (NEMSs): Nature produces nanosized machines. Nanomotors exist in biological systems such as the flagellar motor in bacteria. Flagella are long, thin, blade-like strucutes that extend from the bacteria. The motion of these flagella propel the bacteria through water. These whip-like structures are made to move by a biological nanomotor consisiting of a highly structured conglomerate of protein molecules anchored in the membrane of the bacterium. The motor has a shaft and a structure about the shaft resembling an armature. However, the motor is not driven by electromagnetic forces, but rather by the breakdown of adenosine triphosphate (ATP) energy-rich molecules, which cause a change in the shape of the molecules. Applying the energy gained from ATP to a molecular ratchet enables the protein shaft to rotate. Perhaps the study of biological nanomachines will provide insights that will enable us to improve the design of mechanical nanomachines.

(i) Fabrication:

- Optical lithography is an important manufacturing tool in the semiconductor industry. However, to fabricate semiconductor devices smaller than 100 nm, ultraviolet light o short wavelengths (193 nm) is required, but this will not work because the materials are not transparent at these wavelengths. Electron-beam and X-ray lithography, can be used to make nanostructures, but these processes are not amenable to the high rate of production that is necessary for large-scale manufacturing. Electron beam lithography uses a finely focused beam of electrons, which is scanned in a specific pattern over the surface of a material. It can produce patterned structure on a surface point by point in a serial manner, it cannot produce structures at sufficiently high rates to be used in assembly-line manufacturing processes. X-ray lithography can produce patterns on surfaces having 20-nm resolution, but its mask technology and exposure systems are complex and expensive for practical applications.

- More recently, a technique called nanoimprint lithography has been developed that may provide a low-cost, high-production rate manufacturing technology. Nanoimprint lithography patterns a resist by physically deforming the resist shape with a mold having a nanostructure pattern on it, rather than by modifying the resist surface by radiation, as in conventional lithography. A resist is a coating material that is sufficiently soft that an impression can be made on it by a harder material. A mold having a nanoscale structured pattern on it is pressed into a thin resist coating on a substrate, creating a contrast pattern in the resist. After the mold is lifted off, an etching process is used to remove the remaining resist material in the compressed regions. The resist is a thermoplastic polymer, which is a material that softens on heating. It is heated during the molding process to soften the polymer relative the mold. The polymer is generally heated above its glass transition temperature, thereby allowing it to flow and conform to the mold pattern. The mold can be a metal, insulator, or semiconductor fabricated by conventional lithographic methods. Nanoimprint lithography can produce pattern on a surface having 10-nm resolution at low cost and high rates because it does not require the use of a sophisticated radiation beam generating patterns for the production of each structure.

- The scanning tunneling microscope (STM), uses a narrow tip to scan across the surface of the material about a nanometer above it. When a voltage is applied to the tip, electrons tunnel from the surface of the material and a current can be detected. If the tip is kept at a constant distance above the surface, then the current will vary as the tip scans the surface. The amount of detected current depends on the electron density at the surface of the material, and this will be higher were the atoms are located. Thus, mapping the current by scanning the tip over the surface produces an image of the atomic or molecular structure of the surface. An alternative mode of operation of the STM is to keep the current constant, and monitor the deflection of the cantilever on which the tip is held. In this mode the recorded cantilever deflections provide a map the atomic surface of the surface. The scanning tunneling microscope has been used to build nanosized structures atom by atom on the surface of materials. An adsorbed atom is held on the surface by chemical bonds with the atoms of the surface.

(ii) Applications- Nanodevices and Nanomachines:

- Actuators are devices that convert electrical energy to mechanical energy, or vice versa. It is known that single-walled carbon nanotubes deform when they are electrically charged. An actuator based on this property has been demonstrated using single-walled carbon nanotube paper. Nanotube paper consists of bundles of nanotubes having their long axis lying in the plane of paper, but randomly oriented in the plane. The actuator consisted of 3x20 nm strips of nanopaper 25-50um thick. The two strips are bonded to each other by double-stick Scotch tape. An insulating plastic clamp at the upper end supports the paper and holds the electrical contacts in place. The sheets were placed in a one molar NaCl electrolyte solution. Application of a few volts produced a deflection of upto a centimeter, and could be reversed by changing the polarity of the volatage. Application of an AC voltage produced an osciallation of the cantilever. This kind of actuator is called a bimorph cantilever actuator. Strictly speaking, this actuator is neither a NEMS nor MEMS device because of the size of the electrodes. However, it works because of the effect of charging on the individual carbon nanotubes, and indicates that nanosized actuators employing three single-walled carbond nanotubes are possible.

- Rotaxanes are circular molecules that have been used as molecular switches. Graphenes have been used to create transistors only a single atom thick and 50 atoms long. Researchers at Lawrence Berkeley Livermore Labs have made significant progress on nanoscale devices throughout the early 00s, including a nanotube-based electrostatic nanomotor, a molecular actuator, and a nanoelectromechanical relaxation oscillator. The nanomotor is about 500 nm across, or 300 times smaller than a human hair, and is the smallest motor ever built.
- Further nanoscale devices include a nanotube-threaded lipid membrane, which can move tiny amounts of fluid, even single molecules; the Rice University nanocar, which uses buckytubes for wheels, "walking DNA", DNA molecules that lift and touch down with molecular "legs" just like a walking human being; semiconducting polymer nanostructures with numerous applications including illumination and optical wires.

PROPERTIES OF NANOMATERIALS

1. Introduction

Nanomaterials: Generally, nanomaterials are defined as materials with grain sizes below 100 nm. More stringent: Nanomaterials are materials with special properties depending on their small grain size**.** In many cases, the latter definition restricts nanomaterials to grain sizes below 10 nm.

The second definition is the more useful one, because nanomaterials are expensive. An expensive material without very special properties is senseless. Some nanocrystalline ceramic materials or nanoglasses with particle sizes below 10 nm exhibit interesting physical properties. Except for properties related to grain boundaries, these are properties of single isolated particles. These special properties may be lost in the case that the particles are interacting. This phenomenon leads to the necessity of nanocomposites

Materials behave differently at this scale: Nanomaterials have the structural features in between of those of atoms and the bulk materials. While most microstructured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials.

Why do materials behave differently at the nanoscale? Materials behave differently at this scale for two reasons: Firstly, very small particles have a larger surface area compared to the same amount of material in a larger lump (for example, grains of sand would cover a bigger surface than the same amount of sand compressed into a stone). As the surface of the particle is involved in chemical reactions, the larger surface area can make materials more reactive – grains of salt dissolve in water much more quickly than a rock of salt for example. In fact, some materials that are generally inactive in their larger form can be more reactive in nanoscale. Secondly, when we look at materials on a nanoscale level, the relative importance of the different laws of physics shift and effects that we normally do not notice (such as quantum effects) become more significant, especially for sizes less than 20nm.

This is mainly due to the nanometer size of the materials which render them:

(i) large fraction of surface atoms;
(ii) high surface energy;
(iii) spatial confinement;
(iv) reduced imperfections, which do not exist in the corresponding bulk materials.

Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large fraction of atoms of the materials to be the surface or interfacial atoms, resulting in more “surface” dependent material properties. Especially when the sizes of nanomaterials are comparable to Debye length, the entire material will be affected by the surface properties of nanomaterials. This in turn may enhance or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity.

The nanometer feature sizes of nanomaterials also have spatial confinement effect on the materials, which bring the quantum effects. Nanoparticles can be viewed as a zero dimension quantum dot while various nanowires and nanotubes can be viewed as quantum wires. The quantum confinement of nanomaterials has profound effects on the properties of nanomaterials. The energy band structure and charge carrier density in the materials can be modified quite differently form their bulk count part and in turn will modify the electronic and optical properties of the materials. For example, lasers and light emitting diodes (LED) from both of the quantum dots and quantum wires are very promising in the future optoelections. High density information storage using quantum dot devices is also a fast developing area. Reduced imperfections are also an important factor in determination of the properties of the nanomaterials.

Nanosturctures and nanomaterials favors of a self-purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased materials perfection affects the properties of nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced, the mechanical properties of nanomaterials will be better than the bulk materials. The superior mechanical properties of carbon nanotubes are well known.

Due to their nanometer size, nanomaterials are already known to have many novel properties. Many novel applications of the nanomaterials rose from these novel properties have also been proposed. In this chapter, the properties of nanomaterials including the mechanical, thermal, biological, optical and chemical properties of nanomaterials will be addressed.

2. General Properties

(a)Mechanical Properties

Mechanical properties of materials depend upon the composition on bonds between the atoms viz. covalent, metallic, ionic etc., As a result , purest materials may be inherently weak or strong or brittle. Presence of impurities affects all the properties.

When the size of materials is reduced to nanoscale, materials tend to be single crystals. It has been shown in case of metallic nanocrystalline materials that elastic modulii reduce dramatically. For example in case of magnesium nanocrystalline materials (grains ~12nm size) Young’s modulus was observed to be 3900 N/mm2 as against 4100 N/mm2 for polycrystalline (grain size>1um) magnesium. Palladium nanocrystallites of ~8nm size had Young’s modulus 8800 N/mm2 as against 1230 N/mm2 for polycrystalline palladium.

Plastic deformation in nanocrystallline materials strongly differs from that of polycrystalline bulk counter part. In nickel stress removal results in more effective recovery of the materials as compared to corresponding polycrystalline material.

Hardness of materials is also related to grain size. For copper in micrometer grain size range there is a linear dependence of hardness on particle size. It increase with increase of grain size. However in nanometer size range the hardness increases with decrease of particle size linearly. Similar results are found in case of palladium nanoparticles and microparticles.

Applications of Mechanical Properties of Nanomaterials

Tougher and harder cutting tools: Cutting tools made of nanomaterials, such as tungsten carbide, tantalum carbide, and titanium carbide, are much harder, much more wear-resistant, erosion-resistant, and last longer than their conventional (large-grained) counterparts. Also, for the miniaturization of microelectronic circuits, the industry needs micro drills (drill bits with diameter less than the thickness of an average human hair or 100 μm) with enhanced edge retention and far better wear resistance. Since nanocrystalline carbides are much stronger, harder, and wear-resistant, they are currently being used in these micro drills.

Automobiles with greater fuel efficiency: In automobiles, since nanomaterials are stronger, harder, and much more wear-resistant and erosion-resistant, they are envisioned to be used in spark plugs. Also, automobiles waste significant amounts of energy by losing the thermal energy generated by the engine. So, the engine cylinders are envisioned to be coated with nanocrystalline ceramics, such as zirconia and alumina, which retain heat much more efficiently that result in complete and efficient combustion of the fuel.

Aerospace components with enhanced performance characteristics: One of the key properties required of the aircraft components is the fatigue strength, which decreases with the component's age. The fatigue strength increases with a reduction in the grain size of the material. Nanomaterials provide such a significant reduction in the grain size over conventional materials that the fatigue life is increased by an average of 200-300%. In spacecrafts, elevated-temperature strength of the material is crucial because the components (such as rocket engines, thrusters, and vectoring nozzles) operate at much higher temperatures than aircrafts and higher speeds. Nanomaterials are perfect candidates for spacecraft applications, as well.

Ductile ceramics: Ceramics are very hard, brittle, and hard to machine even at high temperatures. However, with a reduction in grain size, their properties change drastically. Nanocrystalline ceramics can be pressed and sintered into various shapes at significantly lower temperatures. Zirconia, for example, is a hard, brittle ceramic, has even been rendered superplastic, i. e., it can deformed to great lengths (up to 300% of its original length). However, these ceramics must possess nanocrystalline grains to be superplastic. Ceramics based on silicon nitride (Si3N4) and silicon carbide (SiC), have been used in automotive applications as high-strength springs, ball bearings, and valve lifters, and because they possess good formability and machinabilty combined with excellent physical, chemical, and mechanical properties. They are also used as components in high-temperature furnaces.

Better insulation materials: Aerogels are nanocrystalline porous and extremely lightweight materials and can withstand 100 times their weight. They are currently being used for insulation in offices, homes, etc. They are also being used as materials for "smart" windows, which darken when the sun is too bright and they lighten themselves otherwise.

(b)Structural Properties

Small clusters or nanoparticles are not just the fragments of bulk materials. There can entirely different structure as well as bonds and bond strengths in nanomaterials. As an example consider silicon crystal. Bulk silicon crystallizes in diamond structure. Small clusters of silicon atoms can be considered as fragments of the unit cell.

Even though some nanomaterials with slightly large number of atoms (>50-60 atoms) may acquire bulk crystalline materials, it is found that the lattice parameters may not be the same as in the bulk materials. For example, X-ray diffraction patterns of ZnS of 1.4 nm particles had liquid like disorder. However, larger nanocystals of ZnS indeed show same sphalerite (cubic) structure as in the bulk. It has been observed that there is a lattice contraction of ~1 for 1.4 nm ZnS nanoparticles. Other small particles also show upto ~2.3% lattice constant deviations compared to bulk crystalline materials.
Temperature and pressure also have profound effect on crystal structure. With increase in temperature the disordered structure of small particles of ZnS were found to transform to wurtzite (hexagonal) structure. Further, chemical capping, often used in the synthesis of nanoparticles, gets removed and particles tend to agglomerate or coalesce forming large particles.

Effect of pressure on structural properties (using x-ray diffraction) has also been well investigated for some nanoparticles. It has been found that indeed the structural transformations do take place in case of nanoparticles with applied pressure. However, the pressures required for this are larger for nanoparticles than for corresponding bulk material and depend upon the particle size for CdSe nanoparticles. Thus CdSe nanoparticles of 2 to 4 nm size required 4.9 GPa to 3 GPa pressure to transform them from wurtzite to rock salt structure. Bulk CdSe needs just 2.0 GPa for the same transformation.

(c) Melting

A variety of nanoparticles like Au, Ag, CdS etc., have been investigated for their thermal stability and melting. Melting begins at the surface. As the particle size decreases, surface t bulk atom ratio increases dramatically. In small particles or cluster the central atom may be considered as surrounded by first, second, third, … compact shell of atoms. First shell would have 12 atoms, second shell would have 42 atoms and so on. The number of surface atoms is quite large in nanoparticles and surface to bulk atoms ratio goes on increasing with decreasing particle size (or shells). Large surface is related to large surface energy. This energy can be lowered by melting. Melting temperature of gold nanoparticles of 3-4 nm size is reduced by ~500 C compared to bulk melting point.

Melting of nanoparticles is determined either by X-ray diffraction or electron diffraction. Heating increases the lattice parameter and at melting long range order is lost.

(d) Electrical Conductivity

Materials are often classified according to their ability to let current flow through them. Conductivity is defined in terms of the properties of electrons in the solids. Resistivity is the inverse of conductivity. Metals are characterized by very low resistivity (~10-6 ohms.cm). Semiconductors have medium resistivity (few ohmcm) and insulators have larger resistivity (> 10^3 ohm.cm). The resistivity (or conductivity) in solids can be measured in principle by connecting electrically conducting wires to solid material of known geometry, applying a voltage difference across it and measuring the current flowing through it. Current flowing through it is given by Ohm's law. For a metal, current-voltage is a linear graph.

If we reduce the dimensions of metal piece (or introduce a semiconductor nanoparticle or quantum dot) to ~100 nm or less and wish to measure its conductivity, then it is useful to put capacitors on either side so that direct contact between electrodes and metal particle is avoided. There appears then a region around zero voltage for which there is no current flow. This phenomenon is known as Coulomb blockade. Repeated tunneling of single electrons produces what is known as Coulomb Staricase.

Resistivity in nanomaterials is in general larger than that in polycrystalline materials. The electrons get scattered at grain boundaries resulting into increase of resistance. Therefore, electrical resistance of polycrystalline materials is larger than that of corresponding single crystal materials. In materials having nanocrystalline grains have larger number of boundaries exist, compared to polycrystalline materials having micrometer sized grains. Therefore, resistivity of materials having nano sized grains is generally quite large.

Applications of Electrical Properties of Nanomaterials: High energy density batteries. Conventional and rechargeable batteries are used in almost all applications that require electric power. The energy density (storage capacity) of these batteries is quite low requiring frequent recharging. Nanocrystalline materials are good candidates for separator plates in batteries because they can hold considerably more energy than conventional ones. Nickel-metal hydride batteries made of nanocrystalline nickel and metal hydrides are envisioned to require far less frequent recharging and to last much longer.

Large electrochromic display devices; An electrochromic device consists of materials in which an optical absorption band can be introduced, or an existing band can be altered by the passage of current through the materials, or by the application of an electric field. They are similar to liquid-crystal displays (LCD) commonly used in calculators and watches and are primarily used in public billboards and ticker boards to convey information. The resolution, brightness, and contrast of these devices depend on the tungstic acid gel’s grain size. Hence, nanomaterials, such as tungstic oxide gel, are being explored for this purpose.

(e) Optical Properties

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

Surface Plasmons (SP) are the origin of the color of nanomaterials. An SP is a natural oscillation of the electron gas inside a given nanosphere. If the sphere is small compared to a wavelength of light, and the light has a frequency close to that of the SP, then the SP will absorb energy. The frequency of the SP depends on the dielectric function of the nanomaterial, and the shape of the nanoparticle. For a gold spherical particle, the frequency is about 0.58 of the bulk plasma frequency. Thus, although the bulk plasma frequency is in the UV, the SP frequency is in the visible (close to 520 nm)

Suppose we have a suspension of nanoparticles in a host. If a wave of light is applied, the local electric field may be hugely enhanced near an SP resonance. If so, one expects various nonlinear susceptibilities, which depend on higher powers of the electric field, to be enhanced even more.

Luminescence can be excited in some molecules or solids using an external stimulus like electrons, photons or electric field. Semiconductor nanoparticles – doped or undoped- exhibit enchanced luminescence compared to their bulk counterparts.

Applications of Optical Properties of Nanomaterials: Glues containing nanoparticles have optical properties that give rise to uses in optoelectronics. Casings, containing nanoparticles used in electronic devices, such as computers, offer improved shielding against electromagnetic interference. Electrochromic, devices are similar to liquid-crystal displays (LCD), are been developed with nanomaterials. The incorporation of nanomaterials in surface coatings can provide long-term abrasion resistance without significantly effecting optical clarity, gloss, color or physical properties.

(f) Magnetic properties

Magnetism is a very important property of materials as it has diverse applications like information storage, electron circuits, transformers, motors, actuators, sensors and medical field. Magnetic nanoparticles, assemblies of nanoparticles, magnetic nanowires, magnetic thin films or multilayers films and metal oxide films show interesting magnetoresistive or magneto optical properties.

Ferromagnetic materials like Fe, Co, Ni have very interesting behavior below a critical size, characteristic of each material. Bulk ferromagnetic materials have spontaneously magnetized domains. However, below the critical size domain formation is not energetically favoured and materials prefers to be single domain. In such a situation all the spins of atoms are oriented in one direction. Typically, the particles with a size below 100 nm are likely to be single domain. Single domain particles of extremely small size which do not show coercivity hysterisis are known as superparamagnetic materials. In superparamagenetic particles, spins are oriented in one direction and switch coherently in the opposite direction.

Small particles are characterized by large surface to volume ratio. Therefore surfaces and interfaces play an important role their magnetic properties of nanostructures. At surface there is not only the symmetry breaking of the bulk crystal structure but there is a change in the coordination number as well as change in the lattice constant. Such effects can give rise to observation of ferromagnetic behavior of materials which are not ferromagnetic in the bulk form.

Deposition of one kind of material over the other, of a few nanometer thick, and repeating it several times gives rise to a multilayer. The multilayers are characterized by the presence of a large number of interfaces. The properties of multilayers are therefore governed not only by the parent materials but also by their surface and interface properties. Magnetic multilayers can be ferromagentically or antiferromagnetically coupled. This gives rise to magnetoresistivitly which depends upon the orientation of the magnetic layers. Mangetoresistance (MR) is the relative change in electric resistance of a material on the application of magnetic field. The change in the resistivity can be quite large and is known as Giant Magneto Resistance (GMR).

Based on GMR effect multilayer structures have been designed for various applications some of which are magnetic tunnel junction (MTJ) and spin valve. A spin valve is a thin film made up of essentially magnetic tri-layers. One layer is magnetically very soft material, meaning it is very sensitive to small magnetic fields. The other is made of a magnetically ‘hard’ meaning insensitive to fields of moderate size. The central part consists of two magnetic layers, separated by a Cu spacer layer. Spin valves are commercially used in computer read heads.

MTJ material is made of at least two magnetic layers separated by an insulating tunnel barrier.The current flows perpendicular to the film plane. The 3-d transition metal oxides, particularly the manganites which have pervoskite structure have improved device performance as compared to the GMR materials. These oxides display a diverse nature of properties such as paramagnetic to ferromagnetic transition accompanied by insulator to metal transition and realization of high magnetoresistance on application of low magnetic field.

Applications of Magnetic Properties of Nanomaterials: High-power magnets Magnets made of nanocrystalline yttrium-samarium-cobalt grains possess very unusual magnetic properties due to their extremely large surface area. Typical applications for these high-power rare-earth magnets include quieter submarines, automobile alternators, land-based power generators, and motors for ships, ultra-sensitive analytical instruments, and magnetic resonance imaging (MRI) in medical diagnostics.

(g) Chemical Properties

One of the important factors for the chemical applications of nanomaterials is the increment of their surface area which increases the chemical activity of the material.

Applications of Chemical Properties of Nanomaterials: Due to their enhanced chemical activity, nanostructural materials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal. Fuel cell technology is another important application of the noble metal nanoparticles relating the catalysis of the reactions. In the present, the fuel cell catalysts are based on platinum group metals (PGM). Pt and Pt-Ru alloys are some of the most frequently used catalysts from this group. In fact, the use of these metals is one major factor for cell costs, which has been one of the major drawbacks preventing it from growing into a more important technology. One possibility to produce economical catalysts is the use of bimetallic nanoparticles.

3. Metal Nanoparticles – properties

(a) Magic numbers: A high intensity laser bean is incident on a metal rod, causing evaporation of atoms from the surface of the metal. The atoms are then swept away by a burst of helium and passed through an orifice into a vacuum where the expansion of the gas causes cooling and formation of clusters of the metal atoms. These clusters are then ionized by UV radiation and passed into a mass spectrometer that measures their mass:charge ratio. The mass spectrum shows that clusters of 7 and 10 atoms are more likely than other clusters, which means that these clusters are more stable than clusters of other sizes. The ionization potential is the energy necessary to remove the outer electron from the atom. The mamimum ionization potential occurs for the rare-gas atoms. More energy is required to remove electron from filled orbitals than from unfilled orbitals. Peaks are observed at clusters having two and eight atoms. These numbers are referred to as electron magic numbers.

(b) Jellium model: The jellium model envisions a cluster of atoms as a large atom. The positive nuclear charge of each atom of the cluster is assumed to be uniformly distributed over the sphere of the cluster.

(c) Geometric Structure: Generally the crystal structure of large nanoparticles is the same as the bulk structure with somewhat different lattice parameters. X-ray diffraction studies of 80-nm aluminium particles have shown that it has the face-centered cubic (FCC) unit cell, which is the structure of the unit cell of bulk aluminium. However, in some instances it has been shown that small particles having diameters of <5nm may have different structures. For example, it has been shown that 3-5 nm gold particles have an icosahedrdal structure rather than the bulk FCC structure.

(d) Electronic structure: When atoms form a lattice, the discrete energy levels of the atoms are smudged out into energy bands. The term density of states refers to the number of energy levels in a given interval of energy. For a metal, the top band is not totally filled. In the case of a semiconductor the top occupied band, called the valence band, is filled, and there is a small energy separation referred to as the band gap between it and the next higher unfilled band.
When a metal particle having bulk properties is reduced in size to a few hundered atoms, the density of states in the conduction band, the top band containing electrons, changes dramatically. The continuous density of states in the band is replaced by a set of discrete energy levels, which may have energy level spacings larger than the thermal energy and gap opens up. The small cluster is analogous to a molecule having discrete energy levels with bonding and antibonding orbitals. Eventually a size is reached where the surface of the particles are separated by distances which are in the order of the wavelengths of the electrons. In this situation the energy levels can be modeled by the quantum-mechanical treatment of a particle in box. This is referred to as the quantum size effect.
The color of material is determined by the wavelength of light that is absorbed by it. The absorbtion occurs because electrons are induced by the photons of the incident light to make transitions between the lower-lying occupied levels and higher unoccupied energy levels of the materials. Clusters of different sizes will have different electronic structures, and different energy-level separations. Light induced transitions between these levels determines the color of materials. This means that clusters of different sizes can have different colors, and the size of cluster can be used to engineer the color of material.

(e) Reactivity: Since the electronic structure of nanoparticles depends on the size of the particle, the ability of the cluster to react with other species should depend on cluster size. This has important implications for the design of catalytic agents. High catalytic activity is observed for gold nanoparticles smaller than 3-5 nm, where the structure is icosahedrdal instead of the bulk FCC arrangement. This work has led to the development of odor eaters for bathrooms based on gold nanoparticles on a Fe_2O_3 substrate.

4. Semiconducting nanoparticles- properties

(a) Optical properties: Nanoparticles made of cadmium, germanium, or silicon are not themselves semiconductors. A nanoparticles of Si can be made by laser evaporation of a Si substrate in the region of helium gas pulse. The beam of neutral clusters is photolyzed by a UV laser producing ionized clusters whose mass to charge ratio is then measured in a mass spectrophotometer.

The most striking property of nanoparticles made of semiconducting elements is the pronounced changes in their optical properties compared to those of the bulk material. There is significant shift in the optical absorption spectra toward the blue (shorter wavelength) as the particle size is reduced.

In a bulk semiconductor a bound electron-hole pair, called an exciton, can be produced by a photon having an energy greater than that of the band gap of the material. The band gap is the energy separation between the top filled energy level of the valence band and the nearest unfilled level in the conduction band above it. The photon excites and electron from the filled band to the unfilled band above. The result is a hole in the otherwise filled valence band, which corresponds to an electron with an effective positive charge. Because of the Columb attraction between the positive hole and the negative electron, a bound pair, called an exciton, is formed that can move through the lattice. The separation between the hole and the electron is many lattice parameters. The existence of the exciton has a strong influence on the electronic properties of the semiconductor and its optical absorption.

An exciton can move in the crystal whose center of mass motion is quantized. Different kinds of excitons are identified in a variety of materials. When the electron-hole pair is tightly bound with distance between electron and hole comparable to lattice constant then it is called Frenkel exciton. At the other extreme, one may have an exciton with electron-hole separation much larger compared to lattice constant. Such a weakly bound electron-hole pair is called Mott-Wannier exciton.

Cd_2P_2 is a dark brown semiconductor with energy gap of approximately 0.5 eV. When its particles are made, it progressively passes through a series of colours like brown, red, yellow and white with particle size changing from ~30A to ~15A. For ~15 A particles the band gap increases to 4 eV. The same is true for CdS. The bulk semiconductor with energy gap of 2.42 eV is orange in colour. As the particles become smaller and energy gap increases it becomes yellowish and ultimately white.

(b) Luminescence:

Luminescence can be excited in some molecules or solids using an external stimulus like electrons, photons or electric field. Semiconductor nanoparticles- doped or undoped- have been widely investigated as they exhibit enhanced luminescence compared to their bulk counterparts.

(i)photoluminescence: When the external source is photons, the luminescence is known as photoluminescence. An electron from a valence band can be excited to a level in the conduction band if photon of sufficient energy to make a transition is available. This process leaves a hole in the valence band. The excited electron can loose energy by emission of photon in a relatively shorter time before it can relax and make a radiative transition.

(ii) Electroluminescence: Luminescence observed by the application of an electric field to a material is known as electrolumnisence. It can be observed by applying either low or high field; accordingly it is classified as ‘injection luminescence’ and ‘high field electroluminescence’ respectively. Light emitting diodes are based on the principle of minority carrier injection in a diode. High field electroluminescence is used in ‘display panel’. Emission of electron by application of very high electric field is known as field emission.

(iii)Cathodoluminescence: Electrons of very high energy striking a semiconductor material produce luminescence known as ‘cathodoluminescence’. The incident electrons here are from some filament or field emission cathode. Phenomenon of cathodoluminescence is used in oscilloscope, TV etc.,

(iv) Thermoluminescence: In semiconductors with large band gaps it is found that if they are excited at very low temperatures with photons in the UV range, on heating to some temperature which depends upon the dopant ions, light is emitted even in the absence of any other stimulus. The phenomenon is known as thermoluminescence or after glow. Thermoluminescence is quite strong in nanomaterials. Thermoluminescence has been reported for ZnS nanoparticles doped with copper.

(c) Photofragmentation

It has been observed that nanoparticles of silicon and germanium can undergo fragmentation when subjected to laser light from a Q-switched Nd:YAG laser. The products depend on the size of the cluster, the intensity of laser light, and the wavelength.

(d) Coulombic explosion

Multiple ionization of clusters causes them to become unstable, resulting in very rapid high-energy dissociation or explosion. The fragment velocities from this process are very high. The phenomenon is called Coulombic explosion.

5. Nanoceramics - properties

(I) Chemical
Acid-Base Behavior of Insulating Metal Oxide Surfaces

- Remarkable ability to chemically adsorb a wide variety of molecules
  - Environmental benefits
  - Chlorinated hydrocarbons, phosphorus compounds
- Enhanced ability to dissociate variety of organic molecules on their surfaces.

Unusual Adsorptive Properties

(II) Physical/Mechanical Properties

a. Improved Sintering and Hardness
b. Reduced Brittleness and Enhanced Ductility and Superplasticity

- Nanophase powder compact more easily in sintering process
- Successful sintering enhances hardness of materials
- Nanophase powder densify at faster rates